POLYURETHANE - POLYMETHYL METHACRYLATE GRAFT COPOLYMERS

A Thesis by Diane WILSON

September 1988

Submitted as a part of a PhD degree

and for the Diploma of Imperial College

Department of Chemistry
Imperial College of Science and Technology
University of London

ABSTRACT

Graft copolymers of polyurethanes and poly(methyl methacrylate) are currently of interest to the paint industry. When used as interfacial agents, they provide a means of producing stable blends of the two constituent homopolymers.

Several segmented polyurethanes were synthesised containing various radically reactive groups. Polyurethanes containing pendent propenyl groups along the polymer backbone were found to be unreactive towards free-radical graft copolymerisation with methyl methacrylate.

However, the formation of polyurethane macromonomers containing either terminal methacrylate or α-methyl styrene groups, or a pendent methacrylate group dispersed along the polyurethane backbone, readily copolymerised with methyl methacrylate to form graft copolymers of a variety of shapes.

Isolation of the pure graft copolymers proved to be difficult by the usual solvent extraction or fractional precipitation techniques. However, separation was achieved by means of preparative gel permeation chromatography (Prep-GPC).

Characterisation of the polyurethanes, the graft copolymers, and their crude reaction products (consisting of graft copolymer and unreacted polyurethane) was carried out using such techniques as ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy, differential scanning calorimetry (DSC), GPC, stress / strain measurements, impact tests, scanning electron microscopy, and rheological tests on the polymer solutions.

ACKNOWLEDGEMENTS

For his invaluable supervision and help over the last three years, my thanks go to Dr.M.H.George. I also wish to indicate my appreciation of the practical assistance donated by Mr.T.Chui, Mr.P.Lam, Mr.S.Pearce, Dr.S.Varma, Mr.A.S.Coote, and all of the other members of the Polymer Chemistry Research Group. Others persons who should be included are the technical staff of the Chemistry Department, especially Mr.G.Tucker, Mr.R.N.Sheppard, Mr.J.N.Bilton, and Mr.R.Carter.

I am also indebted to the help offered by Dr.A.Palluel, Dr.R.Redman, Mr.E.West, Mr.T.Strivens, and Mr.S.Phelan of ICI (Paints) PLC, Slough.

My thanks go to the past and present members of the Old Building Physical Chemistry Coffee Club and the members of the Prof.W.J.Albery research group for providing light relief from the research work.

Last, but not least, I wish to express my gratitude to my husband, Peter, and to all the members of our joint family and friends outside of the College for their endless support.

CONTENTS

ABSTRACT 2

ACKNOWLEDGEMENTS 3

CONTENTS 4

LIST OF TABLES 12

LIST OF FIGURES 15

LIST OF ABBREVIATIONS 19

CHAPTER 1: INTRODUCTION TO POLYURETHANES 21

1.1 History and Applications 21

1.2 Synthesis of Polyurethane Block Copolymers 22

1.2.1 General Chemistry 22

1.2.2 Components of a Polyurethane Block Copolymer 26

1.3 Characterisation of Polyurethanes 34

1.3.1 Introduction to the Structure of Polyurethane Elastomers 34

1.3.2 Nuclear Magnetic Resonance (NMR) Spectroscopy 35

1.3.3 Infrared (IR) Spectroscopy 37

1.3.4 Differential Scanning Calorimetry (DSC) 40

1.3.5 Dynamic Mechanical Thermal Analysis (DMTA) 42

1.3.6 Stress / Strain Measurements and Impact Tests 44

1.3.7 Gel Permeation Chromatography (GPC) 49

1.3.8 Other Techniques 50

CHAPTER 2: GRAFT COPOLYMERS OF POLYURETHANES AND POLY(METHYL METHACRYLATE) 52

2.1 Acrylic and Methacrylic Polymers 52

2.1.1 Introduction 52

2.1.2 Synthesis 53

2.1.3 Properties of Poly(methacrylate)s 56

2.1.4 Modification and Crosslinking of Acrylic Polymers 65

2.2 Polyurethane Graft Copolymers 69

2.2.1 Methods of Synthesising Graft Copolymers 72

2.2.2 Isolation of Graft Copolymers 113

2.2.3 Uses of Graft Copolymers 115

CHAPTER 3: CHARACTERISATION OF POLYMERS FOR USE IN SURFACE COATINGS 117

3.1 Introduction 117

3.2 Evaluation of the Properties of Surface Coatings 119

3.2.1 Barrier Properties 119

3.2.2 Mechanical Properties 121

3.2.3 Ageing Properties 122

3.2.4 Rheological Properties 123

3.2.5 Other Properties Used to Characterise Surface Coatings 138

CHAPTER 4: EXPERIMENTAL 140

4.1 Purification of Chemicals 140

4.1.1 Solvents 140

4.1.2 Monomers and Other Reagents 141

4.2 Physical and Analytical Experimental Methods 143

4.2.1 High Vacuum Equipment 143

4.2.2 Infrared (IR) Spectroscopy 144

4.2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy 144

4.2.4 Microanalysis 145

4.2.5 Centrifuge 145

4.2.6 Rotary Evaporation 145

4.2.7 Turbidimetric Titrations 145

4.2.8 Adsorption Column Chromatography 146

4.2.9 Gel Permeation Chromatography (GPC) 146

4.2.10 High Performance Liquid Chromatography (HPLC) 159

4.2.11 Differential Scanning Calorimetry (DSC) 160

4.2.12 Stress / Strain Measurements 161

4.2.13 Impact Tests 162

4.2.14 Rheological Properties of Polymer Solutions 164

4.2.15 Scanning Electron Microscopy (SEM) 167

4.3 Reactions of a Saturated Polyurethane, PU1 167

4.3.1 Synthesis of PU1 167

4.3.2 Reactions of PU1 168

4.4 Polymers Based on Erythrol: Attempted Syntheses of Polyerythrol (PER) and the Copolymer of Erythrol and Methyl Methacrylate [P(ER-CO-MMA)] 169

4.5 Polyurethanes Based on Erythrol 169

4.5.1 Synthesis of Polyurethane PU2 169

4.5.2 Attempted Homopolymerisation of PU2 and Attempted Graft Copolymerisation of PU2 with Methyl Methacrylate [P(U2-G-MMA)] 170

4.5.3 Synthesis of Polyurethane PU3 171

4.5.4 Attempted Homopolymerisation of PU3 and the Copolymerisation of PU3 with Methyl Methacrylate [P(U3-G-MMA)] 171

4.5.5 Separation of P(U3-G-MMA) from the Starting Materials 172

4.6 Synthesis of Polyurethanes Terminated with 2-Hydroxyethyl Methacrylate (HEMA) 172

4.6.1 Termination of Both Ends of the Molecule (PU4) 172

4.6.2 Termination of One End of the Polyurethane Molecule (PU5) 173

4.7 Synthesis of a Polyurethane Terminated at One End with a,a-Dimethyl-Meta-Isopropenyl-Benzyl-Isocyanate, m-TMI (PU6) 174

4.8 Attempted Synthesis of Glyceryl Monomethacrylate, GMM, Through the Hydrolysis of Glycidyl Methacrylate, GM 174

4.8.1 General Experiments 174

4.8.2 HPLC Experiments 175

4.9 Synthesis of Polyurethanes Based on Glyceryl Monomethacrylate 176

4.9.1 Polyurethane Containing Many Units of Glyceryl Monomethacrylate (PU7) 176

4.9.2 Polyurethane Containing One Unit of GMM (PU8) 177

4.10 Grafting Reactions of PU4 with Methyl Methacrylate [P(U4-G-MMA)] 177

4.11 Grafting Reactions of PU7 with Methyl Methacrylate [P(U7-G-MMA)] 178

4.12 The Reactions of PU5, PU6, and PU8 179

4.12.1 Attempted Homopolymerisation of PU5, PU6, and PU8 179

4.12.2 Grafting Reactions of PU5 [P(MMA-G-U5)], PU6 [P(MMA-G-U6)], and PU8 [P(U8-G-MMA)] 179

4.13 Separation of the Graft Copolymers of Section 4.12 from the Starting Materials 180

4.13.1 Solvent Extraction 180

4.13.2 Turbidimetric Titrations 183

4.13.3 Fractional Precipitations 184

4.13.4 Adsorption Column Chromatography 185

4.13.5 Preparative Gel Permeation Chromatography, Prep-GPC 186

4.14 Preparation of Films for Mechanical Testing 187

4.15 Storage of Polymers 187

CHAPTER 5: RESULTS AND DISCUSSION 189

5.1 Reactions of the Saturated Polyurethane, PU1 189

5.1.1 Synthesis of PU1 189

5.1.2 Reactions Using PU1 190

5.2 Polymers Based on Erythrol: Attempted Synthesis of PER and P(ER-CO-MMA) 193

5.3 Polyurethanes Based on ER 194

5.3.1 Synthesis of Polyurethane PU2 194

5.3.2 Attempted Homopolymerisation of PU2 and Attempted Graft Copolymerisation with Methyl Methacrylate 198

5.3.3 Synthesis and Reactions of the Polyurethane PU3 200

5.3.4 Attempted Homopolymerisation of PU3 and the Graft Copolymerisation of PU3 with MMA [P(U3-G-MMA)] 200

5.4 Attempted Syntheses of Glyceryl Monomethacrylate (GMM) Through the Hydrolysis of Glycidyl Methacrylate (GM) 223

5.4.1 General Experiments 225

5.4.2 HPLC Experiments 225

5.5 Reactions of Polyurethanes Containing Many Methacrylate Units (PU4 and PU7) 228

5.5.1 Reactions of PU4 228

5.5.2 Reactions of PU7 233

5.6 The Reactions of the Polyurethanes PU5, PU6, and PU8 238

5.6.1 The Syntheses of the Polyurethanes 238

5.6.2 Attempted Homopolymerisation of PU5, PU6, and PU8 242

5.6.3 Graft Copolymerisation of PU5, PU6, and PU8 with MMA 243

5.7 Separation of the Graft Copolymers from their Starting Materials 257

5.7.1 Solvent Extraction 258

5.7.2 Turbidimetric Titrations 261

5.7.3 Fractional Precipitations 262

5.7.4 Adsorption Column Chromatography 264

5.7.5 Prep-GPC 265

5.8 Characterisation of the Graft Copolymers of PU5, PU6, and PU8 266

5.8.1 Molecular Weight Analysis 266

5.8.2 Microanalysis Results 272

5.8.3 Spectroscopic Analysis 273

5.9 Thermal and Mechanical Properties of the Graft Copolymers and their Blends with Unreacted Polyurethane 281

5.9.1 DSC Studies 281

5.9.2 Stress / Strain Tests 286

5.9.3 Impact Tests 291

5.10 Rheological Properties of the Graft Copolymers and their Blends with Unreacted Polyurethane 293

5.10.1 Viscometry Tests 293

5.10.2 Dynamic (Oscillation) Tests 302

5.11 Scanning Electron Microscopy 310

5.12 Effect of Storage of the Graft Copolymers 316

CHAPTER 6: CONCLUSIONS AND FUTURE WORK 318

6.1 Conclusions 318

6.2 Future Work 320

APPENDICES

Appendix I Program to Calculate the Area Under a Peak of a GPC Chromatogram Between Two Specified Points 323

Appendix II Program to Calculate the Secant Modulus, Breaking Strain, and Breaking Stress of Samples that were Subjected to Impact Tests, Using the Raw Data Obtained from the Impact Tester 326

REFERENCES 327

LIST OF TABLES

CHAPTER 1

1.1	Relative Reactivity of Isocyanates with Butanol	27
1.2	Summary of the Results of the Work of Delides et al.	38
1.3	Polyurethane IR Absorption Wavelengths and Wavenumbers	39
1.4	Features of Stress / Strain Curves Associated with Polymer Properties	46

CHAPTER 2

2.1	Klein's Results Showing the Effect of Side Group Chain Length on (Meth)acrylate Polymer Properties	58
2.2	Influence of Branching of the Side Chain on the Softening Points of Poly(methacrylate) Homopolymers	60
2.3	Properties of Poly(methyl methacrylate)s Polymerised by Different Methods	63
2.4	Functional Monomers Used in the Preparation of Thermosetting Acrylic Copolymers	67
2.5	Typical Monomers Used in the Preparation of Thermosetting Acrylic Polymers	68

CHAPTER 4

4.1	Purification of Solvents	140
4.2	Purification of Monomers and Other Reagents	141
4.3	Summary of the Reactions of PU1	168
4.4	Summary of the Reactions Synthesing PER and P(ER-CO-MMA)	169
4.5	Summary of the Homopolymerisation of PU2 and the Copolymerisation of PU2 with MMA	170
4.6	Summary of the Homopolymerisation of PU3 and the Formation of the Graft Copolymer [P(U3-G-MMA)]	171

4.7	Hydrolysis Reactions of GM	174
4.8	Summary of The Grafting Reactions of PU4	178
4.9	Summary of the Grafting Reactions of PU7	178
4.10	Summary of the Homopolymerisation Reactions of PU5, PU6, and PU8	179
4.11	Summary of the Synthesis of PMMA and the Grafting Reactions of PU5, PU6, and PU8 with Methyl Methacrylate	181
4.12	The Concentrations of Solutions Used for Turbidimetric Titrations	184
4.13	Solvent and Non-Solvent Combinations Used for Fractional Precipitations	185
4.14	Solvent Systems Used for Column Chromatography	186
4.15	Summary of Experiments to Determine the Effect of Light and Air Upon Samples	188

CHAPTER 5

5.1	Molecular Weight Analysis Results for PU2	195
5.2	Results of the Solubility Tests Performed on PU2	198
5.3	Results from the Quantitative GPC Experiments Performed on the Crude Products of the P(U3-G-MMA) Reaction	216
5.4	Microanalysis Results for PU3, PMMA, and P(U3-G-MMA)	216
5.5	Stress / Strain Results for PMMA and the Polymers Based on PU3	221
5.6	Results from the Quantitative GPC Experiments Performed on the Crude Products of the P(MMA-G-U5) Reactions	248
5.7	Results from the Quantitative GPC Experiments Performed on the Crude Products of the P(MMA-G-U6) Reactions	252
5.8	Results from the Quantitative GPC Experiments Performed on the Crude Products of the P(U8-G-MMA) Reactions	256
5.9	Molecular Weight Averages for PU5 and the Graft Copolymers P(MMA-G-U5) as Evaluated by GPC (with Respect to PS Standards)	267

5.10	Estimation of the Average Number of PU5 Branches per Graft Copolymer Molecule for P(MMA-G-U5)	269
5.11	Molecular Weight Averages for PU6 and the Graft Copolymers P(MMA-G-U6) as Determined by GPC (with Respect to PS Standards)	269
5.12	Estimation of the Average Number of PU6 Branches per Graft Copolymer Molecule for P(MMA-G-U6)	270
5.13	Molecular Weight Averages for PU8 and the Graft Copolymers P(U8-G-MMA) as Evaluated by GPC (with Respect to PS Standards)	271
5.14	Estimation of the Average Number of PU8 Branches per Graft Copolymer Molecule for P(U8-G-MMA)	271
5.15	%-Polyurethane Contents of the Graft Copolymers of PU5, PU6, and PU8 as Obtained from the Microanalysis Results	272
5.16	^{13}C-NMR Chemical Shifts Observed for the Carbon Atoms of the Groups Present in PU5, PU6, and PU8	280
5.17	Stress / Strain Results	287
5.18	Results of the Impact Tests	292
5.19	Results of the Oscillation Tests on the 20% w/v DMF Solution of PMMA, PU6, PU6 / PMMA Blend, and the Mixtures of Graft Copolymers with Unreacted Polyurethanes	307

LIST OF FIGURES

CHAPTER 1

1.1	The Urethane Linkage	22
1.2	Representation of a Segmented Polyurethane Block Copolymer	25
1.3	Canonical Forms of an Isocyanate	27
1.4	DABCO	33
1.5	Typical Tensile Stress / Strain Curve for Polymers	45

CHAPTER 2

2.1	General Structure of (Meth)acrylic Polymers	52
2.2	T_gs of Linear (Meth)acrylic Homopolymers	59
2.3	General Representation of a Linear Block Copolymer	70
2.4	General Representation of a Graft Copolymer	70
2.5	General Representation of a Crosslinked Polymer	71
2.6	ACV	86
2.7	ACP	86
2.8	A Typical Turbidimetric Titration Curve	114

CHAPTER 3

3.1	Diagram Showing the Approximate Shear Rate Ranges Applying to Various Aspects of Paint Flow	123
3.2	Diagram Representing Simple Shear	124
3.3	Rheological Flow Types	125
3.4	Viscosity / Shear Curves for Polymers with Broad and Narrow Molecular Weight Distributions (MWDs)	128
3.5	Thixotropic Effect	129
3.6	Rheopectic Effect	130

3.7	Time Profile of a Periodic Simple Shear Experiment with the Shear Oscillating Sinusoidally	131
3.8	Vectoral Representation of the Components of the Complex modulus, G^*	133

CHAPTER 4

4.1	Analytical GPC Equipment	147
4.2	Typical GPC Calibration Curve for the UV Detector, Showing the Equation of the Curve	150
4.3	Prep-GPC Using the Waters Pump	153
4.4	Calibration of the Waters Prep-GPC Apparatus Using the Dye Isatin	155
4.5	Typical GPC Chromatogram Indicating the Dividing Point Between Fractions Collected and Fractions Discarded for a Combination of Materials with No Clear Distinction Between Them	156
4.6	HPLC of a Mixture of Two Materials Using the Recycle Facility	157
4.7	Prep-GPC Apparatus Using the Altex Pump	158
4.8	Determination of the T_g of a Sample from DSC Measurements	161
4.9	Diagram of the Shape of Sample for Stress / Strain Measurements Using the "Minimat" Equipment	161
4.10	Diagram of the Clamping Unit Containing a Polymer Sample as Used for Impact Tests	162
4.11	Diagram of the Dimensions of, and the Forces Felt by, the Sample Before and After the Impact Test	163
4.12	Rheometer Fixed with 5° Cone and Plate, and Other Attachments Which Could be Used	165
4.13	Apparatus Used for the General Synthesis of a Polyurethane	167

CHAPTER 5

5.1	GPCs of PU1 and the Reaction Products PU1/PMMA[1] and [2] (UV Detector)	191
5.2	GPCs of PU2 and the Products of the Reactions	196

	of PU2	
5.3	IR Spectrum of PU2	197
5.4	^{1}H-NMR Spectrum of PU2	197
5.5	GPCs of PU3 and the Products of the Reaction of PU3 (RI Detector)	201
5.6	Prep-GPC of the Products of the P(U3-G-MMA) Reaction Using the Waters Equipment	203
5.7	IR Spectrum of PU3	204
5.8	IR Spectrum of PMMA	205
5.9	IR Spectrum of P(U3-G-MMA)	206
5.10	^{1}H-NMR Spectrum of PU3	207
5.11	^{1}H-NMR Spectrum of PMMA	208
5.12	^{1}H-NMR Spectrum of P(U3-G-MMA)	209
5.13	^{13}C-NMR Spectrum of PU3	210
5.14	^{13}C-NMR Spectrum of PMMA	211
5.15	^{13}C-NMR Spectrum of P(U3-G-MMA)	212
5.16	DSC Thermograms for PMMA	218
5.17	DSC Thermograms for PU3	220
5.18	DSC Thermogram for P(U3-G-MMA) (Run 2)	222
5.19	HPLC Chromatograms for Experiment (3)	227
5.20	GPCs of PU4 and the Soxhlet Extract of P(U4-G-MMA)[1]	232
5.21	GPCs of PU7 and the Products of the Reaction P(U7-G-MMA)[4]	235
5.22	GPCs of PU5 and its Reaction Products	244
5.23	GPCs of PU6 and its Reaction Products	251
5.24	GPCs of PU8 and its Reaction Products	255
5.25	Graphical Results for the Turbidimetric Titration 4.13.2.7	263
5.26	IR Spectra of PU8 and P(U8-G-MMA)[3]	274
5.27	^{1}H-NMR Spectra of PU5 and P(MMA-G-U5)[5]	275
5.28	^{1}H-NMR Spectra of PU6 and P(MMA-G-U6)[3]	276

5.29	1H-NMR Spectra of PU8 and P(U8-G-MMA)[2]	277
5.30	^{13}C-NMR Spectra of PU6 and P(MMA-G-U6)[3]	279
5.31	DSC Thermograms for PU8	282
5.32	DSC Thermograms for P(U8-G-MMA)[1]	283
5.33	Graph of σ_s Versus $\dot{\gamma}$ for the 20% w/v DMF Solutions of PMMA, 1 : 1 w/w Blend of PU6 and PMMA, and PU6	295
5.34	Graphs of σ_s and η Versus $\dot{\gamma}$ for the Graft Copolymers of PU6: P(MMA-G-U6)[1], [2], and [3]	296
5.35	Graphical Results of the Viscometry Tests Performed on the Solutions of P(MMA-G-U5)-MIX[1], [2], [3], and [7]	297
5.36	Graphical Results of the Viscometry Tests Performed on the Solutions of P(MMA-G-U6)-MIX[1], [2], [3], and [7]	298
5.37	Graphical Results of the Viscometry Tests Performed on the Solutions of P(U8-G-MMA)-MIX[1], [2], [3], and [7]	299
5.38	Graphical Results of the Oscillation Tests Performed on the Solution of P(MMA-G-U6)[1]	304
5.39	Graphical Results of the Oscillation Tests Performed on the Solution of P(MMA-G-U6)[2]	305
5.40	Graphical Results of the Oscillation Tests Performed on the Solution of P(MMA-G-U6)[3]	306
5.41	SEM of PU8	311
5.42	SEM of P(MMA-G-U5)[1]-MIX	312
5.43	SEM of P(MMA-G-U5)[3]-MIX	313
5.44	SEM of P(U8-G-MMA)[3]	314

ABBREVIATIONS

The following list contains the abbreviations used for compounds and chemicals which occur frequently in this thesis.

AA	Acrylic acid
ACN	Acrylonitrile
AIBN	2,2'-Azo-bis-iso-butyronitrile
AM	Acrylamide
BD	Butane diol
BMA	n-Butyl methacrylate
BPO	Benzoyl peroxide
DBTL	Dibutyl tin dilaurate
DMF	Dimethyl formamide
DMSO	Dimethyl sulphoxide
ED	Ethane diol
ER	Erythrol
GM	Glycidyl Methacrylate
GMM	Glyceryl monomethacrylate
HDI	Hexamethylene diisocyanate
HEMA	2-Hydroxyethyl methacrylate
$H_{12}MDI$	4,4'-Dicyclohexyl methane diisocyanate
HQ	Hydroquinone
IBMK	Iso-butyl methyl ketone
IEM	Isocyanatoethyl methacrylate
MAA	Methacrylic acid
MAC	Methacryloyl chloride
MDI	4,4'-Diphenyl methane diisocyanate
MMA	Methyl methacrylate
NVP	N-Vinyl pyrrolidone

PEG	Polyethylene glycol
PMMA	Poly(methyl methacrylate)
PPG	Polypropylene glycol
PS	Polystyrene
PTMEG	Polytetramethylene ether glycol
PU1	A polyurethane based on MDI, BD, and PTMEG
PU2	A polyurethane based on MDI, ED, PEG 1000, and ER
PU3	A polyurethane based on H_{12}MDI, BD, PTMEG 2000, and ER
PU4 & PU5	Polyurethanes based on MDI, BD, PTMEG 2000, and HEMA
PU6	A polyurethane based on MDI, BD, PTMEG 2000, and m-TMI
PU7 & PU8	Polyurethanes based on MDI, BD, PTMEG 2000, and GMM
TDI	Toluene diisocyanate
m-TMI	a,a-Dimethyl meta-isoprenyl-benzyl-isocyanate
THF	Tetrahydrofuran

CHAPTER 1

INTRODUCTION TO POLYURETHANES

1.1 HISTORY AND APPLICATIONS

Polyurethanes were discovered in 1937 by Prof. Otto Bayer[1,2] and his co-workers of I.G. Farbenindustrie, Germany. Bayer initially investigated the reaction between diisocyanates and diamines, producing polyureas[3], but these materials did not have the required properties for plastic and fibre applications. However, the reactions of diisocyanates with dialcohols, forming the first polyurethanes, had more commercial significance.

Since that time, the importance of polyurethanes has increased due to their versatility. The chemical composition and structure of the polymer can be designed to give the desired physical and mechanical properties. There are many texts detailing the development of polyurethanes since their discovery[3-10].

Of the present day market, 90% is controlled by foams[4]. Low density, flexible foams, consisting of partially crosslinked, open cells, through which air can freely diffuse, are used in the upholstery and bedding industries.

Low density, rigid foams, which are highly crosslinked, closed cell structures, combine good mechanical strength with considerable insulating properties. Chlorofluoromethane gas is introduced into the closed "bubbles" to reduce the thermal conductivity of the material compared to those filled with air. Rigid foams are used for applications requiring good thermal insulation, such as for refrigeration and the insulation of buildings. The foams can also be sandwiched between metal, other plastics, paper, or wood to give composite materials of use in the construction industry.

High density flexible foams are divided into moulded, self-

skinning foams and microcellular elastomers. These have applications in the automotive industry (for upholstery and vehicle trimmings) and in shoe manufacturing (for soles and synthetic uppers).

The remaining 10% of the polyurethane market is split between solid elastomers, adhesives, binders, coatings, and paints. The materials have excellent abrasion resistance and are also resistant to chemical attack by many chemicals and solvents.

The scope of this thesis will be restricted to the discussion of polyurethane elastomers. Reference to the general texts mentioned previously will yield more comprehensive information about the other applications of polyurethanes.

1.2 SYNTHESIS OF POLYURETHANE BLOCK COPOLYMERS

The polymers classified as polyurethanes do not necessarily consist primarily of urethane groups [fig. (1.1)], and the term is used for convenience.

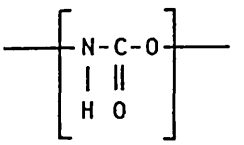
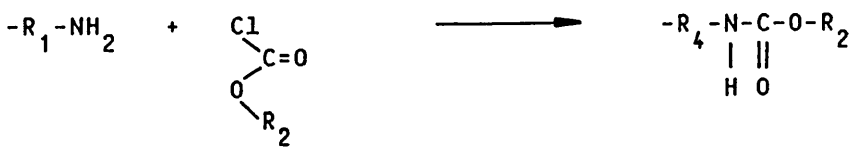


FIG. (1.1): THE URETHANE LINKAGE

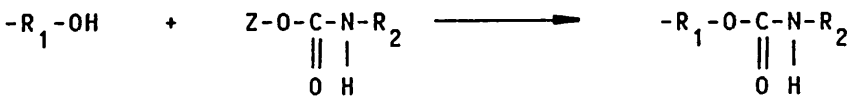
The chemistry of polyurethanes has been extensively reviewed in many publications[3-10]. The following sections are intended to summarise the salient features.

1.2.1 GENERAL CHEMISTRY

Urethanes are generally considered to be the esters of carbamic acid or the amide esters of carbonic acid. Polyurethanes can be synthesised by the reactions of bischloroformates with diamines and carbamic esters with diols[6]:

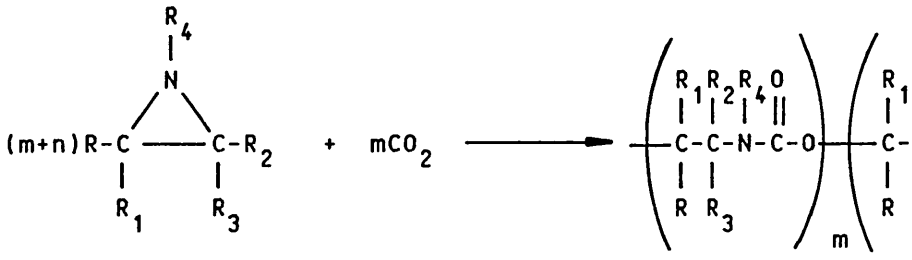


(1.1)



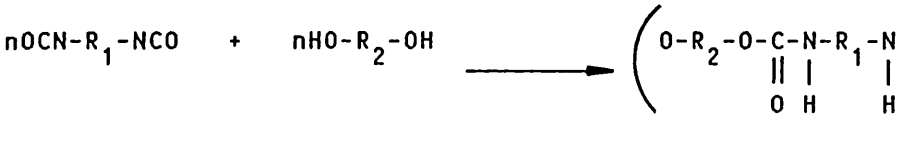
(1.2)

Union Carbide[11] patented the copolymerisation of aziridines and carbon dioxide to form copolymers of polyurethanes and polyaziridines:



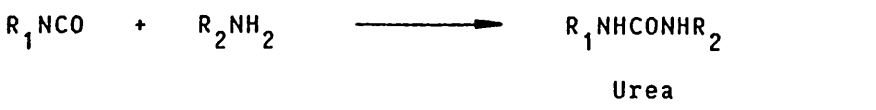
(1.3)

However, by far the most popular route to producing polyurethanes is through the step-growth polymerisation of a diisocyanate with a diol:



(1.4)

The -NCO group will react with any molecule containing an active hydrogen atom, e.g thiols and halogen acids. Apart from alcohols, useful compounds can be produced by reacting isocyanates with amines and carboxylic acids[6]:



(1.5)

Urea

$$R_1NCO + R_2COOH \longrightarrow \left[R_1NHC(=O)-O-C(=O)-R_2 \right] \longrightarrow \underset{\text{Amide}}{R_1NHCOR_2} + CO_2 \qquad (1.6)$$

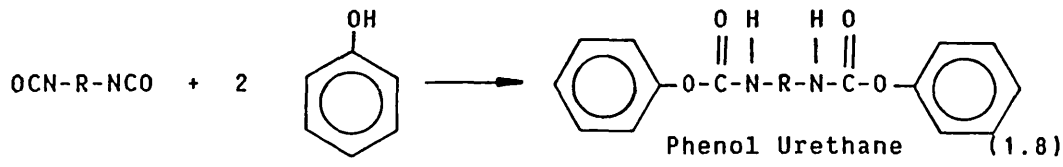
A urea group group can be indirectly formed by the reaction of water with an isocyanate[6]:

$$R\text{-}NCO + H_2O \longrightarrow [\ RNHCOOH\ ] \longrightarrow RNH_2 + CO_2$$

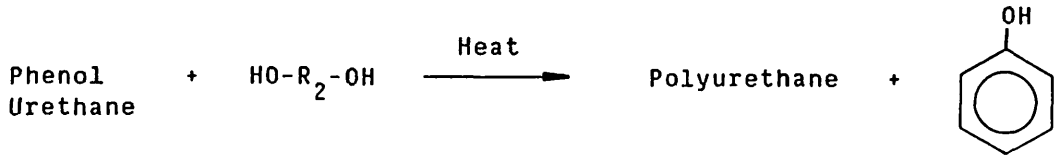
$$RNH_2 \xrightarrow{+\ R\text{-}NCO} RNHCONHR \qquad (1.7)$$

Reactions (1.6) and (1.7) are utilised for the production of polyurethane foams, using the CO_2 formed as the "blowing agent"[4].

"Blocked isocyanates" are formed when an isocyanate compound is reacted with phenol. The material decomposes back to its components at high temperatures. These compounds have been used industrially to create systems in which the phenol urethane (the blocked isocyanate) and the diol are mixed together, but polyurethane formation does not occur until the temperature is raised. However, the volatile side product has restricted the use of these systems to coating applications[12].



(1.8)



(1.9)

Several side reactions can occur during polymerisations using isocyanates which lead to the formation of chain branching or cross-linking. The more important ones are[6]:

$$-R_1-NCO \quad + \quad -R_2-NHCO-R_3- \longrightarrow \begin{array}{c} -R_2-NCO-R_3- \\ | \\ CONH-R_1- \end{array} \qquad (1.10)$$

Acyl Urea

$$-R_1-NCO \quad + \quad -R_2-NHCONH-R_3- \longrightarrow \begin{array}{c} -R_2-NCONH-R_3- \\ | \\ CONH-R_1- \end{array} \qquad (1.11)$$

Biuret

$$-R_1-NCO \quad + \quad -R_2-NHCOO-R_3- \longrightarrow \begin{array}{c} -R_2-NCOO-R_3- \\ | \\ CONH-R_1- \end{array} \qquad (1.12)$$

Allophanate

The initial productions of polyurethanes via the isocyanate - diol route were carried out in bulk at temperatures below 200°C (since the polymers are thermally unstable above 220°C). Lyman[13] originated the synthesis of polyurethanes by means of solution polymerisation in 1960.

As mentioned in the introduction, the versatility of polyurethanes arises from the ability to tailor the molecules to meet physical and mechanical requirements. A polyurethane elastomer can be considered to be a segmented block copolymer, the structure of which can be represented as [fig. (1.2)]:

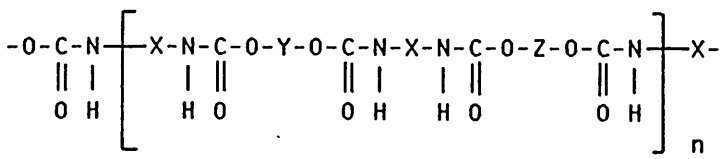


FIG. (1.2): REPRESENTATION OF A SEGMENTED POLYURETHANE BLOCK COPOLYMER

X represents the diisocyanate unit and Y is a short chain diol, which may be flexible or rigid, called a chain extender. Z is a dihydroxy terminated prepolymer, also called a "polyol", which introduces a flexible block into the polymer chain. By varying the ratio of the components Y and Z, the final polymer can range from a soft, jelly-like material to a rigid, hard plastic.

The polyurethane molecule, therefore, consists of a series of hard and soft segments. The diisocyanate and the chain extender constitute the "hard" block, and the flexible polyol is the "soft" block.

Polyurethanes can be synthesised by a "two-shot" process[6], in which the polyol and the diisocyanate are reacted together to give a prepolymer. This is then chain extended.

The "one-shot" method of preparation involves mixing all of the polyurethane's components together simultaneously. This generates a more random structure than the two-shot process.

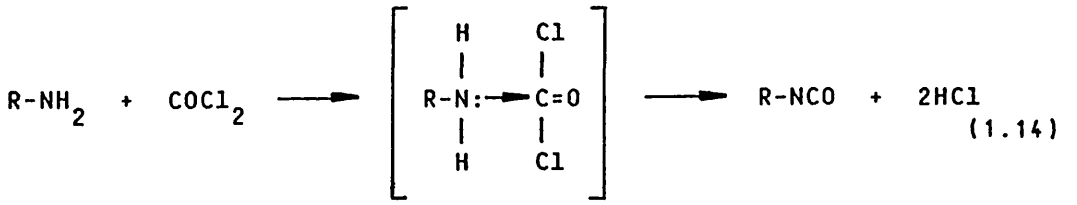
1.2.2 COMPONENTS OF A POLYURETHANE BLOCK COPOLYMER

1.2.2.1 ISOCYANATES

The first aliphatic isocyanates were synthesised by Wurtz[14]. The method involved reacting organic sulphates with cyanates:

$$(R)_2SO_4 + 2KCNO \longrightarrow 2R\text{-}NCO + K_2SO_4 \qquad (1.13)$$

Walsh[12] reviews the more recent routes used to synthesise isocyanates. At present, the general commercial preparation consists of the phosgenation of the relevant amine[13]:



(1.14)

The most frequently used diisocyanates for polyurethane preparation are 2,4- and 2,6-toluene diisocyanate (TDI), 4,4'-diphenyl methane diisocyanate (MDI), the saturated analogue of MDI 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$), hexamethylene diisocyanate (HDI), 1,5-naphthalene diisocyanate (NDI), and isophorone diisocyanate (IPDI).

Aromatic diisocyanates are far more reactive towards amines and alcohols than those that are aliphatic. Frisch et al.[15], reacted several diisocyanates with 1-butanol at 25°C in 2-ethoxyethylacetate, using the catalyst dibutyltin dilaureate (DBTL). They measured k_{cat} (in units of $kg^{3/2}mole^{-3/2}min^{-1}$) and found the following results [table (1.1)]:

TABLE (1.1): RELATIVE REACTIVITY OF ISOCYANATES WITH BUTANOL[15]

ISOCYANATE	k_{cat}
$H_{12}MDI$	6
HDI	10
TDI (80/20 ratio of 2,4- to 2,6- isomers)	28
MDI	150

The electronic structure of isocyanates is such that the following canonical forms are possible [fig. (1.3)][3]:

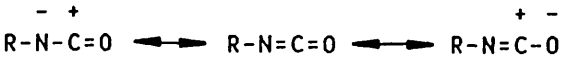
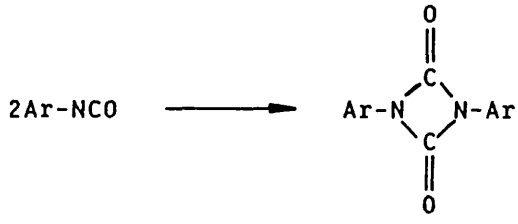


FIG. (1.3): CANONICAL FORMS OF AN ISOCYANATE

Aromatic isocyanates enable further electron delocalisation to occur involving the aromatic groups. This increases their susceptibility to nucleophilic attack at the positive carbon atom, and hence their greater reactivity compared to aliphatic isocyanates.

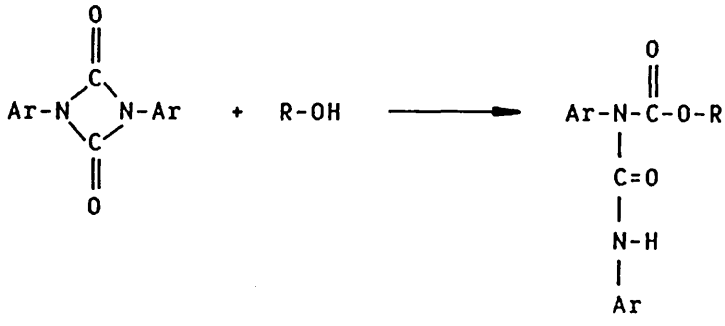
However, aromatic isocyanates are more prone to UV and thermal degradation. Therefore, the aliphatic analogues are used in instances where colour stability is required.

Aromatic isocyanates dimerise at low temperatures to form "uretidine diones"[3] [equation (1.15)]. The reaction is catalysed by acidic or basic catalysts[16].



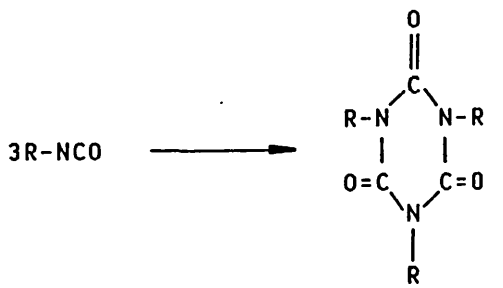
(1.15)

The dimerisation not only destroys the balance of reagents for the step-growth polymerisation of polyurethanes, but also introduces a potential site for branching and crosslinking [equation (1.16)]:



(1.16)

Both aliphatic and aromatic isocyanates have the ability to trimerise at high temperatures to form trisubstituted isocyanurates:



(1.17)

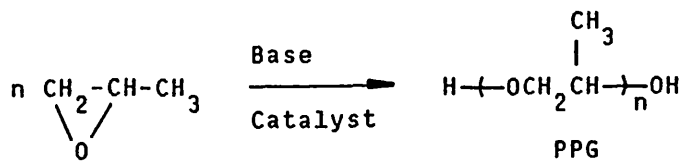
Again, acidic or basic catalysts promote the reaction[16]. The trimer is relatively stable in the temperature range 150 - 200°C. The trimerisation reaction also upsets the balance of reagents in the polyurethane synthesis, and can lead to chain branching.

1.2.2.2 POLYOLS

The type and concentration of polyol used for polyurethane syntheses can have a dramatic effect on the properties of the polymer. In general, polymers containing a high proportion of polyol soft segment will be pliable and possess good extensibility and elastic recovery. Those with a low soft segment content will be hard, rigid plastics.

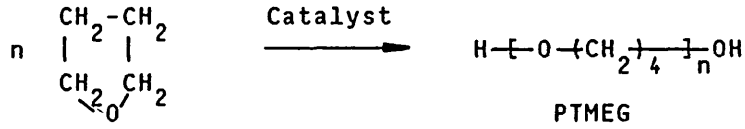
In theory, any flexible, αω-hydroxy polymer can be utilised. However, the more popular polyols used for polyurethane elastomers are polyether-glycols and polyester-glycols. The polyester polyols tend to be more expensive and prone to hydrolysis[4].

Polyether-glycols, such as polyethylene glycol (PEG) and polypropylene glycol (PPG) are usually synthesised by the base catalysed addition polymerisation of the relevant monomeric epoxide[6]:



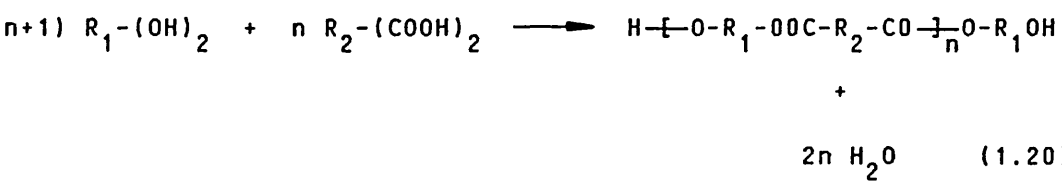
(1.18)

Polytetramethylene ether glycol (PTMEG) is synthesised from tetrahydrofuran, hence it is sometimes called poly(tetrahydrofuran) (PTHF)[6]:



(1.19)

Polyester-polyols are formed by the reaction of a dibasic acid (e.g. adipic, sebacic, or phthalic acid) with a diol such as ethylene glycol, 1,2-propylene glycol, or diethylene glycol[6]:



(1.20)

If chain branching or crosslinking is required, a polyol of high functionality can be synthesised by reacting the dibasic acid with compounds such as glycerol or sorbitol. Using ethanolamine introduces amide linkages into the polyol.

Polyurethanes based on polyester polyols are more easily hydrolysed than those containing polyether glycols. However, they are less easily oxidised, more stable at high temperatures, and have better tensile properties[4]. Due to the presence of polar groups, polyesters can readily crystallise.

PTMEG homopolymer is a crystalline solid polymer with a melting point of ~45°C[17]. However, when incorporated into the polyurethane,

the PTMEG soft segment cannot crystallise, due to steric hindrances, so long as the segment's length is below a critical value[17]. For elastomers, crystallisation of the soft segment is undesirable, and it is important that its T_g is below the service temperature of the material.

Due to its structural regularity, PTMEG is considered to be one of the best polyether glycols for producing elastomers with outstanding properties[18]. Pechhold et al.[19] and Petrović et al.[17,20] investigated the effect of soft segment concentration, molecular weight (proportional to length), and molecular weight distribution of the soft segment on the mechanical, physical, and morphological properties of polyurethanes based on MDI, butane-1,4-diol (BD), and PTMEG.

Pechhold et al. found that the optinum molecular weight of PTMEG for the synthesis of polyurethanes with ideal elastomeric properties was in the range of 1800 - 2100. They also found that a broad molecular weight distribution for the polyol gave polyurethanes with better performance than a narrow distribution.

Petrović et al. found that the polyurethane density was higher for those containing PTMEG that could crystallise, and that the T_g of the soft segment was strongly dependent on its length.

In general, polyethers are less compatible with MDI than polyesters. Therefore, there is a higher degree of phase separation in the polyurethane elastomer[4].

When using commercial polyols, their "hydroxyl value", or OHV, has to be carefully considered. This is a measure of the concentration of isocyanate reactive hydroxyl groups per unit weight of polyol, and is expressed in mg KOH/g. The OHV of a polyol is related to its molecular weight and functionality[6]:

$$\text{OHV (mg KOH/g)} = \frac{56.1 \times \text{functionality}}{\text{molecular weight}} \times 1000 \qquad (1.21)$$

The OHV is usually quoted by the manufacturers, and the polyol's equivalent weight, or molecular weight per -OH group, can be calculated using the formula[6]:

$$\text{Equiv. Weight} = \frac{56.1 \times 1000}{\text{OHV}} \qquad (1.22)$$

1.2.2.3 CHAIN EXTENDERS

Chain extenders are low molecular weight diols, diamines, or hydroxyamines. Those with a functionality greater than 3 induce chain branching or crosslinking. The polyurethane or polyurea resulting from the chain extension reaction are components of the "hard" or "rigid" segment of the polymer. Typical chain extenders are ethane diol (ED), butane-1,4-diol (BD), and ethylene diamine (EDA). BD is usually prepared from acetylene[5]:

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow[\substack{100^\circ C \\ 5\text{ atms.} \\ CuC_2}]{CH_2O} \underset{\substack{\text{1,4-Butyne-} \\ \text{diol}}}{HOCH_2C{\equiv}CCH_2OH} \xrightarrow[\substack{80\text{-}130^\circ C \\ 200\text{-}300 \\ \text{atms.}}]{H_2} \underset{\text{BD}}{HO\text{-}(CH_2)_4\text{-}OH} \qquad (1.23)$$

Diamines react with -NCO faster than diols, and the hard segment produced has a higher degree of hydrogen bonding. This gives the material a higher hard segment T_g and thermal stability[4].

The intermolecular H-bonding between the hard segments of the polyurethane act as physically bonded, crystalline centres dispersed in a soft segment matrix. The hard block, therefore, acts as a reinforcing filler.

For chain extenders of the general structure $X-(CH_2)_n-X$, where X is either $-NH_2$ or -OH, the resulting packing density and melting point of the hard segment domains are greatest when n is even[4,21].

1.2.2.4 CATALYSTS

The catalysts that are generally used for polyurethane formation are aliphatic or aromatic tertiary amines, organometallic compounds of tin, mercury, or lead, alkali metal salts of carboxylic acids and phenols, and symmetrical triazine derivatives[4].

In the presence of a catalyst, the isocyanate / primary alcohol reaction follows second order kinetics[22]. However, the branching or crosslinking side reactions [equations (1.10) - (1.12)] and trimerisation become important at high conversions and, since they involve the isocyanate group, the kinetics move to higher orders, and the rate equation becomes more complicated[23].

Typical tertiary amine catalysts are N,N-dimethylaminoethanol, N,N-dimethylcyclohexylamine (catalyst SFC), and 1,4-diazo-[2,2,2]-bicyclo-octane (DABCO) [fig. (1.4)]:

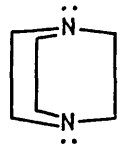


FIG. (1.4): DABCO

The mechanism of catalysis involves the donation of electrons from the tertiary nitrogen to the carbonyl of the isocyanate, thus forming a complex intermediate[4]. Increasing the strength of the base and the steric shielding of the nitrogen increases its catalytic activity[6]. The use of polar solvents can also increase the catalytic effect by stabilising the polarisation of the -NCO group.

Organometallic catalysts, such as stannous octoate, dibutyltin

dilaurate (DBTL), and phenyl mercuric propionate, form an intermediate complex with the isocyanate and the hydroxyl group of the diol[4]. Yilgor and McGrath[22] studied the effect of the catalysts DBTL, $SnCl_4.5H_2O$, $Zn(CH_3COO)_2.2H_2O$, and $Hg(CH_2COO)_2$ on the reaction between $H_{12}MDI$ with butanol in toluene at 100°C. All of the catalysts were effective, with DBTL having the highest efficiency. However, the selectivity for urethane formation, as opposed to side reactions, was best for the Hg and Sn salts (selective up to 90% conversion), whereas DBTL deviated at ~30% conversion and the Zn compound was not selective at all.

Hostettler and Cox[24] found that a combination of tin catalysts with tertiary amines led to a synergistic increase in catalytic effect. These mixtures are most commonly used in the production of polyurethane foams[6].

1.3 CHARACTERISATION OF POLYURETHANES

1.3.1 INTRODUCTION TO THE STRUCTURE OF POLYURETHANE ELASTOMERS

Polyurethane elastomers are block copolymers with a two-phase structure. Petrović et al.[20] considered that at a soft segment concentration of 20%, the soft phase was dispersed in the hard matrix. At a concentration of 40 - 60%, the material would consist of two phases with an interlocking structure. At greater soft segment concentrations, the arrangement would be such that the hard domain would be dispersed in the soft matrix.

There is much evidence of phase mixing of the hard and soft domains. Seymour et al.[25] estimated that 60% of the polyether - urethane N-H groups were H-bonded to the urethane carbonyls (urethane - hard block interactions). The rest were associated with the ether oxygens (urethane - soft block interactions).

Although the relevant contributions could not experimentally be

determined, it was expected that more polar polyesters would attain a higher percentage of the urethane H-bonds than polyethers.

Bonart et al.[26] considered the H-bonding within the hard segment, by comparing the heat distortion temperatures (HDTs) of polyurethanes based on MDI - BD and MDI - pentane diol hard block systems. On finding that the BD system was the more stable, they suggested that the hard-block consisted of a three-dimensional network of H-bonds, with transverse crosslinking of urethane groups in different directions. The lamellar arrangement of the hard block would give rise to the spherulite structure observed in semi-crystalline polyurethanes.

The following techniques can be used to characterise the structure, morphology and properties of elastomeric polyurethanes, as well as determining their molecular sequences within the molecules and their molecular weight distributions.

1.3.2 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

NMR spectroscopy is useful for determining the microstructure of polymers (e.g. the microtacticity of the sample) and their chemical composition. Although, theoretically, any nucleus with a spin of 1/2 can be monitored using NMR, the most popular nuclei are ^{1}H and ^{13}C.

For solution NMR, the concentration of the polymer in the solvent has to be kept low in order to keep its viscosity as low as possible. A high viscosity leads to line broadening.

For the NMR measurement of solid polymers, the method of analysis has to modified to accommodate for this line broadening effect. "Magic angle rotation" and pulse methods[27] have been developed, and so insoluble, crosslinked polymers can now be analysed.

Sumi et al.[28] were among the first to investigate polyurethane elastomers by solution ^{1}H-NMR. They found that the resonance signal

for the N-H of the urethane or urea groups could not be seen when non-polar solvents, such as CCl_4 or chloroform, were used. However, sharp signals were observed for polar solvents, such as dimethyl sulphoxide (DMSO), N,N-dimethylacetamide (DMA), acetone, or pyridine. The resonance signals for the N-H for allophanate and biuret groups were identifiable in any solvent.

Their explanation was that the relaxation effect of the ^{14}N quadrupole broadened the signal so that it was not observed in non-polar solvents. A polar solvent, however, would increase the N-H distance, thus weakening the influence of the N quadrupole.

Sumi and co-workers' results show that DMSO solutions of model compounds have chemical shifts for the N-H group of 5.70 - 8.58δ (urea), 8.60 - 9.70δ (urethane), 9.6 - 10.25δ (biuret), and 10.62 - 10.67δ (allophanate). Hence, performing proton NMR on a polyurethane sample gives an estimate of the extent of side reactions that may have occurred during its synthesis.

The ^{1}H-NMR spectrum of a polyurethane also shows strong resonances for the polyether or polyester from which it was prepared. These tend to have similar chemical shifts as the polyol homopolymer.

Despite its lack of sensitivity due to the low natural abundance of the isotope, ^{13}C-NMR is a very useful tool for elucidating the chemical structure of polymers. Complex splitting patterns due to neighbouring atoms can be removed, revealing a less complicated spectrum dependent mainly upon electron density for chemical shifts. However, for quantitative measurements, consideration has to be taken to allow for relaxation and the phenomenon known as the "Nuclear Overhauser Effect" (NOE), which affects line intensity.

Delides et al.[29] analysed certain monomers used for polyurethane synthesis, polyurethanes based on various polyesters, MDI, and BD, and

several urethane model compounds by ^{13}C-NMR. Using an extension of Grant and Paul's[30,31] additive scheme for predicting the chemical shifts of alkanes, the authors calculated the shifts for the C atoms in their compounds and compared these values to those found experimentally. Good correlation was found. Table (1.2) indicates some of their results which are relevant to the experimental work carried out for this project.

The authors also found that for polyester-urethanes, the chemical shift of the urethane carbonyl was different depending on whether it was as a result of the reaction between MDI and BD or MDI and the polyester glycol.

1.3.3 INFRARED (IR) SPECTROSCOPY

IR spectroscopy has a very important role in polyurethane elastomer characterisation. It can be used to follow chain-extension or crosslinking processes, as well as identifying the various groups within the polymer sample. Table (1.3) lists the wavelength and wavenumbers of the absorptions of several groups present in polyurethanes[6].

IR spectroscopy can also be used to determine the degree of ordering within the polyurethane sample. For example, Miller et al.[32] used FT-IR to investigate the degree of hard and soft segment interaction in polyurethanes, based on PTMEG, MDI, and BD, with varying hard segment length distributions. They found that the N-H group of the hard segment urethane (absorption region 3500 - 3200cm^{-1}) was virtually completely H-bonded for every sample, and that no free N-H absorption (~3420cm^{-1}) existed. As the hard segment content increased, the wavenumber of the H-bonded N-H absorption shifted to a higher value, corresponding to a higher energy.

The carbonyl absorption band was split into two peaks; C=O

TABLE (1.2): SUMMARY OF THE RESULTS OF THE WORK OF DELIDES ET AL.

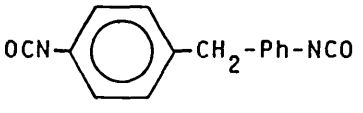
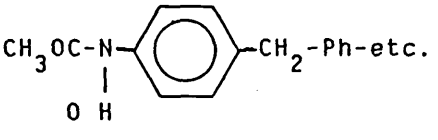
COMPOUND		^{13}C CHEMICAL SHIFTS (ppm) Predicted	Observed
BD	$HOCH_2CH_2CH_2CH_2OH$ 1 2	C_1 62.0 C_2 29.4	60.9 29.1
PTMEG	$HOCH_2CH_2CH_2CH_2(OCH_2CH_2CH_2CH_2)_nO(CH_2)_4OH$ 4 3 1 2	C_1 71.5 C_2 27.7 C_3 30.3 C_4 60.5	69.8 26.1 29.4 62.7
PEG	$HOCH_2CH_2O(CH_2CH_2O)_n(CH_2)_2OH$ 3 2 1	C_1 72.2 C_2 62.8 C_3 74.4	69.9 60.3 72.5
MDI	6 5 4 3 2 1 	C_1 43.3 C_2 141.1 C_3 128.9 C_4 124.5 C_5 130.8 C_6 -	40.69 138.2 129.8 124.7 131.5 124.7
MDI-dimethyl urethane 7 6 5 4 3 2 1		C_1 43.3 C_2 138.5 C_3 136.5 C_4 127.9 C_5 117.9 C_6 - C_7 -	41.9 137.10 135.5 128.7 118.3 153.6 51.6
BD-MDI	$-CH_2CH_2OCONH-$ 1 2	C_1 - C_2 -	25.5 63.8

TABLE (1.3): POLYURETHANE IR ABSORPTION WAVELENGTHS AND WAVENUMBERS

FUNCTIONAL GROUP	WAVELENGTH OF MOST INTENSE BAND (μm)	WAVENUMBER (cm^{-1})
-NCO	4.4	2273
-C=O (Uretidione)	5.61-5.63	1776-1783
-C=O (Isocyanurate)	5.85-5.92	1709-1689
-C=O (Urethane)	5.75 (Films & elastomers) 5.75-5.85 (Solutions)	1739-1700 1709-1739
-C=O (Urea)	5.9-6.1	1639-1695
-C=O (Allophanate & biuret)	5.71-5.85 6.85-7.06	1709-1751 1416-1460
NH (Amide II band)	6.5	1538
NH (Stretch)	3.0	3333
C-O (Aliphatic ether)	9.3	1075
C-O (Stretch &/or deformation)	8.1	1235
C=C (Skeletal stretch of benzene)	6.2	1613

involved in H-bonding was centred at $1700cm^{-1}$, and that corresponding to free C=O was at $1732cm^{-1}$. The fraction of bonded C=O, i.e. the fraction of hard domain, went up as the hard segment length increased. At the same time, more hard segments were introduced into the soft domain.

The authors also found that polyurethanes synthesised by the single step method had more phase separation than multi-step samples.

IR dichroism is used to study the orientation of particular chemical groups during deformation. Gibson et al.[33] describe the theory behind this technique. An example of its use for polyurethanes is the work of Allegrezza et al.[34]. Polyether-urethanes were synthesised with PTMEG as the soft segment and a hard segment of piperazine extended with the bischloroformate of BD. This gave a hard block incapable of forming H-bonds.

The samples were subjected to deformation. At all strains, the soft segment aligned itself with the direction of the stretch. When the load was removed, it relaxed to a random configuration. The hard segment, however, was aligned transverse to the stress direction at low strains, but re-orientated at high strains to lie in the same direction. After re-orientation, the hard segment relaxed very little on removal of the load.

It should be noted that polyurethanes with H-bonding had a lower hard segment re-orientation, due to the greater strength of inter-segment bonding.

1.3.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC, and similarly DTA, are very important thermo-analytical techniques for determining the thermal properties of polymers. They both involve measuring the amount of heat absorbed from or emitted to the surroundings by a polymer sample, compared to a reference. The

measurements can be taken at various time intervals for an isothermal run, or at various temperatures during a temperature program. This enables heat capacities, melting enthalpies, transition temperatures, and specific heats to be determined. Using this data, information on the phase transitions, melting and crystallisation processes, purity, decomposition, etc., for the polymer can be assessed.

Chapter four of reference (27) describes the experimental arrangement and general uses of DSC and DTA.

Polyurethane elastomers has been extensively studied by DSC, and references (7) and (33) give a review of recent literature. In general, three groups of transitions are observed; those at temperatures below -30°C, corresponding to the T_g of the soft segment, transitions in the region 80 - 150°C, and those above 160°C, corresponding to the collapse of the hard block H-bonding.

Seymour and Cooper[35], found that annealing a polyurethane elastomer caused the transition at 80°C to move towards higher temperatures, until it merged with those at 150°C and 160°C. Their explanation implies the existence of short and long range ordering within the hard blocks. As long as the temperature is below the T_g of the hard block, only the short range order is affected by annealing, hence the change in temperature of the transitions. However, H-bonding disruption occurs when the temperature is > T_g of the hard block. For a pure MDI / BD polymer, the T_g is 109°C[36].

Petrović et al.[17] studied the DSC data for a series of polyurethane elastomers based on PTMEG, MDI, and BD for various soft segment lengths and concentrations. They found that the soft segment concentration needed to be above ~50% to observe the T_g of the soft segment, that its value was independent of the concentration, but was affected by the chain length, following the relationship:

$$T_g = T_g^{\infty} - \frac{B}{M} \qquad (1.24)$$

where T_g and T_g^{∞} were those of the soft segment in the elastomer and at infinite molecular weight respectively, M was the elastomer's soft segment molecular weight, and B was a constant.

The authors found that soft segments of $\bar{M}_n$ 650 and 1000 did not crystallise, unlike the coresponding homopolymer of PTMEG. However, T_m was independent of soft segment concentration for PTMEG 2000, occurring at 15 - 20°C. This showed that complete phase separation existed.

The hard segment properties depended upon its concentration and length. T_m of the hard segment was observed for a soft segment concentration $\leqslant$ 60%. In some cases two endotherms were recorded. One of these may have been the decomposition of the urethane link at ~200°C.

1.3.5 DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

DMTA involves subjecting a polymer sample to a sinusoidally varying strain. The resulting stress is also sinusoidal and leads the strain by a phase angle, δ. This phase difference arises from the time required for molecular rearrangements to occur. The strain, ε^*, is related to the angular frequency, ω, and the maximum amplitude, ε_o, by the expression[33]:

$$\varepsilon^* = \varepsilon_o.\exp(i\omega t) \qquad (1.25)$$

The stress response, σ^*, is, therefore:

$$\sigma^* = \sigma_o.\exp(i\omega t + \delta) \qquad (1.26)$$

The stress / strain relationship becomes:

$$\sigma^* = E^*.\varepsilon^* = (E' + iE'').\varepsilon^* \qquad (1.27)$$

where E' is the storage modulus and is related to the elastic response component in phase with the oscillation, and E'' is the loss modulus and is the result of viscous flow component 90° out of phase. The complex modulus, E^* (= E' + E''), can be expressed as:

$$E^* = \frac{\sigma_o}{\varepsilon_o}.\exp(i\delta) \qquad (1.28)$$

The technique of DMTA involves measuring E', E'', $|E^*|$ (= σ_o/ε_o), or tan(δ) (= E''/E'), with ω and ε_o fixed and the temperature varying uniformly. Alternatively, the temperature can be held constant with ω varying.

Information provided gives details about T_m, T_g, phase separation, and mechanical properties of polymers. Temperature scans taken at various values of ω can give the activation energies of relaxation processes[33].

Many studies have been performed on polyurethane elastomers. Huh and Cooper[37] carried out DMTA measurements on H-bonded polyurethanes whilst Samuels et al.[38] and Ng et al.[39] worked with non-bonded polyurethanes. Petrović et al.[20] investigated the effect of soft segment concentration on polyurethane elastomers containing PTMEG as the polyol.

In general, it is found that a low temperature transition occurs which corresponds to the T_g of the amorphous soft segment. If the phase is relatively pure, the transition temperature is virtually equal to the T_g of the free homopolymer. Another transition is

observed at a high temperature, corresponding to the breaking down of the hard segment H-bonding. Secondary transitions are also observed at ~-125°C, especially in the tan(δ) curve, and are designated γ transitions. These indicate the onset of localised motion in the polyether $(CH_2)_x$ sequences.

For polyurethanes with a soft segment of $\bar{M}_n$ > 2000, melting transitions are observed at -21°C for the soft segment. The polyether T_g was lower for non-H-bonded polyurethanes compared to those with H-bonding of the same hard segment concentration.

Pechhold et al.[19] found that the values of E'' (the loss modulus) and tan(δ) in the service region were greater for a polyurethane based on PTMEG 1000 than for an equivalent one containing PTMEG 2000. For polyether polyols with narrow molecular weight distributions, E' was lower and E'' and tan(δ) were greater compared to those with broad distributions. This was probably due to the absence of low molecular weight oligomers.

As the degree of phase mixing increases, there is a decrease in the gradient of the curves for E' transitions, and the E'' peaks are broadened.

1.3.6 STRESS / STRAIN MEASUREMENTS AND IMPACT TESTS

A useful technique for determining the morphology and mechanical properties of elastomers is the constant strain rate, uniaxial tensile test. The method involves measuring the force induced as the sample is stretched at a constant rate of extension. Information is acquired of the initial modulus or stiffness, yield stress, ultimate strength, ultimate elongation, and capacity for strain energy dissipation[33,40].

If the experiment is run in a cyclic mode, the strain energy hysteresis and permanent elongation are monitored. Thus, data

concerning the stress transfer mechanisms in the microstructure, and the mechanical disruption and reorganisation of microdomains can be evaluated.

Figure (1.5) is the generalised tensile stress / strain curve for plastics[41].

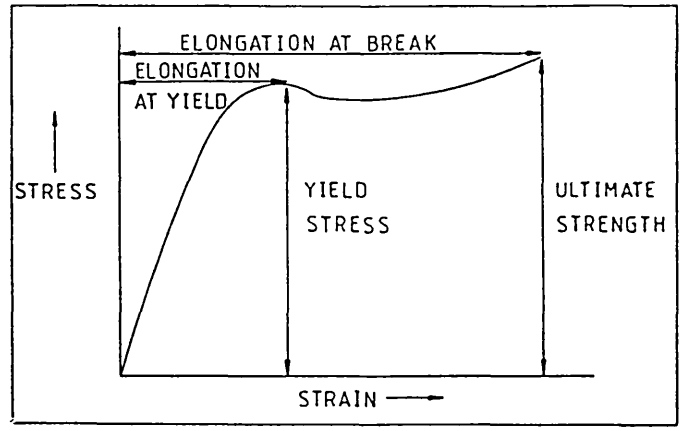


FIG. (1.5): TYPICAL TENSILE STRESS / STRAIN CURVE FOR POLYMERS

If a rectangular strip of polymer of length x_o and cross-sectional area A is subjected to a balanced pair of forces, F, such that its length changes to $x_o + \delta x$, where δx is small, the stress, σ (= F/A), follows Hooke's Law and is related to the resultant strain, ε (= $\delta x/x_o$), by the expression[42]:

$$\sigma = E.\varepsilon \qquad (1.29)$$

where E is Young's modulus.

Table (1.4) indicates the mechanical properties of various polymer types as shown by their stress / strain curves[41].

TABLE (1.4): FEATURES OF STRESS / STRAIN CURVES AS ASSOCIATED WITH POLYMER PROPERTIES

CHARACTERISTICS OF POLYMER	FEATURES OF STRESS / STRAIN CURVE			
	MODULUS	YIELD STRESS	ULTIMATE STRENGTH	ELONGATION AT BREAK
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Yield Stress	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

In some cases, Young's modulus cannot be determined, particularly for certain elastomers which show no Hookean region[43]. It is, therefore, convenient to define another parameter, the "secant modulus", which can be used as a measure of the stiffness of materials. Bendit[43] defines the secant modulus as that derived from the gradient of the straight line passing through the origin of the material's stress / strain curve and a point on the curve corresponding to a particular strain.

For segmented copolymers in general, the behaviour of a strained material is dependent upon the size and concentration of the hard segment domains and their resistance to plastic deformation, the ability of the segments to align themselves in the direction of the strain, and the susceptibility of the soft segment to crystallise whilst under strain[33].

Seymour et al.[44,45] studied samples of polyurethane of ~50% w/w hard segment content and a soft segment of molecular weight 2000 using the technique of IR dichroism. They found that the hard segments orientate transverse to the direction of stress, but realigned to lie parallel with it at higher strains. If the strain was fixed, this re-

orientation was time dependent, and the modulus decreased with increasing temperature.

For samples having the blocks lengths half of those above, the orientation of the hard segments was always parallel to the direction of the stress, and less relaxation was observed. Their explanation was that the shorter blocks led to less crystallinity, hence the domains were easier to deform and disrupt.

Section 1.3.3 describes the work of Allgrezza et al.[34], and their work using IR dichroism to investigate the effect of deforming polyurethanes with non-H-bonded hard segments.

The modulus of an elastomer is dependent upon the rigidity and morphology of the hard segment domains, whereas its elastoplastic properties at high strains are proportional to the domain restructuring ability, ductility, and the behaviour of the mixed hard and soft segment interfacial regions[33].

Fu and co-workers[46] studied three types of polyurethane elastomer based on PTMEG, the polyester-polyol polycaprolactone glycol (PCL), and polybutadiene glycol (PBD). The degree of interphase H-bonding due to the polyol was greater for the PCL-based polyurethane than for that based on PTMEG. The PBD-polyurethane contained no H-bonding.

Polyurethanes were synthesised with a range of hard block contents consisting of 2,4-TDI and BD, producing amorphous hard segments. They found that the PCL-polyurethanes had the best tensile strength and toughness because of the bonding within the soft segment and the possibility of strain induced crystallisation. Indeed, the T_gs of the hard segments were less than the T_m of the polyester soft segment.

The PTMEG-based polyurethanes showed good mechanical properties if the hard segment was at least five units long; i.e. greater phase separation and a higher T_g for the hard segment improved the values of

the modulus whilst retaining a large %-elongation.

PBD-polyurethanes showed poorer mechanical properties. However, induced crosslinking during moulding gave reasonable values for the moduli.

Petrović and co-workers'[20] tests on the effect of soft segment concentration and length on the mechanical properties of polyurethane elastomers showed that a concentration of 40-60% gave the best results. However, although materials with a soft segment concentration > 60% suffered from plastic flow at high extensions, their strength could be improved by introducing a few crosslinks with peroxides or excess isocyanate. The properties of samples having a soft segment concentration < 40% were improved by heating the materials.

There appeared to be no relation to strength and soft segment length. Elongation at break increased with larger soft segment concentrations, although necking and plastic flow affected those with > 60%.

Pechhold et al.[19] found that the modulus of PTMEG-based polyurethanes increased as the hard segment concentration increased. However, if the hard / soft segment ratio was kept constant, the modulus at 100% extension, and to some extent at 300% extension, increased with the molecular weight of the polyol in the sequence 650 < PTMEG1000 < 1800, probably due to increasing soft segment crystallisation. Polyurethanes containing PTMEG of a narrow molecular weight distribution had lower moduli, but greater elongation at break, than those with broad distributions.

Petrović and Ferguson[47] studied the properties of amine extended segmented polyurethanes. They found that the tensile strength decreased with a soft segment concentration > 50%, but the elongation at break increased continually as the amount of soft segment increased.

The impact test is a method of assessing the toughness or shock resistance of a particular material. There are two principal types of test: the pendulum impact test (Izod or Charpy test methods) and the "falling dart" technique.

The Izod or Charpy tests[4] allow a pendulum of known mass to fall through a known height and at its lowest point of swing strike a polymer specimen of known dimensions. The impact energy is then measured.

The "falling dart" technique allows a dart or Charpy striker to fall vertically through a known height set so that the striker hits the sample at known speed. The tip of the striker contains a piezoelectric crystal, and the small charge which develops on impact is measured. Values of tensile strength and elongations are ascertained.

1.3.7 GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC is a convenient method of determining the molecular weight distribution of a polymer. The experimental arrangement is very similar to that of HPLC, except that the mechanism of separation by the GPC column depends upon the molecular size of the polymer. The column is packed with a material containing many pores of varying sizes; small molecules can diffuse freely into the pores, but larger molecules are restricted. As a result the larger molecules elute first, followed by the smaller ones.

The column can be calibrated with monodisperse standards of a known molecular weight and a calibration curve can be produced. This can be used to calculate the molecular weight averages of other materials, but only with respect to the standards. Other techniques, such as colligative property measurements, light scattering, and viscosity methods, will lead to the evaluation of absolute molecular

weight averages.

GPC is also limited in that its separation depends on molecular size rather than weight. Hence, a comb shaped molecule would elute after a longer time interval because it is more compact than a linear molecule of the same molecular weight distribution.

GPC is useful, however, for checking the purity of polymers, since it will detect solvents and unreacted monomers, and for monitoring changes in the molecular weight distribution of polymers after certain reactions, e.g. grafting processes or degradation.

1.3.8 OTHER TECHNIQUES

Electron microscopy can be used to determine information about the domain structure of polyurethane elastomers. Koutsky et al.[48] were the first to examine polyether and polyester polyurethanes using transmission electron microscopy (TEM). After staining some of their samples with iodine, which preferentially attacked the aromatic sections of the hard segment, they found that the electron micrograph contained dark regions of size 30-100 Å in width for the polyester urethane and 50-100 Å for the polyether urethane.

TEM has also been used to study the spherulitic structure of polyurethanes[49].

Small angle x-ray diffraction (SAXS) can be used to investigate structural features ranging from 20-2000 Å in size. Usually 1.542 Å wavelength Cu-K_α x-rays are used. The technique involves probing the electron density distribution of the polymer, and the intensity of the scattered data gives information on the morphology of the material.

Wide angle x-ray diffraction (WAXD) can determine the degree of crystallinity in a polymer, the size of crystallites and their

orientation.

Small angle light scattering (SALS) investigates the morphological structures of 1000-100,000 Å in size. Therefore, it can be used to examine polyurethane spherulites.

Gibson et al.[33] review the recent literature concerning the techniques of SAXS, SALS, and WAXD, and their application to the determination of polyurethane elastomer structures.

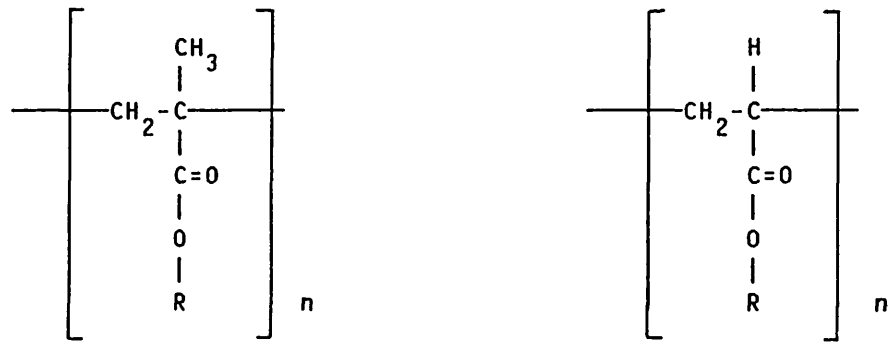
CHAPTER 2

GRAFT COPOLYMERS OF POLYURETHANES AND POLY(METHYL METHACRYLATE)

2.1 ACRYLIC AND METHACRYLIC POLYMERS

2.1.1 INTRODUCTION

For the purpose of this thesis, the acrylic polymers and copolymers considered will be those based upon the esters of acrylic and methacrylic acid, with particular emphasis towards methyl methacrylate (MMA) and its polymers. The general structures of these polymers are shown in fig. (2.1), where R is usually H, an aliphatic or aromatic group, or an ion:



POLY(METHACRYLATE) POLY(ACRYLATE)

FIG. (2.1): GENERAL STRUCTURE OF (METH)ACRYLIC POLYMERS

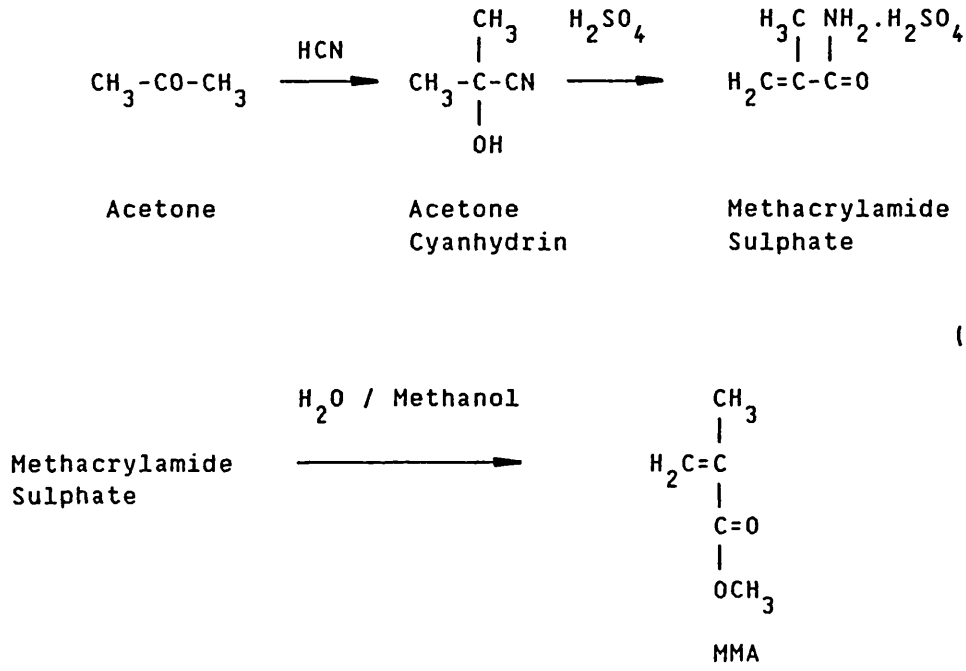
Acrylic and methacrylic polymers are used extensively in the field of protective coatings. Their properties which enable excellent coatings to be produced are high outdoor durability, water-white colour, clarity, resistance to discolouration at high temperatures, flexibility, toughness, resistance to chemical fumes, alkalis, acids, and water, high gloss and gloss retention, and low pigment reactivity[50].

The first (meth)acrylic polymer to be produced commercially was poly(methyl acrylate) by Rohm and Haas AG of Germany in 1927. It was Hill of ICI (UK) who initially prepared poly(methyl methacrylate),

(PMMA), in about 1930, and found it to be a potentially useful compound. However, the cost of the raw materials was prohibitive, and it was in 1932 that Crawford, also of ICI, developed a new, commercially feasible synthesis. Production began in 1934. One of the first applications of sheet PMMA was for the glazing of World War 2 aircraft[51].

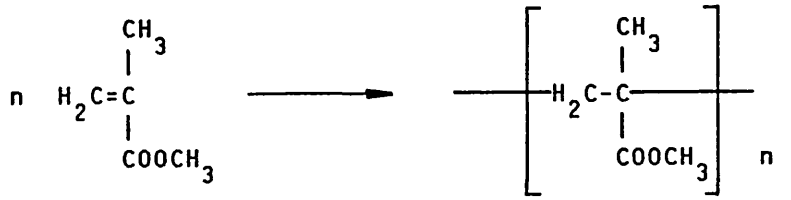
2.1.2 SYNTHESIS

MMA is synthesised from the product of the reaction between acetone and hydrogen cyanide. The acetone cyanhydrin formed is heated with sulphuric acid to form methacrylamide sulphate. This is then reacted without isolation with water and methanol to give the monomer[40,51].



MMA is a colourless liquid with a sweet, pungent odour and a boiling point of 100.5°C. Commercial MMA is usually inhibited for storage purposes.

The production of PMMA from MMA can be achieved by free-radical addition, anionic, or co-ordination polymerisation methods[40].



(2.2)

For commercial free-radical addition polymerisation, bulk, solution, suspension, and emulsion techniques are used[51].

2.1.2.1 BULK POLYMERISATION

Bulk polymerisation[51] of PMMA is used to produce polymer sheets. Initially a "syrup" is made, consisting of partially polymerised material (~20% degree of conversion), by stirring the monomer with, for example, benzoyl peroxide, (BPO), at 90°C for 10 minutes. The syrup is then cooled, and colourant, plasticizer, and UV absorber are added.

The liquid is then poured into a casting cell, consisting of two glass plates, separated by a rubber gasket, and held together by spring loaded clamps. As the polymerisation progresses, there is a shrinkage of volume of ~20%, which is compensated for by the clamps. The cell is then passed through a heating tunnel for 15 hours at 40°C, followed by 1 hour at 95°C. The sheet is then removed. The molecular weight of the PMMA is typically ~10^6.

A variation of this method is used for rod production. The syrup is poured into vertical aluminium tubes, and these are slowly lowered into a bath at 40°C. As the lower part polymerises, it contracts and the syrup above moves down the tube. Thus, homogeneous rods are produced.

2.1.2.2 SOLUTION POLYMERISATION

Solution polymerisation[51] is used for some surface coatings.

However, the solids content for paint applications is limited to 20 - 30% in order to keep the viscosity manageable.

Industrially, the polymerisation is carried out in either benzene, toluene, or a ketone, e.g. methyl ethyl ketone, (MEK). Azo or peroxide initiators are used (0.2 - 1% by weight of the monomer). The reaction is carried out at 90 - 110°C under a slight pressure. As the reaction tends to be vigorous, the monomer is added slowly over 1 - 4 hours. A wide molecular weight distribution is produced, with an average molecular weight of ~90,000. The final solution is used directly.

2.1.2.3 SUSPENSION POLYMERISATION

Suspension polymerisation[51] is used to produce injection moulding and extrusion grades of PMMA. It is usually carried out batch-wise in a reactor capable of withstanding pressures of 3 - 4 atmospheres.

A typical formulation is:

MMA	100 parts (w/w)
Water	200
Magnesium Carbonate	3 (Suspending agent)
Benzoyl Peroxide	0.2 (Initiator)

The reaction is carried out under nitrogen, and the mixture is heated to 80°C. Since the reaction is exothermic, the temperature usually rises to 120°C, and consequently the pressure increases. The process is complete after 1 hour. The suspension is then cooled and acidified with sulphuric acid to remove the suspending agent. The beads of polymer are then filtered, washed, and dried.

Molecular weights tend to be in the region of 60,000. The beads can be moulded, compounded with additives, extruded or granulated.

2.1.2.4 EMULSION POLYMERISATION

Emulsion polymerisation[51] can be used for the production of surface coatings. Stable dispersions, or latices, can have workable viscosities at solids contents of 50 - 60%. However, aqueous latices tend to produce water sensitive paints because they contain hydrophilic colloids or surfactants. Also, long drying times are required because of the high latent heat of vaporisation of water. Therefore, an "organosol" is used, where the PMMA is dispersed in a suitable organic liquid.

Polymer that has been prepared by conventional emulsion polymerisation cannot be used to create the dispersion as the coating produced would still contain hydrophilic species. Therefore, the organosol is prepared "in situ" and non-aqueous emulsion polymerisation is performed. This requires the use of hydrophobic surfactants, such as rubber-PMMA graft copolymers.

2.1.3 PROPERTIES OF POLY(METHACRYLATE)S

2.1.3.1 CLARITY

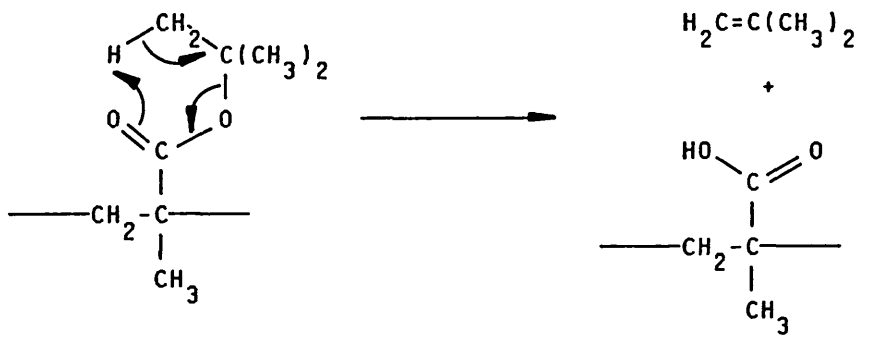
PMMA absorbs very little visible light. Only 4% reflection occurs at the polymer - air interface, and 92% of the normal incident light is transmitted through a sheet of the polymer[51].

2.1.3.2 STABILITY

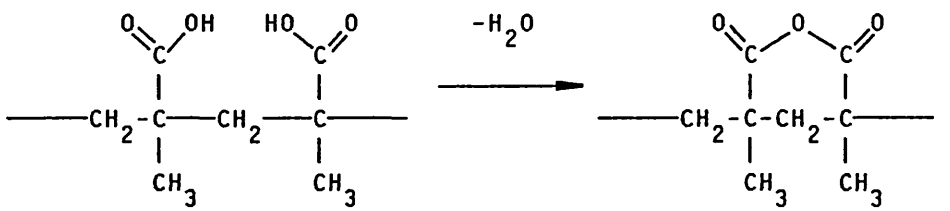
Poly(methacrylate)s tend to be very stable to UV light and oxygen, and are more resistant towards hydrolytic attack, compared to poly(acrylate)s, due to the absence of the tertiary hydrogen atom[50]. However, PMMA is attacked by dilute acids, such as hydrocyanic and hydrofluoric acids, and concentrated oxidising acids. PMMA can be converted into poly(sodium methacrylate) by using strong conditions only, such as molten sodium hydroxide[51].

Above 200°C, PMMA decomposes, and between 350 - 450°C, an "unzipping" reaction of the polymer backbone yields a virtually quantitative amount of monomer. However, poly(methacrylate)s of higher esters do not degrade totally to their monomers, and poorer yields are obtained as the length of the alkyl chain and the degree of branching increases[51].

For example, the decomposition of poly(tert-butyl methacrylate) involves ester decomposition to give polymethacrylic acid, which then loses water to form the anhydride:



(2.3)



(2.4)

The stability of PMMA can be increased by saturating the reactive ends of the polymer chains which have undergone termination by disproportionation[52].

2.1.3.3 SOLUBILITY

PMMA prepared by free-radical polymerisation is amorphous and is soluble in moderately H-bonded solvents such as ketones, esters, THF, unsymmetrical chlorinated hydrocarbons, and aromatic hydrocarbons. As the length of the alkyl ester group of the poly(methacrylate)s

increases, so does their ability to dissolve in aliphatic hydrocarbons, alcohols, and naphtha[50].

2.1.3.4 TENSILE STRENGTH AND TOUGHNESS

Klein[53] studied the effect of the alkyl side chain on the tensile strength and elongation of poly(methacrylate)s and poly(acrylate)s. The results are summarised in table 2.1.

TABLE (2.1): KLEIN'S RESULTS SHOWING THE EFFECT OF SIDE GROUP CHAIN LENGTH ON (METH)ACRYLATE POLYMER PROPERTIES.

POLYMER OF	TENSILE STRENGTH [Pa (psi)]	ELONGATION AT BREAK (%)
MMA	6.90×10^7 (10,000)	1
Ethyl methacrylate	3.72×10^7 (5,400)	25
n-Butyl methacrylate	3.45×10^6 (500)	300
Methyl acrylate	6.93×10^6 (1,005)	750
Ethyl acrylate	2.28×10^5 (33)	1,800
n-Butyl acrylate	2.07×10^4 (3)	2,000

In general, methacrylates tend to be harder and less flexible than acrylates. This is probably due to the presence of the methyl group at the α-carbon atom restricting the free rotation of the chains. Also, the polarisation of the methacrylate chains, also due to this methyl group, results in a closer packing of the chains, thus affecting the mechanical properties[50].

Increasing the alkyl side chain length also affects the mechanical properties. It has been found[50] that increasing the side chain length reduces the strength of the polymers. The effect has a linear dependence up to C_8 for poly(acrylate)s and C_{12} for

poly(methacrylate)s. Above these values, side chain crystallisation increases the polymers' hardness.

Branching within the alkyl side chain also increases the hardness and decreases the elongation of the polymers compared to their linear isomers. This is because the branched materials can pack more closely, and the bulkier groups hinder rotation of the polymer chains[51].

Abrasion and impact resistance of acrylic polymers depends upon the molecular weight of the material[50]. The higher the molecular weight, the greater the toughness and abrasion resistance of polymer films. However, after the molecular weight reaches a value of ~100,000 - 200,000 for amorphous polymers, little improvement occurs on further molecular weight increase.

2.1.3.5 THERMAL PROPERTIES

Edwards[54] showed how the number of carbon atoms in the alkyl chain affects the T_g of poly(acrylate)s and poly(methacrylate)s. The results are summarised in fig. (2.2).

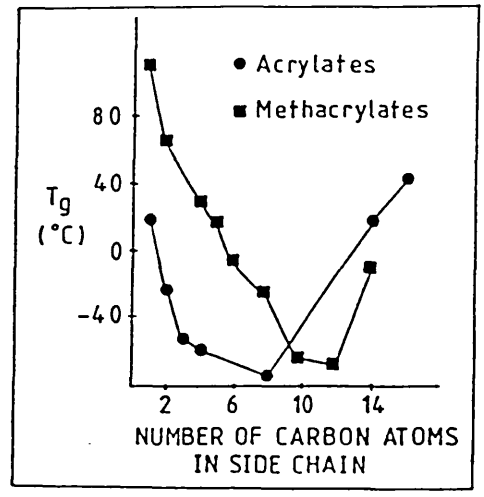


FIG. (2.2): T_gS OF LINEAR (METH)ACRYLIC HOMOPOLYMERS

Increasing the length of the side chain decreases the T_g of the

polymer because they are becoming more rubbery up to the point where crystallisation occurs.

For paints and coatings, the softening point (which is related to the T_g) is more important than the actual T_g. Table (2.2) shows the effect of branching of the alkyl side chain of poly(methacrylate)s on the softening point[55].

TABLE (2.2): INFLUENCE OF BRANCHING OF THE SIDE CHAIN ON THE SOFTENING POINTS OF POLY(METHACRYLATE) HOMOPOLYMERS

ALKYL GROUP	SOFTENING POINT (°C)
CH_3-	125
CH_3-CH_2-	65
CH_3-CH_2-CH_2-	38
CH_3-CH_2-CH_2-CH_2-	33
CH_3-CH(CH_3)-	95
CH_3-CH_2-CH(CH_3)-	62
CH_3-CH(CH_3)-CH_2-	70

Polymers with branched alkyl groups have higher softening points than their unbranched isomers due to their better packing and hindered rotation.

2.1.3.6 TACTICITY OF POLY(METHYL METHACRYLATE)

The configuation of PMMA can be syndiotactic, atactic, or isotactic. NMR can be used to determine the stereoregular configurations of a sequence of successive repeat units up to five units long[40].

The resonances of the methylene protons of PMMA can be analysed in order to determine the relative number of sequences of two monomer units (dyads) that have syndio (racemic, r) and iso (meso, m) configurations.

Monitoring the α-methyl proton resonance enables the determination of the relative numbers of 3-monomer sequences (triads) with mm, mr, and rr symmetry.

^{13}C-NMR enables the determination of the symmetry of tetrads and pentads (4- and 5-monomer units respectively).

This information can be used to estimate whether the probability, P_m, of adding the next monomer unit with the same configuration (meso) as the last one is independent of the configuration of the growing chain, and if so, to determine its value. For predominantly syndiotactic PMMA, P_m is 0.24[40].

2% solutions of isotactic and syndiotactic PMMA in chloroform were studied at 120°C by proton NMR[56]. The ester methyl group protons had resonances at 6.41τ (3.59δ) for all samples.

For the backbone methylene group it was found that for a syndiotactic sample, i.e. the adjacent unit had the opposite configuration to a particular unit, the protons were magnetically equivalent, and one resonance was observed at 8.18τ (1.82δ).

For an isotactic link, however, the two units had the same configuration and so magnetic symmetry was eliminated. The result of the spin-spin interactions gave a quadruplet consisting of two doublets centred at 7.83τ (2.17δ) and 8.46τ (1.54δ). A polymer containing a mixture of configurations would contain all of the resonances.

The α-methyl groups gave three separate resonances depending upon the two neighbouring units. For isotactic links either side of a particular unit (mm configuration), the resonance was at 8.80τ

(1.20δ). With an isotactic link on one side and a syndiotactic link on the other (mr configuration), the resonance appeared at 8.96τ (1.04δ). For syndiotactic links on both sides (rr configuration), the resonance was observed at 9.09τ (0.91δ). For a polymer predominantly isotactic, the resonance at 8.80τ would be the strongest, and for a predominantly syndiotactic sample, the resonance at 9.09τ would be the strongest.

^{13}C-NMR has the advantage that the proton-decoupled spectrum is less complex than the proton NMR spectrum, and the resonances of the various carbon atoms of PMMA in different configurations are well-defined. However, quantitative results are complicated by effects such as spin-relaxation and NOE. Although some reports believe that stereochemical environment will not affect the ^{13}C spin-relaxation times, Levy[57] has found that for poly(butyl methacrylate), the values of these relaxation times, for mr and rr configurations, can vary by ~50% for an individual polymer. Lyerla et al.[58] and Inoue et al.[59] found that for polymers with different overall tacticities, the variation was even greater.

Fox et al.[60] described the polymerisation and properties of several PMMA samples with different stereochemical arrangements. Hummel[61] summarises their work [table (2.3)].

TABLE (2.3): PROPERTIES OF POLY(METHYL METHACRYLATE)S POLYMERISED BY DIFFERENT METHODS

TYPE	T_g (°C)	M.Pt. (°C)	DENSITY AT 30°C (Amorphous) ($g.cm^{-3}$)	POLYMERISATION CONDITIONS	ASSUMED STRUCTURE
I	115	200	1.19	Free-radical at low temperature. Anionic in highly solvating media	Isotactic, crystallis-able
II	45	160	1.22	Organolithium compounds (anionic) in hydrocarbons	Syndiotactic, crystallis-able
III	60-95	170	1.20-1.22	Low temperature anionic in media of moderate solvating power for cations	Isotactic-syndiotactic block copolymer
Conven-tional	104	-	1.188	Radical catalysts at room temperature	Essentially random with a high degree of syndiotac-ticity

For free-radical polymerisation, the product is mainly syndiotactic, but the proportion of isotactic structure increases with increasing temperature of polymerisation[62,63].

For anionic polymerisation, the tacticity of the product depends upon the solvating power of the solvent used. The effect of solvent is assigned to the specific solvation (co-ordination) of ion pairs[64,65,66]. Contact-ion pairs tend to produce isotactic polymerisation, while ion pairs separated by solvent appear to favour syndiotactic polymers. Bolker[52] reviews the various mechanisms proposed which explain these phenomena.

Several authors have studied the stereochemical structures of various PMMA samples by means of IR spectroscopy.

Fox et al.[67] found large diferences in the 1065 and 750cm^{-1}

regions for the spectra of PMMA samples which had been polymerised under different conditions and were in crystalline and amorphous states.

Miller et al.[68] found that for the spectrum for a crystalline sample of PMMA, which was presumably isotactic, characteristic bands appeared at 955cm^{-1} and 755cm^{-1}. Also, several bands were missing that were normally present for a sample of conventional PMMA at 1063, 965, 913, 825, and 747cm^{-1}.

Baumann et al.[69] found that spectral bands near 1475, 1060, 965, 909, 824, and 806cm^{-1}, which were present in syndiotactic and conventional PMMAs, were missing for isotactic, the most obvious being the disappearance of the band at 1060cm^{-1}.

Korotov et al.[70] studied the spectrum of conventional and isotactic PMMA. They discovered that bands at 962 and 854cm^{-1}, that were characteristic for isotactic PMMA, were missing for the conventional PMMA.

The general concensus of opinion was that conventional PMMA had a predominantly syndiotactic structure.

Hummel and Busse[71] scanned the far IR spectra from 15μm - 24μm for syndiotactic and isotactic PMMA. They found that the band at 557cm^{-1} was stronger for the isotactic sample than the syndiotactic material. The maximum band for the syndiotactic sample was near to 552cm^{-1}. A doublet with maxima at ~506 and ~482cm^{-1} was also sensitive to tacticity. The band at 506cm^{-1} increased in size with the syndiotactic content of the polymer.

As can be seen from table (2.3), there is a variation in T_g between syndiotactic and isotactic PMMA. Shetter[72] discovered that the shorter the alkyl chain of the series of poly(methacrylate)s, the

greater the difference between the T_gs of the isotactic and syndiotactic forms. PMMA, therefore, shows the largest difference.

This variation in T_g is considered to be due to the difference in energy between the rotational isomers (trans, t, and gauche, g) of the polymer[73]. Yoon and Flory[74] calculated that the energy difference between the gt state and the tt state for PMMA was 7.1 kJ mol^{-1} (1.7kcal mol^{-1}) for a syndiotactic dyad, but only 4.6 kJ mol^{-1} (1.1kcal mol^{-1}) for an isotactic dyad. Hence, a syndiotactic PMMA sample has a larger T_g due to this larger energy difference. Bywater and Toporowski[75], however, argue that the higher T_g of syndiotactic PMMA is due to its higher rotational barriers, since the isotactic polymer is dynamically more flexible.

Fernandez-Martin et al.[76] performed DSC studies on monodisperse, heterotactic-like (containing a large proportion of heterotactic triads, mr) PMMA samples over a wide range of $\bar{M}_n$s. The use of monodisperse samples enabled the authors to extrapolate to T_g^{∞}, the value for infinite chain length. Their results indicate that the relevant T_gs for the various forms of PMMA are 314K for pure isotactic, 365K for atactic, and 398K for pure syndiotactic PMMA.

2.1.4 MODIFICATION AND CROSSLINKING OF ACRYLIC POLYMERS

2.1.4.1 COPOLYMERISATION

Acrylic monomers will readily copolymerise with each other and many other types of polymer. This has resulted in great commercial interest in acrylic copolymers for a wide variety of uses. By varying the amount of each component in the copolymer, the properties can be tailored for specific applications. For instance, Fox[77] proposed the following equation for calculating the T_g of a copolymer from the values of the homopolymers:

$$\frac{1}{T_{g(copolymer)}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \qquad (2.5)$$

where W_1 and W_2 are the weight fractions of each acrylic monomer in a copolymer, T_{g1} and T_{g2} are the glass transition temperatures of the relevant homopolymers. However, this is an oversimplification and several modifications have been proposed[50].

An important function of copolymerisation is for the internal plasticization of polymers for use as surface coatings. For example, copolymers having T_gs of 35 - 60°C have good reflow and hardness properties for thermosetting vehicle finishes. Thermoplasticity can be obtained by adding external plasticizers such as butyl benzyl phthalate, butyl phthalate, or dioctyl phthalate. However, migration of these plasticizers to the film surface can occur, and their evaporation ages the film. Hence, plasticization by copolymerisation alleviates this problem[50].

Copolymerising MMA and acrylates with methacrylic or acrylic acid increases the functionality of polymers used for surface coatings. Thus, the adhesion properties of the resin are greatly improved. However, there is an upper limit to the amount of functional monomer which can be used to ensure that the films retain their hydrophobic nature[50].

Styrene is frequently copolymerised with acrylic monomers to reduce cost and to contribute to the hardness and water, alkali, detergent, salt spray, humidity, and stain resistance of films. However, as the quantity of styrene increases, the flexibility, light stability, and gloss retention on outdoor exposure of the film decreases[50].

Incorporation of vinyl chloride polymers and copolymers can increase the flexibility and adhesion of acrylic resins[50]. Bazuin et al.[78] review acrylic resins modified by ionic compounds. The presence

of ionic groups improves the mechanical and bulk properties of the polymers due to the formation of ion aggregates in the molecules.

2.1.4.2 CROSSLINKING OF ACRYLIC RESINS

Thermosetting acrylic copolymers are usually terpolymers[51]. The first monomer provides the polymer with hardness and rigidity, the second monomer introduces flexibility, and the third provides pendent reactive groups which are sites for crosslinking. The inclusion of crosslinks increases the polymer's hardness and resistance to solvents, chemicals, and detergents. Solomon[79] lists the various functional monomers copolymerised with acrylic monomers in order to synthesise thermosetting acrylic resins [table (2.4)].

TABLE (2.4): FUNCTIONAL MONOMERS USED IN THE PREPARATION OF THERMOSETTING ACRYLIC COPOLYMERS

REACTIVE GROUP	MONOMER
Epoxide	Glycidyl (meth)acrylate Allyl-glycidyl ether
Amine	Dimethyl-amino-ethyl methacrylate Vinyl pyridine tert-Butyl-amino-ethyl methacrylate
Anhydride	Maleic anhydride Itaconic anhydride
Hydroxyl	Allyl alcohol, monoallyl ethers of polyols 2-Hydroxyethyl methacrylate (HEMA) Hydroxypropyl methacrylate Hydroxypropyl acrylate
Amide	(Meth)acrylamide Maleamide
Methylol amide & Alkyl ethers	N-Methylol (meth)acrylamide etc., & corresponding ethers
Isocyanate	Vinyl isocyanate Allyl isocyanate

Carboxylic groups can be inserted by the use of (meth)acrylic acids. However, itaconic acid is preferred as it imparts better

humidity resistance and adhesion properties[50].

The two most commonly used functions are the hydroxyl and carboxylic groups. The hydroxyl-type acrylics are crosslinked with amino resins, giving hard, rigid films with controlled flexibility. Carboxylic type acrylics are crosslinked with epoxy resins which impart greater flexibility and adhesion to metals than the hydroxyl-type. Table (2.5) lists the typical monomers used to prepare thermosetting acrylic resins, and their contribution to the final polymer's properties[80].

TABLE (2.5): TYPICAL MONOMERS USED IN THE PREPARATION OF THERMOSETTING ACRYLIC POLYMERS

MONOMER	INFLUENCE ON FILM PROPERTIES
MMA Styrene Vinyl toluene Acrylonitrile	Hardness
Ethyl Butyl 2-Ethyl-hexyl } (Meth)acrylates Butyl maleate	Flexibility
Acrylamide Butoxy-methacrylamide Hydroxy-alkylacrylates Glycidyl acrylates Acrylic acid	Crosslinks
(Meth)acrylic acid Maleic anhydride	Cure accelerator

2.1.4.3 GRAFT COPOLYMERISATION

Graft copolymerisation of acrylic polymers is used to improve the hardness and strength of materials such as rubber and cellulose, and at the same time, these materials impart their favourable qualities onto the acrylic resin. Graft copolymers are also used as interfacial agents between acrylic and, for example, rubber matrices, thus

improving the adhesion between the two phases. Griffith et al.[81,82] compared the toughness of two phase interpenetrating networks, consisting of a rubber and a polymer of a vinyl monomer, with and without the presence of grafted material. They found that samples prepared by grafting techniques were up to 3 times more efficient in promoting toughness than the same weight fraction of mechanically blended rubber.

As the aim of this research project was to graft PMMA with an elastomeric polyurethane, in order to improve the mechanical properties of the PMMA, a full account of the current literature concerning this type of grafted system will follow.

2.2 POLYURETHANE GRAFT COPOLYMERS

The combination of two or more polymeric species can generate a new material of enhanced properties. Physically blending two types of polymer has its limitations, particularly if microphase separation occurs within the blend due to the incompatiblity of its constituents. This reduces the strength of the blend. However, if the polymers are linked together by chemical bonds, phase separation is restricted, and the new material produced, referred to as a copolymer, will have a combination of the properties of its components.

Depending upon their basic structures, the copolymers can be defined as:

(A) Linear Block Copolymers

These are linear macromolecules containing two or more sequences of homopolymeric species. The general representation is shown in fig. (2.3):

```
--------AAAAAAAAAAAABBBBBBBBBBB-------BBBBBBBAAAAAAA-------
```

FIG. (2.3): GENERAL REPRESENTATION OF A LINEAR BLOCK COPOLYMER

where A and B are the constituent monomers.

(B) Grafted Block Copolymers

These are branched macromolecules with a "backbone" of one polymeric species to which several side chains of anothers polymeric material are attached [fig. (2.4)]:

```
--------AAAAAAAAAAAAAA--------------AAAAAAAAAAAA-------
             B                          B
             B                          B
             B                          B
             B                          B
             B                          B
             B                          B
             |                          |
             |                          |
             |                          |
```

FIG. (2.4): GENERAL REPRESENTATION OF A GRAFT COPOLYMER

A crosslinked 3-dimensional network structure can be formed if the terminal units of the side chains are attached to two individual polymer backbones [fig. (2.5)]:

```
                                        |
                                        |
                                        B
                                        B
                                        B
----------AAAAAAAAAAA---------AAAAAAAAAAA-----------
               B                 B
               B                 B
               |                 |
               |                 |
               B                 B
               B                 B
-----------AAAAAAAAAAAAA-------AAAAAAAAAAAAA----------
                     B
                     B
                     B
                     |
                     |
```

FIG. (2.5): GENERAL REPRESENTATION OF A CROSSLINKED POLYMER

(C) Interpenetrating Networks (IPNs)

IPNs are special types of polymer blends whose structures consist of two crosslinked polymers which are entangled, and hence have a fixed arrangement. There are two methods of synthesing IPNs. The two-shot method involves swelling one network with the components of the second, which are polymerised and crosslinked in situ. For the one-shot process all of the monomers are mixed together and the two networks are formed simultaneously. The latter method of preparation implies that the two networks are polymerised by different modes of polymerisation, e.g. addition and step-growth, otherwise the IPN system would be complicated by side reactions[83].

As mentioned previously, the aim of this research project was to produce graft copolymers of elastomeric polyurethanes and MMA. The following section discusses the various ways of synthesising graft copolymers in general. Where possible, examples of the application of these methods will be quoted from the current literature concerning

the production of polyurethane graft copolymers. This will be followed by a description of the methods of separating graft copolymers from their starting materials and side products and a discussion about the uses of the final products.

2.2.1 METHODS OF SYNTHESISING GRAFT COPOLYMERS

2.2.1.1 TRANSFER TO POLYMER[84,85]

The abstraction of a labile atom by growing radicals during the free-radically initiated polymerisation of an unsaturated monomer has been well documented. The process is known as a chain transfer reaction, and can occur between the growing chains and the initiator, monomer, solvent, polymer, or another growing chain. The propagating chain thus terminates and a new radical is formed simultaneously. The transfer constant, C_s, is defined as:

$$C_s = \frac{k_{tr}}{k_p} \qquad (2.6)$$

where k_{tr} and k_p are the rate constants for chain transfer and propagation respectively.

For the synthesis of graft copolymers, chain transfer with the polymer is the important step. Consider the polymerisation of the monomer M in the presence of the polymer -P-P-P-P-. Abstraction of a labile hydrogen or halogen atom, X, from the polymer by the growing radical generates a new macroradical. Monomer addition to this radical produces the graft copolymer. If the initiator is represented as I-I, the reaction scheme is:

$$\mathrm{I\text{-}I} \longrightarrow 2\mathrm{I}^{\bullet} \qquad (2.7)$$

$$\mathrm{I}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{I\text{-}M}^{\bullet} \qquad (2.8)$$

$$\mathrm{I\text{-}M}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{I\text{-}M\text{-}M}^{\bullet} \quad \text{etc.}$$

$$\mathrm{I\text{-}M\text{-}(M)_n\text{-}M}^{\bullet} + \text{-P-P-P-P-} \longrightarrow \mathrm{I\text{-}M\text{-}(M)_n\text{-}M\text{-}X} + \text{-P-P-P-P-}^{\bullet} \qquad (2.9)$$

$$\text{-P-}\underset{\bullet}{\mathrm{P}}\text{-P-P-} + \mathrm{M} \longrightarrow \text{-P-P-P-P-}\underset{\mathrm{M}^{\bullet}}{|} \qquad (2.10)$$

$$\text{-P-P-P-P-}\underset{\mathrm{M}^{\bullet}}{|} + \mathrm{M} \longrightarrow \text{-P-P-P-P-}\underset{\mathrm{M}\underset{\mathrm{M}^{\bullet}}{|}}{|} \quad \text{etc.}$$

Alternatively, the initiator radical could undergo a transfer reaction directly with the polymer producing the same macroradical:

$$\mathrm{I}^{\bullet} + \text{-P-P-P-P-} \longrightarrow \mathrm{I\text{-}X} + \text{-P-}\underset{\bullet}{\mathrm{P}}\text{-P-P-} \qquad (2.11)$$

This mode of synthesis of graft copolymers was first suggested by Flory[86]. For efficient initiation of grafting, the polymer has to successfully compete for the radicals with the other species present.

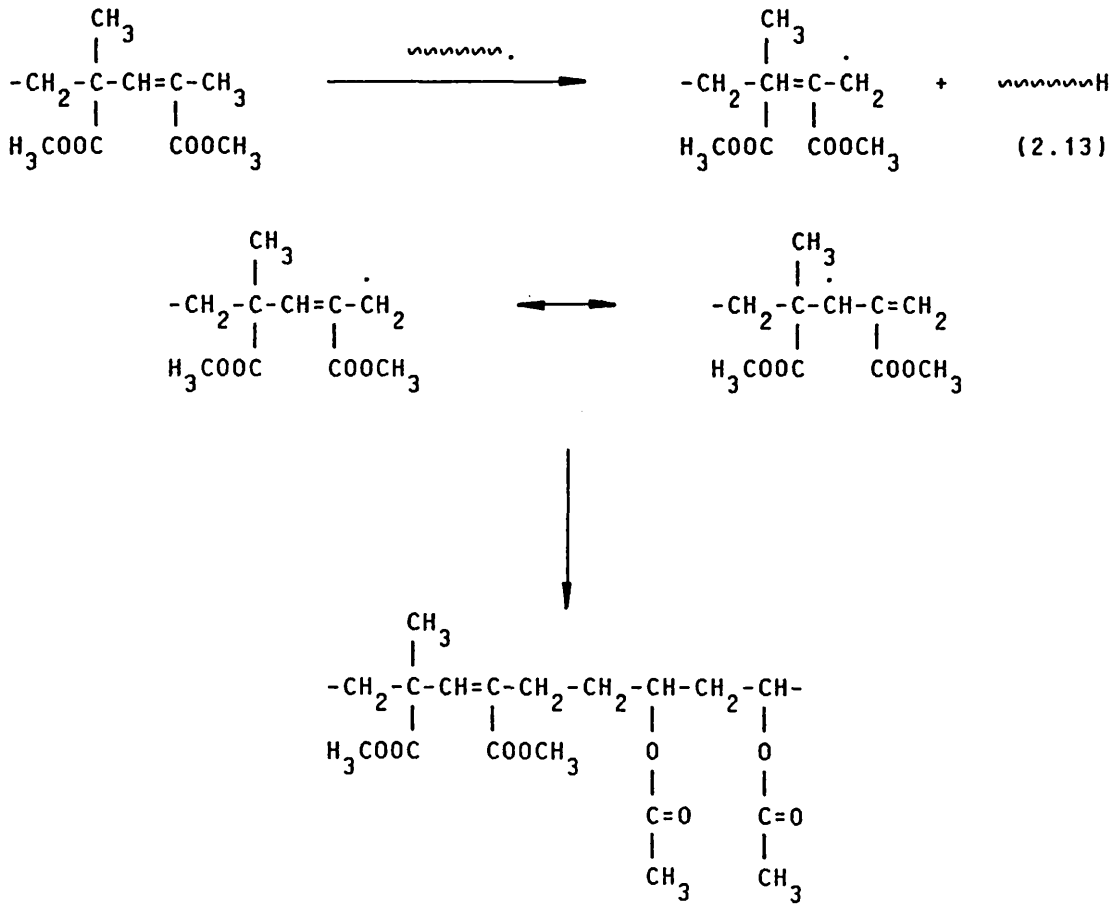
The transfer of radicals between the initiator fragments and the polymer give rise to a phenomenon called the "initiator effect". It has been shown that the grafting efficiency, defined as:

$$\text{Grafting Efficiency} = \frac{\text{Weight of Grafted Monomer}}{\text{Weight of Grafted Monomer} + \text{Weight of Homopolymer}} \qquad (2.12)$$

can be greatly affected by the initiator used. For example, Smets et al.[87] showed that the polymerisation of MMA in the presence polystyrene (PS) yielded appreciable amounts of graft copolymer if benzoyl peroxide (BPO) was used as the initiator. However, using azo-iso-butyronitrile (AIBN) or di-tert-butyl peroxide as the initiator

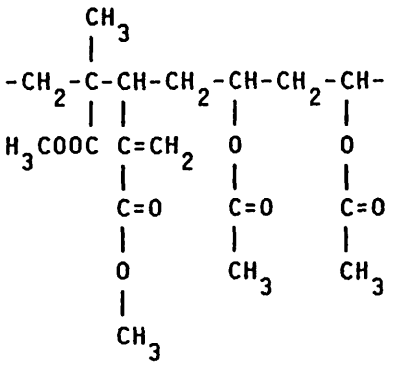
reduced the amount of grafting to insignificant quantities. The grafting of vinyl acetate onto PMMA was independent of the nature of the initiator[87].

Chain termination by disproportionation plays an important role in the polymerisation of PMMA (as demonstrated by Bevington et al.[88,89] using ^{14}C-labelled initiators). The unsaturated terminal groups produced are sensitive to radical attack due to their allylic structure and the presence of the labile H atoms in the α-positions with respect to the double bonds. This is illustrated by the polymerisation of vinyl acetate in the presence of disproportionated PMMA[84].



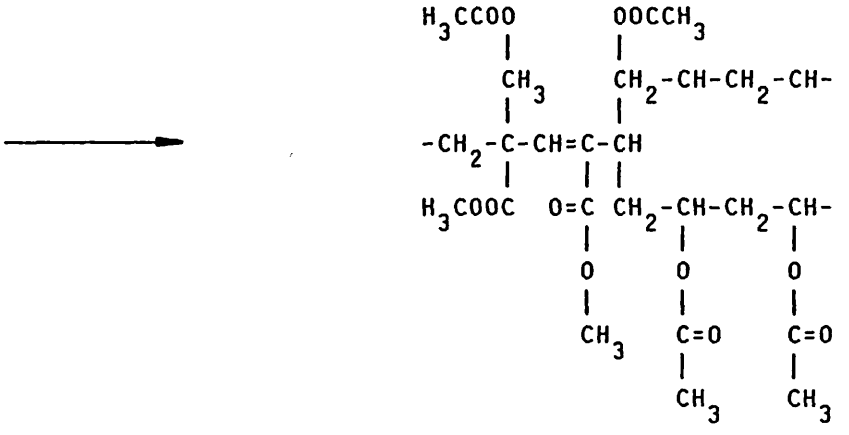
(2.13)

or



(2.14)

This forms a block copolymer which can be transformed into a graft copolymer by the repetition of the reaction mechanism.



(2.15)

Grafting to polymers by the transfer mechanism has been frequently used to graft vinylic or acrylic monomers to natural rubber[90] and chlorinated rubber. Anbazhagan et al.[91,92] grafted chlorinated rubber (Chlorub-40) with ethyl acrylate, n-butyl methacrylate (BMA), and 2-hydroxyethyl methacrylate (HEMA), using BPO as the initiator. An isocyanate terminated polyurethane was then synthesised based on a castor oil-PPG prepolymer (molecular weight 2000) and TDI. The polyurethane and the grafted chlorinated rubber (which contained -OH groups in the grafts due to the presence of the HEMA units) were mixed together to form a crosslinked network.

The preparations of polyurethane graft copolymers using the transfer to polymer method have mainly involved the modification of

the soft segment of the polyurethane elastomer. The dihydroxy prepolymer usually undergoes grafting prior to its reaction with the diisocyanate.

Kuryla et al.[93] reported the polymerisation of vinyl monomers in the presence of excess polyether using AIBN and BPO as the initiators. They found that they achieved large percentages of grafted species, but they do not quote any values. The isolated products of the AIBN and BPO polymerisations had similar properties, and there was no evidence of the initiator effect.

Allen et al.[94], however, investigated the effect of polymerising MMA, using AIBN as the initiator, in the presence of PPG (m.w. 2000) and a model urethane compound consisting of the product of the reaction between MDI and PPG. They found no evidence of grafting.

Morimoto et al.[95] synthesised a polyurethane prepolymer from PTMEG (m.w. 1280) and MDI. 40 parts of this prepolymer were mixed with 42 parts of acrylonitrile (ACN), methyl acrylate (8 parts), and n-octyl mercaptan (0.8 parts), and were suspension polymerised for 5h at 70°C with lauroyl peroxide (1 part) and poly(vinyl alcohol) (0.3 parts). This process formed an ACN-MDI-methyl acrylate-PTMEG graft copolymer.

Kuriyama et al.[96] treated PPG (m.w. 4000) with BMA in the presence of AIBN. Isophorone diisocyanate and γ-isocyanatopropyl-triethoxysilane were added to produce a silicone modified polyurethane.

Another example of preparing grafted polyethers for polyurethane synthesis is the work of Katayama et al.[97]. Propylan 333 and N,N-dimethyl aniline were treated with a solution of BPO and ACN, and polymerised for 5h to give a grafted polyether-polyol which had a lower discolouration than that prepared in the presence of BPO or AIBN alone. The polyol was then used to synthesise a polyurethane based on

HDI.

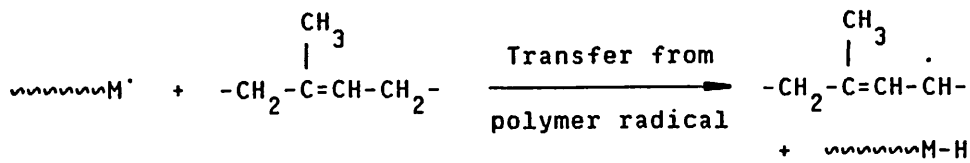
2.2.1.2 RADICAL ATTACK ON UNSATURATED POLYMERS

The addition of a growing polymer radical to unsaturated groups in a different polymer is another method of producing graft copolymers. Prepolymers containing unsaturated terminal groups will be discussed in section (2.2.1.3) concerning macromonomers. This section refers to unsaturated functions that are dispersed along the polymer chains. The free-radical polymerisation of a vinyl monomer in the presence of an unsaturated polymer is probably one of the easiest synthetic methods of producing graft copolymers. The disadvantage is that large amounts of homopolymer can also be formed.

Many investigations have utilised the unsaturation present in natural rubber. A study of twenty natural rubber samples of Standard Malaysian Grades indicated the presence of 0.1 to 1.1% unsaturation in the form of pendent vinyl groups[90]. A radical site on a backbone molecule can be formed by the abstractive or additive attack of an initiator radical, $I^{\cdot}$, on the double bond, or by chain transfer from a growing polymer radical[98].

$$I^{\cdot} + -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2- \xrightarrow{\text{Addition}} -CH_2-\underset{\underset{I\cdot}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH-CH_2- \qquad (2.16)$$

$$\xrightarrow{\text{Abstraction}} -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\overset{\cdot}{CH}- + I-H \qquad (2.17)$$



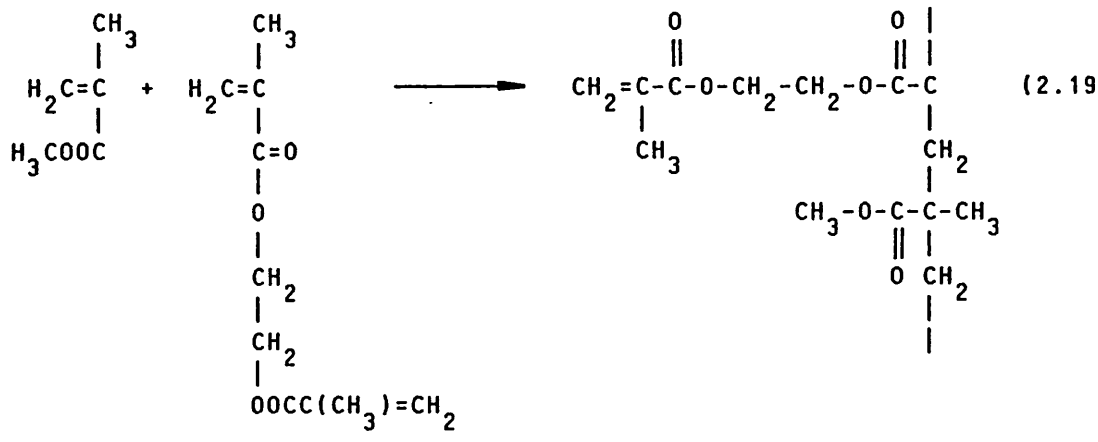
(2.18)

The graft copolymerisation of rubber is greatly influenced by the initiator effect. Initiators such as BPO produce radicals which have a strong tendency to abstract H atoms, and hence have high grafting efficiencies. AIBN, however, generates the relatively weak H-abstracting 2-cyanoisopropyl radical[99] and yields mainly homopolymer[98].

It is unlikely that the chain transfer from a growing polymer radical would occur because of the low reactivity of 1,2-disubstituted ethylenes in radical polymerisation[98]. Addition reactions also need favourable orientation of the double bond and, therefore, require the correct configuration of the polymer chain[100]. H-abstraction yields a resonance stabilised allylic radical, hence energetic considerations tend to favour this mechanism.

Polybutadiene behaves in a similar fashion to natural rubber in that the nature of the initiator affects the grafting efficiency. BPO[101] and dicumyl peroxide[102] have higher grafting yields than AIBN[101].

Smets et al.[103] copolymerised MMA with small amounts of ethylene dimethacrylate to a low degree of conversion. This produced a macromonomer with a unsaturated group within the molecule.



(2.19)

The molecule was then copolymerised with ethyl acrylate or styrene.The major disadvantage of this method of synthesis of large unsaturated molecules is that crosslinking can be a side reaction.

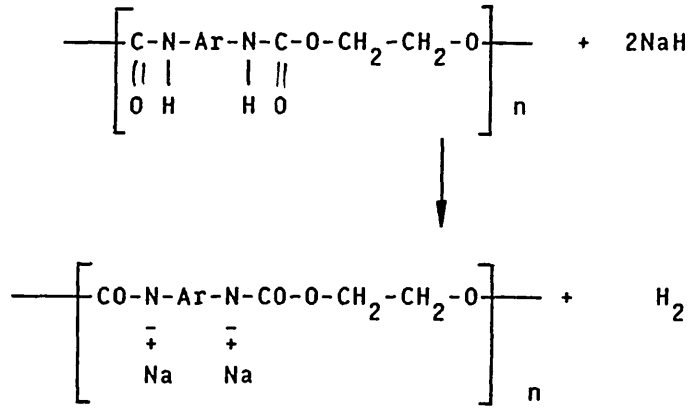
The introduction of radically reactive unsaturated groups into polyurethanes has been carried out by various workers. Egboh et al.[104-107] studied the grafting of various monomers onto segmented polyurethane elastomers based on either PPG or PEG, MDI, BD, and cis-2-butene-1,4-diol (BDU). They found that when grafting acrylamide (AM), methacrylonitrile (MACN), and MMA onto the unsaturated polyurethane, the graft yield was proportional to the monomer concentration and the reaction time. Using AIBN as the initiator gave relatively higher graft yields than BPO for AM, whereas the reverse was true for MMA and MACN.

The self-initiated grafting of methacrylamide (MAM) onto the unsaturated polyurethane formed insoluble gels at high conversions[105]. The grafting of N-vinyl pyrrolidone (NVP) onto the polyurethane was successful when using AIBN as the initiator, but was unsuccessful when using BPO[107]. It was found that the percentage grafting rose with increasing initiator concentration up to 40mmol dm^{-3}. At higher concentrations, the percentage grafting decreased.

Gujral[108] studied the grafting of HEMA and ACN onto unsaturated polyurethanes based on PPG, PEG, or PTMEG and MDI, BD, and BDU. BPO and AIBN were used as initiators, and the polymerisations were carried out at 70°C in DMF. Gujral found that poly(urethane-g-ACN) could not be completely separated from its reaction side-products (i.e. unreacted polyurethane and PACN homopolymer).

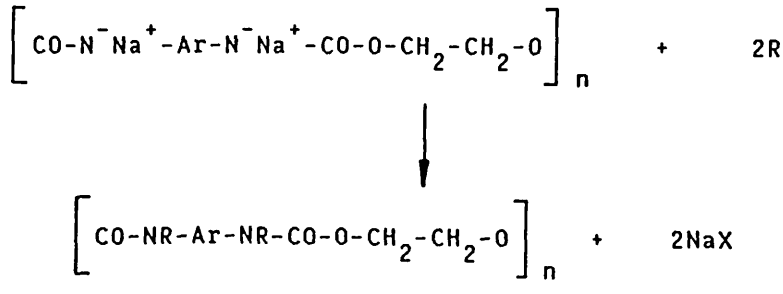
Davison[109] incorporated the diol erythrol (but-1-ene-3,4-diol, $H_2C{=}CHCH(OH)CH_2OH$) into a polyurethane based on MDI and BD, thus producing an unsaturated polymer with pendent alkene groups. The polyurethane was grafted with acrylic acid (AA) to give poly(urethane-g-AA).

Beachell et al.[110,111] prepared two types of polyurethane based on ED and either TDI or MDI. Unsaturation was introduced into the polyurethanes by nitrogen substitution. The urethane protons were removed first by sodium hydride, a strong base.



(2.20)

An alkyl halide was then added to form a N-substituted polymer:



(2.21)

By using the halides of compounds such as bromoethyl acrylate or acryloyl chloride, pendent unsaturated groups were introduced into the polyurethane molecule. Methyl acrylate, MMA, and styrene were then grafted to the polyurethanes by free-radical initiation using BPO. Although monomer conversions were kept low deliberately in order to prevent crosslinking, conversions from 50 - 70% were achieved without gelation.

Hitachi Ltd.[112] patented a polyurethane system which involved the incorporation of ACN-grafted hydroxy terminated 1,4-polybutadiene into the soft segment of the polyurethane. The polyol was grafted prior to use and was mixed with PPG-trimethylolpropane ether, ungrafted 1,4-polybutadiene, Cl_3CF, siloxane, triethylene diamine, and MDI to form the final product.

Toyoda Gosei Co. Ltd.[113] produced a polyurethane based on BDU, BD, MDI, and poly(butylene adipate). The polyurethane was grafted with ethyl methacrylate and MMA.

Kuriyama et al.[114] synthesised a polyurethane based upon PTMEG, poly(ethylene itaconate), and MDI. The polymer was grafted with octyl acrylate using BPO as the initiator.

Takai[115] prepared a polyurethane from a mixture of adipic acid, BD, and itaconic acid (in the ratio 2920 : 2160 : 292), ED, and MDI. The polyurethane was grafted with MMA, ethyl acrylate, and dimethylaminoethyl methacrylate, thus forming a grafted polyurethane system containing quaternary ammonium groups.

2.2.1.3 GRAFT COPOLYMERISATION BY THE USE OF MACROMONOMERS

A macromonomer (macromolecular monomer) is a polymer which has been synthesised such that it contains a terminal unit of unsaturation which can undergo addition-type copolymerisation with a vinylic or acrylic monomer. The copolymerisation reaction generates a graft copolymer, with the macromonomer molecules incorporated constituting the grafts. The importance of macromonomers has only recently been recognised. The majority of uses, particularly for polyurethanes, have been for the production of crosslinked networks by the use of αω-unsaturated macromonomers. However, the intention of this literature survey is to describe the research into the use of these polymers for grafting purposes only.

The numerous methods of synthesising macromonomers have been extensively reviewed[116,117], together with the kinetics of their homopolymerisation and copolymerisation reactions[118]. The following discussion is a summary of the more important techniques.

(A) SYNTHESIS OF MACROMONOMERS BY MEANS OF ANIONIC POLYMERISATION

The direct methods of synthesising macromonomers through anionic polymerisation include:

(i) The use of an usaturated organometallic initiator. For example, Waack et al.[119-121] prepared an organolithium compound, vinyl lithium, by the exchange reaction between tetravinylzinc and butyl lithium:

$$(H_2C{=}CH)_4Zn \quad + \quad 4BuLi \longrightarrow 4H_2C{=}CHLi \quad + \quad Bu_4Zn \qquad (2.22)$$

The initiator formed could be used to prepare PS and other anionically polymerised materials. The drawback was that the allylic double bond introduced at the end of the polymer molecules had a low

reactivity towards radicals, and so copolymerisation of these macromonomers was difficult.

(ii) Using the reactivity of the active site at the end of the polymer chains (after initiation by an organometallic compound) when the polymerisation is complete. If an unsaturated electrophile is added to deactivate the "living polymer", a reactive group can be introduced into the molecule. For example, PMMA that has been initiated by BuLi can be deactivated by $BrCH_2CH{=}CH_2$ (allyl bromide)[122].

The indirect methods of macromonomer synthesis by anionic polymerisation involve:

(iii) Deactivating the living polymer with a compound that is capable of undergoing further reaction with other materials in order to form the macromonomer.

For example, Quirk et al.[123] found that styryl carbanions react with CO_2 to give carboxy end groups which can further react with other compounds.

(iv) Double bond formation by spontaneous deactivation.

For example, living PS anions, with sodium cations, that are kept for long periods or are heated to around 60°C undergo a colour change[117]. This is caused by the elimination of NaH from the active sites[124]. A double bond is produced at the end of the polymer.

(B) SYNTHESIS OF MACROMONOMERS BY MEANS OF CATIONIC POLYMERISATION

Macromonomers of heterocyclic monomers, e.g. THF, can be produced by:

(i) Initiation by an unsaturated compound.

For example, it has been proposed that 3-phenylallyl bromide can be reacted with $AgSbF_6$ in THF solution, to produce a poly-THF macromonomer with a terminal styryl unit[125]:

$$\longrightarrow \quad Ph\text{-}CH{=}CH\text{-}CH_2\text{-}(\text{-}O(CH_2)_4\text{-})_n\text{-}O\text{-}Ph \qquad (2.23)$$

(ii) The end-capping of the living polymer chains using an unsaturated nucleophile.

Asami et al.[126] used p-vinyl phenoxide to deactivate the THF polymerisation which had been initiated by triethyloxonium tetrafluoroborate.

(iii) Cationic transfer reactions.

Katz and Zewi[127] synthesised difunctional poly(dimethylsiloxane), (PDMS), by means of a cationic process. The cyclic tetramer of PDMS was polymerised in the presence of a disiloxane containing carboxy groups. This compound acted as a transfer agent and the polymer was terminated with carboxylic groups at both ends. Reaction of these acid groups with HEMA gave the di-unsaturated product.

(iv) The polymerisation of vinylic monomers by the "inifer"-type method.

Kennedy et al.[128-131] devised a way of producing ω-functional macromonomers of vinyl monomers. An initiator system consisted of, for example, an allyl or benzyl halide with boron trichloride, BCl_3. This readily initiated the polymerisation of monomers such as iso-butene or α-methylstyrene. The reaction scheme proposed is as follows:

$$RCl + BCl_3 \rightleftharpoons [R^+BCl_4^-] \quad \text{Complex formation} \quad (2.24)$$

$$[R^+BCl_4^-] + CH_2{=}C\!\!\begin{smallmatrix}/\\ \backslash\end{smallmatrix} \longrightarrow R\text{-}CH_2\text{-}\overset{|}{\underset{|}{C}}{}^+BCl_4^- \quad \text{Initiation} \quad (2.25)$$

$$\sim\!\sim\!\sim CH_2\text{-}\overset{|}{\underset{|}{C}}{}^+BCl_4^- + H_2C{=}C\!\!\begin{smallmatrix}/\\ \backslash\end{smallmatrix} \longrightarrow \sim\!\sim\!\sim CH_2\text{-}\overset{|}{\underset{|}{C}}{}^+BCl_4^-$$

$$\text{Propagation} \quad (2.26)$$

$$\sim\!\sim\!\sim CH_2\text{-}\overset{|}{\underset{|}{C}}{}^+BCl_4^- \longrightarrow \sim\!\sim\!\sim CH_2\text{-}\overset{|}{\underset{|}{C}}\text{-}Cl + BCl_3$$

$$\text{Anion splitting} \quad (2.27)$$

$$\sim\!\sim\!\sim CH_2\text{-}\overset{|}{\underset{|}{C}}{}^+BCl_4^- + RCl \longrightarrow \sim\!\sim\!\sim CH_2\text{-}\overset{|}{\underset{|}{C}}\text{-}Cl + [R^+BCl_4^-]$$

$$\text{Transfer to RCl} \quad (2.28)$$

RCl is acting as an initiator and a transfer agent, hence the process is termed "inifer".

(C) SYNTHESIS OF MACROMONOMERS BY MEANS OF FREE-RADICAL POLYMERISATION

Synthesis of macromonomers by means of free-radical polymerisation can be achieved by several methods:

(i) By using a functional initiator.

The primary radical formed on the homolytic fission of an initiator molecule adds to a monomer on initiation. If the initiator contains a reactive group, the final polymer would be terminated by this function. However, this method of synthesising macromonomers relies upon several conditions. The termination of the polymer has to occur by disproportionation, as opposed to combination, so as to ensure that the polymer is not end-capped at both ends with the functional group. Also, transfer reactions to the monomer or solvent

have to be negligible, otherwise the macromonomer molecules would not contain the maximum number of functional groups.

Examples of functional initiators are azo-bis-4-cyanovaleric acid (ACV) and azo-bis-4-cyanopentanol (ACP).

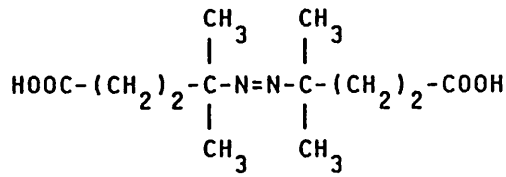


FIG. (2.6): ACV

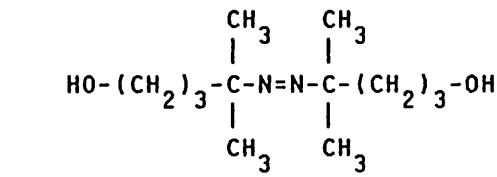


FIG. (2.7): ACP

Brosse et al.[132,133] produced αω-dihydroxy polybutadiene by using hydrogen peroxide as the initiator.

(ii) By using a functional transfer agent.

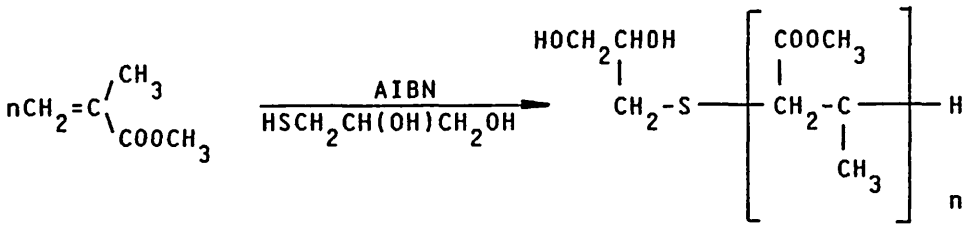
Transfer agents are usually used in free-radical polymerisations to control the molecular weight of the polymer formed. If an efficient transfer agent is used with a large transfer constant, functional of one chain end can be achieved.

2-Mercaptoethanol, $HS-CH_2-CH_2-OH$, has been used as a transfer agent during the polymerisation of MMA[134]. The polymer molecules produced were terminated at one end with an hydroxyl group, which was reacted with methacryloyl chloride to convert it to an unsaturated group.

Thioglycolic acid, $HS-CH_2-COOH$, has been used as a transfer agent

for the polymerisation of monomers such as MMA, styrene, and stearyl methacrylate[117]. The polymer formed is terminated with a carboxylic acid group which can be reacted with glycidyl methacrylate to introduce unsaturation.

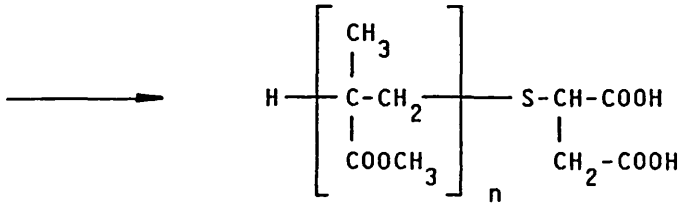
Chujo et al.[135] free-radically polymerised MMA in the presence of α-thioglycerol. This produced a polymer which was terminated at one end with a dihydroxy group:



(2.29)

The MMA macromonomer was then reacted with TDI or HDI, along with BD, to produce a grafted polyurethane.

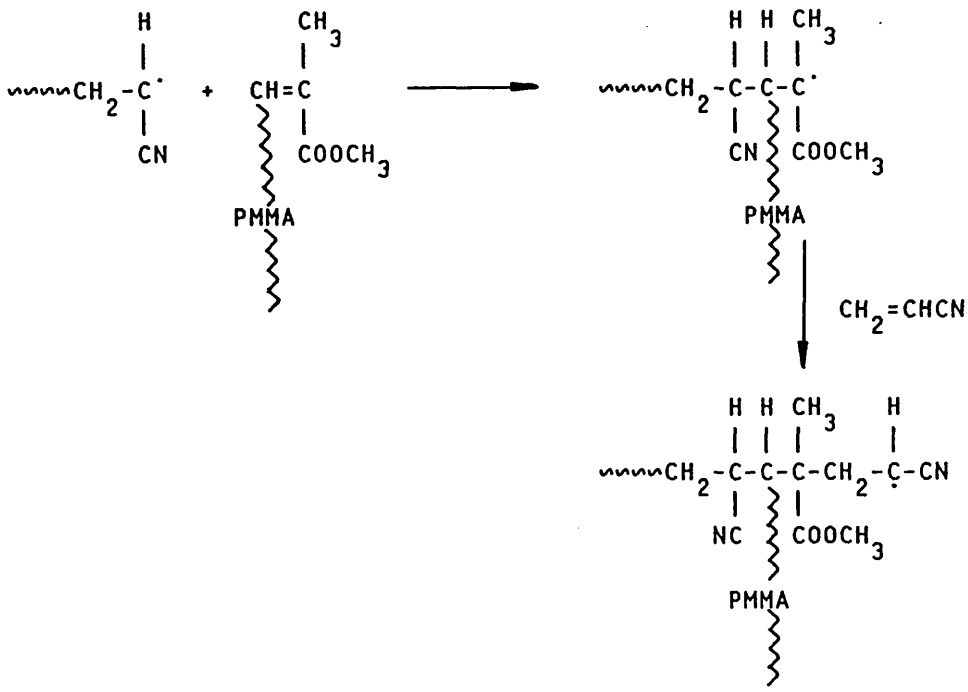
Yamashita et al.[136] polymerised MMA in the presence of thiomalic acid and produced a polymer terminated at one end with a dicarboxlylic acid group.



(2.30)

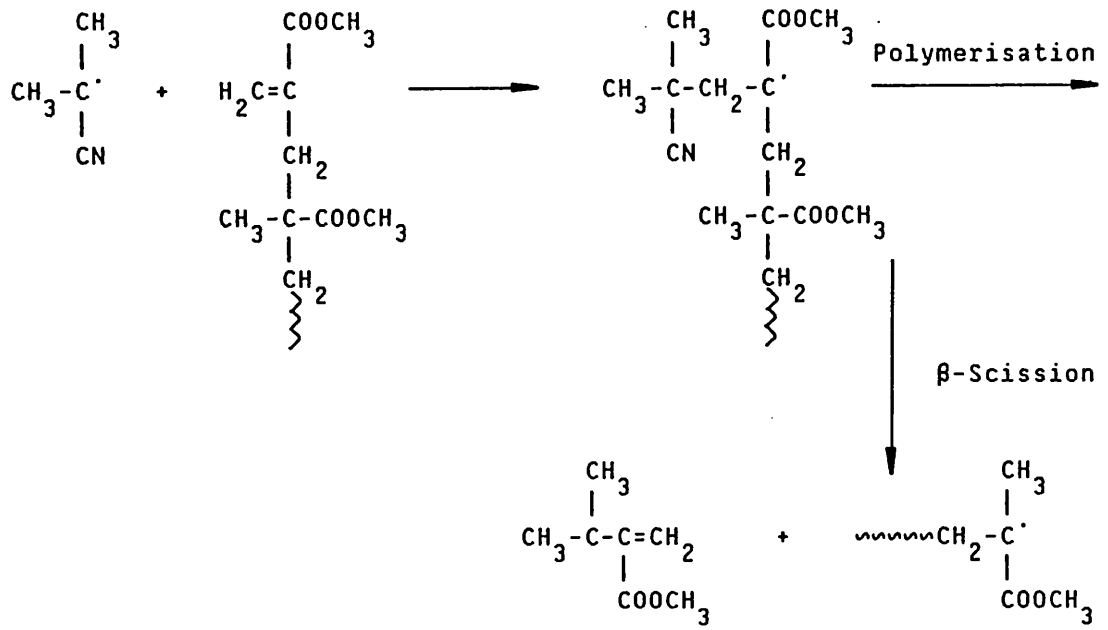
(iii) Using the unsaturated group formed by the disproportionation of polymer radicals during free-radical synthesis.

Bamford and White[137] copolymerised ACN with a PMMA macromonomer that contained terminal double bonds due to the disproportionation of the polymer radicals formed during its synthesis.



(2.31)

Cacioli et al.[138] free-radically polymerised MMA, using methyl azo-iso-butyrate as the initiator, in the presence of the transfer agent cobalt(II) tetraphenyl porphyrin. This enabled PMMA oligomers ($\bar{M}_n$ ~1000) to be produced with terminal unsaturated groups (due to its termination by disproportionation). The oligomers were copolymerised with ethyl acrylate, styrene, MMA, ACN, and vinyl acetate, but did not homopolymerise. The authors found that the macromonomer was readily attacked by the initiator radical, but the new radical thus produced had a low reactivity. β-Scission of this radical could regenerate another macromolecule.



(2.32)

Many side reactions could follow. The β-scission reaction is important during the copolymerisation with other monomers as the production of another polymerisable macromonomer, which could contain sections of the comonomer's homopolymer, would mean that the side chains would consist of PMMA and the comonomer.

(D) SYNTHESIS OF MACROMONOMERS BY THE REACTION OF UNSATURATED COMPOUNDS WITH FUNCTIONAL TERMINAL GROUPS OF POLYMERS FORMED BY STEP-GROWTH POLYMERISATION

This section is concerned with the synthesis of macromonomers by the reaction of a terminal group of a polymer, synthesised by step-growth polymerisation methods, with an unsaturated compound containing an antagonistic functional group. This type of reaction is particularly useful in the synthesis of polyurethane macromonomers.

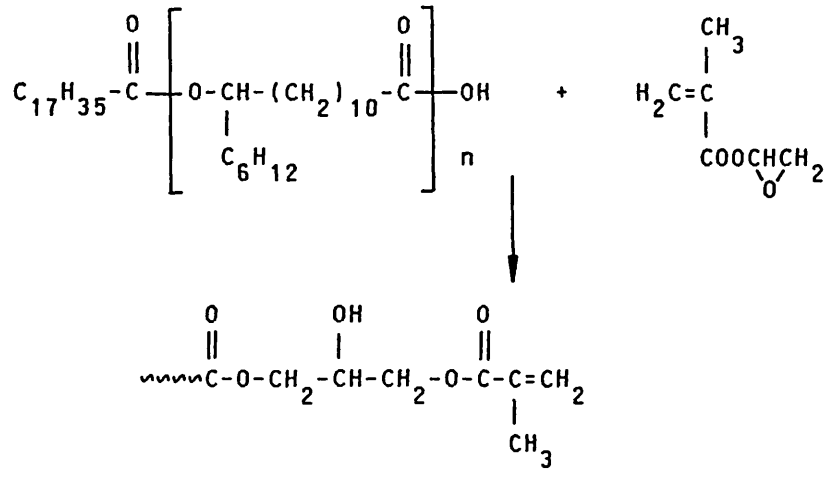
In general, it is preferential to perform the step-growth polymerisation by the reaction of bifunctional monomers carrying the relevant functional groups on the same molecule, i.e. having the structure A-B (where A and B are antagonistic functions). The final

polymer would then contain molecules with equal amounts of A and B functions at either end, but they would be randomly distributed, 25% A--A, 25% B--B, and 50% A--B. If one of these functional groups can be reacted with an unsaturated compound, a macromonomer can be synthesised.

For example, Hudecek et al.[139,140] mixed the polyester poly(butanediol-adipate) with hydroxy end groups with the product of the reaction of HEMA and MDI. This yielded a polyurethane with a methacrylate end group. The polyurethane was then copolymerised with HEMA to form a graft copolymer containing polyester-urethane grafts. The same authors produced oligourethanes from the reaction of HDI, BD, and HEMA[141-143], and HDI, diethylene glycol, and HEMA[144] which were copolymerised with ethyl acrylate, butyl acrylate, HEMA, AM, and NVP. Electron microscopy showed that each graft copolymer was a two-phase system consisting of a crystalline phase with oligourethane grafts.

Hayes[145] prepared a polyurethane prepolymer from PTMEG 2000, BD, and MDI. The polyurethane was then capped at one end with isocyanatoethyl methacrylate (IEM), $OCNCH_2CH_2OOCC(CH_3)=CH_2$. The method of synthesis was such that there would have been a distribution of 50% singly end-capped molecules, 25% doubly end-capped molecules, and 25% non-functional molecules. The polyurethane macromonomer underwent free-radical graft copolymerisation with MMA. Grafting was achieved, but the product was not isolated or characterised.

Theodore and Chatta[146] created a macromonomer from the reaction of capped poly(12-hydroxystearic acid) with glycidyl methacrylate.

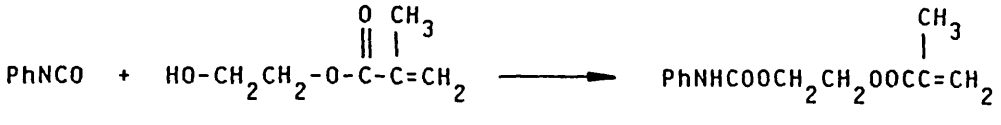


(2.33)

The macromonomer was copolymerised with a mixture of MMA and HEMA. IEM was then added to react with the hydroxyl groups of the resulting graft copolymer. This produced another macromonomer capable of producing crosslinked networks when copolymerised with acrylic monomers.

Maslyuk et al.[147] synthesised oligourethanes containing terminal reactive methacrylate and photoinitiating benzoin groups by two types of procedure. The 1-step method involved reacting a polyol, e.g. PPG, with an equimolar mixture of two mono-isocyanates obtained by reacting 2,4-TDI with HEMA or benzoin, PH-CH(OH)-CO-Ph. For the 2-step procedure, the polyols were reacted first with TDI, followed by benzoin, then HEMA. Irradiation of these macromonomers with UV light initiated their homopolymerisation or copolymerisation with various comonomers.

Sorokin et al.[148] reacted phenyl isocyanate with HEMA. The product was then copolymerised with BMA.



(2.34)

The reactivity ratios for the copolymerisation reaction were evaluated and were found to be 0.23 for the urethane compound and 0.34

for BMA. The product of the reactivity ratios being less than 1 indicated that alternation occurred in the final product.

(E) HOMOPOLYMERISATION OF MACROMONOMERS

The rate of homopolymerisation of macromonomers should be affected by three factors[117]:

(i) the low concentration of active sites,

(ii) the inaccessibilty of the terminal unit of unsaturation due to steric hindrance,

(iii) the growing radical would also be hindered and would find it difficult to approach other molecules.

Since the macromonomer consists of many chain segments, the possibility of transfer reactions with these segments is very high. Therefore, chain branching can occur.

Macromonomers have been homopolymerised mainly by means of free-radical polymerisation[117,118]. Anionic homopolymerisation of macromonomers requires that the unsaturated end unit is susceptible to attack by carbanionic sites, and that the polymer chain does not contain proton donating or electrophilic groups which could deactivate the living polymer.

(F) COPOLYMERISATION OF MACROMONOMERS WITH OTHER MONOMERS

The free-radical copolymerisation of a macromonomer with vinylic or acrylic comonomers is a way of synthesising graft copolymers. In theory, the process follows the general rules of copolymerisation, and the radical reactivity ratios, r, can be determined. This gives a measure of the ability of each species present to enter the final polymer.

If the macromonomer is represented as M and the comonomer as A, the instantaneous composition of the copolymer is expressed as[117]:

$$\frac{d[A]}{d[M]} = \frac{[A].(r_a.[A] + [M])}{[M].(r_m.[M] + [A])} \tag{2.35}$$

where [A] and [M] are the concentrations of A and M respectively at time t, d[A] and d[M] are the amounts of A and M consumed between times t and (t + dt), and r_a and r_m are the reactivity ratios of A and M and are equal to:

$$r_a = \frac{k_{aa}}{k_{am}} \tag{2.36}$$

$$r_m = \frac{k_{mm}}{k_{ma}} \tag{2.37}$$

where k_{aa} and k_{am} are the rate constants for the addition of A and M to radical A respectively, and k_{mm} and k_{ma} are the corresponding rate constants for radical M.

Since macromonomers are polymers, their concentration, with respect to the concentration of A, is usually quite low. Therefore, equation (2.35) reduces to:

$$\frac{d[A]}{d[M]} = r_a . \frac{[A]}{[M]} \tag{2.38}$$

if [A] >> [M]. Equation (2.38) integrates to:

$$r_a = \frac{\ln\{[A]_o/[A]\}}{\ln\{[M]_o/[M]\}} = \frac{\ln(1 - x_a)}{\ln(1 - x_m)} \tag{2.39}$$

where $[A]_o$ and $[M]_o$ are the initial molar concentrations of A and M in the reaction mixture, and x_a and x_m are the fractional conversions of A and M at time t. Hence, r_m has no importance in the process as long

as the molar quantity of M used is low.

Therefore, the ratio of the molar amounts of A and M included in the copolymer is proportional to the ratio of their molar amounts in the feed. However, deviations from this behaviour occur at high conversions.

If $r_a > 1$, the consumption of A is faster than that of the macromonomer. As the conversion increases, the proportion of M in the feed increases, and, therefore, the proportion of grafts included in the copolymer also increases. The opposite is true if $r_a < 1$.

Rempp et al.[117,118] define the probability of finding an AA diad anywhere along the copolymer chain as:

$$\begin{aligned} p_{aa} &= F_a \cdot \frac{k_a.[A]}{k_{aa}.[A] + k_{am}.[M]} \\ &= F_a \cdot \frac{r_a.f_a}{r_a.f_a + f_m} \\ &= (F_a)^2 \end{aligned} \qquad (2.40)$$

where f_a and f_m are the molar proportions of A and M in the monomer mixture, and F_a is the mole-% of A units in the copolymer formed instantaneously. Also, the probability of finding AM and MA diads can be represented as:

$$p_{am} = p_{ma} = F_m \cdot \frac{f_m}{r_a.f_a + f_m} = F_m \cdot \frac{r_a.f_a}{r_a.f_a + f_m} = F_a.F_m \qquad (2.41)$$

and the probability of finding MM diads is expressed as:

$$p_{mm} = F_m^2 = \frac{f_m^2}{(r_a.f_a + f_m)^2} \approx 0 \qquad (2.42)$$

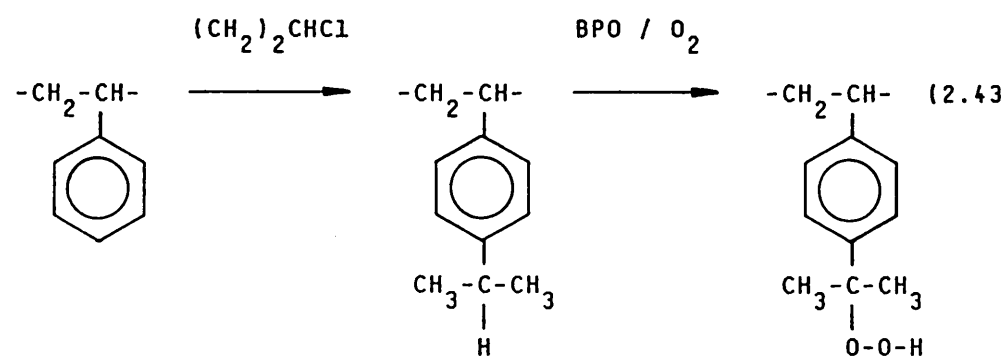
as long as $f_m < 0.05$.

Therefore, provided the molar amount of M is small, the instantaneous distribution of M units along the backbone (and, therefore, the grafts) formed instantly follow Bernouillian statistics.

2.2.1.4 INITIATION OF GRAFT COPOLYMERISATION BY THE THERMAL HOMOLYSIS OR REDOX ACTIVATION OF AZO-GROUPS OR PEROXIDES INTRODUCED INTO THE POLYMER BY CHEMICAL MEANS

The incorporation of azo or peroxide groups into polymer molecules introduces a potential grafting site. The functional group will undergo homolytic fission at high temperatures, and form a reactive radical.

Hydroperoxide groups can be introduced into polymers with suitable side groups by direct oxidation. For example, Metz and Mesrobian[149] alkylated polystyrene with isopropyl chloride, and then oxidised the side groups using BPO and preheated oxygen gas. The peroxidised material was then used to initiate the redox polymerisation of MMA.



(2.43)

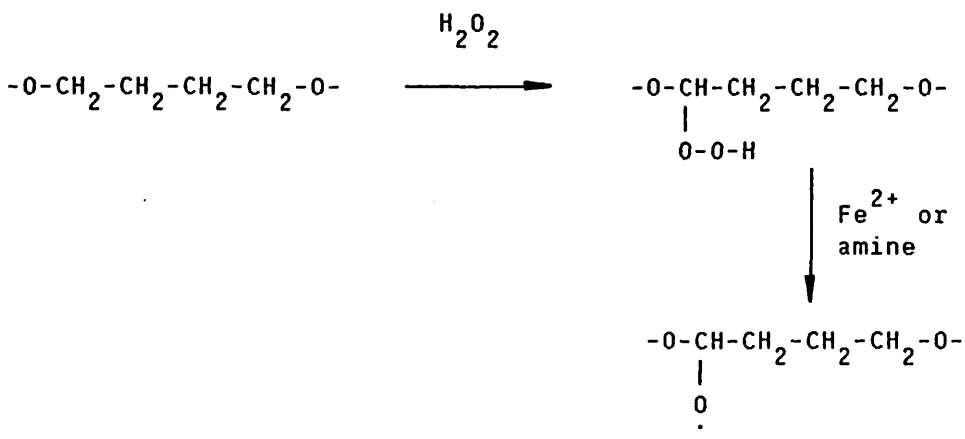
Another method of introducing hydroperoxide groups is by ozonization[84,150]. At high temperatures, the hydroperoxide sites split into radicals that can initiate grafting and homopolymerisation.

The introduction of peroxide groups into a polymer by oxidative methods is affected by the degradation of the main polymer chain. To overcome this problem, Smets et al.[151,152] synthesised poly(methyl acrylate-g-styrene) by heating dioxane / styrene solutions at 75°C in the presence of different amounts of a copolymer of methyl acrylate and t-butyl peracrylate.

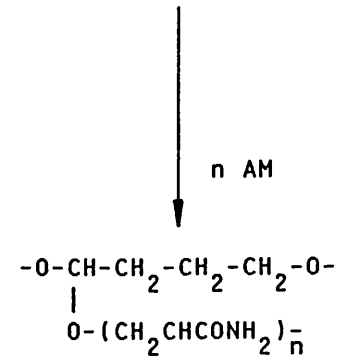
Feng et al.[153] introduced hydroperoxy groups onto the surface of a polyether-urethane, based on MDI, BD, and PTMEG, by oxidising the polyurethane film in H_2O_2 solution under UV light. The resulting oxidised polymer was then reacted with ferrous ions or N,N-dimethyltoluidine to initiate graft copolymerisation.

It was found that graft copolymerisation occurred mainly at the polyether soft segment, because of the susceptibility of the ether linkages to oxidation. The urethane group was inert to oxidation.

In another publication[154], the same authors repeated the process but did not irradiate the polyurethane with UV light. Grafting of AM or HEMA to the polyurethane's surface was carried out. Homopolymerisation could be prevented by washing away any free H_2O_2 after the oxidation process. This meant that the only initiating groups were on the polymer backbone. The proposed reaction scheme was:



(2.44)

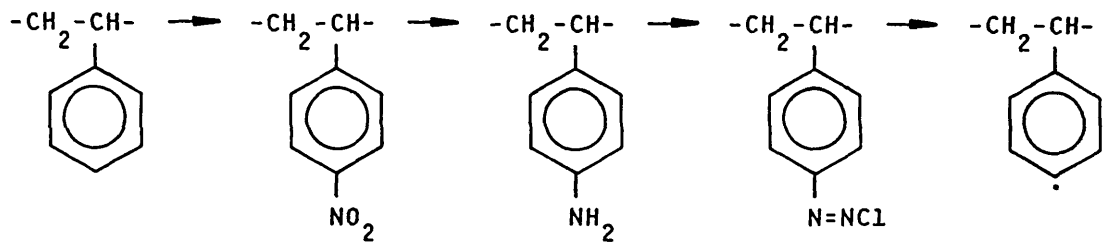


A poly(ether-ester) (PEES) based upon PTMEG showed greater reactivity than the polyether-urethane to the controlled oxidation method of graft copolymerisation. This was due to the easier introduction of hydroperoxy groups by oxidative methods for the PEES.

Huang et al.[155] also used irradiation of polyether-urethane films by sunlight or UV light in the presence of H_2O_2. Their polyurethanes were based on MDI, PTMEG, and BD or ED. Hydroperoxy groups were introduced onto the surface of their films. The polyurethanes were then grafted, in the presence of ferrous ions, with either sodium-6-sulpho-hexyl acrylate (SSHA) or sodium-8-sulpho-octyl acrylate (SSOA), (general formula $CH_2{=}CHCOO(CH_2)_nSO_3^-Na^+$, n=6 and 8 for SSHA and SSOA respectively).

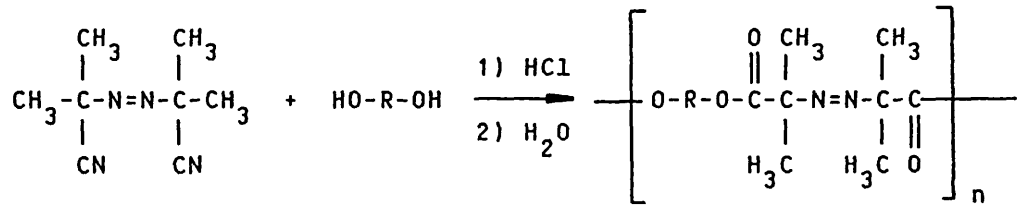
The hydrophilicity of the acrylate grafted films were compared to those grafted with the corresponding methacrylate compounds. The acrylate-grafted polyurethanes had a greater hydrophilicity than the methacrylate-grafted polymers. This was due to the absence of the methyl group.

Valentine and Chapman[156] nitrated PS, and then reduced and diazotised the resulting polymer. The diazotised PS decomposed in the presence of a ferrous salt to give polymeric phenyl radicals which were sites for grafting.



(2.45)

Simionescu et al.[157] have reported the reaction of AIBN with a diol or epoxide, to yield a polymer containing azo groups capable of decomposing and acting as initiators for free-radical polymerisation.



(2.46)

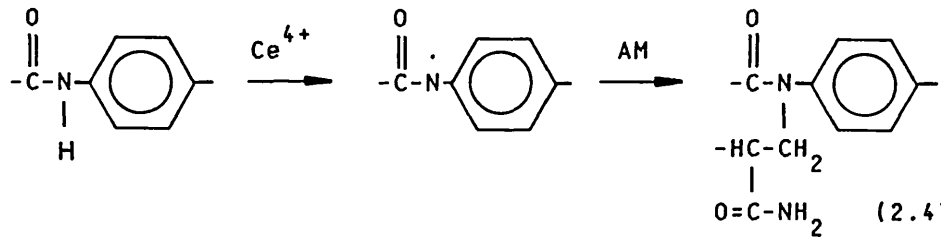
2.2.1.5 GRAFT COPOLYMERISATION BY MEANS OF REDOX INITIATION

There are many different redox systems which can be used to initiate graft copolymerisation onto polymers. In general, the methods involve the interaction of the redox system with the polymer backbone. Mansour and Nagaty[150] review the various combinations of initiators which can be used to graft onto cellulose by redox techniques. The more popular systems involve the use of ceric ions, ferrous / hydrogen peroxide, persulphate ions, peroxydiphosphate ions[158], permanganate / oxalic acid[159], V^{5+}, Mn^{3+}, Ti^{3+}, the uranyl cation, periodate, and bromate anions as the initiators.

Ratner et al.[160] developed portable apparatus for the modification of the surface of commercial PDMS or Tygothane C210A (polyurethane) tubing. The grafting reactions were initiated by either irradiation techniques or Ce^{4+} ions.

Feng et al.[154,161] grafted AM and HEMA onto a polyurethane based

on BD, MDI, and PTMEG using ceric ammonium nitrate as the redox initiator. By studying equivalent reactions with model organic compounds, the authors found that grafting occurred at the urethane group of the hard segment:



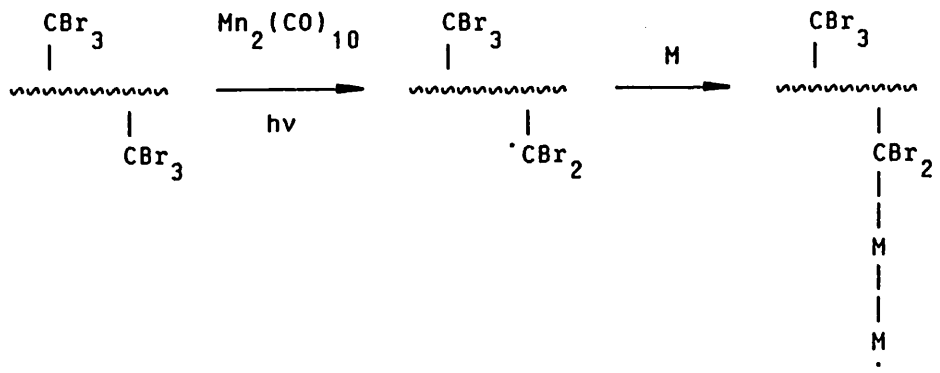
(2.47)

The amount of grafting increased with increasing concentration of AM and Ce^{4+} initiator (up to a concentration of 5.0mmol l^{-1}, after which a sharp decrease occurred). Varying the concentration of the polyurethane had no effect.

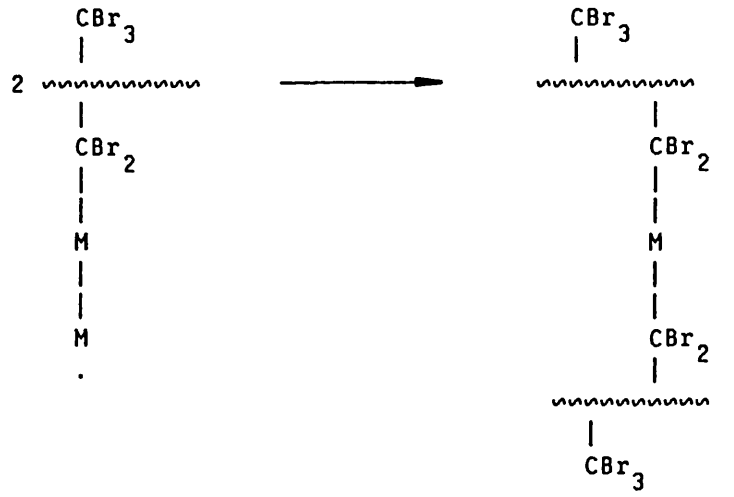
Feng et al.[154] also grafted AM and HEMA to a PEES based on PTMEG. They found that it was less reactive towards Ce^{4+} than the polyurethane (in contrast to their reactions using H_2O_2), and had to be swollen with acetic acid prior to the reaction.

Ogura[162] prepared a urethane modified poly(vinyl alcohol) and copolymerised the resulting polymer with ethyl acrylate and styrene in the presence of $K_2S_2O_8$.

The production of radicals by the interaction of an organo-halide and a transition metal compound has been reviewed by Bamford[163]. If a polymer chain contains side chains consisting of organo-halide, then these groups can be used in conjunction with a transition metal derivative to initiate grafting to the polymer. If termination by combination occurs, a crosslinked network is formed.



(2.48)



(2.49)

Initiation can be induced thermally or photochemically. For thermal reactions, the hexacarbonyls of group IVB metals can be used in the temperature range of 60 - 90°C. $Mn(CO)_6$ is the most reactive[164]. The compound undergoes ligand displacement with a molecule of monomer, and then a redox reaction with a halide generates the radical:

$$Mo(CO)_6 + M \rightleftharpoons M\text{---}Mo(CO)_5 + CO \qquad (2.50)$$

(2.51)

where A is an atom on the polymer attached to the halogen atom.

Photoactive transition metal derivatives include the deca-carbonyls of group VII, such as manganese and rhenium. Light of wavelength 436nm can be used for $Mn_2(CO)_{10}$, whilst $Re_2(CO)_{10}$ requires shorter wavelengths (~365nm)[166]. In the presence of an additive, S, the major reactions that occur are:

$$Mn_2(CO)_{10} + h\nu \longrightarrow Mn_2(CO)_{10}^{*} \xrightarrow{S} S\text{---}Mn(CO)_5 + Mn(CO)_5 \qquad (2.52)$$

$$S\text{---}Mn(CO)_5 + \underset{\underset{AX}{|}}{\sim\sim\sim\sim} \xrightarrow{\text{Slow}} Mn^{(I)}(CO)_5X + \underset{\underset{A^{\bullet}}{|}}{\sim\sim\sim\sim} \qquad (2.53)$$

$$Mn(CO)_5 + \underset{\underset{AX}{|}}{\sim\sim\sim\sim} \xrightarrow{\text{Fast}} Mn^{(I)}(CO)_5X + \underset{\underset{A^{\bullet}}{|}}{\sim\sim\sim\sim} \qquad (2.54)$$

Similar reactions occur with $Re_2(CO)_{10}$, with S = M. Hence, grafting onto a polymer is carried out in two stages. Firstly, the carbonyl is irradiated in the presence of the monomer (and an additive, if necessary). The resulting liquid is then added to the halogenated polymer, and macroradicals are produced which initiate the grafting reaction.

Bamford and Middleton[164] used transition metal derivatives as initiators for grafting to a halogenated polyether-urethane. The hydrogen atom on the nitrogen of the urethane link was replaced by a halogen atom (Cl or Br) by the use of acidified aqueous hypochlorite or hypobromite solutions. $Mo(CO)_6$, $Mn_2(CO)_{10}$ (with the additive acetylacetone), and $Re_2(CO)_5$ were used as initiators in order to graft (meth)acrylic acid, hydroxypropyl methacrylate, HEMA, and MMA to polyurethanes.

2.2.1.6 RADIATION-INDUCED GRAFT COPOLYMERISATION

Graft copolymerisation of a preformed polymer with another monomer can be induced by irradiating the material with ionising radiation, such as high energy electrons, X-rays, or γ-rays.

There are basically three techniques available for producing graft copolymers[165]:

(A) Direct irradiation of the polymer and monomer mixture. Free radicals are formed on both the polymer and the monomer, and hence both homopolymer and graft copolymer are produced. The production of homopolymer is dependent upon the sensitivity of the monomer.

(B) If the polymer is pre-irradiated in vacuo or in the presence of an inert gas, "trapped" radicals are produced. If the polymer is then immersed in the monomer, grafting is initiated.

(C) If the polymer is irradiated in the presence of air or oxygen, peroxide groups are introduced into the material. When the polymer is immersed in the monomer, these groups decompose to generate radicals which initiate grafting.

Chapiro[166] proposed the following reaction scheme for a polymer, -P-P-P-P-, which has been subjected to consistant radiation in the presence of air:

$$\text{-P-P-P-P-} \xrightarrow{\text{Irradiation}} \text{-P-}\underset{\cdot}{\text{P}}\text{-P-P-} + \text{H}^{\cdot} \qquad (2.55)$$

```
-P-P-P-P-   +   O2   ------>   -P-P-P-P-
   ·                              |
                                  O
                                  |
                                  O
                                  ·
```

(2.56)

```
-P-P-P-P-   +   -P-P-P-P-   ------>   -P-P-P-P-   +   -P-P-P-P-
   |                                     |                ·
   O                                     O
   |                                     |
   O                                     O
   ·                                     |
                                         H
```

(2.57)

```
-P-P-P-P-   +   -P-P-P-P-   ------>   -P-P-P-P-
   |               ·                     |
   O                                     O
   |                                     |
   O                                     O
   ·                                     |
                                         O
                                         |
                                      -P-P-P-P-
```

(2.58)

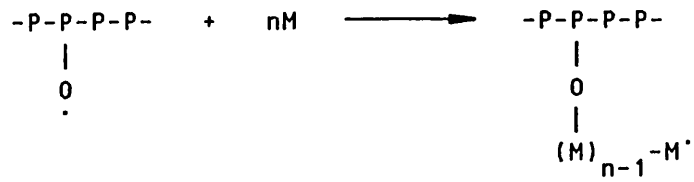
The peroxide bonds of equations (2.57) and (2.58) decompose at high temperatures to form peroxy radicals, which, in the presence of a monomer, M, initiate grafting to the backbone.

```
                      Heat
-P-P-P-P-   ------>   2 -P-P-P-P-
   |                       |
   O                       O
   |                       ·
   O
   |
-P-P-P-P-
```

(2.59)

```
                      Heat
-P-P-P-P-   ------>   -P-P-P-P-   +   HO·
   |                     |
   O                     O
   |                     ·
   O
   |
   H
```

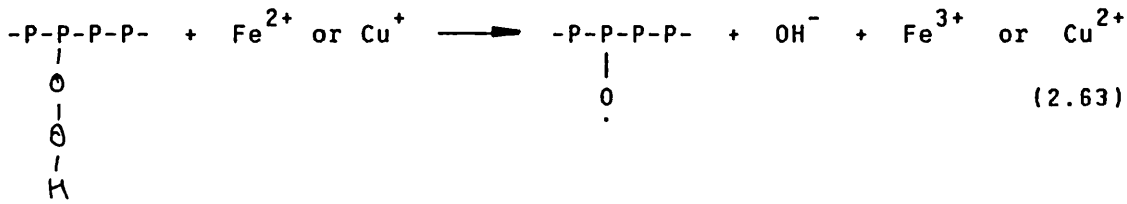
(2.60)



(2.61)

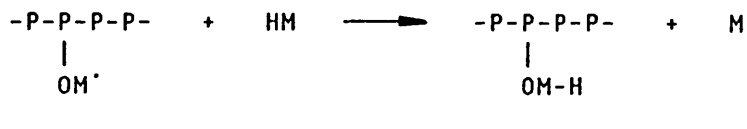
(2.62)

The formation of homopolymer can be reduced by the introduction of redox catalysts, e.g. Cu^{+} and Fe^{2+} salts. In this case, cleavage of the hydroperoxide can occur at room temperature, but without the formation of the hydroxyl radical.



(2.63)

Hence, in the presence of monomer, grafting can occur onto the polymer backbone. However, chain transfer reactions can occur, involving the abstraction of a hydrogen atom from the monomer by the polymer radical. Thus, a monomer radical is formed which can initiate the production of homopolymer.



(2.64)

(2.65)

Skraba et al.[165] irradiated samples of a polyether-urethane flexible foam with two types of ionising radiation, i.e. with γ-radiation, from a 1200 Curie Co^{60} source, and high energy electrons, by means of a 2MeV Van de Graff generator.

By carrying out two separate procedures, the polyurethane was grafted with AM, AA, or methacrylamide, in the presence of ferrous ammonium sulphate or cuprous chloride. Procedure (i) involved pre-irradiating the foam, and then immersing it in a 10% aqueous solution of monomer containing 0.01% Fe^{2+} or Cu^{+} ions. The reaction was performed under a blanket of nitrogen gas.

Procedure (ii) was similar to (i), but there was no nitrogen purge.

It was found that no grafting occurred without the redox catalysts. Both methods produced homopolymer, with the most being formed for procedure (i).

The extent of grafting was inversely proportional to the radiation dose rate. Despite needing a higher dose to peroxidise the polyurethane foam than the Co^{60} source, the electron accelerator proved to be the best means of irradiating large quantities of polyurethane. The Co^{60} source, however, provided a low dose, high volume radiation process, with the ability to penetrate deeply into the material.

Hayakawa and Yamakita[167] found that pre-irradiation at low temperatures was more effective, compared to simultaneous irradiation, for grafting 2-hydroxyethyl acrylate, HEMA, and vinyl acetate onto the open-cell polyurethane foams Motopren SC (a polyester-urethane) and Colorfoam ECS (a polyether-urethane).

Irradiation by γ-rays has been used frequently to modify the surface of polyurethane tubes and films for medical puposes. Sharma et al.[168] irradiated samples of a polyether-urethane-urea, with γ-rays from a Co^{60} source, in the presence of HEMA, and in a nitrogen atmosphere.

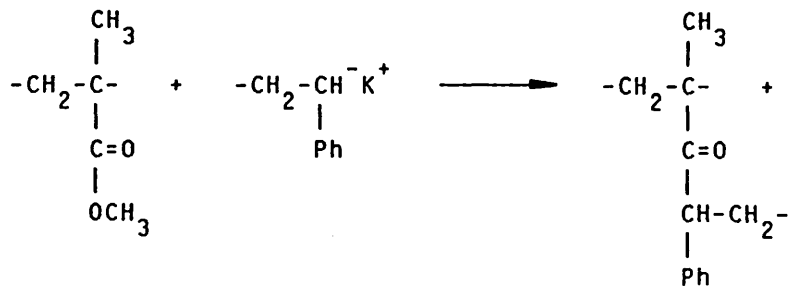
Jansen et al.[169-172] grafted HEMA, 2,3-epoxypropyl methacrylate, AM, 2,3-dihydroxypropyl methacrylate, and NVP onto the surface of

polyether-urethane films or tubes by means of γ-radiation. The materials were pre-swelled with the monomer for a certain amount of time, and were then irradiated in the absence of the surrounding monomer. It was found that the tensile strength and elongation at break decreased with increasing grafting yield. However, materials with grafting yields of < 5mg cm^{-2} had the same mechanical properties as those that were ungrafted.

Egboh et al.[173] grafted NVP onto a segmented polyurethane based on PTMEG, MDI, BDU, and BD, using γ-radiation as the method of initiation. Their technique involved dissolving the polyurethane and the monomer together in dimethyl formamide (DMF), degassing the solution, and sealing it in an ampoule under vacuum prior to irradiation.

2.2.1.7 IONIC SYNTHESES OF GRAFT COPOLYMERS

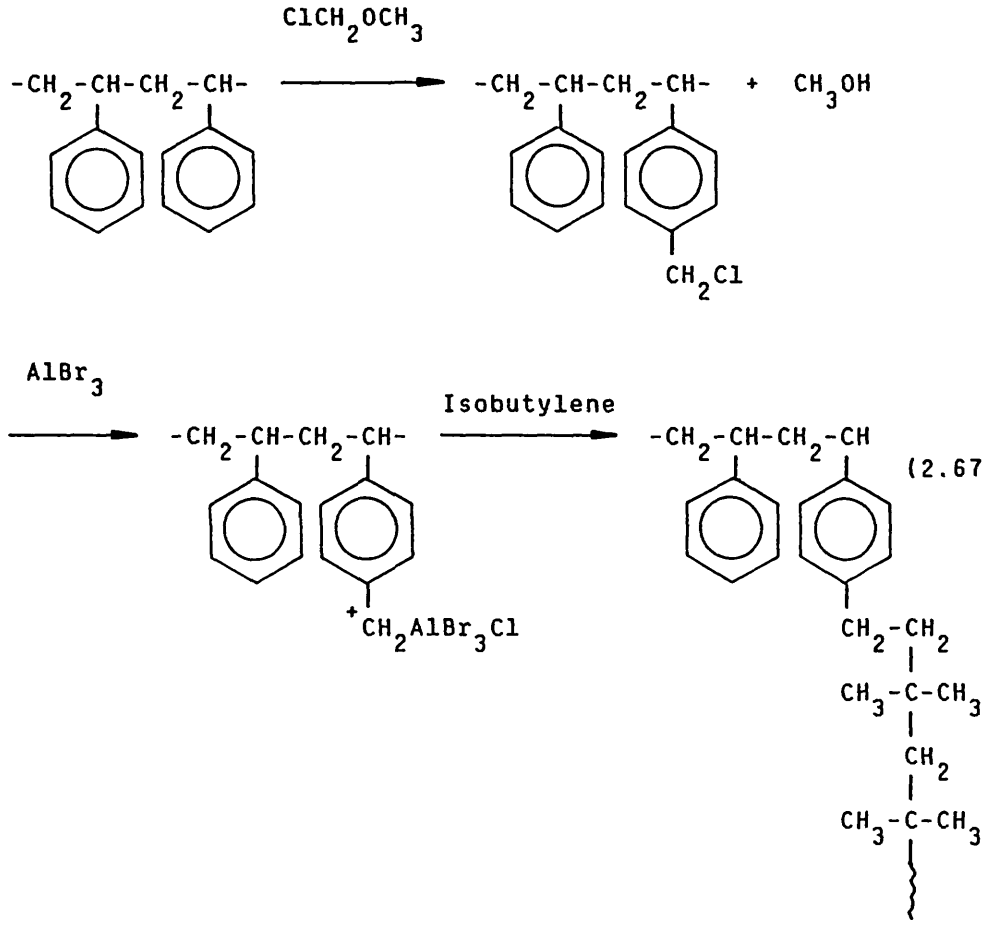
Graft copolymers can be prepared by the attack of a "living" polymer on the backbone of a preformed polymer[174]. For example, living PS can react with PMMA to produce poly(MMA-g-styrene)[175]. The attack takes place at the ester groups of the PMMA.



(2.66)

Haas et al.[176,177] investigated the ionic chain transfer reaction between the polystyryl carbonium ion and poly-p-methoxy-styrene, to form poly(p-methoxystyrene-g-styrene). However, it was found that alkyl vinyl ethers, isobutylene, and NVP could not be grafted onto

PS, poly(vinyl toluene), or poly(p-methoxystyrene) by this method. Kockelbergh and Smets[178] used chloromethylated PS, in the presence of $AlBr_3$, to initiate the polymerisation of isobutylene by a carbonium ion mechanism.

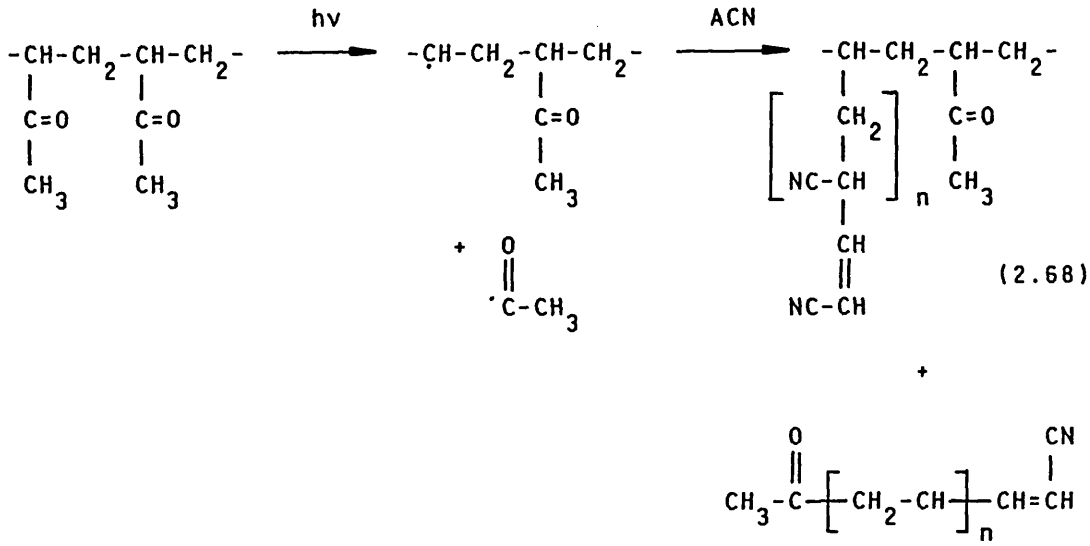


(2.67)

2.2.1.8 PHOTOCHEMICAL METHODS OF PRODUCING GRAFT COPOLYMERS

Jones[179] prepared poly(styrene-g-MMA) by irradiating benzene solutions of brominated PS with UV radiation in the presence of MMA. An average of 1.2 - 5.9 PMMA chains were grafted onto each PS backbone molecule.

Polymers containing vinyl ketones can be photo-irradiated directly to produced radical sites for grafting. Guillet et al.[180-182] irradiated poly(methyl vinyl ketone), with radiation of wavelength 313nm, in the presence of ACN, to produce poly(methyl vinyl ketone-g-ACN).



(2.68)

Groups which contain chlorine atoms within a polymer molecule can be photolysed when they are activated by the proximity of a second polar group. Thus, Miller[183] synthesised copolymers of α-chloro-acrylonitrile with ACN and AM.

Only a few polymer systems can be directly photoinitiated, but the use of a photosensitizer, e.g. benzophenone, increases the scope of this method[84].

Craubner[184,185] partially nitrosated polymers containing peptide groups within their molecules (which included a polyurethane based on 1,6-hexamethylene diamine and the bischloro-carbonic acid ester of BD). Typical nitrosating agents suitable for use were liquid or gaseous dinitrogen tetroxide, nitrosyl chloride, aqueous or anhydrous nitrous acid, and alkyl nitrides.

The N-nitroso-N-aryl-acylamines produced rearranged to diazo esters. Irradiation, with near UV or visible radiation, or heat caused these compounds to decompose, losing N_2 and CO_2. In the presence of monomers, the radicals thus formed initiated copolymerisation. Hence, by this method, the polyurethane was block-copolymerised with MMA. By introducing unsaturated N-nitroso acylamines (e.g. $R_1CH{=}CHC(O)N(NO)R_2$) branched or crosslinked polymers can be formed.

$$R_1\text{-NH-CO-}R_2 \xrightarrow[-H_2O]{\text{Nitrosating Agent}} \underset{\text{N-Nitroso-N-acylamine}}{R_1\text{-N(NO)-CO-}R_2} \longrightarrow \underset{\text{Diazo ester}}{R_1\text{-N=N-O-CO-}R_2} \qquad (2.69)$$

$$\xrightarrow{h\nu \text{ or heat}} R_1 + {}^{\cdot}OOC\text{-}R_2 + N_2 \xrightarrow[-CO_2]{h\nu \text{ or heat}} R_1^{\cdot} + R_2^{\cdot}$$

$$R_1^{\cdot} + H_2C{=}CHX \longrightarrow R_1\text{-}CH_2\text{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^{\cdot} \xrightarrow{(n-1)M} R_1\text{-}M_n \qquad (2.70)$$

If the polymer contains more than one nitroso group, then biradicals are produced on decomposition, which generate more complicated products.

Chain transfer reactions can also yield homopolymer and branching.

Kawaguchi et al.[186] used light of a wavelength $\leqslant$ 320nm to graft vinyl monomers of the formula $R_1C(=CH_2)COR_2$, where R_1 is H or alkyl and R_2 is NH, OH, $NHCH_2OH$, or OR_1, onto a moulded polyurethane article.

2.2.1.9 OTHER METHODS OF PRODUCING GRAFT COPOLYMER

Preformed polymer molecules, which contain functional groups capable of undergoing chemical reactions, can couple with similar polymers, containing antagonistic groups, in order to form graft or block copolymers.

For example, Akcelrud and Gomes[187,188] prepared a graft copolymer, consisting of a PMMA backbone with polyurethane side chains, by the application of a condensation type reaction between

complementary reactive groups. Initially, a copolymer was prepared of MMA and HEMA. This copolymer contained hydroxyl functions at intervals along the polymer chain. Secondly, a polyurethane prepolymer was synthesised from TDI and PPG with a terminal isocyanate unit. The polymers were then coupled together through the reaction of the backbone hydroxyl groups of the MMA / HEMA copolymer and the terminal -NCO of the polyurethane.

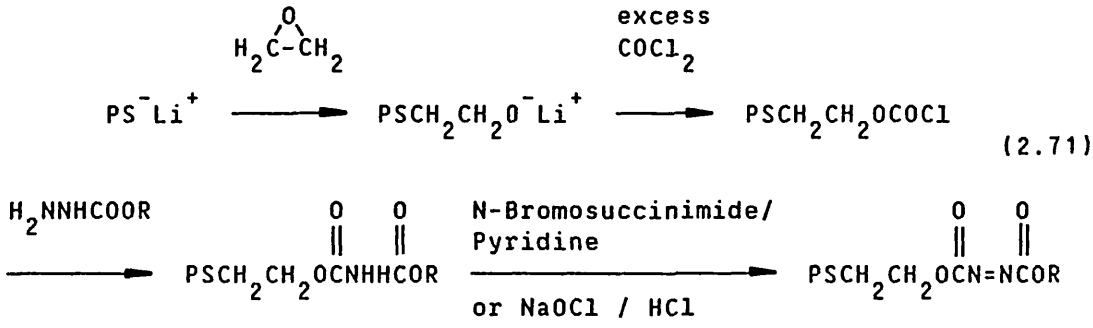
A major problem was gelation due to the presence of polyurethane molecules terminated at both ends with isocyanate groups. Gel formation was also significant when the copolymer contained high concentrations of hydroxyl groups.

The isolated graft coplymers were characterised by DSC. The thermograms showed two transitions at -60°C (due to the T_g of the polyurethane's polyether segment) and 90°C (corresponding to the T_g of the PMMA). When the polyurethane content of the graft copolymers was < 20%, no polyurethane soft segment transition was observed until the sample had been heat treated.

Tensile tests showed that the polyurethane had a reinforcing effect on the graft copolymer up to 15% polyurethane content. However, the modulus decreased as the % polyurethane content increased. This latter effect was probably due to internal plasticization caused by the soft segment of the polyurethane. After 15%, there was a marked variation in the slope of the stress / strain curve, indicating a change in morphology, possibly due to a change from a one-phase system to a two-phase system. It was concluded that the components of the graft copolymer were compatible up to ~15% polyurethane content.

Another example of the coupling reaction of two polymers is the work of Campbell et al.[189]. A sample of monofunctional PS was grafted to an unmodified polydiene, utilising the "ene" addition reaction of azodicarboxylates to allylic double bonds. Firstly, styrene was

anionically polymerised using butyl lithium as the initiator. The living polymer was terminated with ethylene oxide, and then underwent a series of reactions in order to convert the end function into an azodicarboxylate group.



(2.71)

The functional polystyrene was then grafted to unsaturated materials such as synthetic polyisoprene, natural rubber, or polybutadiene.

The general reaction with the polydiene backbone was as follows:

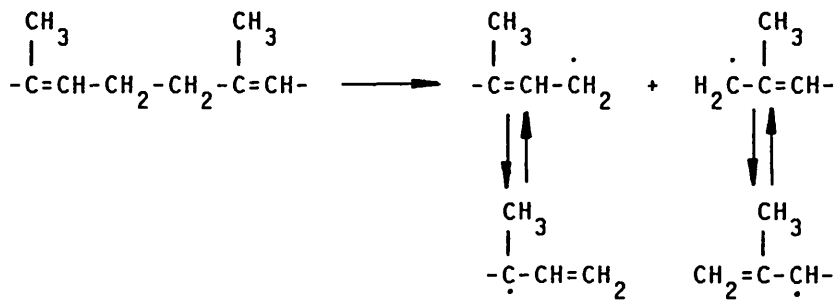
(2.72)

Another technique for preparing graft copolymers is referred to as the mechanico-chemical synthesis[84]. If a sufficient stress is applied to a polymer, homolytic or heterolytic scission of a C-C or other chemical bond can occur. This type of degradative process occurs during the milling and extrusion of polymers in the viscoelastic state, the ultrasonic irradiation of polymer solutions under cavitation conditions, the high speed stirring, shaking, freezing, and

thawing of polymer solutions, the discharge of high voltage sparks through polymer solutions, and the swelling of crosslinked or highly entangled polymers.

Thus, graft copolymers can be prepared by either subjecting a mixture of polymers to mechanical degradation or exposing a polymer to degradation in the presence of a monomer.

This method is frequently used for grafting to rubber. The weakest bond in natural or synthetic rubber is the polyisoprene CH_2-CH_2 linkage. Polyisoprenyl radicals are formed by mechanico-chemical scission[90]:



(2.73)

However, many side reactions can occur, including gelation. Hence, this method of synthesising graft copolymers is uncontrollable.

Campbell et al.[190] carried out the same grafting reaction between a sample of monofunctional PS and a polydiene, as in their previous publication[189] (q.v.), but performed the reaction by mechanically mixing the components in the absence of a common solvent. The temperature of the reaction had to be above the T_g of the PS. The results of several experiments showed that the reactive end groups and intensive mixing were essential for grafting to occur.

Mendis et al.[191] prepared a "Hevea plus" type natural rubber (NR)-g-MMA graft copolymer by means of the electrochemical initiation of MMA in the presence of NR. Only small yields of graft copolymer

were formed if a NR - MMA emulsion was subjected to electrolysis. However, yields were improved if MMA, or if MMA with ferrous sulphate and tetraethylene-pentamine (TEP) were added after the NR had been electrolysed. The results showed that the NR was acting as a macroradical and that hydroperoxide groups were being formed during the initiation.

2.2.2 ISOLATION OF GRAFT COPOLYMERS

The crude product of a graft copolymerisation usually contains unreacted prepolymer, homopolymer of the grafted monomer, and other possible side products that have to be removed. There are several methods of isolation which are described below:

2.2.2.1 FRACTIONAL PRECIPITATION

Fractional precipitation involves the addition of a non-solvent to a solution of a polymer mixture. The precipitated polymer fractions can be isolated. Rempp et al.[118] claim that fractional precipitation is the most efficient way to separate unreacted macromonomers from graft copolymers due to the large difference in molecular weight between the two polymers. They state that the precipitant should be a non-solvent of the backbone and of the grafts.

Turbidimetric titration is an analytical technique which can be used to show the presence of graft copolymers and to determine the precipitation ranges of the polymers. The technique involves measuring the amount of turbidity resulting from the addition of a precipitant to a dilute polymer solution. The turbidity is expressed as the ratio of the light absorbed at partial precipitation to the amount of light absorbed at complete precipitation[85]. A titration curve of turbidity versus volume of precipitant added is plotted. In theory, a curve such as fig. (2.8) should be obtained.

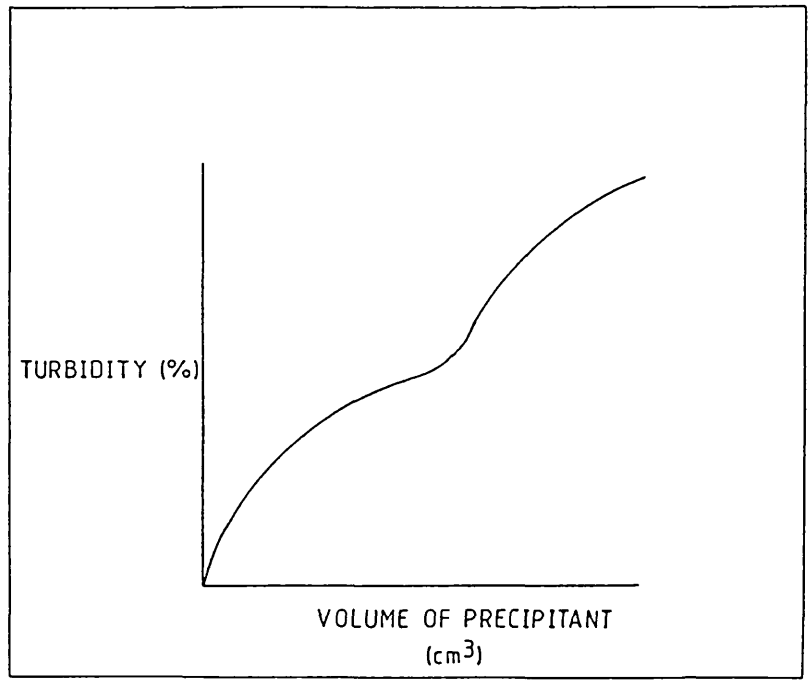


FIG. (2.8): A TYPICAL TURBIDIMETRIC TITRATION CURVE

The inflexion distinguishes between the precipitation of the various species in the polymer mixture.

2.2.2.2 SELECTIVE PRECIPITATION

Selective precipitation[85] is a variation of the fractional precipitation technique. However, only one of the polymers is precipitated with a certain non-solvent. If this technique can be used, clean separations can be achieved.

2.2.2.3 FRACTIONAL ELUTION

In fractional elution, a polymer mixture is treated with successive solvent / non-solvent mixtures which contain progressively larger amounts of the solvent. If a solvent for only one of the species is used, selective elution can be carried out[85].

2.2.2.4 COMBINED ELUTION AND PRECIPITATION

If during fractional precipitation co-precipitation of the polymer species occurs, or if there is no gap between the titres for the precipitation ranges of the materials, then extraction of one of the polymers with a solvent which does not dissolve any other polymer of the mixture can be used, followed by fractional or selective precipitation of the remaining mixture[84].

2.2.2.5 PREPARATIVE GEL PERMEATION CHROMATOGRAPHY (PREP-GPC)

Prep-GPC uses the same principle of separation of polymer mixtures as analytical GPC, but larger quantities of material can be used. If the eluting fractions are collected, a mixture of polymers of different molecular sizes can be separated. However, the disadvantage of this technique is that only small amounts of product can be isolated per run compared to the other methods of separation.

2.2.3 USES OF GRAFT COPOLYMERS

Graft copolymers have several applications[192]:

(A) The reinforcement of rubbery materials.

(B) The modification of rubber based adhesives.

(C) The formulation of high impact strength polymers.

Theoretically, the presence of discontinuities, or nuclei, in the path of a fracture increases the resistance of the material to the impact causing the fracture. Therefore, if particles of a different phase can be dispersed uniformly in glassy polymers, e.g. PMMA, then its impact resistance will increase. If the microparticles of material,e.g. rubber, are blended with the polymer, incompatibility

and microphase separation weaken the resulting polymer mixture. However, graft copolymers of the constituent polymers act as interfacial or nucleating agents, thus stablising the mixture of homopolymers and graft copolymers.

(D) As surface active agents.

Graft copolymers can be used as suface active agents if it can be dispersed between two usually immiscible liquids.

(E) For improvement of the physical properties of fibres.

For example, PACN fibres have problems in dyeing and dye retention. The presence in the fibre of graft copolymers with monomers which can readily accept the dyes, e.g. AM, NVP, and methacrylonitrile, can greatly improve the fibre's properties.

(F) For use as ion exchange membranes.

Monomers such as styrene, methyl acrylate, ethyl acrylate, and ACN, can readily be grafted onto film forming polymers, e.g. polyethylene, polypropylene, and nylon. The grafts can then be chemically converted in situ to ion exchange resins or acid type membranes.

For example, Yanagita et al.[193] grafted with 4-vinyl pyridine or 2-methyl-5-vinyl pyridine, which can be quartenised with methyl iodide, in order to produce membranes of a high basicity.

CHAPTER 3

CHARACTERISATION OF POLYMERS FOR USE IN SURFACE COATINGS

3.1 INTRODUCTION

Unprotected surfaces are open to attack by their local environmental conditions. Applying a thin layer of paint to the surface is an effective method of shielding an object from its surroundings. Surface coatings are used for[194]:

(A) waterproofing

(B) corrosion protection

(C) insulation

(D) decoration

(E) flame-proofing

(F) the production of printed circuit boards and photographic film.

The different types of paint are classified as[195,196]:

(i) Fillers or Stoppers.

These are materials with a high solids content and typically are highly pigmented, so that they can dry hard without shrinkage and can be rubbed down to provide a smooth surface. They are used to treat surfaces containing imperfections such as indentations.

(ii) Primers.

Primers are applied to either filled or unfilled surfaces in order to improve the adhesion of the following layers of paint.

(iii) Sealers.

These are used to prevent the movement of materials from one coat of paint to another. Also, they are used to improve adhesion between

coats.

(iv) Surfacers or Undercoats.

These are applied over the filler or primer. They are highly pigmented to give good opacity and to give thickness to the paint film.

(v) Finishing Coats or Top-coats.

These are the last layers to be applied. If there is no pigment, the paint is called a varnish. "Lacquers" are thermoplastic solutions of paints or varnishes, and "enamels" are thermosetting paints.

In general, a paint consists of three basic components, a pigment, which can be decorative and protective, a binder or film-former, which holds everything together, and a liquid or solvent. Occasionally the film-former / liquid mixture is termed the "vehicle" for the pigment[195].

Binders are divided into two major categories, i.e. natural and synthetic resins. Natural resins include rosin (or calophony), which is obtained from pine trees, and lac (shellac), which is a product of the larvae of the insect Lacifer lacea[197].

Synthetic resins include the alkyd resins, unsaturated polyester resins, amino resins, epoxy resins, polyamides, polyurethanes, and vinyl and acrylic resins[197].

Information concerning the choice of pigment or solvent for a particular paint system is beyond the scope of this thesis, and can be found in general texts[50,195,197].

The aim of this research project was to modify PMMA, which, together with its copolymers, forms the basis of many paints which are used, for example, in the motor car industry. The following section is designed to introduce the techniques used in the paint industry to evaluate the properties of surface coatings particularly affected by the nature of the binder. However, emphasis will be placed only on those techniques which have been performed during the course of the research work. For the other techniques, references to general texts will be given.

3.2 EVALUATION OF THE PROPERTIES OF SURFACE COATINGS

3.2.1 BARRIER PROPERTIES

In order to protect the material onto which it has been coated, a paint film has to be impervious to water and corrosive gases and liquids. Permeation of these substances through the paint can affect the adhesion of the film to, and corrode, the substrate. The permeation of gases through a polymer film can be described by Fick's law[50]:

$$\bar{P} = D \frac{\Delta c}{\Delta p} \qquad (3.1)$$

where $\bar{P}$ is the permeability coefficient, D is the diffusion coefficient, and Δc and Δp are the concentration and pressure gradients. Therefore, $\bar{P}$ is dependent upon the diffusivity and a phase-boundary coefficient relating the gas concentration inside the polymer to the gas pressure outside the polymer.

The liquid permeation flux per unit thickness of film, Q, can be expressed as[50]:

$$Q = D_{(c=0)} \cdot \varrho_1 \cdot \alpha \cdot c^* \cdot \exp(\varphi \cdot c^*) \qquad (3.2)$$

where D is the diffusion coefficient, ϱ_1 is the density of the liquid, α is the amorphous volume fraction in the dry polymer, c^* is the volume of liquid sorbed per unit volume of amorphous polymer, and φ is the volume of amorphous polymer per unit volume of sorbed liquid.

Corrosion of metals is an electrochemical reaction. For example, the anodic reaction occuring during the corrosion of steel can be represented as[50]:

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (3.3)$$

The electrons pass through the steel to the cathode, where several reactions can occur according to the pH-value and the availability of oxygen:

$$2e^- + 2H^+ \longrightarrow H_2 \qquad (3.4)$$

$$2e^- + 2H^+ + \frac{1}{2} O_2 \longrightarrow H_2O \qquad (3.5)$$

$$2e^- + H_2O + \frac{1}{2} O_2 \longrightarrow 2OH^- \qquad (3.6)$$

A paint film can prevent electrochemical corrosion either by providing a barrier to one of the reactants (ions, oxygen, or water), or by inhibiting the passage of the electrons.

Paul[50] reviews the research that has been carried out concerning the measurement of the permeability of surface coatings.

3.2.2 MECHANICAL PROPERTIES

Paint films behave as viscoelastic materials. The mechanical performance of a particular coating can be evaluated with the paint in the form of a free film or as a complete coating / substrate system.

The stress / strain behaviour of the free films can be evaluated by static and dynamic methods[50]. The static measurements include creep and stress relaxation, the constant strain rate, uniaxial tensile test, or impact tests. For a viscoelastic material, the stress relaxation can be described as[50]:

$$\sigma(t) = G(t).\gamma_o \qquad (3.7)$$

where γ_o is the constant strain applied, $\sigma(t)$ is the resulting stress measured as a function of time, and $G(t)$ is the relaxation modulus.

In a creep experiment, a constant stress, σ_o, is applied, and the time dependence of the strain is measured under the influence of σ_o. The time dependent strain, $\gamma(t)$ is expressed as[50]:

$$\gamma(t) = J(t).\sigma_o \qquad (3.8)$$

where $J(t)$ is the creep compliance.

The constant strain rate tensile test and impact test are described in Chapter 1 (sections 1.35 and 1.36), together with dynamic measurements by means of DMTA. Paul[50] describes the experiments to assess the creep and stress relaxation behaviour of paint films.

The experiments which are performed upon coated substrates include the evaluation of[50]:

(A) Indentation Hardness.

This is a measure of the resistance of the coating when it is deformed by a body pressing into it.

(B) Scratch Hardness.

This is usually evaluated by determining the hardest pencil required to fail to scratch the paint film.

(C) Impact Resistance.

This can be determined by, for example, forcing a spherical indentor against the test panel at an impact velocity in the range 0 - 2500cm s^{-1}. The minimum velocity, v_m, at which visible damage at the impact point occurs and the area, A, of the damage are recorded.

(D) Pendulum Hardness.

To measure this quantity, an indentor is allowed to roll backwards and forwards on a horizontal coating. The coating causes the amplitude of the rolling to decrease with time. The pendulum hardness is the time for the amplitude to reduce to half of its original value.

(E) Bending Tests.

These tests are demonstrated by the Mandrel test. The coating ia applied to a metal panel, which is then bent around various cylinders of different diameters, with the coating on the outside of the bend. The smaller the diameter of the cylinder at which cracks appear in the film, the greater the flexibilty of the coating.

3.2.3 AGEING PROPERTIES

Paint films can be degraded by sunlight, moisture, temperature changes, oxygen, and other atmospheric contaminants. However, under

the usual conditions of use, this degradation occurs slowly. Hence, for the ageing properties to be evaluated over a convenient timescale, accelerated exposure tests need to be carried out. After the films have undergone the required treatment, their performance is determined by monitoring the degree of chalking, cracking, blistering, scaling, hardness, and general appearance.

Paul[50] describes the testing methods used for accelerated exposure tests performed outdoors and in the laboratory.

3.2.4 RHEOLOGICAL PROPERTIES

Rheology is the study of the flow and deformation of materials. The study of the rheology of a paint enables the optinum conditions for the paint's preparation, application, and film formation to be determined. Fig. (3.1) illustrates the typical shear rate ranges for different coating processes[198].

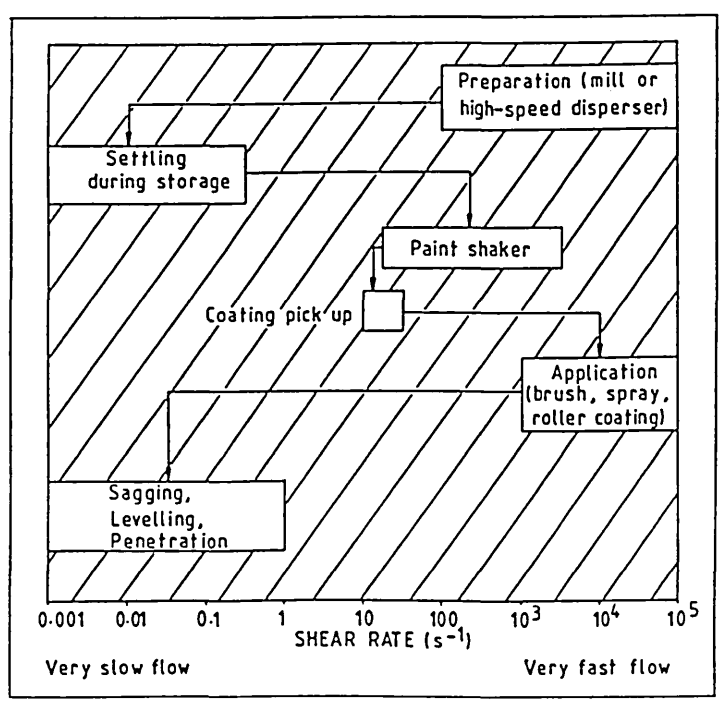


FIG. (3.1): DIAGRAM SHOWING THE APPROXIMATE SHEAR RATE RANGES APPLYING TO VARIOUS ASPECTS OF PAINT FLOW

3.2.4.1 TYPES OF RHEOLOGICAL BEHAVIOUR

The classical theory of hydrodynamics, or Newton's law, states that the applied stress, or shear, to a viscous liquid is proportional to the rate of strain, but is independent of the strain itself[199]. Simple shear be demonstrated in fig. (3.2)[200], where F is the applied force, v is the resulting velocity, i denotes the direction of flow, and j represents the perpendicular distance between the two principal planes which are parallel to the i-axis.

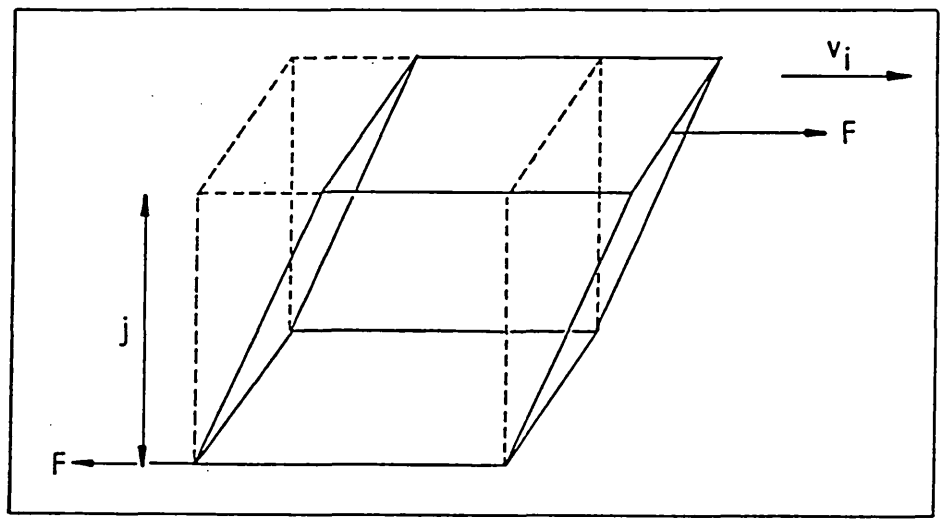


FIG. (3.2): DIAGRAM REPRESENTING SIMPLE SHEAR

Simple shear can be expressed mathematically as:

$$\eta = \frac{\sigma_s}{\dot{\gamma}(t)} \qquad (3.9)$$

where η is the coefficient of viscosity, σ_s is the shear stress, i.e. the shearing force per unit area, and $\dot{\gamma}(t)$ is the shear rate (itself a function of shear stress). The shear rate can be expressed as:

$$\dot{\gamma}(t) = \frac{dv_i}{dj} \tag{3.10}$$

If a liquid obeys Newton's law, then a plot of σ_s versus $\dot{\gamma}(t)$ is linear, passes through the origin, and has a gradient of η.

However, classical Newtonian behaviour is not always followed. Other types of rheological behaviour can occur. A selection of the more important types, as described by their σ_s vs. $\dot{\gamma}$ curves, are shown in fig. (3.3)[200].

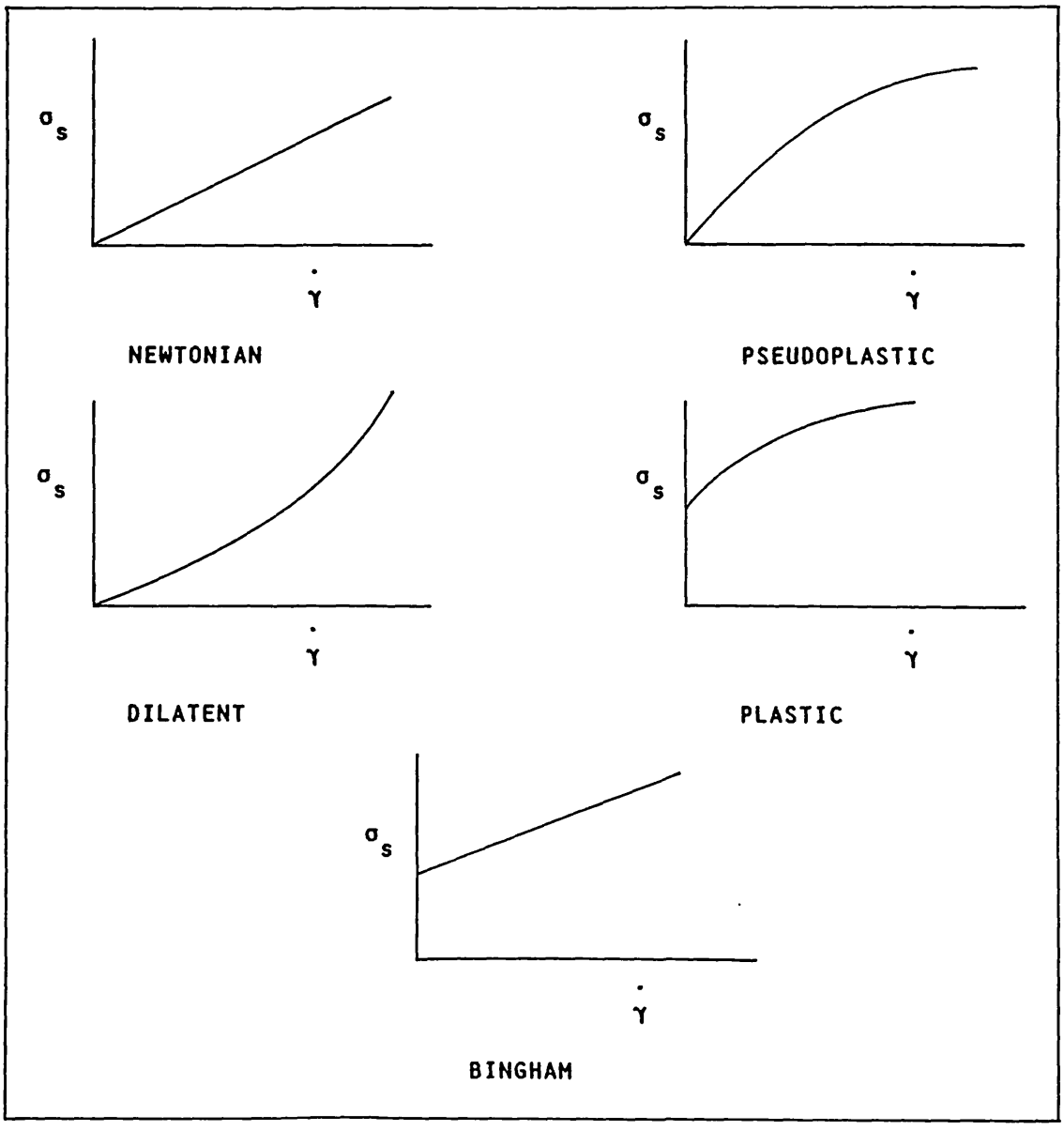


FIG. (3.3): RHEOLOGICAL FLOW TYPES

Pseudoplasticity and dilatancy are described by the "power law"[200]:

$$\sigma_s = \eta_N . \dot{\gamma}(t)^n \qquad (3.11)$$

where η_N is the "zero shear" (Newtonian) viscosity, and $n > 1$ for dilatant systems, $n < 1$ for pseudoplastic systems, and $n = 1$ for Newtonian liquids.

A Bingham flow type can be expressed as[200]:

$$\sigma_s - \sigma_{sy} = \eta . \dot{\gamma}(t) \qquad (3.12)$$

where σ_{sy} is the "yield stress". Below σ_{sy}, the material will not flow and $\dot{\gamma}(t) = 0$ and $\eta = \infty$. When σ_s exceeds σ_{sy}, the material behaves like a liquid.

Plastic behaviour differs from Bingham type in that after the yield stress has been achieved, apparent pseudoplastic behaviour is observed.

The various types of rheological behaviour observed can be explained on a molecular basis[200]. A polymer solution or melt can be considered to consist of entangled molecules. If the act of applying a shearing force does not disturb these entanglements, then the material behaves as a Newtonian liquid.

However, if the applied force causes the molecular entanglements to be broken down, and the molecules re-orientate in the direction of the shear, they present less resistance to flow. The overall entropy of the system is reduced, and the viscosity appears to decrease. This is the cause of pseudoplastic behaviour.

It is possible that when the molecular entanglements have been completed, and the overall structure consists of shear orientated molecules, the flow curve may develop into a linear plot, and a Newtonian region is observed as the shear rate increases.

If, as the shear rate increases, the entangled molecules start to exert a frictional force on their neighbours, the molecules begin to collect together and present a resistance to flow. This is the basis of dilatancy. This sort of behaviour is uncommon among plastics, but is found in heavily filled systems and some PVC pastes.

Bingham type behaviour occurs in crowded, two-phase systems, e.g. clays, mineral slurries[200], foams, emulsions, and pigment dispersions[50].

Fox et al.[201] state that for polymers such as PS, PMMA, poly(iso-butylene) and PDMS, at sufficiently low shear rates so that the viscosity was Newtonian, and provided that the chain length, Z, (or molecular weight) was above a critical value, Z_c:

$$\log \eta = 3.4.\log \bar{Z}_w + k \qquad (3.13)$$

where $\bar{Z}_w$ is the weight average chain length of the polymer (proportional to $\bar{M}_w$), and k is a temperature dependent constant.

Z_c is ~600 for many polymers. Below Z_c, the viscosity is dependent upon a power of $\bar{Z}_w$ in the range 1.75 - 2.0.

Williams et al.[202] developed an equation (the Williams-Landel-Ferry, or WLF, equation) which related the melt viscosity of a polymer to its T_g (or to some other reference temperature). The general form of the WLF equation is[40]:

$$\log (a_T) = \frac{-17.44.(T - T_g)}{51.6 + T - T_g} \qquad (3.14)$$

where a_T (sometimes called the "shift factor") is the ratio of the viscosity at temperature T, η_T, to that at the T_g, η_{Tg}[42]. The equation holds over the temperature range T_g to $(T_g + 100)$ K.

Equation (3.14) can be combined with equation (3.13) to give the temperature relationship of η[40]:

$$\log \eta = 3.4.\log \bar{Z}_w - \left\{\frac{-17.44.(T - T_g)}{51.6 + T - T_g}\right\} + k' \qquad (3.15)$$

where k' is a constant dependent only upon the type of polymer.

The viscosity dependence on shear rate is affected by the molecular weight distribution of the polymer. It has been found that there is a drop in η occurring over a broader range of shear rates for polymers with a broad molecular weight distribution than for those of a narrow distribution. Hence the viscosity / shear-rate measurements give qualitative information about the weight distributions in a polymer sample [fig. (3.4)][40].

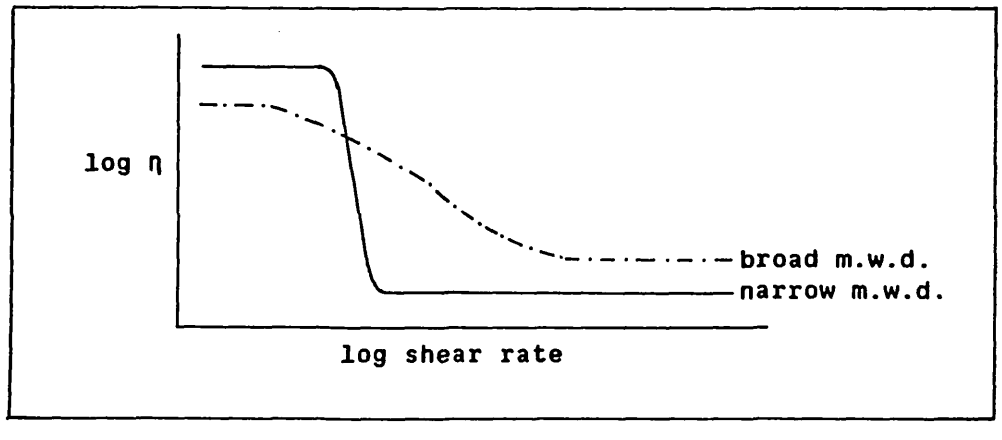


FIG. (3.4): VISCOSITY / SHEAR CURVES FOR POLYMERS WITH BROAD AND NARROW MOLECULAR WEIGHT DISTRIBUTIONS (M.W.D.S)

3.2.4.2 TIME DEPENDENT EFFECTS[200]

If the random molecular entanglements of a polymer sample change gradually rather than immediately upon the application of a shearing force, then the timescale of the viscosity measurements is important.

When carrying out a shear stress versus shear rate experiment, it is important not only to record measurements up to the required maximum shear rate, but, also, to repeat the measurements in the reverse direction (i.e. maximum to minimum). If any time dependent effects are present, a hysteresis loop is obtained which is characteristic for the material (provided that it is sufficiently rested before the experiment is repeated). Time dependent effects are observed in pseudoplastic and dilatant materials.

(A) THIXOTROPY

Thixotropy is observed in certain pseudoplastic flow types. It is defined as an "isothermal and reversible time dependent loss of viscosity as a result of the application of shear"[200] [fig. (3.5)].

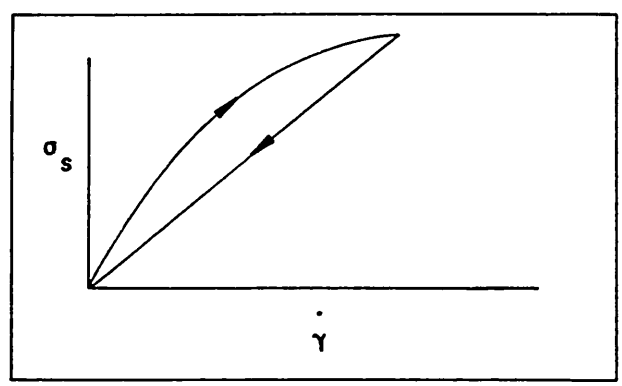


FIG. (3.5): THIXOTROPIC EFFECT (THE ARROWS INDICATE THE DIRECTION OF MEASUREMENT)

All thixotropic materials are pseudoplastic, but not all pseudoplastic materials are thixotropic.

(B) RHEOPEXY

Rheopexy is the time dependent effect observed in some dilatant compounds. It is also referred to as "negative thixotropy"[200], and on a molecular basis implies that the structure present on the downcurve of the experiment is greater than on the upcurve [fig. (3.6)].

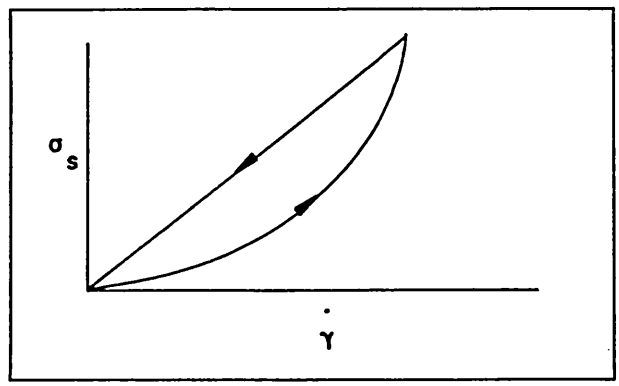


FIG. (3.6): RHEOPECTIC EFFECT

All rheopectic materials are dilatant, but the reverse is not necessarily true.

3.2.4.3 DYNAMIC (PERIODIC) EXPERIMENTS[199]

Simple shear can be mathematically represented as:

$$\sigma_s(t) = \int_{-\infty}^{t} G(t-t').\dot{\gamma}(t')\ dt' \qquad (3.16)$$

where $\sigma_s(t)$ and $\dot{\gamma}(t')$ are the shear stress and shear rate expressed as functions of time, $G(t-t')$ is the relaxation or shear modulus, and the integration is carried out over all past times t' up to the present time t. Equation (3.16) is usually written in a form similar to equation (3.7)[42]:

$$\sigma_s = G.\gamma_s \qquad (3.17)$$

where γ_s is the shear strain, or shear per unit distance between the shearing surfaces.

In dynamic experiments, the stress is varied sinusoidally at a frequency of v Hz or ω (= $2\pi v$) rads.s^{-1}. This is equivalent to performing a non-periodic experiment over the time $t = \omega^{-1}$. It is found that the resulting strain will also vary sinusoidally, but will be out of phase with the stress by the phase angle δ [fig. (3.7)][199].

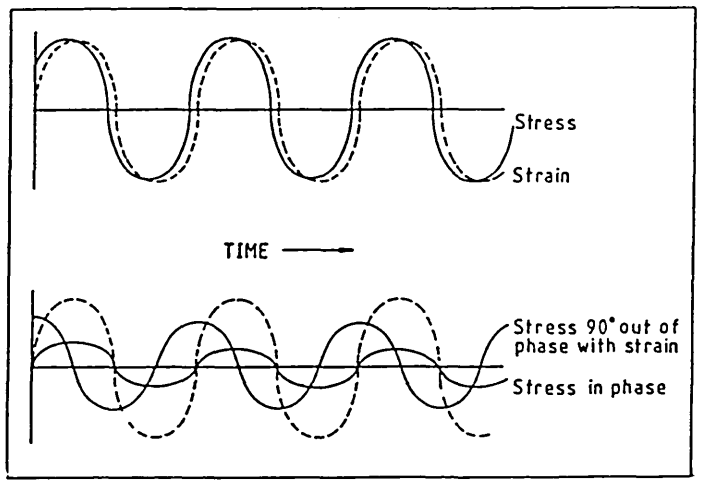


FIG. (3.7): TIME PROFILE OF A PERIODIC SIMPLE SHEAR EXPERIMENT WITH THE SHEAR OSCILLATING SINUSOIDALLY

If the strain, γ_s, is represented as[199]:

$$\gamma_s = \gamma_s^o.\sin(\omega t) \qquad (3.18)$$

where γ_s^o is the maximum amplitude of the strain, then:

$$\dot{\gamma} = \frac{d\gamma_s}{dt} = \omega.\gamma_s^o.\cos(\omega t) \qquad (3.19)$$

If this expression is substituted into equation (3.16), and if (t-t') is replaced by s, $\sigma_s(t)$ can be expressed as:

$$\sigma_s(t) = \int_0^\infty G(s).\omega.\gamma_s^o.\cos[\omega(t-s)]\ ds \qquad (3.20)$$

$$= \gamma_s^o.[\omega.\int_0^\infty G(s).\sin(\omega s)\ ds].\sin(\omega t) + \gamma_s^o.[\omega.\int_0^\infty G(s).\cos(\omega s)\ ds].\cos(\omega t) \qquad (3.21)$$

From equation (3.21), the term in sin(ωt) is in phase with the strain, and the term in cos(ωt) is 90° out of phase with the strain. The equation can be re-written as:

$$\sigma_s = \gamma_s^o.[G'.\sin(\omega t) + G''.\cos(\omega t)] \qquad (3.22)$$

where G' is termed the shear storage modulus, and is a measure of the energy stored per cycle, and G'' is the shear loss modulus, and is a measure of the energy lost per cycle. Both of these moduli are frequency dependent.

σ_s is also related to the phase angle, δ, between the stress and the strain:

$$\sigma_s = \sigma_s^o.\sin(\omega t + \delta) \qquad (3.23)$$

$$= \sigma_s^o.\cos(\delta).\sin(\omega t) + \sigma_s^o.\sin(\delta).\cos(\omega t) \qquad (3.24)$$

where σ_S^o is the maximum amplitude of the stress.

Comparing equations (3.22) and (3.24) shows that:

$$G' = \left[\frac{\sigma_s^o}{\gamma_s^o} \right] .\cos(\delta) \qquad (3.25)$$

$$G'' = \left[\frac{\sigma_s^o}{\gamma_s^o} \right] .\sin(\delta) \qquad (3.26)$$

$$\frac{G''}{G'} = \tan(\delta) = \frac{\text{energy dissipated}}{\text{energy stored}} \qquad (3.27)$$

Experimentally, the magnitude of the complex modulus, $|G^*|$, is measured. G^* is related to G' and G'' by the expression:

$$G^* = G' + iG'' \qquad (3.28)$$

Therefore:

$$|G^*| = \frac{\sigma_s^o}{\gamma_s^o} = (G'^2 + G''^2)^{\frac{1}{2}} \qquad (3.29)$$

This can be represented vectorially [fig. (3.8)]:

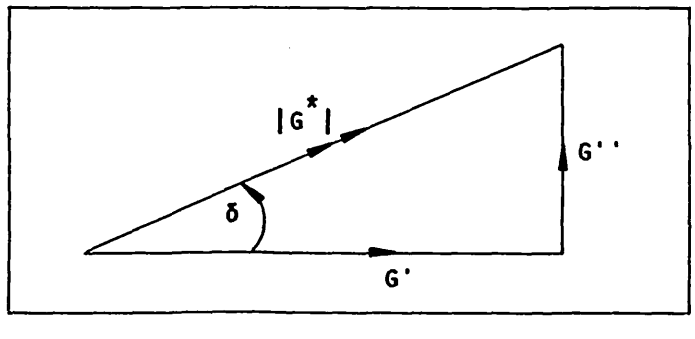


FIG. (3.8): VECTORAL REPRESENTATION OF THE COMPONENTS OF THE COMPLEX MODULUS, G^*

The following discussion describes the effects observed, for polymer solutions and melts, when the shear modulus and other parameters, such as tan(δ) and the dynamic viscosity, are measured at various frequencies of oscillation.

(A) THE STORAGE MODULUS, G'

The storage modulus, G', is defined as the component of the stress in phase with the strain divided by the strain, for a sinusoidal shear deformation[199]. It is a measure of the energy stored and recovered per cycle in the system. Usually, a graph of log (G') against log (ω) is plotted.

For viscoelastic liquids, such as dilute polymer solutions and melts of uncrosslinked polymers, G' tends towards zero as the frequency decreases. This implies that the phase angle, δ, between the stress and the strain approaches 90°, and the stored energy per cycle diminishes, and energy dissipation in the form of heat is more dominant. For dilute polymer solutions in theta solvents, it is found that as ω tends towards zero, G' becomes proportional to ω^2.

At high frequencies, G' is independent of molecular weight distribution. At low frequencies, however, G' is higher for polymers of a broad molecular weight distribution than for those with a uniform distribution, but with the same value of $\bar{M}_n$.

For melts of high molecular weight polymers, highly branched polymers, and very lightly crosslinked polymers, two inflections are observed in the curve. The first corresponds to the glass / rubber transition, i.e. it reflects the relative motion of chain segments between entanglements. The second corresponds to long range configurational rearrangements being suppressed by entanglements, i.e. physical crosslinks are being formed.

Highly crosslinked materials or glassy polymers reach an

equilibrium value of G', i.e. the curve flattens to a plateau. This is due to the suppression of chain motion.

(B) THE LOSS MODULUS, G''

The loss modulus, G'', is defined as the component of the stress which is 90° out of phase with the strain divided by the strain[199]. It is a measure of the energy lost or dissipated as heat per cycle. A plot of log G'' vs log ω yield several features.

In the regions where elastic behaviour is dominant, and little energy is lost, G'' << G'. At high values of ω, G'' tends to zero. On a molecular basis, this means that there can be no more molecular or atomic adjustments which are capable of dissipating energy.

For high molecular weight polymers, highly branched materials, and lightly crosslinked polymers, the curve shows a maximum. This occurs because the losses that are due to backbone changes gradually diminish.

For a viscoelastic liquid, G'' is always proportional to ω. For a simple Newtonian liquid:

$$G'' = \omega.\eta \qquad (3.30)$$

over the entire frequency range, where η is the viscosity.

G'' is not affected by molecular weight distribution.

(C) THE DYNAMIC VISCOSITY, η'

The dynamic viscosity, η', is defined as the ratio of the stress in phase with the rate of strain, divided by the rate of strain[199]. It has the dimensions of viscosity, and is the real part of the complex viscosity, η^*, which is defined in a similar manner to G^*:

$$\eta^* = \eta' - i\eta'' \tag{3.31}$$

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} \tag{3.32}$$

If the strain, $\gamma(t)$, is represented as:

$$\gamma(t) = \gamma_s^o . e^{i\omega t} \tag{3.33}$$

then the rate of strain, $\dot{\gamma}(t)$, is equal to:

$$\dot{\gamma}(t) = i\omega\gamma_o . e^{i\omega t} = i\omega\gamma(t) \tag{3.34}$$

Using a combination of equations (3.9) and (3.17), it can be shown that:

$$\eta^* = \frac{G^*}{i\omega} \tag{3.35}$$

and the individual components are:

$$\eta' = \frac{G''}{\omega} \tag{3.36}$$

$$\eta'' = \frac{G'}{\omega} \tag{3.37}$$

The real part, or in-phase component, η', also called the dynamic viscosity, is a useful quantity for describing uncrosslinked polymer melts and solutions, since at low values of ω, $\eta' \rightarrow \eta$ (the steady flow viscosity). However, as ω increases, η' decreases, reaching values much lower than η.

(D) THE LOSS TANGENT, TAN(δ)

Tan(δ) (= G''/ G') is a measure of the ratio of the energy lost to the energy stored in a sinusoidally varying deformation[199]. The plot of log [tan(δ)] versus log ω reveals several characteristics.

For dilute solutions, tan(δ) is very high because both the solvent and the solute are contributing towards G'', but only the solute contributes to G'.

At low frequencies, tan(δ) is large for uncrosslinked polymer melts, and becomes inversely proportional to the frequency, i.e. tan (δ) decreases as ω increases.

Tan(δ) goes through a maximum for uncrosslinked polymers of a high molecular weight and lightly crosslinked polymers at the transition region between the glass-like and rubber-like phase.

For a very lightly crosslinked material, there can appear a secondary maximum at lower frequencies, corresponding to energy losses due to entanglement slippages.

The loss tangent is a useful quantity to measure, since it can be used to determine bulk properties of polymers and polymer solutions, such as the damping of free vibrations.

(E) OTHER MODULI AND COMPLIANCES WHICH CAN BE MEASURED

Other moduli and compliances (reciprocals of moduli) that can be measured include the creep compliance, J(t), defined as the strain / stress ratio at constant deformation, the stress relaxation modulus, G(t), (introduced in section 3.2.2), defined as the stress / strain ratio at constant deformation (for a perfectly elastic solid J = 1/G), the storage compliance, J'(ω), defined as the strain in phase with the stress divided by the stress during a sinusoidal deformation, and the loss compliance, J''(ω), defined as the strain 90° out of phase with the stress divided by the stress. The characteristics of these

functions are described by Ferry[199].

3.2.5 OTHER PROPERTIES USED TO CHARACTERISE SURFACE COATINGS

Other properties which are evaluated in order to characterise a surface coating include:

(A) Optical Properties.

These are determined by assessing three parameters:

(i) colour

(ii) specular gloss

(iii) hiding power

(B) Adhesion Properties.

The adhesion strength is a measure of the attraction between two surfaces. The performance of a paint is very dependent upon its adhesion to its substrate.

(C) Cratering.

Cratering is caused by the rapid spreading of a paint or a contaminant over the surface of an applied coat.

(D) Skinning.

Skinning is the process whereby a layer of skin is formed at the surface of a paint. It is undesirable as it requires removal before the paint can be used. A series of anti-skinning agents have been formulated to prevent this process from occurring.

(E) Flame Retardancy.

This is characterised by the flash points of the final paint formulations.

(F) Storage Stability.

These factors, and others, are reviewed in detail by Paul[50].

CHAPTER 4

EXPERIMENTAL

4.1 PURIFICATION OF CHEMICALS

4.1.1 SOLVENTS

Table (4.1) lists the solvents used for experimental work and their preparation for use. Those used for reactions involving high purity were initially dried and then fractionally distilled. Other solvents were either distilled only or used as supplied.

TABLE (4.1): PURIFICATION OF SOLVENTS

SOLVENT	SUPPLIER	PREPARATION FOR USE
Acetone	BDH	Dried with anhydrous barium oxide; distilled (b.pt. 56°C; atmospheric); stored over molecular sieves type 4A.
Benzene	May & Baker	-
Butan-2-ol	Rose Chemicals	-
Chloroform	May & Baker	-
$CDCl_3$	Merck, Sharp & Dohme	Contained 1% v/v tetramethylsilane.
Dichloro-methane	BDH	Distilled (b.pt. 40°C; atmospheric)
Diethyl-ether	BDH	-
Dimethyl-formamide (DMF)	Aldrich	For reactions: initially dried with anhydrous BaO followed by distillation (b.pt. 153°C; atmospheric); stored over molecular sieves type 4A. For general use: distilled as supplied.
Dimethyl-sulphoxide (DMSO)	Fluka	Dried for at least 48h with anhydrous calcium hydride; distilled (b.pt. 189°C; atmospheric); stored over molecular sieves type 4A.
d_6-DMSO	Aldrich	$1cm^3$ ampoules used as supplied.
1,4-Dioxane	BDH	Dried with anhydrous BaO; distilled (b.pt. 100°C; atmospheric); stored

		over molecular sieves type 4A.
Ethanol 96	James Burrough	-
Ethyl-acetate	Hopkin & Williams	-
Industrial Methylated Spirit	BDH	-
Iso-butyl-methyl-ketone (IBMK)	BDH	Dried for at least 48h with anhydrous BaO; distilled (b.pt. 117°C; atmospheric); stored over molecular sieves type 4A.
Methanol	May & Baker	-
Tetrahydro-furan (THF)	Aldrich	For reactions: dried using anhydrous BaO; distilled (b.pt. 67°C; atmospheric); stored over molecular sieves type 4A. For general use: distilled as supplied.
Toluene	BDH	Distilled as supplied (b.pt. 111°C; atmospheric).

4.1.2 MONOMERS AND OTHER REAGENTS

Table (4.2) lists the monomers and other reagents used for experimental work, and their preparation for use. In certain cases Analar reagents were employed, and did not undergo further purification.

TABLE (4.2): PURIFICATION OF MONOMERS AND OTHER REAGENTS

MONOMER OR REAGENT	SUPPLIER	PREPARATION FOR USE
Amberlite Resin	Mr.J.N.Bilton Imperial Coll.	-
2,2'-Azo-bis-iso-butyro-nitrile (AIBN)	BDH	Recrystallised from ethanol; stored in freezer.
Barium oxide (anhydrous)	Aldrich	-

Benzoyl-peroxide (BPO)	BDH	Recrystallised from chloroform; stored in freezer.
1,4-Butane-diol (BD)	BDH	Vacuum distilled; stored over molecular sieves type 4A.
Calcium chloride	BDH	-
Copper(I) chloride	BDH	-
Calcium hydride (anhydrous)	Aldrich	-
Dibutyltin-dilaurate (DBTL)	BDH	-
4,4'-Dicyclo hexylmethane diisocyanate ($H_{12}MDI$)	Dupont	Vacuum distilled; stored in a well-sealed vessel at 4°C.
Dimethyl-dichloro-silane solution	BDH	-
a,a-Dimethyl meta-iso-prenyl-benzyl-isocyanate (m-TMI)	Cyanamid	Vacuum distilled; stored in a well-sealed vessel at 4°C.
4,4'-Diphenyl methane-di-isocyanate (MDI)	Bayer	Vacuum distilled; stored in freezer. Care had to be taken prior to use to ensure that no water condensed on the sides of the storage vessel, hence it was allowed to warm to room temperature in a drying dessicator.
Dowex 50W-X8 resin	Mr.J.N.Bilton Imperial Coll.	Initially activated by mixing resin with dilute sulphuric acid; filtered; washed with distilled water; dried in vacuo.
Erythrol (ER)	Dr.I.R. Davison & Mr.P.Lam, Imperial Coll.	Prepared by the hydrolysis of 3,4-epoxybut-1-ene with aqueous sodium carbonate solution (ref. 203).
1,2-Ethane diol (ED)	BDH	Vacuum distilled; stored over molecular sieves type 4A.
Glyceryl mono methacrylate (GMM)	Polysciences	Used as supplied; inhibited with hydroquinone monomethylether, (MeHQ, 3000ppm); stored in freezer;

		allowed to warm to room temperature in a drying dessicator before use.
Glycidyl methacrylate (GM)	Aldrich	-
Hydroquinone (HQ)	BDH	-
2-Hydroxy-ethyl-meth-acrylate (HEMA)	Aldrich	Vacuum distilled; stored over molecular sieves type 4A at 4°C.
Methyl methacrylate (MMA)	Aldrich	Inhibitor removed by washing several times with aqueous sodium hydroxide solution (5% w/v) followed by distilled water; dried over anhydrous BaO for 48h; vacuum distilled; stored at 4°C.
Nitric acid SG 1.42	Hopkin & Williams	-
Nitrogen gas (oxygen free)	BOC	Dried as used by passing through concentrated sulphuric acid, potassium hydroxide pellets, and anhydrous calcium chloride.
Polyethylene glycol 1000 (PEG 1000)	BDH	Neutralised with HCl; dried under vacuum at 90°C. Stored in drying dessicator.
Polytetra-methylene ether glycol 2000 (PTMEG 2000)	Quaker Oats Co.	Vacuum dried at 90°C. Hydroxyl no. = 53 - 59 mg KOH/g, i.e. equivalent weight = 950 - 1058. Stored in a drying dessicator.
Potassium hydroxide pellets	BDH	-
Sodium chloride	BDH	-
Sulphuric acid 98%	May & Baker	-

4.2 PHYSICAL AND ANALYTICAL EXPERIMENTAL METHODS

4.2.1 HIGH VACUUM EQUIPMENT

Addition polymerisation of unsaturated monomers using free

radical initiators is sensitive to air and moisture. A Pyrex glass high vacuum system was constructed to enable air and moisture to be eliminated from reaction mixtures. The pumping system consisted of a high vacuum rotary pump and a mercury diffusion pump. Reaction solutions were prepared in ampoules which were sealed under vacuum before being heated to the required temperature.

Reactions that did not require the use of the vacuum line were carried out in flasks that were sealed with Suba-seal septa (Aldrich). Red rubber septa were used for solution in THF and white rubber septa were used for solutions in DMF. The solution was then purged by inserting a needle through the septum and bubbling dry, O_2-free nitrogen gas through the liquid. A pressure release needle enabled the gases to escape. This was removed before the N_2-gas needle to ensure that the solution was surrounded by an inert atmosphere.

4.2.2 INFRARED (IR) SPECTROSCOPY

IR spectra of reagents, reactants, and products were recorded using a Perkin-Elmer 457G Grating Spectrophotometer, scanning from 4000 to 600cm^{-1}. Solid materials were prepared in nujol and applied to sodium chloride plates. Polymers capable of forming films were either cast as a film on a NaCl plate, using THF as the solvent, or used as a thin free-standing film. Complete removal of the solvent had to be ensured, and all films were dried in vacuo. A standard PS film was used as a reference.

4.2.3 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Personally recorded ^{1}H-NMR spectra were carried out using a Perkin-Elmer R32 90MHz NMR Spectrometer. Solutions were made up in d_6-DMSO or $CDCl_3$ at a concentration of 5 - 10% w/v, and were filtered using syringe filter equipment (Anachem Stainless Steel Filter Holder

containing Whatman Grade 1 filter papers). The NMR tube was stoppered and sealed with Parafilm to prevent contamination of the solvent.

Other NMR spectra were recorded by the NMR Service, Department of Chemistry, Imperial College. Solutions submitted were analysed by a Bruker WM-250 spectrometer operating at 250MHz for ^{1}H-NMR and 62.9MHz for ^{13}C-NMR. ^{13}C-NMR required a much larger concentration of sample. However, a problem with the polymeric materials was that a high concentration led to a very viscous solution which gave spin exchange broadened resonances. Too low a concentration gave weak signals. The optinum concentration was around 15 - 25% w/v.

4.2.4 MICROANALYSIS

Microanalysis was carried out on samples submitted to the Microanalytical Laboratory, Department of Chemistry, Imperial College. Microanalysis was used as a method of verifying results obtained about the composition of materials by other techniques.

4.2.5 CENTRIFUGE

Centrifugation was carried out using the M.S.E. High Speed 18 Refrigerated Centrifuge which could operate to a speed of 18,000rpm at any temperature between -30 to 60 $^{\circ}$C.

4.2.6 ROTARY EVAPORATION

Rotary evaporation of solvents was performed using a Buchi Rotavapor R connected to either a water-vacuum pump or a high vacuum rotary pump.

4.2.7 TURBIDIMETRIC TITRATIONS

The absorbances of the solutions prepared during the turbidimetric titrations were measured using an Evans Electroselenium

Ltd Absorptiometer. The diffraction grafting was set at position ND. Glass cells (Hilger) of dimensions 20 x 23 x 35mm were used for the sample and the reference.

4.2.8 ADSORPTION COLUMN CHROMATOGRAPHY

Adsorption columns were made according to standard techniques[204] using silica gel type S5070 (Rose Chemicals) as the column packing.

4.2.9 GEL PERMEATION CHROMATOGRAPHY (GPC)

4.2.9.1 ANALYTICAL GPC

The experimental arrangement of the equipment used for analytical GPC is shown in fig. (4.1). The solvent used initially was THF. However, this was eventually substituted by DMF. Solvent was pumped from the reservoir by an HPLC pump (Altex Model 110A) set at a flow rate of $1.0cm^3\ min^{-1}$. A sample of low concentration (~0.3% w/v in the eluting solvent) was prepared, and filtered, using a syringe filter system, if any insoluble material was present.

Using a blunt-needled syringe (Hamilton Inc.) several portions of the sample were injected into the stainless steel high pressure sample injector valve (Rheodyne Model 7125 Syringe Loading Sample Injector fitted with 20µl loop) to ensure that any residual material was washed out. After the final injection, the syringe was left in the needle port and the valve was turned through 60° in an anticlockwise direction. The flow of solvent now passed through the sample loop instead of the bypass. It was now safe to remove the syringe without introducing air into the sample loop via the vents.

From the injection valve, the solvent and sample flowed through a prefilter (Anachem, 2µm), a precolumn (Polymer Laboratories 50 x 7.5mm, 5µm mixed porosity "PL Gel") and the main column (Polymer Laboratories 300 x 7.5mm, 5µm mixed porosity "PL Gel"). The eluate

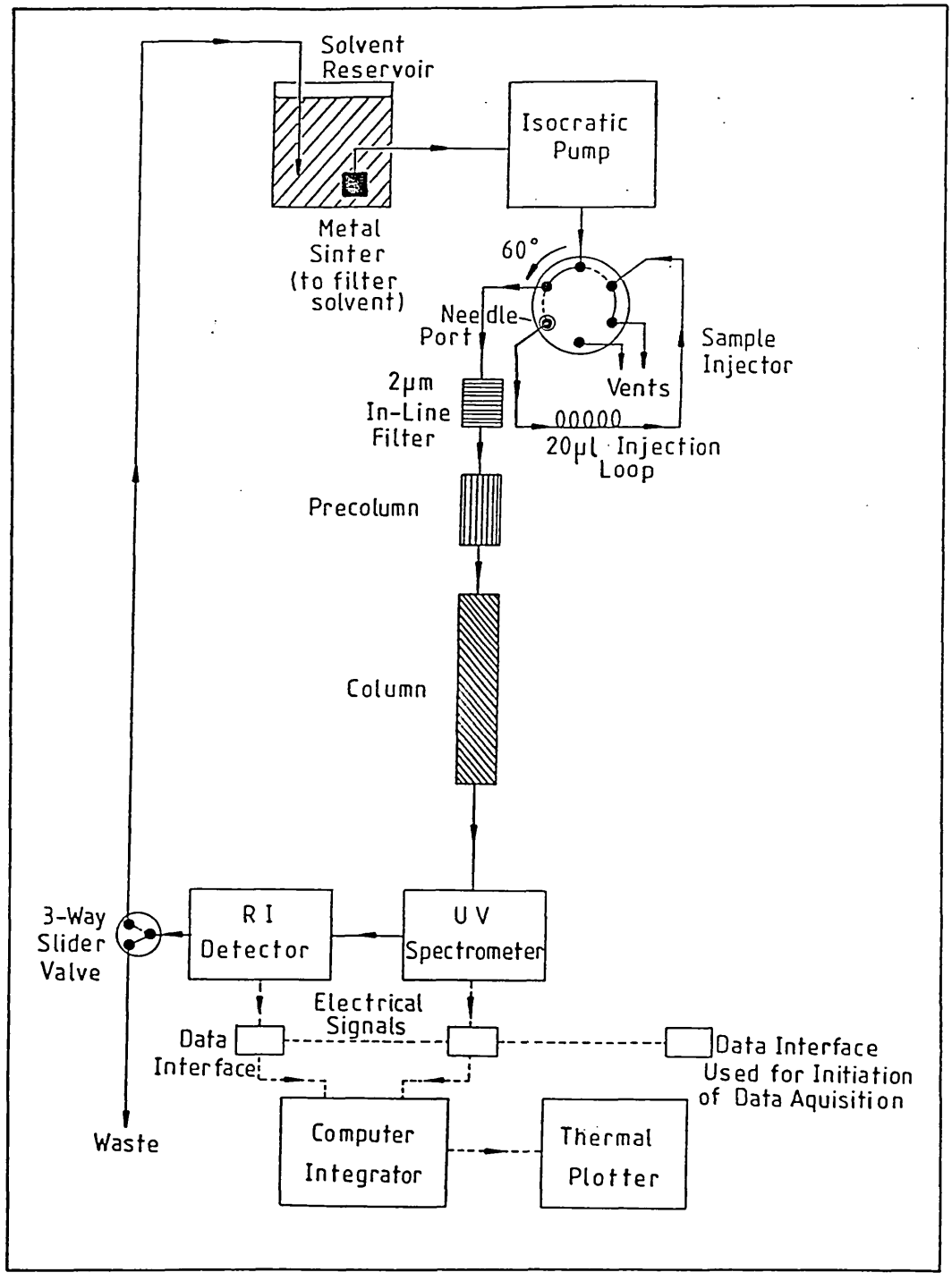


FIG.(4.1): ANALYTICAL GPC EQUIPMENT

then passed through a UV detector (Cecil CE 2012 Reference Channel Variable Wavelength UV Monitor with 8µl flow cell) and then through the sample cell of a refractive index (RI) detector (Knauer Differential Refractometer with 10µl flow cell). The eluate was collected for solvent recovery by distillation.

A 3-way slider valve (Rheodyne) was installed between the RI detector and the waste collector so that solvent could be recycled back to the reservoir when no sample was running. This enabled the apparatus to be continually operating throughout the working day, thus ensuring that the column was equilibrated.

The individual components were linked together using the minimum quantity of stainless steel or PTFE tubing of low internal diameter. The fact that the two detectors were linked in series with a certain amount of dead volume between them meant that the retention times of the polymers observed by the UV detector were 10 - 20s shorter than those for the RI detector. The system was shut down overnight.

The data from the two detectors was collected by a Trilab III Computing Integrator (Trivector Systems Ltd). This was later updated to the Trilab 2000 (Trivector). Each detector was linked to the integrator via a data interface consisting of a voltage to frequency converter (Trivector) which was based on an operational amplifier design. The two separate interfaces were connected to a third multiplexing interface which enabled data to be logged into two channels by the computer.

Data was saved onto magnetic tape (Trilab III system) or onto 5.25 inch floppy disk (Trilab 2000), to be reloaded at a later date.

(A) QUALITATIVE INFORMATION

GPC data, as analysed by the computer, was used as a method of determining whether polymers had been formed or not, whether a change

in molecular size had occurred, or if the sample was contaminated with impurities such as solvents.

The UV spectrometer was usually set at a wavelength of 280nm, corresponding to a region of strong absorbance by the aromatic groups of polyurethanes based on MDI. However, non-aromatic polymers had only weak absorbances in that area, and, therefore, were not observed by the UV detector. The RI detector, however, detected all species present as long as there was a change in refractive index compared to the reference (the eluting solvent). Negative peaks were occasionally observed when using the RI detector.

The discrepancy in the detecting limits of the two detectors was very useful when using GPC as a method of determining whether the grafting of a weakly UV-absorbing monomer onto a polyurethane containing MDI had occurred. The RI detector showed the presence of all polymers, i.e. polyurethane, homopolymer, and graft copolymer. The UV detector, however, only showed materials containing polyurethane. If there was evidence of a new material at a shorter retention time than the original polyurethane (corresponding to an increase in molecular size), it was safely assumed that the monomer had grafted. If there were no new peaks in the UV chromatogram, any new ones observed by the RI detector were probably due to homopolymer.

(B) QUANTITATIVE INFORMATION ACQUIRED FROM GPC

For chromatography in general it can be assumed that the area under a peak on a chromatogram is directly proportional to the concentration of the species responsible for its formation. This rule was applied to GPC. The apparatus was calibrated by running samples of known concentrations. From the calibration those of unknown composition were evaluated. A TRIVECTOR BASIC VSN 6.45 computer program was written (Appendix I) to calculate the area between two

specified limits on a GPC chromatogram. The program was designed to be run by the Trilab 2000 computer.

(C) MOLECULAR WEIGHT ANALYSIS USING GPC

The GPC apparatus was initially calibrated by injecting several samples of linear PS standards (Polymer Laboratories Ltd) of a known, monodisperse molecular weight distribution. Using the GPC calibration program provided (Trivector), $\log_{10}$(molecular weight) of the standards was plotted against peak retention time. The details of the calibration curves were saved onto magnetic tape (Trilab III system) or a 5.25 inch floppy disk (Trilab 2000).

A typical calibration curve is shown in fig. (4.2).

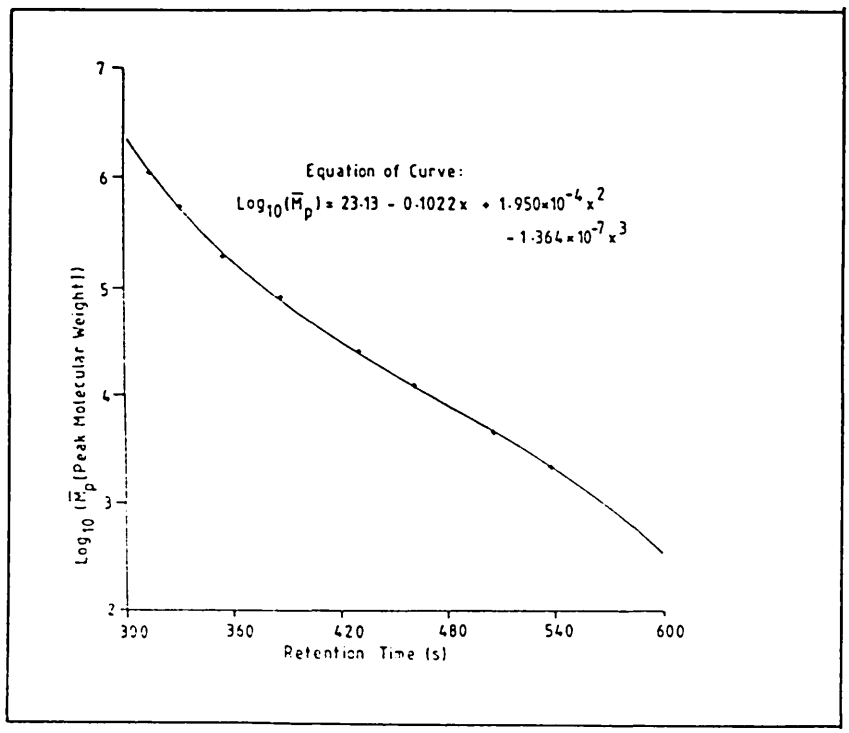


FIG. (4.2): TYPICAL GPC CALIBRATION CURVE FOR THE UV DETECTOR, SHOWING THE EQUATION OF THE CURVE

It was usually a cubic curve. The straight portion in the middle corresponded to the working range of the column, and the asymptotes at

either side indicated the points where severe inaccuracies in the calculation of molecular weight from the calibration occurred. The UV detector and the RI detector were calibrated independently. Re-calibration was carried out whenever an alteration of the apparatus was performed, e.g. the changing of the column or any of the tubing. Thereafter, it was only necessary to re-calibrate after a period of six months to allow for the deterioration of the column.

An internal standard (usually toluene) was injected at the time of calibration. The same standard was injected after experimental runs. The retention time of the standard was used by the "GPC Analysis" (Trivector) program to correct for slight variations in the flow rate.

The analysis program calculated the weight averages of the samples run. It has to be stressed, however, that values quoted, such as $\bar{M}_n$ and $\bar{M}_w$, were with respect to linear PS standards, and were not absolute. Polymers other than PS would have interacted with the column packing in a different manner and, therefore, the retention times would not have been the same for polymers of different composition but of an identical molecular weight distribution. GPC also depended on molecular size and shape rather than molecular weight. Therefore, a comb-like graft copolymer would have appeared to have a smaller molecular weight distribution than its linear counterpart as the molecule was more compact and could have diffused in and out of the pores of the packing more readily.

GPC molecular weight analysis was, therefore, used as a guide rather than an absolute method of determining molecular weight distributions.

4.2.9.2 PREPARATIVE GEL PERMEATION CHROMATOGRAPHY (PREP-GPC)

Two sets of experimental apparatus were utilised using the same Prep-GPC column but different solvent pumps and detectors.

(A) USING THE WATERS HPLC PUMP

The schematic diagram of the experimental arrangement is shown in fig. (4.3). The pump and refractometer and valves came as a complete unit (Waters Associates Prep LC/System 500). Prior to use, the flushing valve was opened and the pump was operated for several minutes to wash and fill the reference channel of the refractometer with the solvent used (DMF). The flushing valve was then closed. The minimum flow rate was set for the pump. This was found to be $\sim 10 cm^3 min^{-1}$ (gauged by measuring the volume of liquid eluted over a specific time). This was a satisfactory flow rate; the maximum flow rate suggested by the column manufacturers was $30 cm^3 min^{-1}$.

Samples of a concentration up to 10% w/v were prepared in DMF. It was very important to filter the solutions, using the syringe-filter system, as the column was not protected by an in-line filter or precolumn.

Using a $5 cm^3$ disposable plastic syringe ("Plastipak", Becton and Dickinson), the sample was injected at the injection port (Omnifit Rotary Sample Injection Valve, usable up to 300psi back pressure, fitted with a $2.5 cm^3$ injection loop). The valve was turned to divert the flow of solvent through the injection loop and, at the same time, the chart recorder was switch on.

The sample passed through the Prep-GPC column (Polymer Laboratories, 300 x 25mm, 10μm mixed porosity "PL-Gel"). The eluate from the column was then separated by a flow splitter; a small portion of the solution flowed through the sample cell of the refractometer, the rest carried on to be collected or discarded. The flow splitting

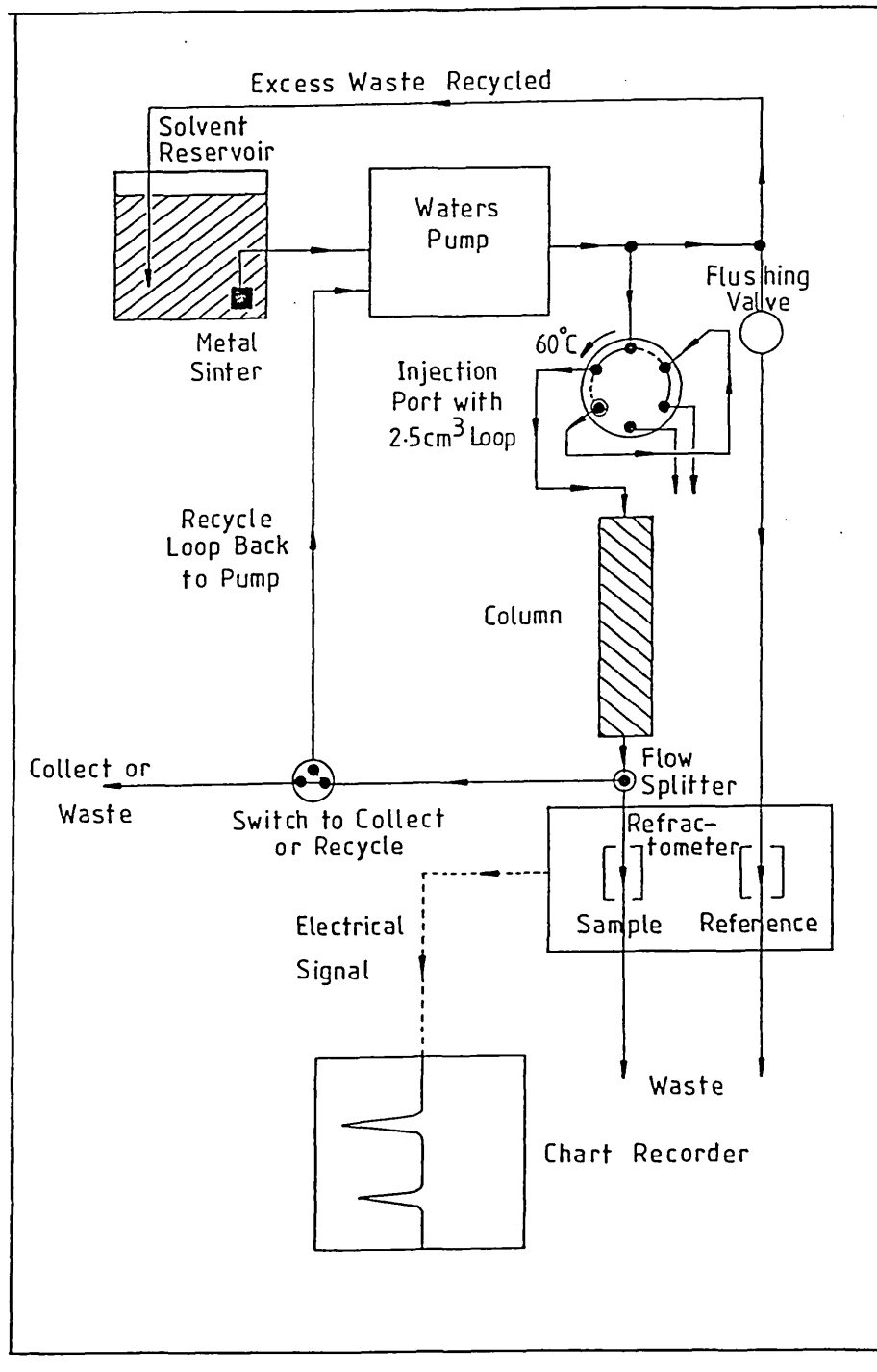


FIG.(4.3): PREP-GPC USING THE WATERS PUMP

ratio was controlled by restricting the aperture of the waste tubing from the refractometer, to ensure that the minimum quantity of liquid was expended. The output from the refractometer was recorded by a chart recorder (Bryans 28000 dual channel).

Since the sample collection ran in parallel with the sample detection, the apparatus had to be initially calibrated, using a DMF solution of the orange dye isatin, to determine the time difference between the response of the detector and the point of collection. As all of the tubing was made of PTFE, it was easy to see the dye eluting. However, the detector responded 3 minutes after the dye had been collected [see fig. (4.4)]. To allow for this during operation, a preliminary run was carried out of the sample, and was used to calculate the time for collection, allowing for the delay in response by the refractometer.

Several fractions of each sample were collected in test-tubes, and each was analysed by analytical GPC to give its composition. Fractions which contained the required material were combined and were rotary evaporated to remove the DMF solvent. Other fractions were discarded.

Certain samples contained two separate species which eluted at close retention times, and hence their peaks on the GPC chromatogram coalesced into one large, broad peak. As it was usually the material of larger molecular size, and, therefore, shorter retention time, that was of interest, fractions which occurred in the intermediate range of the two peaks were discarded [see fig. (4.5)].

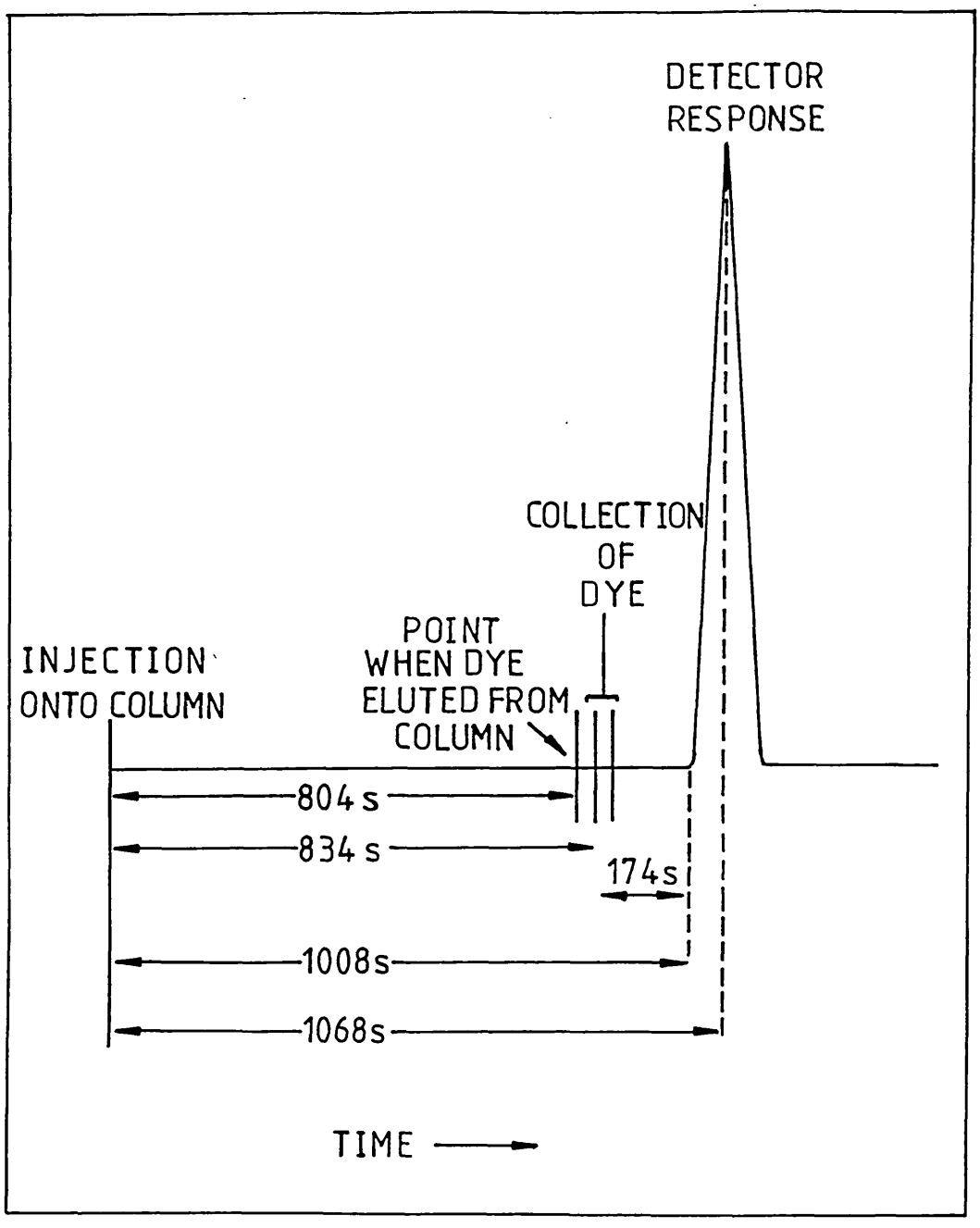
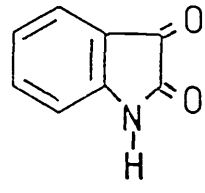


FIG.(4.4): CALIBRATION OF THE WATERS PREP-GPC APPARATUS USING THE DYE ISATIN



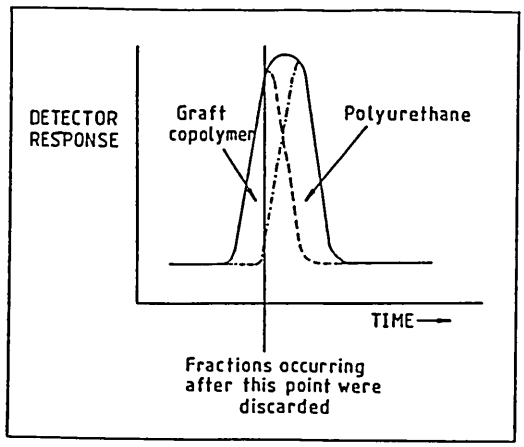


FIG. (4.5): TYPICAL GPC CHROMATOGRAM INDICATING THE DIVIDING POINT BETWEEN FRACTIONS COLLECTED AND FRACTIONS DISCARDED FOR A COMBINATION OF MATERIALS WITH NO CLEAR DISTINCTION BETWEEN THEM.

This meant that the material obtained under these circumstances would have been biased towards the higher molecular weight material.

(B) USING THE WATERS EQUIPMENT IN THE RECYCLE MODE OF OPERATION

Instead of collecting an eluting sample, the recycle valve of the equipment was used to divert the flow of liquid back to the pump. This automatically cut off the supply of solvent from the reservoir. The sample was then repeatedly pumped through the column until the valve was switched back to collect, and the pump resumed pumping solvent.

It was shown[205] that using the equipment for HPLC in the recycle mode improved the separation of materials, with each pass through the column, up to the point where recombination occurred [see fig. (4.6)].

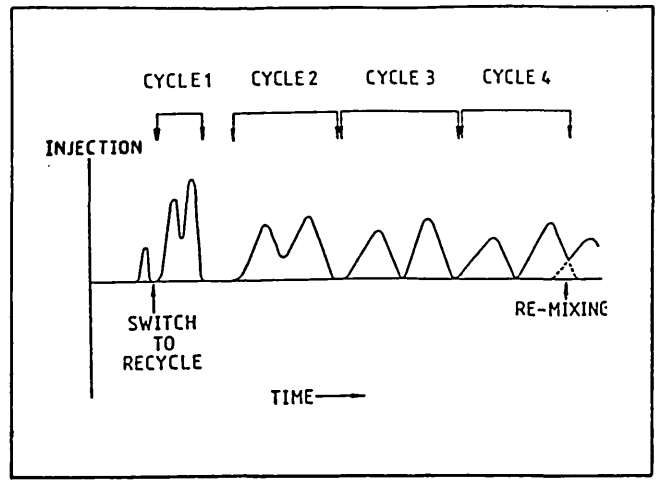


FIG. (4.6): HPLC OF A MIXTURE OF TWO MATERIALS USING THE RECYCLE FACILITY

The recycle facility was utilised for several samples, using the Prep-GPC column, as a method of demonstrating the number of components in the mixtures of materials. However, the equipment was designed to be used with very large, plastic-walled HPLC columns which could contract in volume as solvent was being lost via the waste of the refractometer. The Prep-GPC column was made of stainless steel and could not contract. Hence no more than four recycles were carried out per sample, and the volume of solvent lost by the detector was reduced to a minimum.

(C) PREP-GPC USING THE ALTEX PUMP

A schematic diagram of the experimental apparatus is shown in fig. (4.7). The HPLC pump (Altex Model 110A) was fitted with a semi-preparative head which increased the flow rate set for the pump by a factor of 2.8. The flow rate could be fixed much more accurately than that of the Waters pump, and the optinum value was found to be $4 cm^3 min^{-1}$.

The samples were prepared as previously and were injected into an identical injection port as that used with the Waters equipment. The

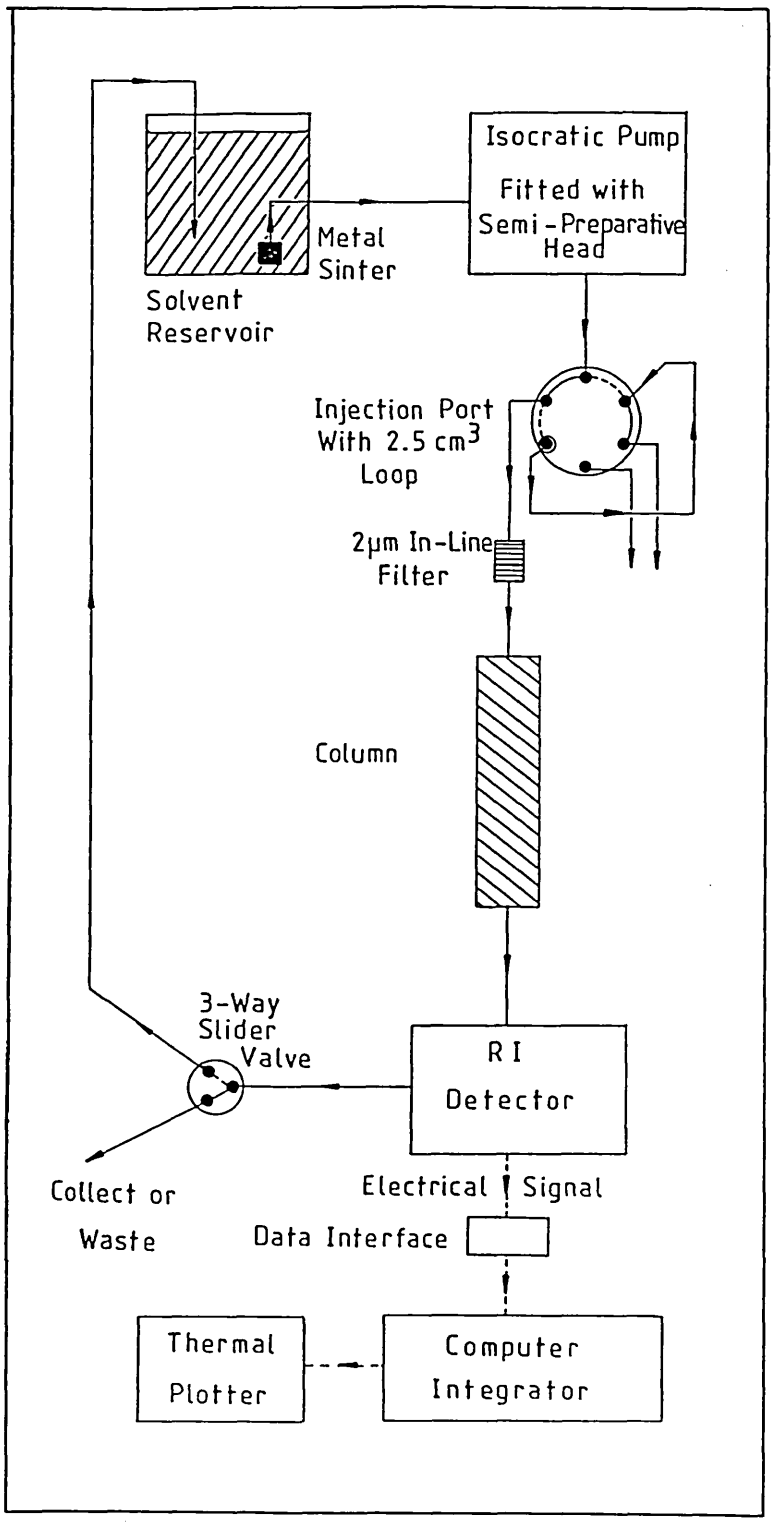


FIG.(4.7): PREP-GPC APPARATUS USING THE ALTEX PUMP

sample, when loaded onto the column, passed through a prefilter (Anachem, 2μm) before reaching the Prep-GPC column (same as before).

The eluting sample next passed to a RI detector (Beckman Model 156 with 10μl flow cell), and from there was collected in fractions. A 3-way slider valve (Rheodyne) was inserted in the line so that the solvent could be diverted back to the reservoir. Hence the equipment could be continually running (this facility was not afforded by the Waters apparatus).

The detector was linked to the Trilab 2000 computer integrator (also used for the analytical GPC equipment) via a separate data interface. This enabled data to be collected by the computer from both the analytical and Prep-GPC detectors simultaneously and independently.

This Prep-GPC arrangement had the advantage that the detector was in series with the collection, hence the apparatus did not require calibrating and the samples progress could be monitored continually by the computer's on-line facility. However, there was no recycle facility.

The fractions collected were analysed by analytical GPC. The required fractions were combined and the solvent removed. The other fractions were discarded.

4.2.10 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

The experimental arrangement was very similar to that of the analytical GPC equipment. The solvent (THF) was pumped by an isocratic pump (Altex Model 110A) at a flow rate of $1.0 cm^3 min^{-1}$.

The sample was injected into a stainless steel high pressure sample injector (Rheodyne Model 7125) fitted with a 20μl injection loop. The solution then flowed through a 10μm ODS HPLC column (packed by Mr. J.N.Bilton, Department of Chemistry, Imperial College) before

passing through a UV spectrometer (Cecil CE 2012 Reference Channel Variable Wavelength UV Monitor) set at a wavelength of 234nm. The sample then flowed to waste.

The output from the UV detector was linked to a chart recorder (Bryans 28000 dual channel).

4.2.11 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC measurements were carried out using a DuPont Instruments Thermal Analysis System 9000 fitted with a DSC plug in module, cooling unit, and high temperature unit. The cooling unit utilised liquid N_2 and was used for runs from -100°C to room temperature. For scans from room temperature to 250°C, the cooling unit was replaced by the high temperature device. The rate of heating used was 10°C min^{-1}.

Samples were placed into aluminium pans of diameter ~6mm, and were covered with an aluminium lid. The reference was an empty pan and lid.

After the high temperature run, the cold unit was returned to the module since this enabled the module to cool to room temperature in a short time. As soon as the apparatus had reached room temperature, the unit was cooled again with liquid nitrogen.

Samples were usually scanned twice, one scan after the other, to see if changes had occurred within the sample.

When analysing the data, the T_g of the sample was considered to be the half way point of the inflexion in the curve [see fig. (4.8)].

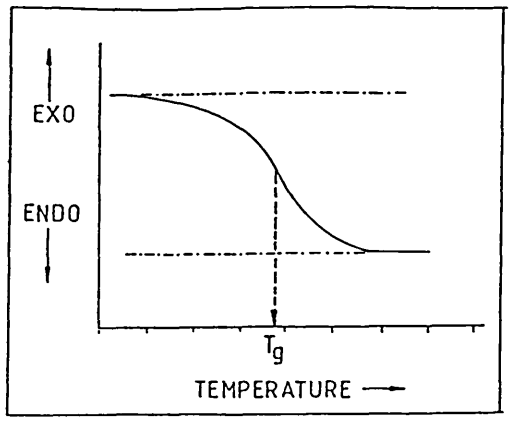


FIG. (4.8): DETERMINATION OF THE T_g OF A SAMPLE FROM DSC MEASUREMENTS

4.2.12 STRESS / STRAIN MEASUREMENTS

The stress / strain properties of the polymers were measured at room temperature using a Polymer Laboratories Miniature Materials Tester ("Minimat") interfaced to an IBM Personal System-2 computer. Polymer films were cast from THF (film thickness ~100 - 500μm) and carefully cut using a scalpel to the required shape (fig. 4.9), which was designed to eliminate failure of the sample at the clamping position. All of the specimen's dimensions were measured accurately.

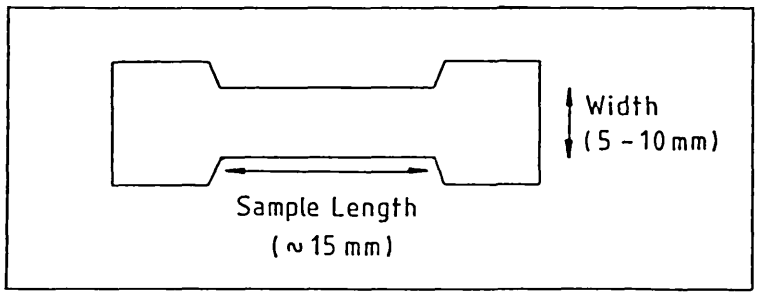


FIG. (4.9): DIAGRAM OF THE SHAPE OF SAMPLE FOR STRESS / STRAIN MEASUREMENTS USING THE "MINIMAT" EQUIPMENT

A crosshead speed of 10 mm min^{-1} was used. A graph of load versus extension was plotted by the computer. This was manually analysed to calculate Young's modulus and other mechanical data.

At least three separate specimens of each sample were tested to ensure reproducibility and to attain the average values of the data available.

4.2.13 IMPACT TESTS

Impact tests ("Falling Dart" technique) were performed using a Rosand Precision Ltd Instrumental Falling Weight Impact Tester Type 5 interfaced to a Commodore 8032-SK computer. The instrument was fitted with a Charpy striker. Strips of polymer film of a known thickness (100 - 500μm) were cut with a length > 80mm and width 10mm. The strips were then placed in a clamping unit [see fig. (4.10)]. The unit was designed so that the geometry of the system was known.

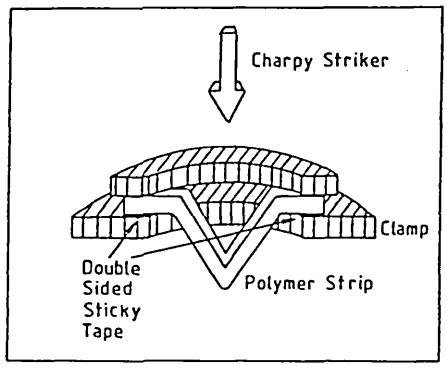


FIG. (4.10): DIAGRAM OF THE CLAMPING UNIT CONTAINING A POLYMER SAMPLE AS USED FOR IMPACT TESTS

The polymer sample was secured in position using double sided sticky tape to ensure that it did not slip in the clamp. The unit was then placed in the apparatus and the striker was raised to the height which would result in the polymer being struck at a particular speed. The striker was released, and after hitting the sample the data was transferred to the computer.

The computer analysed the forces experienced by the striker and its displacement. It should have plotted a graph of stress versus l-

strain so that Young's modulus could be calculated. However, a fault in the software created erroneous results. A computer program was written in BASIC (Appendix II), for use on a BBC Model B microcomputer, to calculate the secant modulus, breaking stress, and breaking strain from the unprocessed data from the impact tester.

The theory behind the program is as follows. Fig. (4.11) is a diagram of the polymer sample before and after being struck. F is the force felt by the striker and T is the tension in the sample. D is the displacement of the striker in a vertical direction.

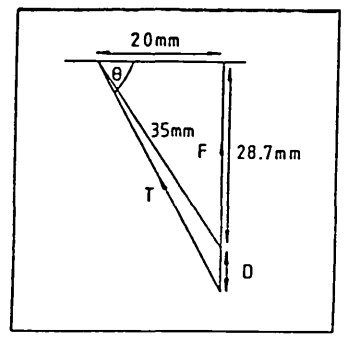


FIG. (4.11): DIAGRAM OF THE DIMENSIONS OF, AND THE FORCES FELT BY, THE SAMPLE BEFORE AND AFTER THE IMPACT TEST

F is related to T by the expression:

$$F = 2.T.\sin\theta \qquad (4.1)$$

The factor of 2 is introduced because there are two halves to the sample. Therefore:

$$T = \frac{F}{2.\sin\theta} \qquad (4.2)$$

If $t = \tan\theta$ [$= (28.7 + D) / 20$], it can be shown using basic rules of trigonometry that:

$$\cos\theta = (1 + t^2)^{-1/2} \qquad (4.3)$$

Therefore, the extended length is equal to $20.[(1 + t^2)^{1/2}]$. From this the percentage extension can be calculated:

$$\% \text{ extension} = \left\{ \frac{20.[(1 + t^2)^{1/2}]}{35} - 1 \right\} \quad (4.4)$$

$$= (E - 1) \times 100 \quad (4.5)$$

where E is the extension ratio [$= (4/7).\{(1 + t^2)^{1/2}\}$].

For small strains:

$$\text{stress} = \frac{T}{\text{Area}} \quad (4.6)$$

$$= \frac{F.[(1 + t^2)^{1/2}]}{2.t.b.d} \quad (4.7)$$

where b is the width of the sample (= 10mm) and d is the thickness of the sample. Since F and D were measured by the computer, the stress and strain of the sample could be calculated. The secant modulus was related to these quantities by the relationships:

$$\text{secant modulus} = \frac{\text{stress}}{\text{strain}} \quad (4.8)$$

$$= \frac{\text{stress}}{E - 1} \quad (4.9)$$

Impact tests were carried out on at least three separate samples of each material to check reproducibility and to achieve the average values of the required data.

4.2.14 RHEOLOGICAL PROPERTIES OF POLYMER SOLUTIONS

The rheological properties of the polymers in solution were investigated using a Bohlin Rheometer VOR interfaced to an IBM Personal Computer XT. A diagram of the sample cell of the apparatus and its attachments are shown in fig. (4.12).

As the base was rotated or oscillated at a certain amplitude and

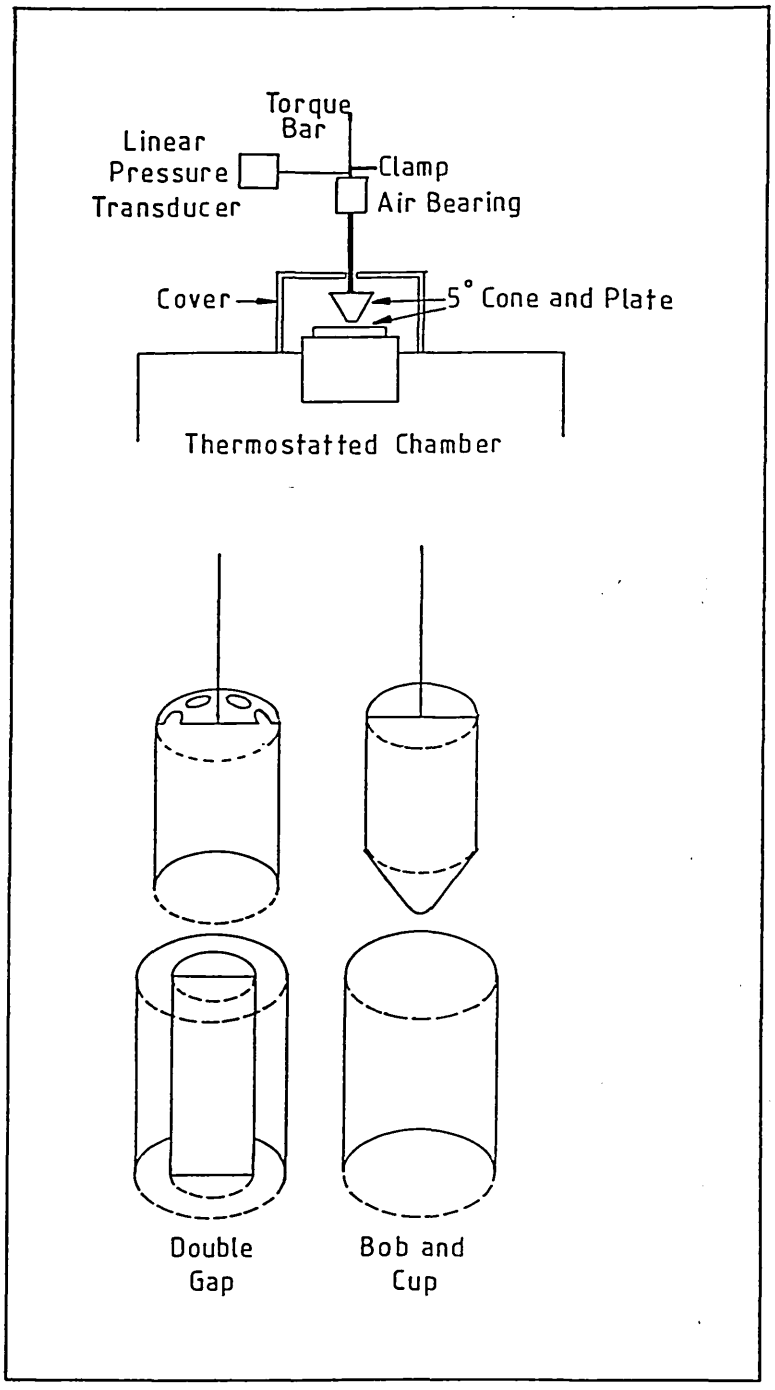


FIG.(4.12): RHEOMETER FIXED WITH 5° CONE AND PLATE, AND OTHER ATTACHMENTS WHICH COULD BE USED

frequency, the torque of the torsion bar was measured by the linear pressure transducer. The data was then converted into the required information by the computer. Several torque bars of different dimensions could be used, depending upon the force exerted.

Initially, THF solutions of the polymers, with concentrations ranging between 10 - 25% w/v, were analysed at 10°C using bob and cup, double gap, and cone and plate attachments. However, rapid evaporation of the solvent caused erroneous measurements. 20% w/v DMF solutions were then analysed at 25°C using the 1° or 5° cone and plate attachments. This was more successful. Both viscosity, shear stress versus shear rate, and oscillatory (dynamic) measurements were performed.

For the viscometry tests, values of the viscosity and shear stress of the sample were taken for a series of different shear rates. For each point, a set time was allocated for the apparatus to attain a particular rate of shear (usually 10s). This was called the strain delay time. A further 10s was allowed for the measurement (the integration time).

Values were taken as the shear rate increased. The measurements were then repeated in the reverse direction (i.e. decreasing shear rate). This was to check the reproducibility of the results and to ascertain whether the system showed any time dependent properties, such as thixotropy.

For the oscillatory tests, values of the dynamic shear modulus, G^*, the moduli G' and G'', the dynamic viscosity, η', and the phase angle, δ, were measured at different frequencies of oscillation. Again, the measurements were taken from the lowest frequency to the highest, and then repeated in the reverse direction.

4.2.15 SCANNING ELECTRON MICROSCOPY (SEM)

SEM was performed using a Joel T200 Electron Microscope with an electron accelerating voltage of 10keV. A disc of polymer film (of thickness ~200μm) was glued to a 1cm aluminium stub and the sample was out-gassed in vacuo for one week.

The edge of the stub and the film were painted with silver suspended in acetone. The acetone was evaporated leaving a layer of silver. This provided a good electrical contact between the polymer and the aluminium (to help to prevent charging of the non-conducting polymer surface).

The surface of the sample was coated with a thin layer of gold using a Hummer Gold Sputterer (also to prevent localised charging). The samples were observed at relatively low magnifications, between 1000 - 5000 times. It was observed that certain samples were damaged by the electron beam.

4.3 REACTIONS OF A SATURATED POLYURETHANE, PU1

4.3.1 SYNTHESIS OF PU1

The synthesis of PU1, and those of all subsequent polyurethanes, were based on the methods of Lyman[13].

MDI (3.6425g, 0.015 mole) was dissolved in DMSO ($10cm^3$) in a 3-necked round bottomed flask arranged as in fig. (4.13):

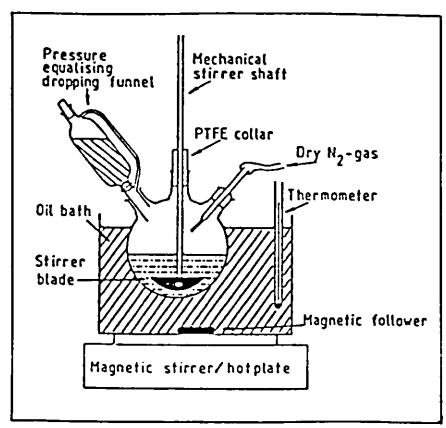


FIG. (4.13): APPARATUS USED FOR THE GENERAL SYNTHESIS OF A POLYURETHANE

The solution was stirred continuously whilst under a cover of dry, O_2-free N_2-gas. The PTFE collar for the stirrer shaft was not a tight fit to allow the gas to escape. All other joints were well-sealed with silicone grease (Dow Corning). The oil bath was maintained at a temperature of 54°C.

PTMEG 2000 (5.2883g, 2.6 x 10^{-3} mole) was dissolved in IBMK ($15cm^3$) and added in a dropwise fashion to the MDI solution. After the addition was completed, DBTL catalyst (2 drops from a Pasteur pipette) was introduced into the reaction mixture. The reaction was then left to react for a further 1h.

BD (1.0721g, 0.012 mole) was dissolved in DMSO ($5cm^3$) and was slowly added to the reaction mixture.

24h 43m after the addition of the PTMEG 2000 solution the resulting polymer was precipitated into distilled water. The PU1 was filtered, washed with clean water, and dried in vacuo to constant weight. The polymer was light brown in colour. The PU was characterised by GPC.

4.3.2 REACTIONS USING PU1

Two reactions were carried out using using different initiators. These are summarised in table (4.3):

TABLE (4.3): SUMMARY OF THE REACTIONS OF PU1

EXPERIMENT REF. NO.	AMOUNT OF PU1 (g)	AMOUNT OF MMA (g)	AMOUNT OF AIBN (g)	AMOUNT OF BPO (g)
PU1/PMMA[1]	1.4986	3.9980	0.0108	-
PU1/PMMA[2]	1.4943	3.9991	-	0.0740

The reactions were carried out in Suba-sealed flasks. Each reaction mixture was dissolved in DMF ($20cm^3$) and the solutions were

purged with N_2-gas and left to react for 24h at 79°C. The products were analysed by GPC.

4.4 POLYMERS BASED ON ERYTHROL: ATTEMPTED SYNTHESES OF POLYERYTHROL (PER) AND THE COPOLYMER OF ERYTHROL AND METHYL METHACRYLATE [P(ER-CO-MMA)]

The quantities of reagents and the reaction times used for these experiments are summarised in table (4.4):

TABLE (4.4): SUMMARY OF THE REACTIONS SYNTHESISING PER AND P(ER-CO-MMA)

REACTION	AMOUNT OF ER (g)	AMOUNT OF MMA (g)	AMOUNT OF AIBN (g)	REACTION TIME
PER	0.2330	-	0.0116	6h
P(ER-CO-MMA)	0.1034	0.9979	0.0100	6h 24m

All reactions were carried out in Suba-sealed flasks. Solutions were made up in THF ($10cm^3$) and were purged with N_2-gas before being left to react for the specified time at 60 - 62°C.

At the end of the reactions, portions of the solutions were withdrawn for GPC analysis. No PER had been formed.

The remainder of the reaction mixture for the synthesis of P(ER-CO-MMA) was poured into distilled water, in order to remove any unreacted ER, and the precipitated polymer was filtered, washed with clean water, and dried in vacuo to constant weight. The ^{1}H-NMR and IR spectra of the polymer were taken.

4.5 POLYURETHANES BASED ON ERYTHROL

4.5.1 SYNTHESIS OF POLYURETHANE PU2

MDI (6.7569g, 0.027 mole) was dissolved in IBMK ($16cm^3$) in a

3-necked round bottomed flask arranged as in fig. (4.13). The oil bath was maintained at a temperature of 76°C. PEG 1000 (8.0004g, 8.0 x 10^{-3} mole) was dissolved in DMSO (11cm^3) and added in a dropwise fashion to the MDI solution over a period of 45m. The reaction was then left for a further 2h at 78°C.

The reaction flask was then removed from the oil bath and allowed to cool slightly. ED (0.6218g, 0.010 mole) and ER (0.8822g, 0.010 mole) were dissolved in DMSO (11cm^3) and added to the reaction mixture over 40m. The flask was returned to the oil bath, and the reaction was left for a further 10h.

After allowing the solution to cool, the resulting polymer was precipitated into distilled water. The PU2 was filtered, washed with clean water, and dried in vacuo to constant weight. ^{1}H-NMR, IR, GPC, and solubility tests were carried out.

4.5.2 ATTEMPTED HOMOPOLYMERISATION OF PU2 AND ATTEMPTED GRAFT COPOLYMERISATION OF PU2 WITH METHYL METHACRYLATE [P(U2-G-MMA)]

The reaction conditions used are summarised in table (4.5):

TABLE (4.5): SUMMARY OF THE HOMOPOLYMERISATION OF PU2 AND THE COPOLYMERISATION OF PU2 WITH MMA

REACTION	AMOUNT OF PU2 (g)	AMOUNT OF MMA (g)	AMOUNT OF AIBN (g)	TEMP. RANGE (°C)	REACTION TIME
PU2 / HOMO-POLYMER	4.0631	-	0.0094	60-61	5h 45m
P(U2-G-MMA)	1.4200	5.7160	0.0151	62-63	6h 40m

The reactions were performed in Suba-sealed flasks. The solutions were made up in THF (15cm^3) and were purged with N_2-gas. The reactants were continually stirred.

The products of the homopolymerisation reaction and the grafting

reaction were precipitated into distilled water and methanol respectively. Each was filtered, washed, and dried in vacuo to constant weight. Samples were analysed by GPC.

The products of the reaction P(U2-G-MMA) underwent Soxhlet extraction, using toluene as the solvent. The GPCs of the toluene extract and the thimble residue were also carried out.

4.5.3 SYNTHESIS OF POLYURETHANE PU3

$H_{12}MDI$ (4.5592g, 0.017 mole) was dissolved in DMSO (6cm^3) in a 3-necked round bottomed flask arranged as in fig. (4.13). The oil bath was kept at 89°C. To this solution was added PTMEG 2000 (4.0810g, 2.0 x 10^{-3} mole) and DBTL catalyst (4 drops from a Pasteur pipette) dissolved in IBMK (20 cm^3). After a further 1h 15m, BD (0.9187g, 0.010 mole) and ER (0.4490g, 5.1 x 10^{-3} mole) dissolved in DMSO (16cm^3) were slowly added to the reaction mixture. After a further 26h, the heating source was removed, and the stirrer and N_2 supply were turned off. The reaction was left for 3 more days at room temperature before precipitating the PU into water. PU3 was filtered, washed, and dried in vacuo. The polymer was then characterised.

4.5.4 ATTEMPTED HOMOPOLYMERISATION OF PU3 AND THE COPOLYMERISATION OF PU3 WITH METHYL METHACRYLATE [P(U3-G-MMA)]

The reaction conditions are summarised in table (4.6):

TABLE (4.6): SUMMARY OF THE HOMOPOLYMERISATION OF PU3 AND THE FORMATION OF THE GRAFT COPOLYMER P(U3-G-MMA)

REACTION	AMOUNT OF PU3 (g)	AMOUNT OF MMA (g)	AMOUNT OF AIBN (g)
PU3 / HOMO-POLYMER	1.4383	-	0.0234
P(U3-G-MMA)	1.5026	3.9974	0.0105

The reactions were carried out in Suba-sealed flasks. The solutions were made up in DMF ($20cm^3$) and were purged with N_2-gas. The reactions proceeded for 24h at 82°C. The final products were precipitated in distilled water, filtered, dried in vacuo, and analysed by GPC.

4.5.5 SEPARATION OF P(U3-G-MMA) FROM THE STARTING MATERIALS

Separation of P(U3-G-MMA) from the unreacted PU3 was achieved by means of Prep-GPC.

Using the Waters equipment in its recycle mode gave evidence of the number of components present.

Characterisation of both the separated and unseparated materials was carried out.

4.6 SYNTHESIS OF POLYURETHANES TERMINATED WITH 2-HYDROXYETHYL METHACRYLATE (HEMA)

4.6.1 TERMINATION OF BOTH ENDS OF THE MOLECULE (PU4)

Initial experiments involved attempting to synthesise an isocyanate-terminated PU prepolymer which would then undergo reaction with HEMA to give the required PU [equation (4.10)].

$$\mathrm{OCN}\sim\sim\sim\sim\sim\sim\mathrm{PU}\sim\sim\sim\sim\sim\sim\mathrm{NCO} + 2\ \mathrm{HOCH_2CH_2OOCC(CH_3)=CH_2} \longrightarrow \mathrm{H_2C=C(CH_3)COOCH_2CH_2OOCNH}\sim\sim\sim\sim\sim\sim\mathrm{PU}\sim\sim\sim\sim\sim\sim\mathrm{NHCOOCH_2CH_2OOCC(CH_3)=CH_2} \quad (4.10)$$

However, the PU prepolymer was difficult to produce as the end groups were very reactive and susceptible to attack by impurities such as water. As a result, end-capping with HEMA could not be carried out using this method. Hence, the general PU synthesis was adapted, and

entailed premixing the HEMA with the MDI before any other reactants were added.

MDI (5.5808g, 0.022 mole) was dissolved in IBMK (20cm^3) in a 3-necked flask arranged as in fig. (4.13). The oil bath was maintained at a temperature of 38°C. To the MDI solution was added HEMA (0.4880g, 3.8 x 10^{-3} mole), catalyst DBTL (5 drops from a Pasteur pipette), and the inhibitor HQ (0.0069g, 6.3 x 10^{-5} mole), all dissolved in DMSO (12cm^3).

After reacting for 2h 35m, PTMEG 2000 (7.4306g, 3.7 x 10^{-3} mole) and BD (1.5077g, 0.017 mole), all dissolved in DMSO (35cm^3), were added slowly. After a futher 4h 20m, the stirrer and N_2 supply were turned off and the reaction was allowed to continue for another 16h. The resulting PU was precipitated into water, isolated, and dried in vacuo. GPC and ^{1}H-NMR of the polymer were performed.

4.6.2 TERMINATION OF ONE END OF THE POLYURETHANE MOLECULE (PU5)

MDI (7.1570g, 0.029 mole) was dissolved in IBMK (20cm^3) in a 5-necked resin flask and was maintained at a temperature of 36°C. This provided a better arrangement than the 3-necked flask as a condensor could be used and a thermometer measured the temperature of the solution rather than the oil bath. To the MDI solution was added slowly HEMA (0.3414g, 2.623 x 10^{-3} mole) and DBTL catalyst (5 drops from a Pasteur pipette) dissolved in DMSO (10cm^3). It was considered unnecessary to add any inhibitor.

The reaction was left for 2h and then PTMEG 2000 (10.3982g, 5.2 x 10^{-3} mole) and BD (2.1085g, 0.023 mole) dissolved in DMSO (40cm^3) were added. After a further 24h, the PU was precipitated into water, filtered, and dried in vacuo. PU5 was then characterised.

4.7 SYNTHESIS OF A POLYURETHANE TERMINATED AT ONE END WITH a,a-DIMETHYL-META-ISOPRENYL-BENZYL-ISOCYANATE, m-TMI (PU6)

MDI (14.1835g, 0.057 mole) was dissolved in DMSO ($40cm^3$) in a 5-necked resin flask, and the solution was maintained at 85°C. To this solution was added slowly PTMEG 2000 (20.6056g, 0.010 mole) in IBMK ($60cm^3$). After reacting for 1h, BD (4.1786g, 0.046 mole), dissolved in DMSO ($20cm^3$), was added.

After a further 1h, the reaction mixture was allowed to cool to 40°C. This took 30m. Then m-TMI (1.0370g, 0.0052 mole) and HQ inhibitor (0.0408g, 3.7×10^{-4} mole) in DMSO ($20cm^3$) were added over 15m, followed by DBTL catalyst (6 drops from a Pasteur pipette).

24h after the addition of the PTMEG 2000 solution, the resulting PU was precipitated into water, filtered, dried in vacuo and characterised.

4.8 ATTEMPTED SYNTHESIS OF GLYCERYL MONOMETHACRYLATE, GMM, THROUGH THE HYDROLYSIS OF GLYCIDYL METHACRYLATE, GM

4.8.1 GENERAL EXPERIMENTS

The following reactions, summarised in table (4.7), involved the hydrolysis of commercial GM:

TABLE (4.7): HYDROLYSIS REACTIONS OF GM

REACTION REF. NO.	HYDROLYSING AGENT (g)	AMOUNT OF AGENT USED	AMOUNT OF GM (g)	AMOUNT OF WATER (cm^3)
4.8.1.1	Sulphuric Acid 98% w/w	$12.5cm^3$	50	75
4.8.1.2	Nitric Acid SG 1.42	$16cm^3$	50	75
4.8.1.3	Potassium Hydroxide Pellets	11.25g	18	200

For each experiment, the reactants were stirred together for 5 days at room temperature. It was important to add the GM to the water solution (rather than vice-versa), so as to prevent rapid heat formation. Initially, the GM was insoluble in the water and formed a separate layer. However, provided that the stirring was efficient, as the hydrolysis proceeded, the reaction mixture became homogeneous, and the GM co-dissolved with the GMM.

Attempted product isolation was different in each case.

For reaction 4.8.1.1, the water solution was extracted with diethyl ether (2 x's 100cm^3) to remove the unreacted GM. The volume of water was reduced by rotary evaporation, and attempts were made to "salt out" the GMM by adding sodium chloride. However, no oily layer separated, and the solution eventually had to be discarded.

For reaction 4.8.1.2, the water was rotary evaporated leaving a yellow liquid. Attempted vacuum micro-distillation of the product, adding HQ as an inhibitor, failed as the material polymerised in the flask.

For reaction 4.8.1.3, the water was removed, and the product was vacuum distilled using CuCl as the inhibitor, and the distillation head was lined with copper wire. Unfortunately, the product polymerised before reaching its boiling point.

4.8.2 HPLC EXPERIMENTS

4.8.2.1 EXPERIMENT 1

Commercial GM (0.2023g) was dissolved in dichloromethane (100cm^3). To this solution was added Amberlite Resin (0.5015g) and distilled water (1cm^3). The resin preferentially floated in the water layer, and so vigorous agitation had to be carried out to ensure that

there was satisfactory mixing of the components. Aliquots ($1cm^3$) of the mixture were taken periodically, filtered, and the solvent evaporated. The resulting material was diluted with THF ($2cm^3$) and HPLC was performed on the solution. No GMM was formed.

4.8.2.2 EXPERIMENT 2

Commercial GM (0.05g) was dissolved in THF ($25cm^3$) containing water ($0.3cm^3$) and activated Dowex 50W-X8 resin (0.5g).The mixture was stirred vogorously, and periodically aliquots of material were taken, filtered, and injected neat into the HPLC column. The final sample was taken after 7 days.

4.8.2.3 EXPERIMENT 3

Dichloromethane was shaken vigorously with water to ensure that it was thoroughly saturated. The two phases were then separated, and a portion of the CH_2Cl_2 mixture ($25cm^3$) was stirred with GM (0.0237g) and activated Dowex 50W-X8 resin (0.238g). Aliquots of the material were taken, filtered, and the solvent evaporated. The resulting liquid was diluted with THF and injected into the HPLC column.

HPLC showed the presence of a new material, and so after 2 days a sample of the CH_2Cl_2 mixture was extracted with water, and prepared for HPLC. The new peak corresponding to the product had disappeared.

4.9 SYNTHESIS OF POLYURETHANES BASED ON GLYCERYL MONOMETHACRYLATE

4.9.1 POLYURETHANE CONTAINING MANY UNITS OF GLYCERYL MONOMETHACRYLATE (PU7)

MDI (3.4793g, 0.0139 mole) was dissolved in DMSO ($10cm^3$) in a 3-necked flask. The temperature of the oil bath was maintained at 79°C. To the MDI solution was added PTMEG 2000 (5.0541g, 2.5×10^{-3} mole)

dissolved in IBMK ($15cm^3$). After reacting for 54m, BD (0.4549g, 5.0×10^{-3} mole), dissolved in DMSO ($5cm^3$),was added dropwise. 30m later, the oil bath was removed, and the solution was allowed to cool to room temperature. This took 40m.

Commercial GMM (1.0147g, equivalent to 6.3×10^{-3} mole) inhibited with MeHQ (3000ppm), HQ (0.0340g, 3.1×10^{-4} mole), and DBTL catalyst (2 drops from a Pasteur pipette), all dissolved in DMSO ($5cm^3$), were added to the reaction mixture.

24h 54m after the addition of the PTMEG 2000 solution, the PU7 was precipitated into water, and the polymer was dried in vacuo. The GPC of the PU was recorded.

4.9.2 POLYURETHANE CONTAINING ONE UNIT OF GMM (PU8)

MDI (3.6121g, 0.014 mole) was dissolved in DMSO ($10cm^3$) in a 3-necked flask. The oil bath was maintained at a temperature of 79 - 80°C. To this solution was added PTMEG 2000 (5.2390g, 2.6×10^{-3} mole) dissolved in IBMK ($15cm^3$). After 48m of reaction, the oil bath was removed and the solution was cooled to room temperature over 18m.

Commercial GMM (0.2102g, equivalent to 1.3×10^{-3} mole), BD (0.9444g, 0.011 mole), HQ (0.0163g, 1.5×10^{-4} mole), and DBTL catalyst (3 drops from a Pasteur pipette), all dissolved in DMSO ($10cm^3$), were added slowly to the reaction mixture. 24h after the addition of the PTMEG 2000 solution, the PU was precipitated into water, filtered, dried in vacuo, and characterised.

4.10 GRAFTING REACTIONS OF PU4 WITH METHYL METHACRYLATE [P(U4-G-MMA)]

Two experiments were carried out with various concentrations of MMA. The amounts of each reactant are summarised in table (4.8):

TABLE (4.8): SUMMARY OF THE GRAFTING REACTIONS OF PU4

SAMPLE	WEIGHT OF PU4 (g)	WEIGHT OF MMA (g)	WEIGHT OF AIBN (g)
P(U4-G-MMA)[1]	2.0019	5.0022	0.0047
P(U4-G-MMA)[2]	1.9997	9.9959	0.0042

Solutions were made in THF (26cm^3), injected into ampoules, degassed using the high-vacuum equipment, sealed under vacuum, and placed in a thermostatted water bath at 51°C for 22h.

When the ampoules were broken open, both solutions were considerably more viscous than before the reaction.

The THF solvent was evaporated for both solutions. The brittle materials obtained were subjected to Soxhlet extraction with THF for 32h. The gel-like residue left in the Soxhlet thimble was dried. It was found to be insoluble in solvents such as DMSO, toluene, and DMF. GPCs were recorded of the THF Soxhlet extraction.

4.11 GRAFTING REACTIONS OF PU7 WITH METHYL METHACRYLATE [P(U7-G-MMA)]

Four experiments were carried out. The amounts of each reactant used are summarised in table (4.9):

TABLE (4.9): SUMMARY OF THE GRAFTING REACTIONS OF PU7

SAMPLE	WEIGHT OF PU7 (g)	WEIGHT OF MMA (g)	WEIGHT OF AIBN (g)	VOLUME OF DMF (cm^3)
P(U7-G-MMA)[1]	1.0000	0.9985	0.0023	15
P(U7-G-MMA)[2]	1.0030	4.9976	0.0400	40
P(U7-G-MMA)[3]	0.9940	5.0061	0.0090	40
P(U7-G-MMA)[4]	1.0059	1.0021	0.0021	40

All solutions were made up in Suba-sealed flasks, purged with N_2-gas, and left to react at 80°C. Solutions [1], [2], and [3] had formed insoluble gels within two or three hours. Reaction [4] was left for 24h, and the resulting polymers were precipitated into distilled water, washed, filtered, and dried in vacuo. The products were analysed by GPC.

4.12 THE REACTIONS OF PU5, PU6, AND PU8

4.12.1 ATTEMPTED HOMOPOLYMERISATION OF PU5, PU6, AND PU8

The homopolymerisation reactions are summarised in table (4.10):

TABLE (4.10): SUMMARY OF THE HOMOPOLYMERISATION REACTIONS OF PU5, PU6, AND PU8

PU-HOMO-POLYMER	AMOUNT OF PU (g)	AMOUNT OF AIBN (g)	SOLVENT	REACTION TEMP. (°C)	REACTION TIME (h)
PU5	0.5001	0.0013	THF	51	27
PU6	1.0009	0.0072	THF	59	24
PU8	1.4880	0.0217	DMF	82	24

Each reaction was carried out in a Suba-sealed flask. Solutions were made up in $20cm^3$ of solvent and were purged with N_2-gas before the reaction.

At the end of the specified time, samples of the solutions were taken and analysed by GPC.

4.12.2 GRAFTING REACTIONS OF PU5 [P(MMA-G-U5)], PU6 [P(MMA-G-U6)], AND PU8 [P(U8-G-MMA)]

For each PU, seven separate reactions were performed, varying either the concentration of the initiator, the reaction time, or the initiator itself. A sample of PMMA was also synthesised.

Each experiment was carried out in a Suba-sealed flask. Solutions

were made up of PU (1.5g), MMA (4.0g) and the initiator in DMF ($20cm^3$), purged with N_2-gas, and left to react for the appropriate time at 80°C.

At the end of the reaction, the resulting polymers were precipitated into water, filtered, dried to constant weight, and characterised. The quantities of the reactants are summarised in table (4.11). The percentage yields quoted are calculated from the formula:

$$\% \text{ Yield} = \frac{\text{Total weight of dried products}}{\text{Total weight of reactants}} \times 100 \qquad (4.10)$$

Characterisation of the product mixtures was then carried out.

4.13 SEPARATION OF THE GRAFT COPOLYMERS OF SECTION 4.12 FROM THE STARTING MATERIALS

4.13.1 SOLVENT EXTRACTION

4.13.1.1 SOXHLET EXTRACTION USING TOLUENE

Samples of the crude products of the grafting reactions of PU5, P(MMA-G-U5), were Soxhlet extracted, using toluene as the solvent, for 16h. GPCs were taken of the thimble residues and the toluene extract. In some cases the harsh conditions caused gelation to occur in the thimble.

The toluene extract was reduced in volume by rotary evaporation. A precipitate was formed which was isolated by centrifuging the mixture. This procedure was repeated several times, each time removing the precipitate, until no more insoluble material appeared on the removal of toluene.

The precipitate and the remaining material in the toluene solution were analysed by GPC.

TABLE (4.11): SUMMARY OF THE SYNTHESIS OF PMMA AND THE GRAFTING REACTIONS OF PU5, PU6, AND PU8 WITH METHYL METHACRYLATE

SAMPLE	WEIGHT OF AIBN (g)	WEIGHT OF BPO (g)	REACTION TIME (h)	% YIELD
PMMA	0.0032		24	
P(MMA-G-U5)[1]	0.0044		24	56.8
[2]	0.0101		24	80.2
[3]	0.0506		24	84.7
[4]	0.1506		24	81.4
[5]	0.0050		48	76.6
[6]	0.0504		48	98.0
[7]		0.0739	24	89.9
P(MMA-G-U6)[1]	0.0046		24	66.8
[2]	0.0104		24	79.8
[3]	0.0499		24	92.1
[4]	0.1505		24	98.7
[5]	0.0054		48	66.5
[6]	0.0510		48	92.6
[7]		0.0733	24	66.5
P(U8-G-MMA)[1]	0.0046		24	74.8
[2]	0.0125		24	66.3
[3]	0.0514		24	74.2
[4]	0.1511		24	90.2
[5]	0.0054		48	69.4
[6]	0.0510		48	84.5
[7]		0.0746	24	82.3

4.13.1.2 SIMPLE SOLVENT EXTRACTION

(A) USING A THF / CHLOROFORM MIXTURE

A 5% w/v solution of the products was made in THF (a good solvent for all of the polymers in the mixture). Chloroform was then added to the well-stirred solution in an attempt to precipitate the free PU5 present, as it was a good solvent for PMMA (and, therefore, should have dissolved the graft copolymer), but was a poor solvent for the PU. However no precipitation occurred.

(B) USING TOLUENE

Samples of the crude products of the P(MMA-G-U5) reactions were stirred in cold toluene. The polymers swelled, but very little material dissolved. The mixtures, therefore, were gently warmed for several hours, filtered, and the polymers in solution recovered. GPCs of the toluene extract and residue were recorded.

(C) USING ACETONE

The products of the reactions of PU5 formed a cloudy suspension in cold acetone. This was centrifuged at -10°C to remove the solid, but the solution still remained opaque. GPC was used to analyse the precipitate and solution.

(D) USING BUTAN-2-OL

A sample of PMMA dissolved in hot butan-2-ol, but precipitated when cold.

This was applied to the products of the P(MMA-G-U5) reactions. However, although a cloudy suspension was obtained in hot butan-2-ol, the insoluble material could not be isolated by centrifugation or filtration, as a slight reduction in temperature caused complete precipitation.

4.13.2 TURBIDIMETRIC TITRATIONS

A sample of the products of reaction P(MMA-G-U5)[5] was Soxhlet extracted, using toluene as the solvent, for several hours. The toluene extract was reduced in volume by rotary evaporation and centrifuged to remove the precipitate formed until no more was formed on removal of solvent. The remaining material in solution was recovered, dried, and analysed by GPC.

A 2.5% w/v solution of this material was made up in toluene and used as a stock solution. Portions of the solution were diluted with various quantities of toluene and were placed in the sample cell of the absorptiometer. The reference cell was filled with an identical volume of neat toluene.

To each cell was added aliquots of methanol, the solutions were stirred with a spatula, and the absorbances were measured. The absorbance of the sample was adjusted to allow for the solvents (subtracting the value for the reference) and for the increase in volume as each aliquot of methanol was added.

Graphs of adjusted absorbance against the volume of methanol added were plotted. The initial concentrations of the toluene solutions are listed in table (4.12).

TABLE (4.12): THE CONCENTRATIONS OF SOLUTIONS USED FOR TURBIDIMETRIC TITRATIONS

TITRATION NO.	CONCENTRATION OF SAMPLE (% w/v)
4.13.2.1	2.5
4.13.2.2	1.2
4.13.2.3	0.5
4.13.2.4	0.2
4.13.2.5	0.1
4.13.2.6	0.09
4.13.2.7	0.04

4.13.3 FRACTIONAL PRECIPITATIONS

The technique of fractional precipitation used involved initially dissolving the sample of products in a good solvent for all of the polymers in the mixture. It was found that concentrations below 1% w/v were too dilute, and the precipitation of fractions produced very fine suspensions which could not be isolated. However, concentrations greater than 5% w/v were too high, and caused large quantities of polymer to be precipitated with the addition of small amounts of non-solvent. Hence, the concentrations used were in the range of 1% - 5% w/v.

The solution was vigorously stirred, and a non-solvent for all of the polymers was added slowly until the liquid became turbid, and the cloudiness did not disappear after being left stirring for several minutes. The mixture was warmed gently until it became a clear solution again. Then it was allowed to cool, occasionally placing the solution in a refrigerator at 4°C in order to quicken the process.

A precipitate formed, which was isolated by decantation or centrifugation. The procedure was then repeated with the supernatent liquid. Each precipitate was dried and analysed by GPC.

Towards the end of the fractionation, the solutions were so dilute that precipitation formed a very fine suspension. The final fraction, therefore, was isolated by rotary evaporation of the solvent / non-solvent mixture.

Several solvent / non-solvent combinations were examined. All of the following fractionations were performed on the products of the grafting reactions of PU5, and are summarised in table (4.13):

TABLE (4.13): SOLVENT AND NON-SOLVENT COMBINATIONS USED FOR FRACTIONAL PRECIPITATIONS

FRACTIONATION REF. NO.	SOLVENT USED	NON-SOLVENT USED
4.13.3.1	THF	Distilled Water
4.13.3.2	THF	Industrial Methylated Spirit
4.13.3.3	DMSO	Distilled Water
4.13.3.4	1,4-Dioxane	Methanol
4.13.3.5	Acetone	Distilled Water

4.13.4 ADSORPTION COLUMN CHROMATOGRAPHY

Three separate solutions were made up in THF of PU5, PMMA, and the products of reaction P(MMA-G-U5)[1].

Several solvent and solvent mixtures were used for the column chromatography experiments. Initially, thin layer chromatography (TLC) was carried out to check the feasibility of a particular solvent system. Portions of the THF solutions were applied to the TLC plates, the THF was allowed to evaporate, leaving the sample. The plate was then placed in a screw-capped jar containing the solvent to a depth of ~0.5cm, and a saturated atmosphere. When the solvent had almost reached the top, the plate was removed, and the solvent was evaporated quickly.

The position of the sample was marked by either staining the plate with iodine, or placing the plate under a UV lamp of wavelength 365nm.

Solvent systems which appeared to achieve a separation were then used for the silica column. A sample of the P(MMA-G-U5)[1] solution in THF was applied to the top of the silica column. The relevant solvent was then run through the column by applying a positive pressure at the top. The eluent was collected in various fractions. The solvent was evaporated, and the residue was analysed by GPC. The various solvent systems used are listed in table (4.14):

TABLE (4.14): SOLVENT SYSTEMS USED FOR COLUMN CHROMATOGRAPHY

EXPERIMENT NO.	SOLVENT / SOLVENT MIXTURE	USED FOR TLC	USED FOR COLUMN
4.13.4.1	THF	Y	N
4.13.4.2	Acetone	Y	N
4.13.4.3	Benzene	Y	Y
4.13.4.4	Benzene followed by THF	N	Y
4.13.4.5	DMF	Y	Y
4.13.4.6	Ethyl acetate	Y	Y

(Y = used, N = not used)

4.13.5 PREPARATIVE GEL PERMEATION CHROMATOGRAPHY, PREP-GPC

Two sets of Prep-GPC equipment were used (section 4.2.9.2).

4.13.5.1 USING THE WATERS EQUIPMENT

The graft copolymers which were separated from unreacted PU using this apparatus were P(MMA-G-U5)[1], [2], [3], and [7], P(MMA-G-U6)[1], [2], and [3], and P(U8-G-MMA)[1], [3], and [7].

The recycle facility was used initially for each sample, as a

check of the number of components in each sample.

4.13.5.2 USING THE ALTEX EQUIPMENT

Further samples of the graft copolymers of the samples in section 4.13.5.1 and those of the other grafting reactions were obtained using the Altex equipment.

The separated graft copolymers were characterised.

4.14 PREPARATION OF FILMS FOR MECHANICAL TESTING

The surface of circular, glass petri-dishes were silanised using 2% dimethyldichlorosilane solution in 1,1,1-trichloroethane according to the manufacturer's instructions. This provided a non-adhesive surface, enabling films to be readily removed from the plates. The petri-dishes had to be of a sufficiently large diameter to ensure that the surface was not convex in shape.

The polymer samples were dissolved in THF and, using a syringe filter system, were filtered directly into the dish. The dish was then placed into a Perspex box, the base of which had been arranged so that it was perfectly flat. The solutions were surrounded by an atmosphere saturated with THF vapour in order to control the rate of solvent evaporation.

After the majority of the THF solvent had evaporated, the films were removed from the plates, and were dried in vacuo.

4.15 STORAGE OF POLYMERS

Polymers in their precipitated form, i.e. in a particulate state, were stored in glass sample tubes at 4°C in the dark. Films were individually protected in polythene bags, and were stored at 4°C without light, as well.

Six samples of the unseparated products of the reactions of section 4.12.2 were arranged to monitor the effect of storing samples at room temperature in the absence or presence of sunlight, and in the absence or presence of air. The experiments are summarised in table (4.15):

TABLE (4.15): SUMMARY OF EXPERIMENTS TO DETERMINE THE EFFECT OF LIGHT AND AIR UPON SAMPLES

SAMPLE OF PRODUCTS	ABSENCE OF LIGHT	PRESENCE OF LIGHT	ABSENCE OF AIR	PRESENCE OF AIR
P(MMA-G-U5)[1][A]	Y	N	N	Y
P(MMA-G-U5)[1][B]	N	Y	Y	N
P(MMA-G-U6)[2][A]	Y	N	N	Y
P(MMA-G-U6)[2][B]	N	Y	Y	N
P(U8-G-MMA)[6][A]	Y	N	N	Y
P(U8-G-MMA)[6][B]	N	Y	Y	N

(Y = Yes, N = No)

Samples that are labelled [A] were prepared by wrapping the sample tubes containing the polymers with aluminium foil. The plastic top was pierced several times to enable air to diffuse in and out of the tube.

Samples labelled [B] were prepared by Suba-sealing sample tubes of the products. The tubes were purged with N_2-gas and were placed in a position exposed to sunlight.

The effect of sunlight and air was assessed by considering the physical appearance and the GPC analysis of the samples after several months of exposure.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 REACTIONS OF THE SATURATED POLYURETHANE, PU1

5.1.1 SYNTHESIS OF PU1

As mentioned in Chapter 4, all polyurethanes were synthesised according to the methods suggested by Lyman[13], utilising the reaction between diisocyanates and diols. Due to the small scale of the polymer preparations, and because subsequent syntheses involved reactions at relatively low temperatures, solution polymerisation was preferred to bulk polymerisation.

It was important to use solvents that did not contain active hydrogens. Lyman[13] found that the preparation of a polyurethane using a 50 / 50 mixture of DMSO and IBMK as the solvent gave 100% yield of polymer on precipitation into water, and the extent of side reactions was minimised. IBMK was a solvent for the components of the polyurethane, but was a non-solvent for the final polymer. The presence of this non-solvent encouraged the complete precipitation of the product. However, at all stages during the polymerisation, the quantity of DMSO in the solvent mixture had to be greater than or equal to the amount of IBMK in order to prevent premature precipitation of the polyurethane.

The GPC of PU1 [fig. (5.1)] showed that a polymer had been formed, as the peak retention time of the material was very much lower than those of its monomers. The polyurethane had a smooth molecular weight distribution, and the chromatogram showed no presence of contaminants such as low molecular weight oligomers, monomers, or solvent residues.

The molar ratios of reactants for PU1 were:

MDI	PTMEG 2000	BD
11	2	9

The theoretical % hard block content was, therefore, 47.1% w/w.

5.1.2 REACTIONS USING PU1

The solvent used for the free-radical polymerisations was dictated by the solvent in general use for the GPC equipment, i.e. either THF or DMF. This enabled aliquots of the reaction mixture to be analysed by GPC directly before isolation of the products. Both were good solvents for all species present in the reaction mixtures, but DMF had the advantage in that it had a much higher boiling point than THF, hence reactions could be performed at higher temperatures.

Fig. (5.1) shows the GPCs of the dried products of the experiments PU1 / PMMA [1] and PU1 / PMMA [2], as obtained using the UV detector. Since the UV detector of the GPC equipment only responded in the presence of the PU, and did not detect PMMA, any reaction, such as grafting onto the polyurethane or degradation, would have registered as a change in the molecular weight distribution of the polymer, as indicated by the chromatogram for this detector. There was no change observed. The GPCs from the RI detector showed the presence of PMMA in the reaction products.

It was concluded that under under these reaction conditions:

(A) The polyurethane did not degrade.

(B) A polyurethane resulting from the reaction between MDI, PTMEG 2000, and BD did not undergo a chain transfer reaction with a growing polymer radical or an initiator radical, by the abstraction of a hydrogen atom, in order to form a macroradical capable of initiating

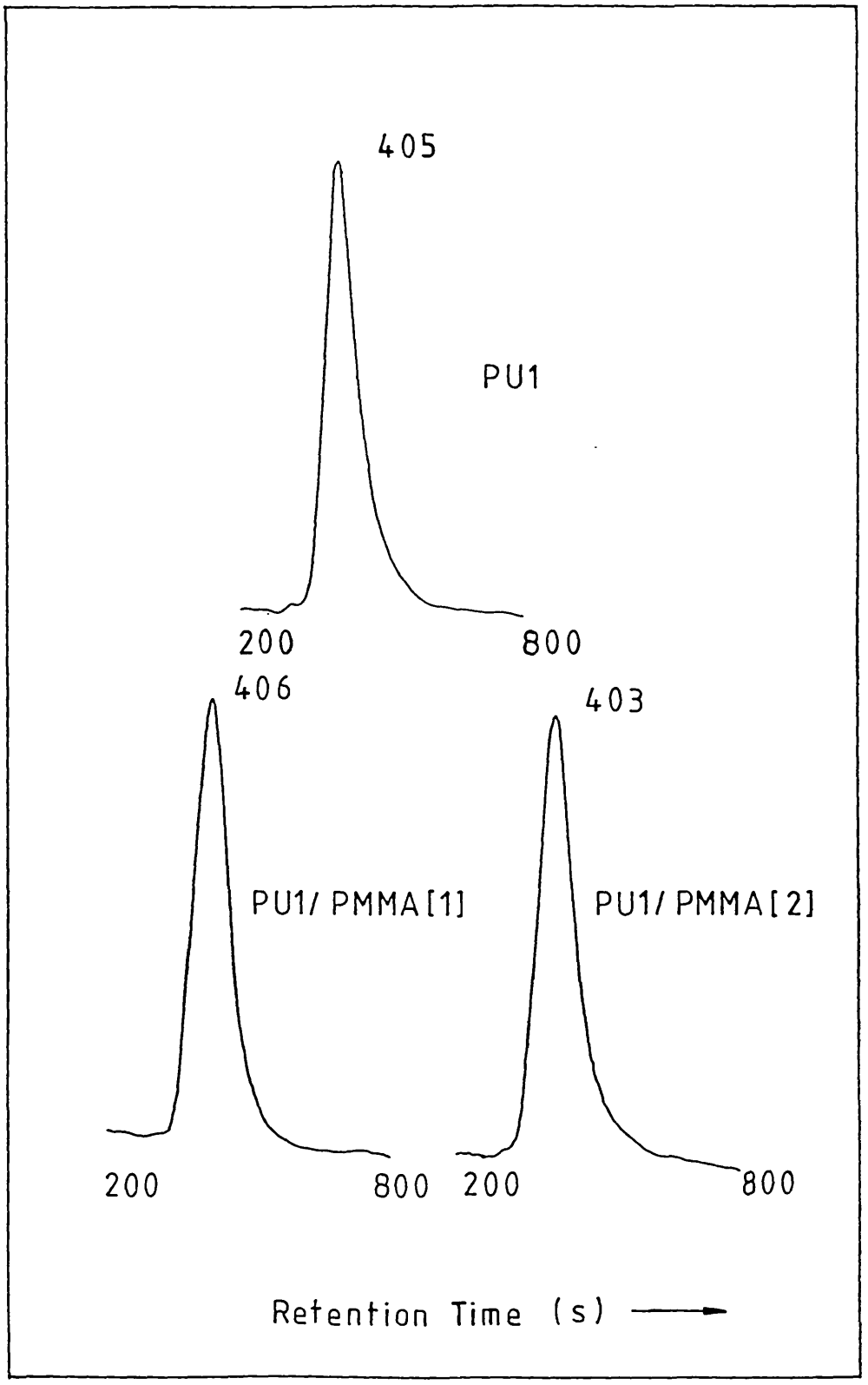
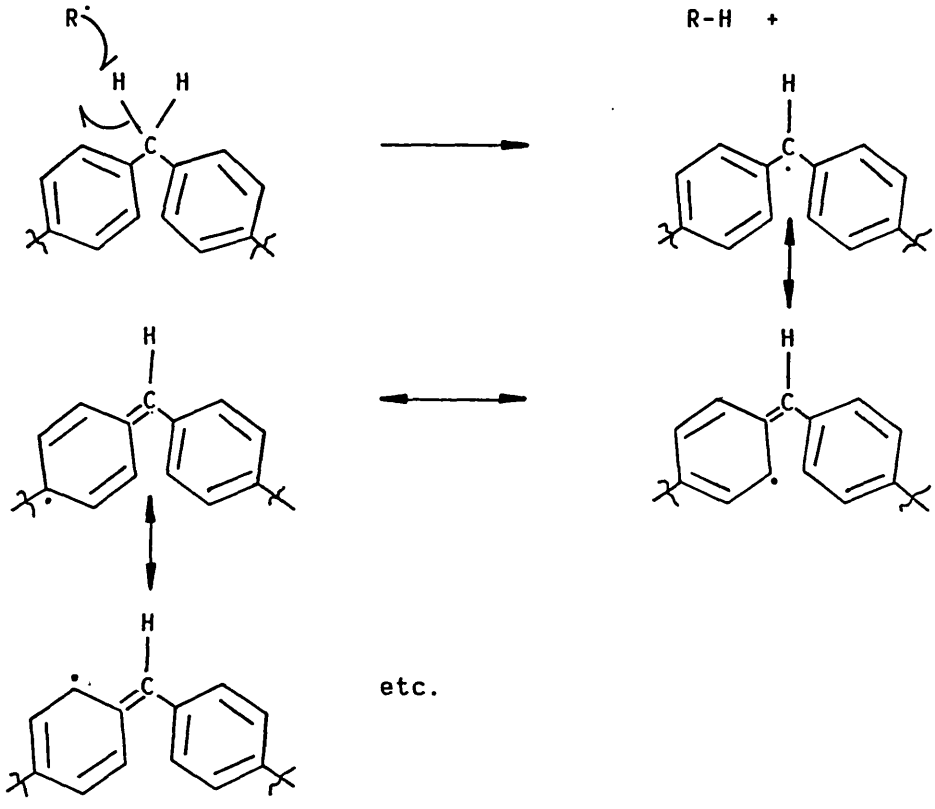


FIG. (5.1): GPC'S OF PU1 AND THE REACTION PRODUCTS PU1/ PMMA[1] AND [2] (UV DETECTOR)

the growth of a PMMA chain from the polyurethane.

(C) Should a free-radical be formed on the polyurethane by the mechanisms suggested in part (B), then the radical species was so stable that the initiation of a PMMA chain did not occur. This may have been possible if, for example, a H atom was abstracted from the central methylene group of the MDI unit of the polymer:



(5.1)

(R$^{\bullet}$ represents a growing PMMA radical or an initiator fragment).

The next stage of investigation involved the introduction of potentially reactive radical sites into the polyurethane molecule to act as a focus for the grafting of PMMA.

5.2 POLYMERS BASED ON ERYTHROL: ATTEMPTED SYNTHESIS OF PER AND P(ER-CO-MMA)

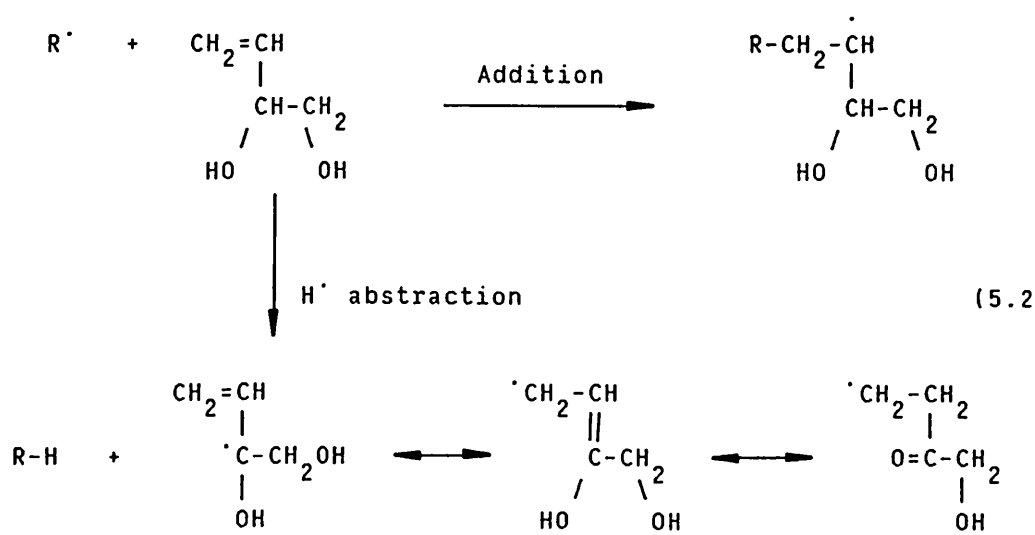
The diol erythrol (ER, but-1-ene-3,4-diol) was considered to be a useful compound for incorporation into a polyurethane, forming a polymer containing many units of unsaturation susceptible to radical attack. Initial experiments were carried out, however, in order to assess the reactivity of the diol under free-radical polymerisation conditions.

ER did not homopolymerise. This was shown by GPC. The chromatogram of the final reaction solution after the attempted homopolymerisation was identical to that of a sample of ER prior to the reaction.

The ^{1}H-NMR and IR spectra of the isolated polymer of the attempted copolymerisation reaction between ER and MMA were identical to those of PMMA alone. Had the two monomers copolymerised, the hydroxyl groups of the ER units would have been easily detected.

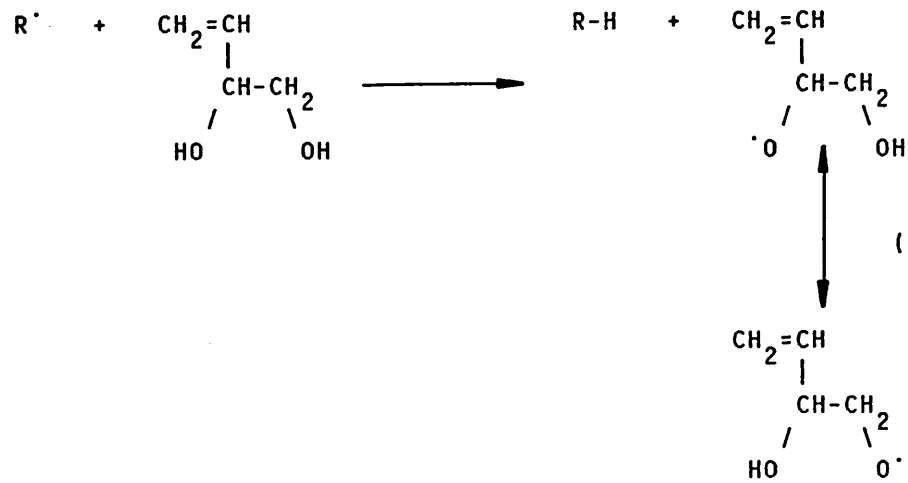
It was concluded that copolymerisation had not occurred.

The apparent lack of reactivity of ER towards free-radical polymerisation was most likely due to allylic radical formation and stabilisation, following the attack by a radical R$^{\bullet}$:



(5.2)

Alternatively, by a transfer reaction, a H atom could be abstracted from a hydroxyl group forming a stabilised radical:



(5.3)

This transfer reaction was probably not highly significant due to the relatively low transfer activity of alcohols towards radical attack.

However, despite this lack of reactivity polyurethanes based upon ER were synthesised.

5.3 POLYURETHANES BASED ON ER

5.3.1 SYNTHESIS OF POLYURETHANE PU2

Due to the availability of chemicals, PU2 had a soft segment consisting of PEG 1000, and was chain extended with ED. All subsequent polyurethanes were based on PTMEG 2000 and BD in order to increase the hydrophobic nature of the polymers, as the intention was to use them in water-repellent surface coatings.

A reaction time of 10h at 78°C was used for the chain extension step to allow for the lower reactivity of the secondary hydroxyl group of ER compared to its primary hydroxyl.

PU2 was synthesised such that the molar ratios of reactants were:

MDI	PEG 1000	ED	ER
27	8	10	10

The theoretical % hard block content of the polyurethane was, therefore, 50.8% w/w.

GPC showed that PU2 had a smooth molecular weight distribution and that the polymer was not contaminated [fig. (5.2)]. Molecular weight analysis by means of GPC gave the following results [table (5.1)].

TABLE (5.1): MOLECULAR WEIGHT ANALYSIS RESULTS FOR PU2 (ALL AVERAGES ARE WITH RESPECT TO PS STANDARDS AND ARE QUOTED TO THE NEAREST WHOLE HUNDRED)

DETECTOR	$\bar{M}_n$	$\bar{M}_w$	Polydispersity ($\bar{M}_w$ / $\bar{M}_n$)
UV detector	6,700	12,200	1.8
RI detector	13,900	15,300	1.1

The UV detector method appeared to give the more accurate result, since the theoretical ratio of $\bar{M}_w/\bar{M}_n$ (= 1 + p, where p was the extent of reaction) should have been 2.0 at high conversions.

Figures (5.3) and (5.4) show the IR and ^{1}H-NMR spectra for PU2. Details of peak assignments can be found in general texts[6,206]. The IR spectrum showed the absorptions of many of the general groups present in the polyurethane, but the alkene absorptions of the ER units were obscured due to their low concentration in comparison to other functions.

The ^{1}H-NMR spectrum contained resonances between δ = 2 and δ = 4.5ppm which were characteristic of aliphatic hydrogens. The aromatic protons of MDI appeared as a set of lines centred at δ = 7.2ppm. The spectrum also indicated the presence of a small amount of urea as well as the urethane resonance. The urea groups probably arose from

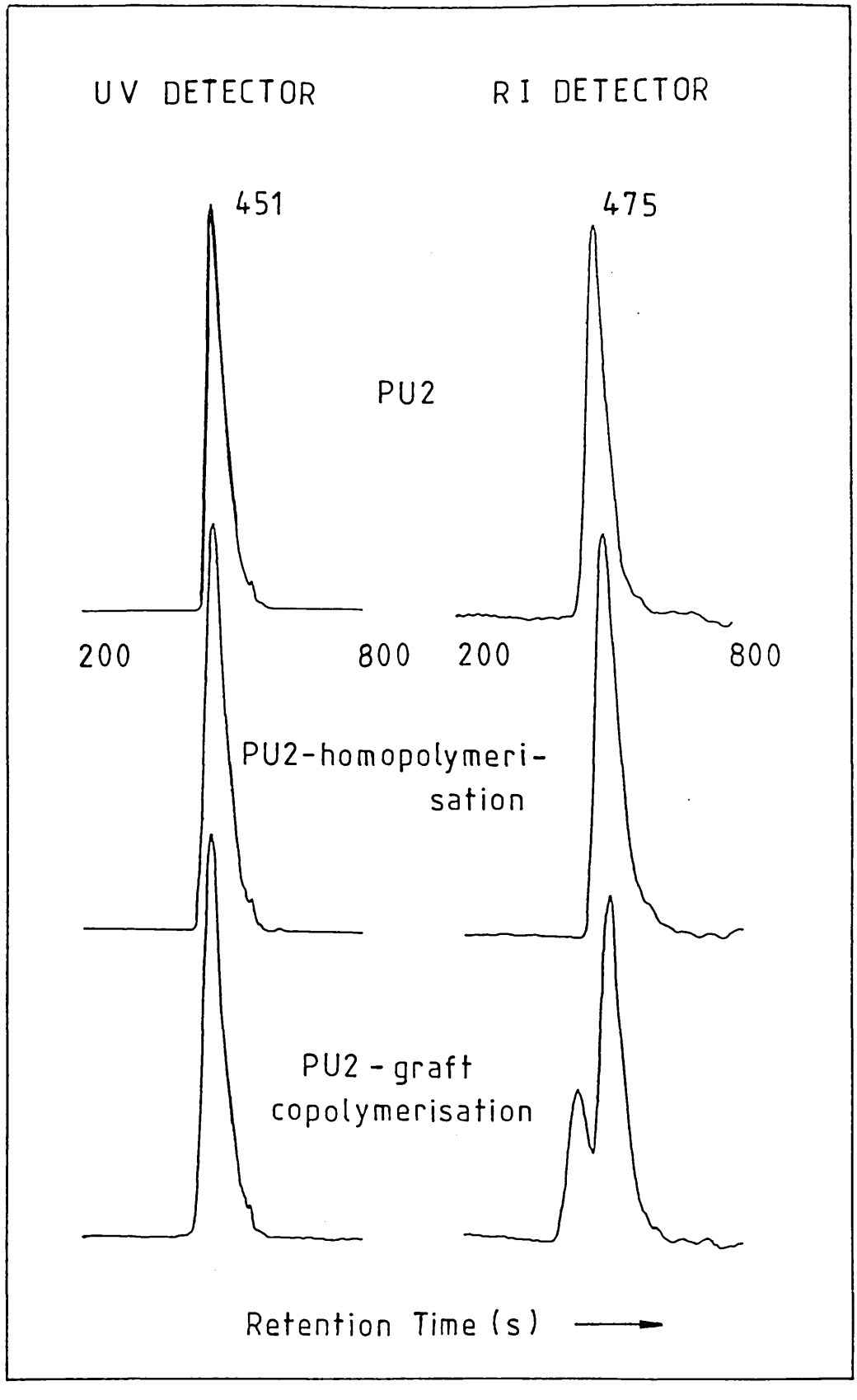


FIG. (5.2): GPC'S OF PU2 AND THE PRODUCTS OF THE REACTIONS OF PU2

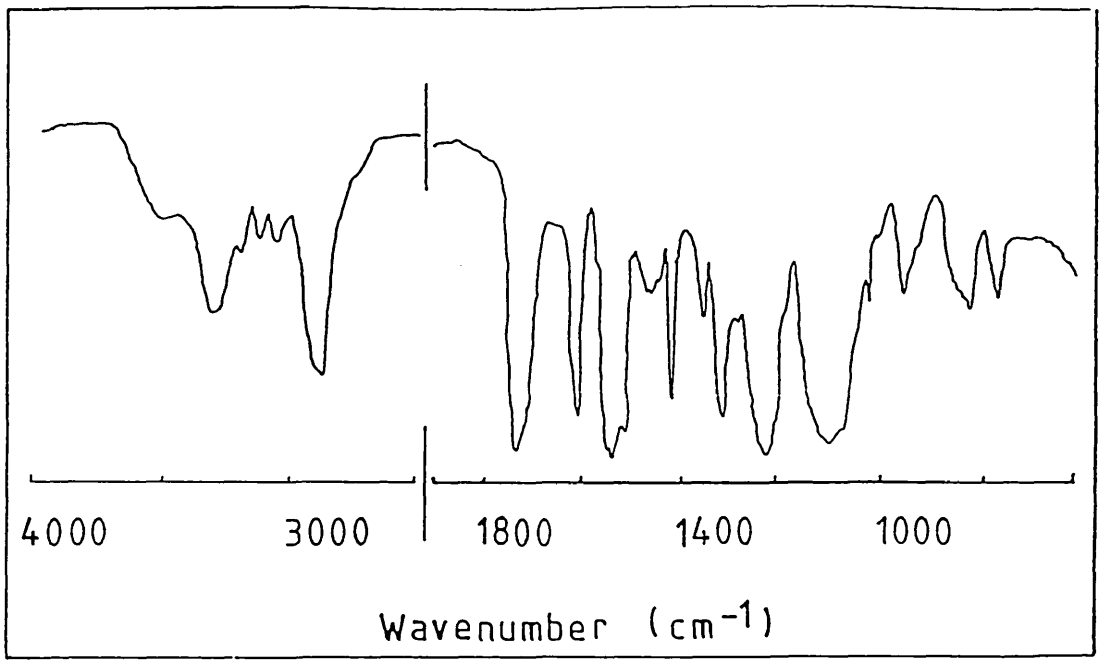
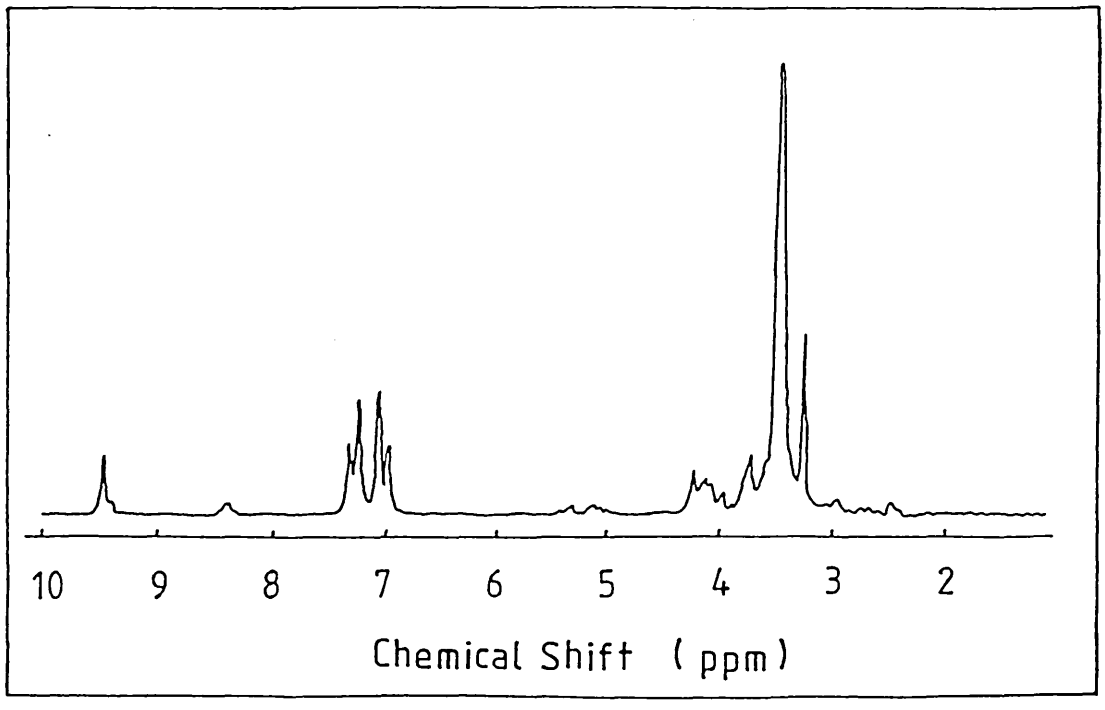


FIG.(5.3): IR SPECTRUM OF PU2

FIG.(5.4): ^{1}H-NMR SPECTRUM OF PU2



contamination of the reaction mixture with water. Reaction of MDI with water yields an amine which then reacts with another isocyanate to give the urea [see equation (1.7)]. Small deviations occurred in the baseline at δ = 5.2ppm and δ = 5.4ppm. These were probably the resonances of the protons of the alkene groups of the ER units, and should have consisted of a doublet and a sextuplet. However, the resonances were too small to distinguish between.

Solubility tests were performed on PU2. The results are shown in table (5.2).

TABLE (5.2): RESULTS OF THE SOLUBILITY TESTS PERFORMED ON PU2

SOLVENT	SOLUBLE IN COLD SOLVENT	SOLUBLE IN HOT SOLVENT
Water	N	N
Acetone	N (swelled with vigorous shaking)	N
Chloroform	Fine suspension	Suspension
IBMK	N	N
DMSO	Y	Y
Methanol	N	N
DMF	Y	Y
THF	Y	Y
Toluene	N	N

(N = non-soluble, Y = soluble)

5.3.2 ATTEMPTED HOMOPOLYMERISATION OF PU2 AND ATTEMPTED GRAFT COPOLYMERISATION WITH METHYL METHACRYLATE

5.3.2.1 HOMOPOLYMERISATION OF PU2

The GPC of the product of the attempted homopolymerisation reaction of PU2 showed that no apparent reaction had occurred [fig.

(5.2)]. Had homopolymerisation taken place, then the GPC of the product should have registered a change in the molecular weight distribution of the polyurethane.

The lack of reactivity of PU2 towards homopolymerisation could have been due to factors mentioned previously, i.e. allylic radical stabilisation or the removal of a hydrogen atom by the initiator. Alternatively, steric hindrance may have prevented an initiated polymer molecule from approaching the unsaturated group of another polyurethane molecule in order to propagate the reaction.

5.3.2.2 ATTEMPTED GRAFT COPOLYMERISATION REACTION

Fig. (5.2) also shows the GPC of the dried products of the attempted graft copolymerisation reaction between PU2 and MMA. The chromatogram from the UV detector showed that no change in the molecular weight distribution of PU2 had occurred. Hence it was concluded that no grafting to the polyurethane had occurred.

The GPC trace for the RI detector, however, showed the presence of PMMA along with the original polyurethane.

The products underwent Soxhlet extraction with toluene. GPC analysis of the thimble residue indicated that the thimble contained mainly unreacted PU2, and only a very small amount of PMMA. The toluene extract consisted chiefly of PMMA, with only a minute quantity of PU2 that had co-dissolved with it.

It was concluded that PU2 was unreactive towards free-radical homopolymerisation and co-polymerisation with MMA under these particular reaction conditions. Davison[109], however, had achieved grafting of AA onto a polyurethane consisting of MDI, BD, and ER. Hence, it was known that the double bond of ER will free-radically co-polymerise with certain monomers. The next stage of the investigation

was to eliminate the possibility of producing stable radicals by means of the MDI units of the polyurethane, i.e. by replacing MDI with its saturated analogue $H_{12}MDI$.

5.3.3 SYNTHESIS AND REACTIONS OF THE POLYURETHANE PU3

The general polyurethane synthesis had to be adapted for PU3 to allow for the lower reactivity of the isocyanate groups of $H_{12}MDI$ compared to MDI [see table (1.1)]. Due to the absence of aromatic groups, PU3 could not be detected by the UV detector of the GPC equipment. However, it gave a large response for the RI detector [fig. (5.5)]. The relative molar ratios of the reactants for PU3 were:

$H_{12}MDI$	: PTMEG 2000	: BD	: ER
17	2	10	5

and the theoretical % hard block content was 59.2% w/w.

The molecular weight analysis of PU3 by GPC estimated that its $\bar{M}_n$ was 117,500, $\bar{M}_w$ was 396,500, and polydispersity was 3.4.

PU3 was characterised by microanalysis, IR spectroscopy, ^1H and ^{13}C-NMR, and DSC. The mechanical properties of the polyurethane were assessed from stress / strain measurements. The results from these techniques will be discussed later.

5.3.4 ATTEMPTED HOMOPOLYMERISATION OF PU3 AND THE COPOLYMERISATION OF PU3 WITH MMA [P(U3-G-MMA)]

5.3.4.1 ATTEMPTED HOMOPOLYMERISATION OF PU3

Fig. (5.5) shows the GPC of the reaction products of the homopolymerisation reaction of PU3. As for PU2, no apparent change in the molecular weight distribution of the polyurethane had occurred. This lack of reactivity towards homopolymerisation was probably due to

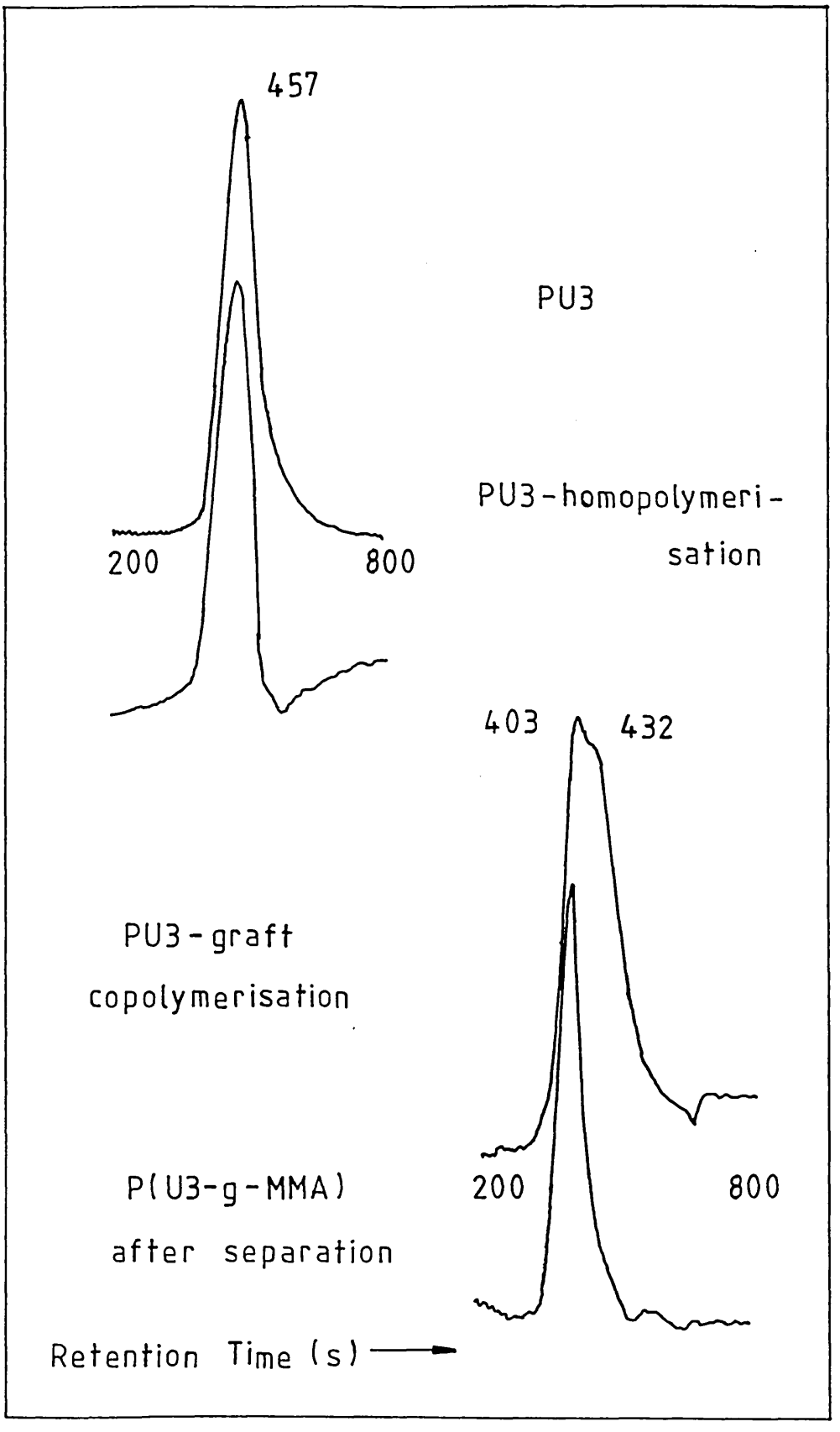


FIG. (5.5): GPC'S OF PU3 AND THE PRODUCTS OF THE REACTIONS OF PU3 (RI DETECTOR)

the same factors as for PU2 (section 5.3.2.1).

5.3.4.2 COPOLYMERISATION OF PU3 WITH MMA [P(U3-G-MMA)]

Fig. (5.5) also shows the GPC of the reaction products of the copolymerisation reaction of PU3 with MMA. Quite plainly there was unreacted PU3 at the end of the reaction. A new material of a seemingly larger molecular size than PU3 had been synthesised, but due to the fact that the RI detector responded to all species present in the mixture, analytical-GPC alone could not be used to determine whether or not grafting onto the polyurethane had occurred. This new peak could have been PMMA homopolymer.

Prep-GPC was performed on the crude reaction products using the Waters equipment in its recycle mode. Fig. (5.6) is the chromatogram obtained after three complete cycles. On each cycle, the peak broadened, but eventually separated into two coalescing peaks. It was concluded that there was only two types of material present in the mixture, one being unreacted PU3.

The two polymers were separated by Prep-GPC using both the Waters and the Altex equipment. Fig. (5.5) displays the analytical-GPC of the P(U3-G-MMA) after separation. The peak retention time of the separated polymer (385s) was lower than that of the second component of the product mixture (403s). This was because the lower molecular weight fractions obtained by Prep-GPC were discarded so as to ensure that all traces of unreacted PU3 were eliminated.

The isolated polymer was analysed by microanalysis, IR spectroscopy, and ^{1}H and ^{13}C-NMR to determine whether or not it contained any PU3. Figures (5.7) to (5.15) show the spectroscopic data obtained. The spectra are compared to those of PU3 and a sample of PMMA synthesised under the conditions described in section 4.12.2.

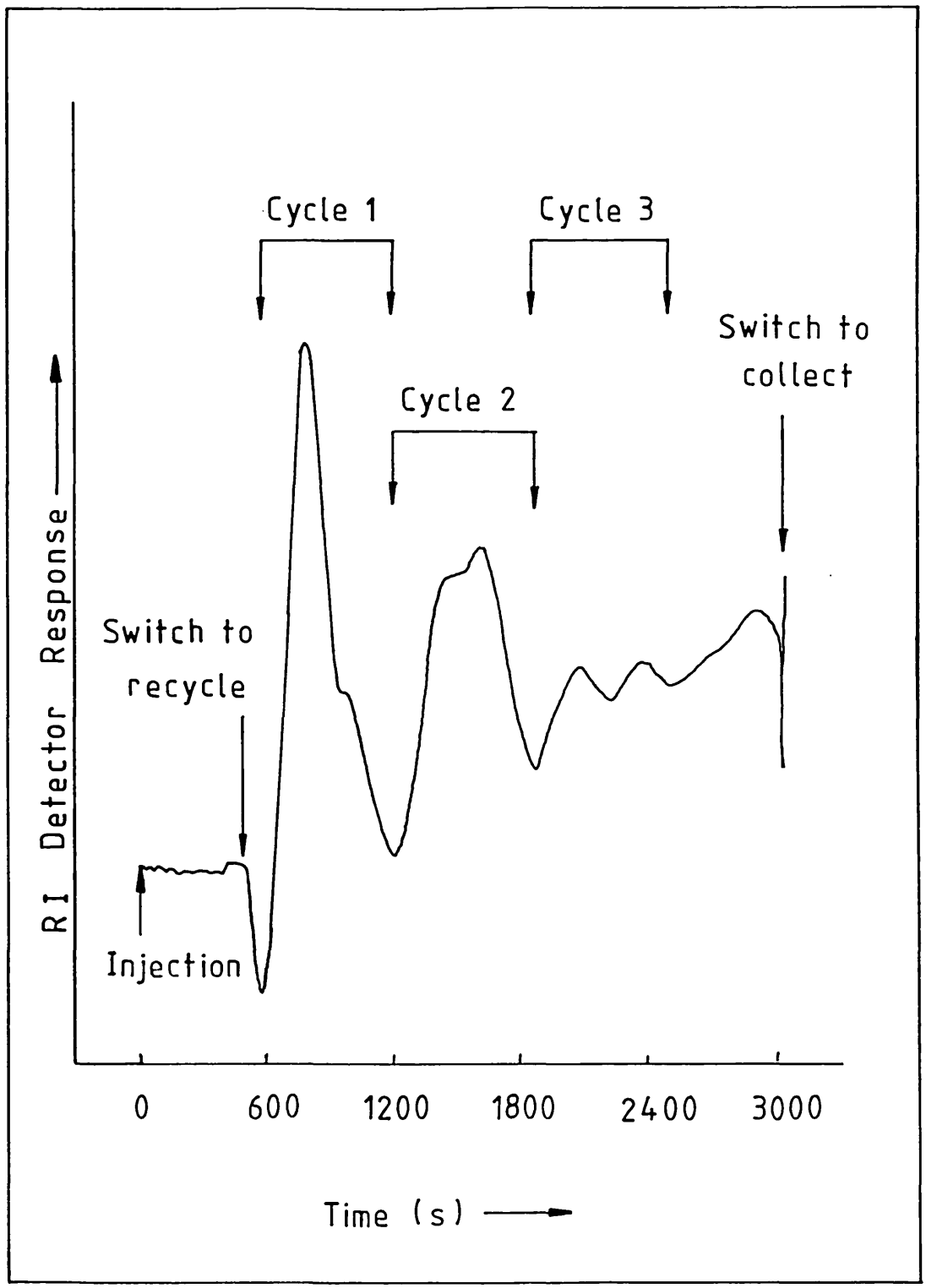


FIG. (5.6): PREP-GPC OF THE PRODUCTS OF THE P(U3-G-MMA) REACTION USING THE WATERS EQUIPMENT

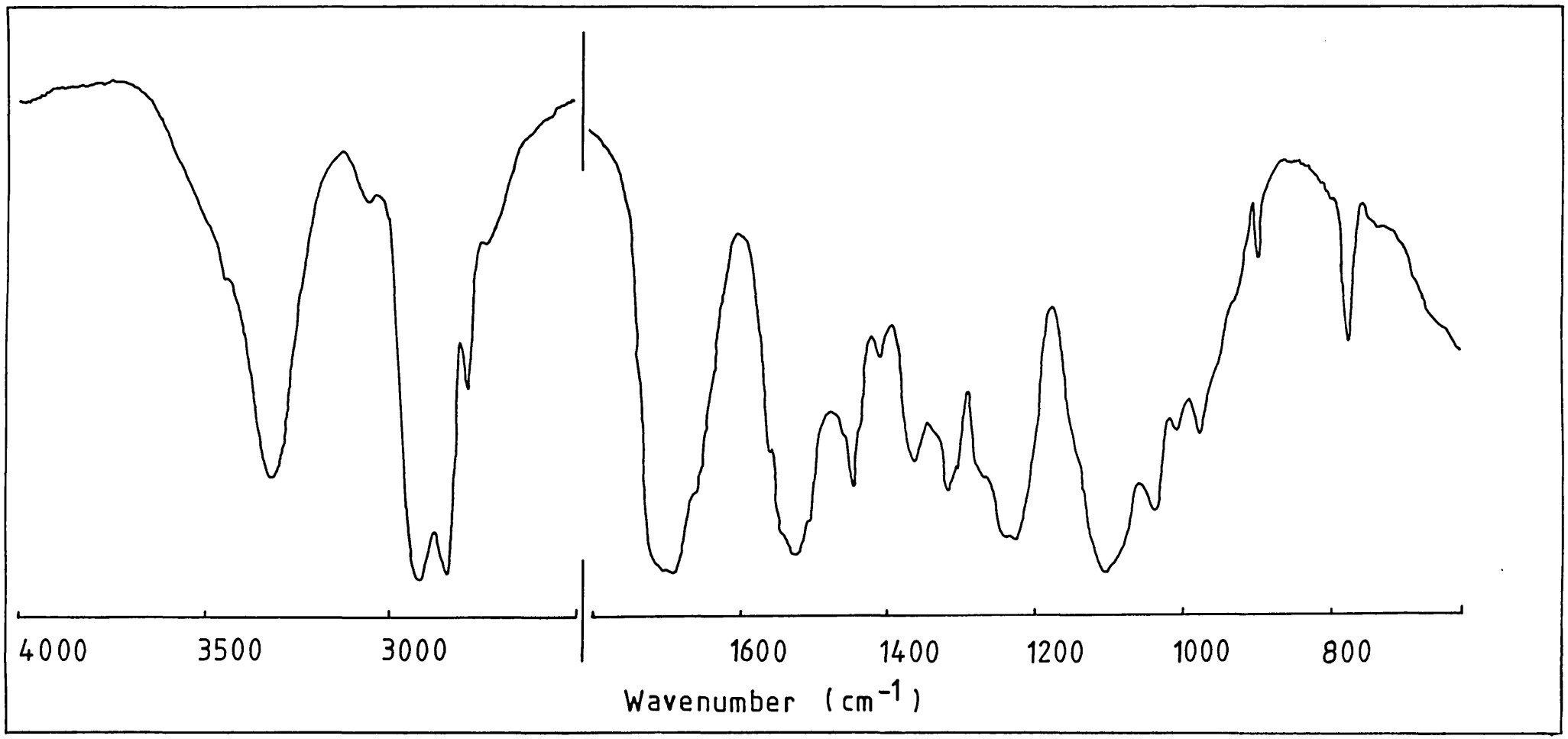


FIG.(5.7): IR SPECTRUM OF PU3

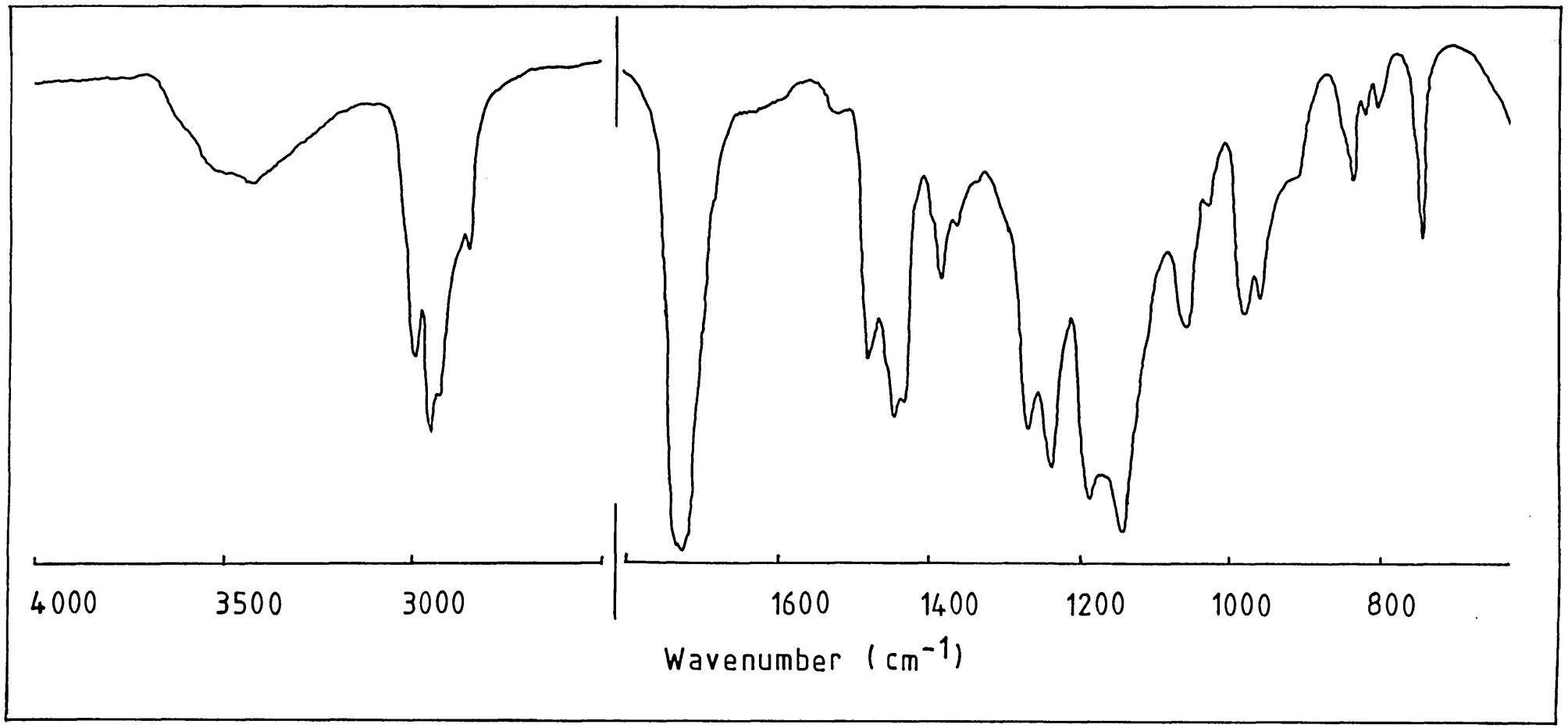


FIG. (5.8): I R SPECTRUM OF PMMA

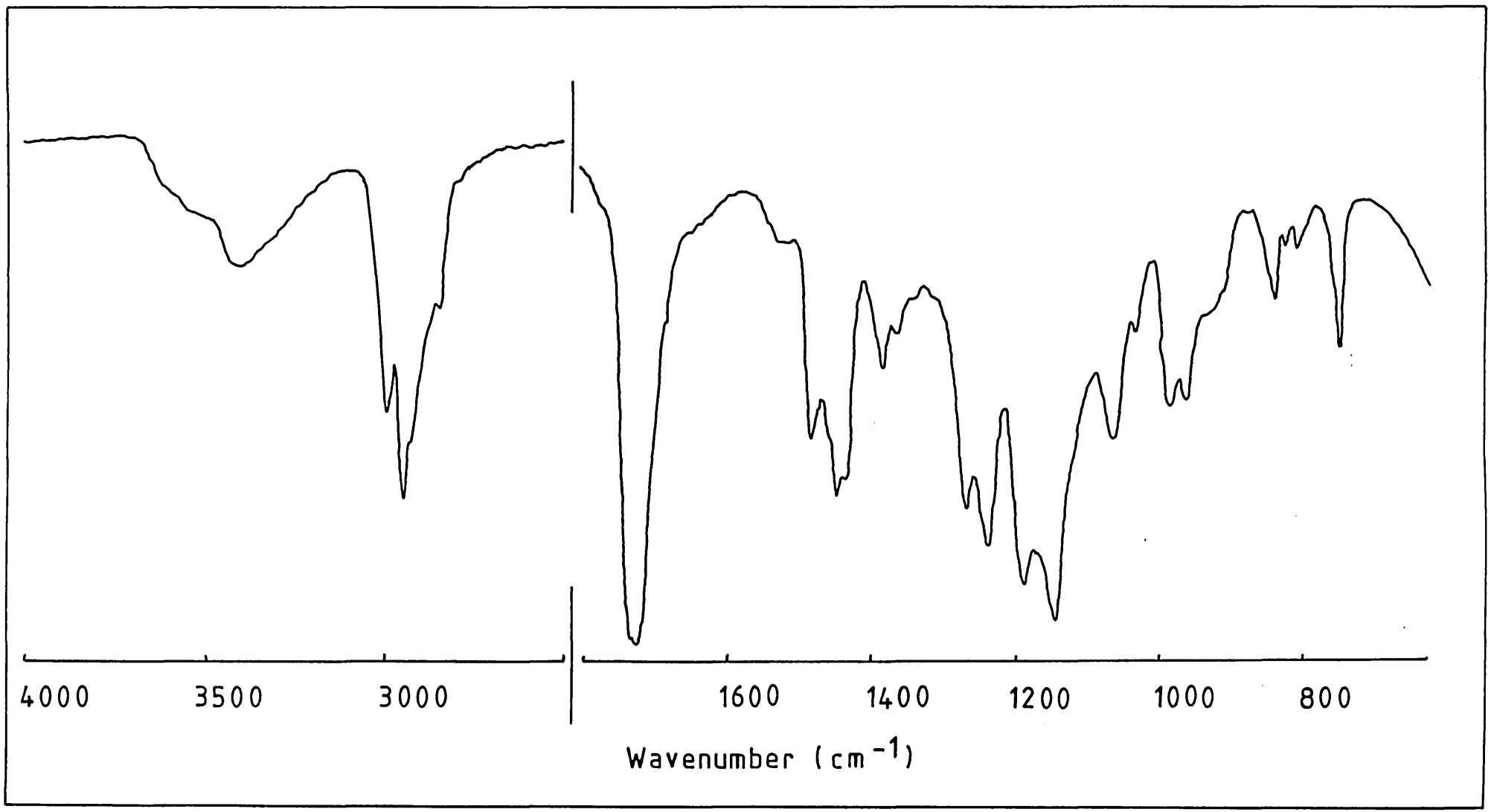


FIG.(5.9): I R SPECTRUM OF P(U3-G-MMA)

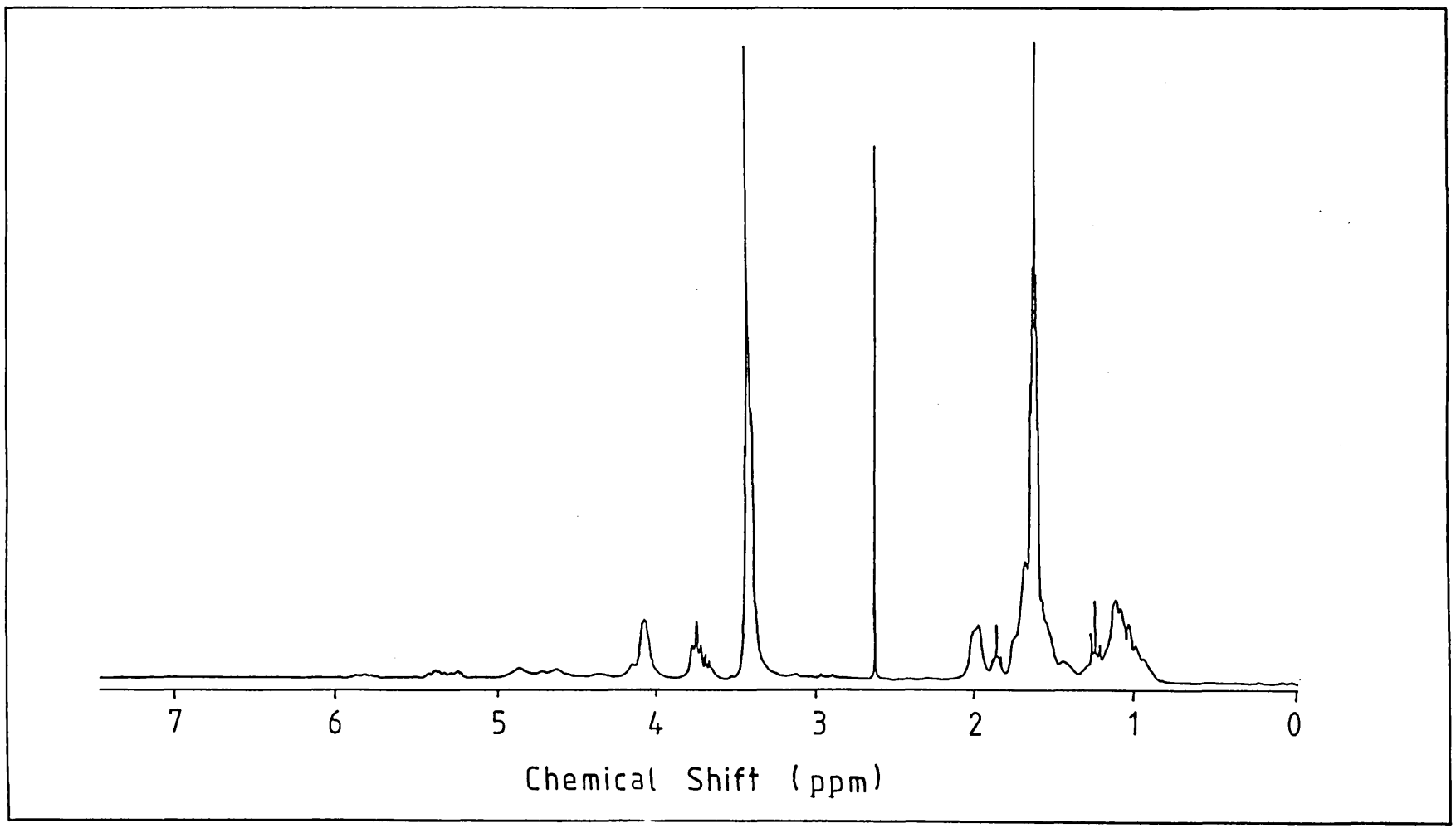


FIG.(5.10): ^{1}H-NMR SPECTRUM OF PU3

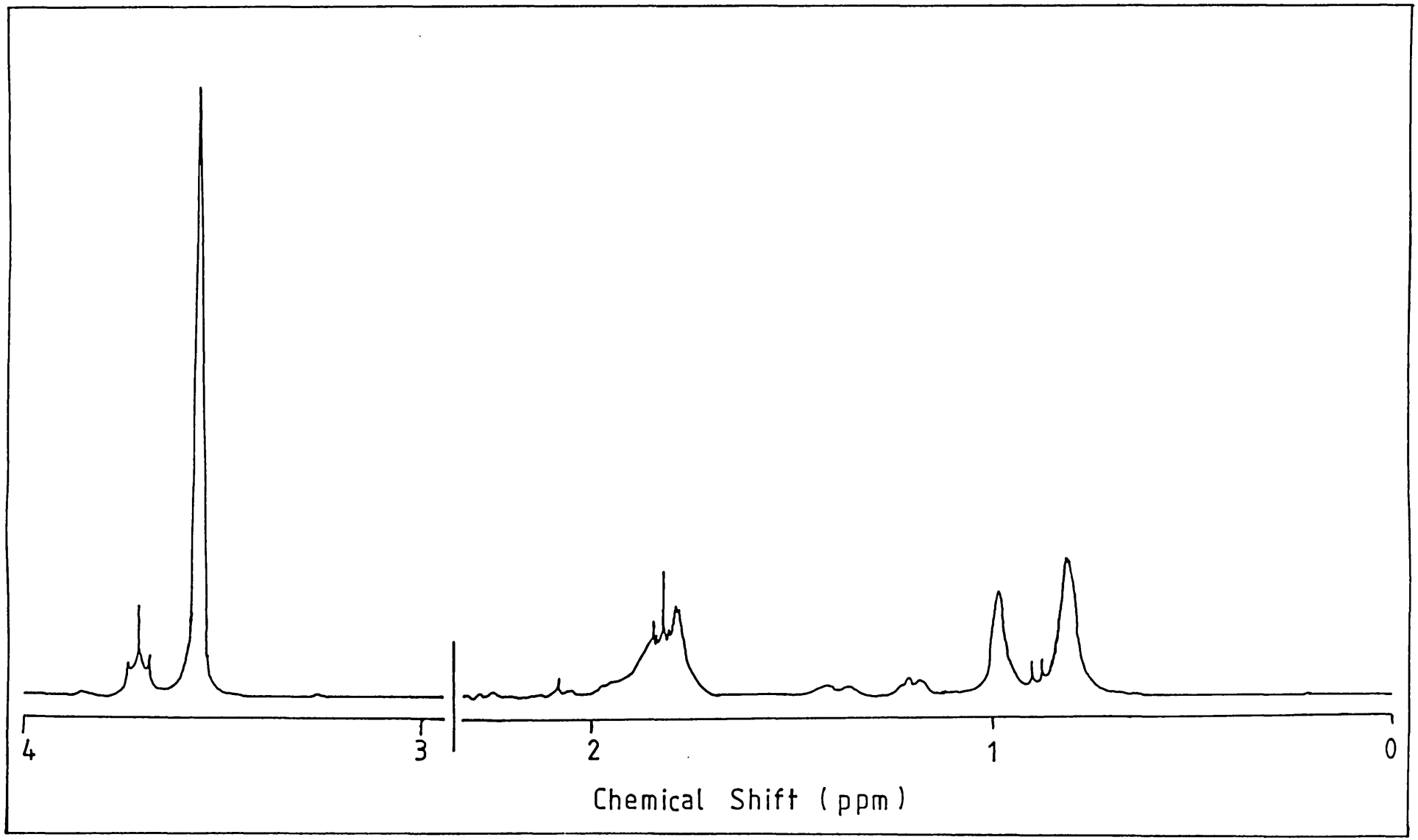


FIG.(5.11): ^{1}H-NMR SPECTRUM OF PMMA

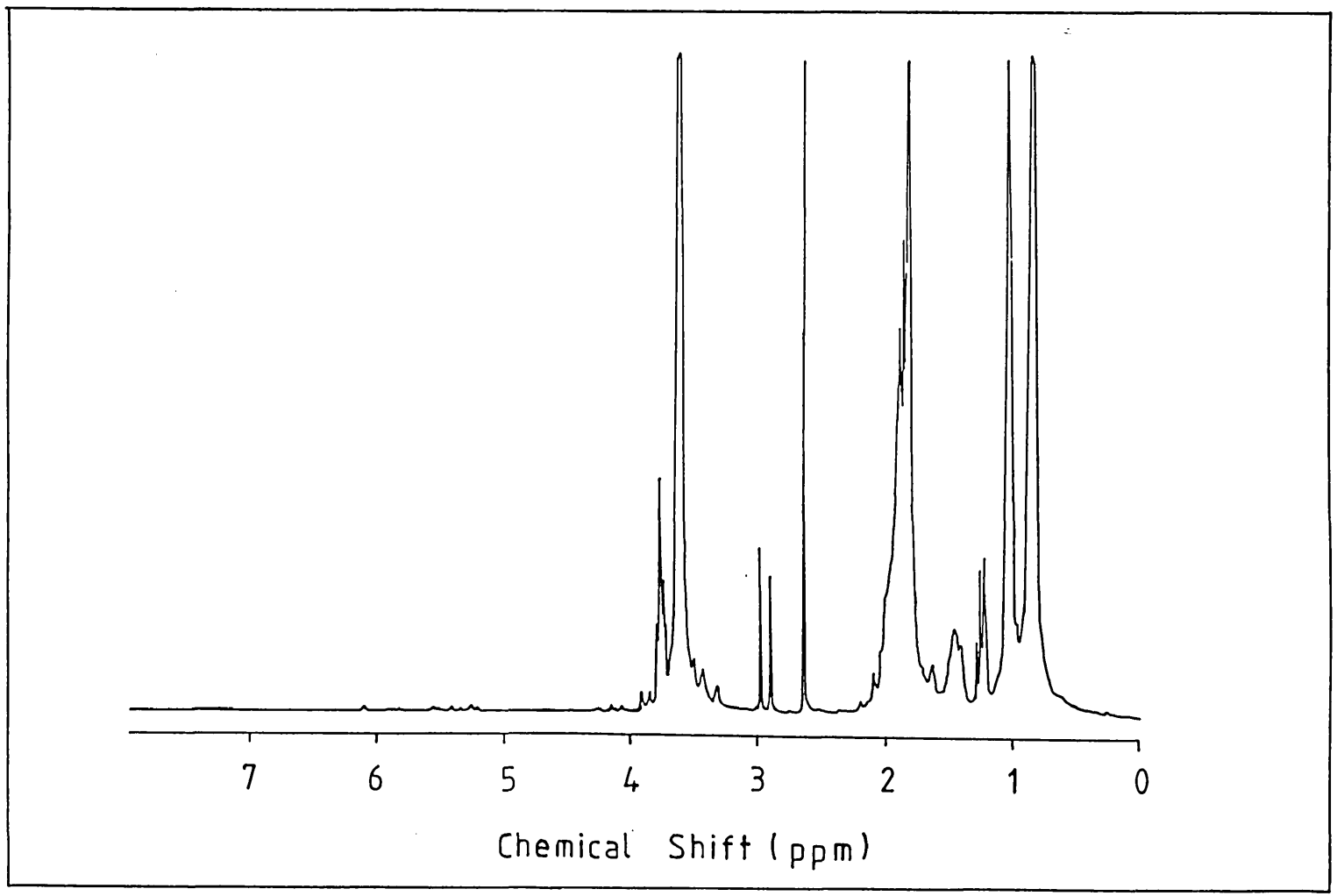


FIG. (5.12): ^{1}H-NMR SPECTRUM OF P(U3-G-MMA)

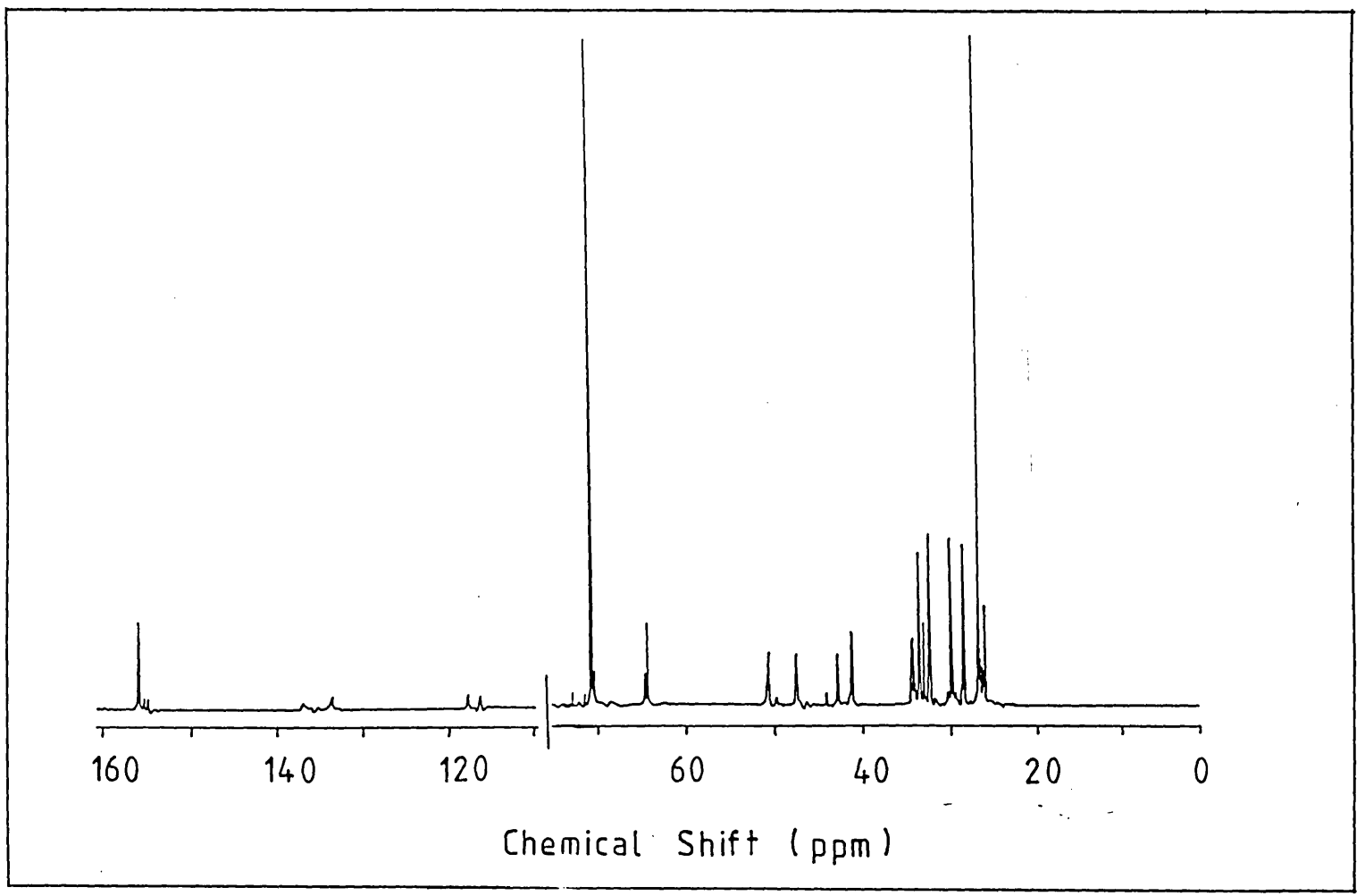


FIG.(5.13): ^{13}C-NMR SPECTRUM OF PU3

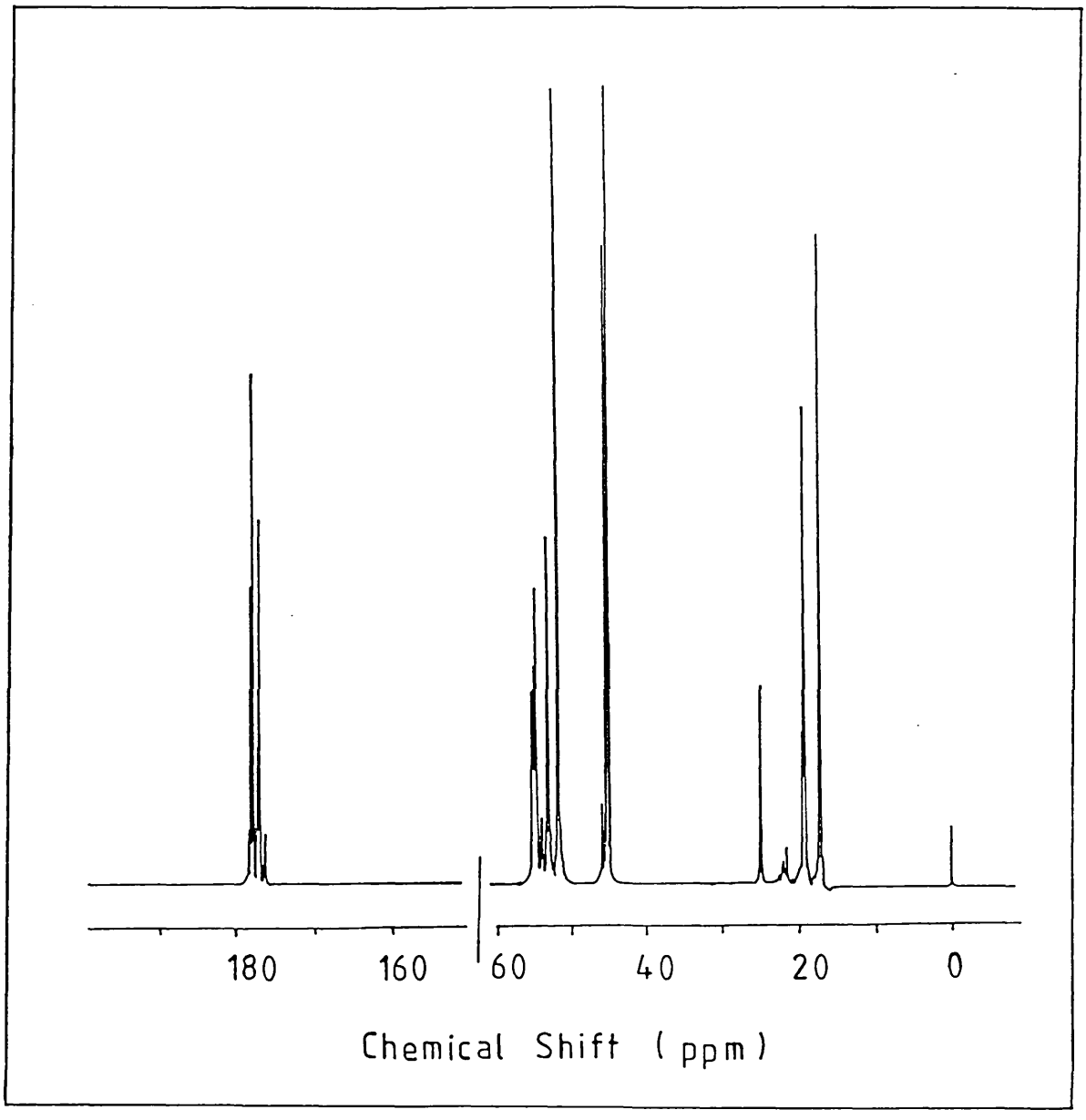


FIG. (5.14): ^{13}C - NMR SPECTRUM OF PMMA

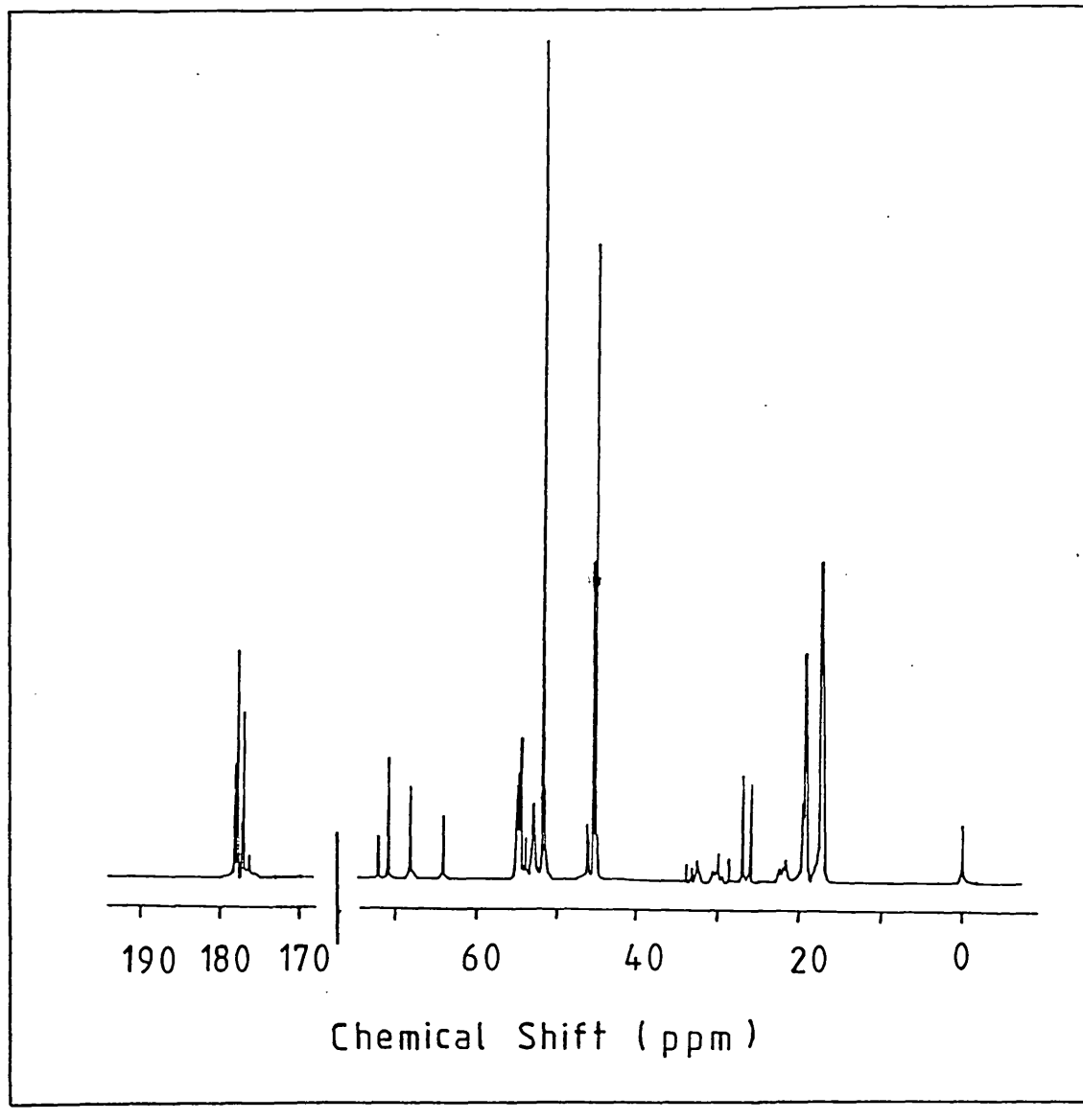


FIG. (5.15): ^{13}C-NMR SPECTRUM OF P(U3-G-MMA)

(A) IR SPECTROSCOPY

The IR spectrum of PU3 [fig. (5.7)] was as expected. A strong absorption band was found between 3100 and 3700cm^{-1}, indicating that the polyurethane contained H-bonded and non-H-bonded N-H groups in the urethane links. The broad carbonyl absorption centred at 1700cm^{-1} also reinforced this assumption.

The IR spectrum of PMMA [fig. (5.8)] was typical of that of a PMMA sample containing a high proportion of syndiotactic links[61].

The IR spectrum of P(U3-G-MMA) [fig. (5.9)] mainly resembled that of PMMA. However, since many of the bands of the polyurethane coincided with those of PMMA, IR spectroscopy was not considered as an adequately sensitive technique for determining whether the product was a graft copolymer of PU3 and MMA.

(B) ^{1}H-NMR

The ^{1}H-NMR spectrum of PU3 [fig. (5.10)] extended only as far as $\delta \approx 6$ppm since it had no aromatic content. The urethane proton resonance was not observed because the solvent used was $CDCl_3$. As explained in Chapter 1, section 1.3.2, when using non-polar solvents, the urethane proton resonances are not detected due to the broadening of the peak by the relaxation effect of the ^{14}N quadrupole.

The resonances between $\delta \approx 0$ and 3ppm were due to the cyclohexyl hydrogens of the H_{12}MDI units of the polyurethane. The peaks were complicated by the different configurations available for cyclohexyl groups (i.e. chair and boat forms), and by the non-equivalence of the equatorial and axial hydrogens.

Between $\delta \approx 3$ to 4.5ppm, the resonances due to the hydrogens of the polyether segments and the saturated portions of the chain

extenders were observed. As for PU2, the alkene resonances were found at $\delta \approx 5$ppm. These were also too small for detailed analysis.

The ^{1}H-NMR spectrum for PMMA [fig. (5.11)] was typical for this polymer[207]. No resonances were observed above $\delta = 4$ppm. A quantitative estimation of the tacticity of the polymer was evaluated from the integral traces of the resonances. For example, the peaks at $\delta = 0.8$, 1.0, and 1.2ppm corresponded to the resonances of the α-methyl protons of the polymer in syndiotactic, atactic, and isotactic configurations respectively. Analysis of the integrals indicated that the PMMA sample contained ~57% syndiotactic links, ~36% atactic links, and ~7% isotactic links. These results were as expected due to the conditions of the polymerisation of the sample (see section 2.1.3.6).

The spectrum for P(U3-G-MMA) [fig. (5.12)] was a combination of those of PU3 and PMMA, although the resonances corresponding to the polyurethane content of the material were relatively small.

(C) ^{13}C-NMR

The ^{13}C-NMR spectrum of PU3 [fig. (5.13)] was less complicated than the ^{1}H-NMR spectrum. Between 28 and 51ppm, there were several resonances which corresponded to the carbon atoms of the H_{12}MDI units of the polymer. At ~117ppm and ~134ppm, small peaks were observed. These represented the unsaturated groups present in the polyurethane due to the ER units. The former corresponded to the terminal $=CH_2$ group and the latter to the -CH= group. The urethane carbonyl resonance appeared at ~166ppm.

The ^{13}C-NMR spectrum of the PMMA sample [fig. (5.14)] was typical of those described in the literature[208]. The various tacticities of

the sequences of monomers units could be plainly seen in the spectrum, but quantitative analysis of the relative ratios was avoided due to NOE and spin-lattice relaxation effects (q.v.).

Resonances at 17, 20, and 22ppm corresponded to the α-methyl group in syndiotactic, atactic, and isotactic configurations repectively. The resonances at 45 - 47ppm belonged to the quarternary C atoms of PMMA. The resonances between 53 - 56ppm and 176 - 179ppm were equivalent to the $-CH_2-$ and the carbonyl C atoms respectively. All of these indicated the tacticity of the sample. The largest resonances were those of the syndiotactic C atoms, the smallest belonged to the isotactic atoms, and the atactic resonances were situated in between. The peak at 52ppm corresponded to the $-O-CH_3$ carbon atom, and showed no configurational effects.

The spectrum for P(U3-G-MMA) [fig. (5.15)] was again a combination of the PU3 and PMMA spectra, with the PMMA part being more dominant. The strong resonances for PU3 at 27ppm and 71ppm were the most prominent of the polyurethane's resonances. The PMMA part had a similar tacticity to the PMMA homopolymer.

(D) QUANTITATIVE ANALYTIC-GPC AND MICROANALYSIS RESULTS

Analytical-GPC was used to determine the quantity of unreacted PU3 left at the end of the copolymerisation reaction. A sample of the PU3 of a known concentration was initially analysed, and the area under the peak was calculated using the computer program of Appendix I. A sample of the crude products of the copolymerisation reaction was then analysed, and the program was used to determine the area of the chromatogram corresponding to the unreacted PU3. The procedure was repeated several times in order to estimate the errors involved.

Having assessed the quantity of unreacted polyurethane, and

assuming that the total amount of PU3 added to the reaction mixture (1.50g) was completely recovered at the end of the reaction in one form or another, a calculation was performed to evaluate the quantity of polyurethane in the P(U3-G-MMA). The results are listed in table (5.3)

TABLE (5.3): RESULTS FROM THE QUANTITATIVE GPC EXPERIMENTS PERFORMED ON THE CRUDE PRODUCTS OF THE P(U3-G-MMA) REACTION

CALCULATED %-UNREACTED PU3 AT END OF REACTION (%)	TOTAL YIELD OF REACTION (g)	AMOUNT OF UNREACTED PU3 (g)	YIELD OF P(U3-G-MMA) (g)	AMOUNT OF PU3 IN P(U3-G-MMA) (g)	%-PU3 IN P(U3-G-MMA) (%)
29 (± 1)	4.70	1.36 (± 0.05)	3.34 (± 0.05)	0.14 (± 0.05)	4.0 (± 1)

Microanalysis was performed on samples of PU3, PMMA, and P(U3-G-MMA). Since PMMA contained no nitrogen, any N content of the P(U3-G-MMA) would have arisen from the presence of PU3. If PU3 contained y% N w/w, and P(U3-G-MMA) contained z% N w/w, then the %-PU3 content of the copolymer was calculated from the formula:

$$\%\text{-PU3 content} = \frac{z}{y} \times 100 \qquad (5.4)$$

Table (5.4) lists the results obtained.

TABLE (5.4): MICROANALYSIS RESULTS FOR PU3, PMMA, AND P(U3-G-MMA)

SAMPLE	%-C CONTENT w/w (%)		%-H CONTENT w/w (%)		%-O CONTENT w/w (%)		%-N CONTENT w/w (%)	
	CALC.	FOUND	CALC.	FOUND	CALC.	FOUND	CALC.	FOUND
PMMA	60.0	59.9	8.0	8.4	32.0	31.7	-	-
PU3	65.6	65.1	9.5	10.2	18.8	19.9	6.1	4.8
P(U3-G-MMA)		57.8		8.2		33.5		0.5

From the microanalysis results, the %-PU3 content for P(U3-G-MMA), according to equation (5.4), was 10.4% w/w (using the found %-N content value for PU3).

Spectroscopic and other data indicated the presence of a small amount of PU3 contained within the product of the copolymerisation reaction. However, the PU3 content was so small that it was highly probable that any graft copolymer was dispersed amongst PMMA homopolymer. If their molecular sizes were similar, all species would elute with similar retention times when carrying out GPC. There was always the possibility that the PU3 content of the new material arose from contamination, despite the precautions taken to eliminate the possibility of unreacted PU3 mixing with the product. However, it was unlikely that contamination would be as much as 4% w/w, as calculated by analytical GPC.

DSC and stress / strain measurements were performed on PU3, PMMA, P(U3-G-MMA), and the mixture of products [P(U3-G-MMA)-MIX] to act as a comparison for later work.

(E) DSC RESULTS

The DSC results for PMMA are shown in fig. (5.16). Three separate runs were performed on the same sample to investigate the effect of annealing the polymer. Run (1) showed two transitions, the first occurring between 0°C and 45°C (centred at ~23°C) and the second between 90°C and 135°C (centred at ~113°C). The transitions showed the signs of stress-relaxation, i.e. as the polymer moved through a transition, the increase in molecular motion enabled the chain to relax and the energy was dissipated as heat as a new equilibrium was reached. This was indicated by an increase in the heat-flow when the

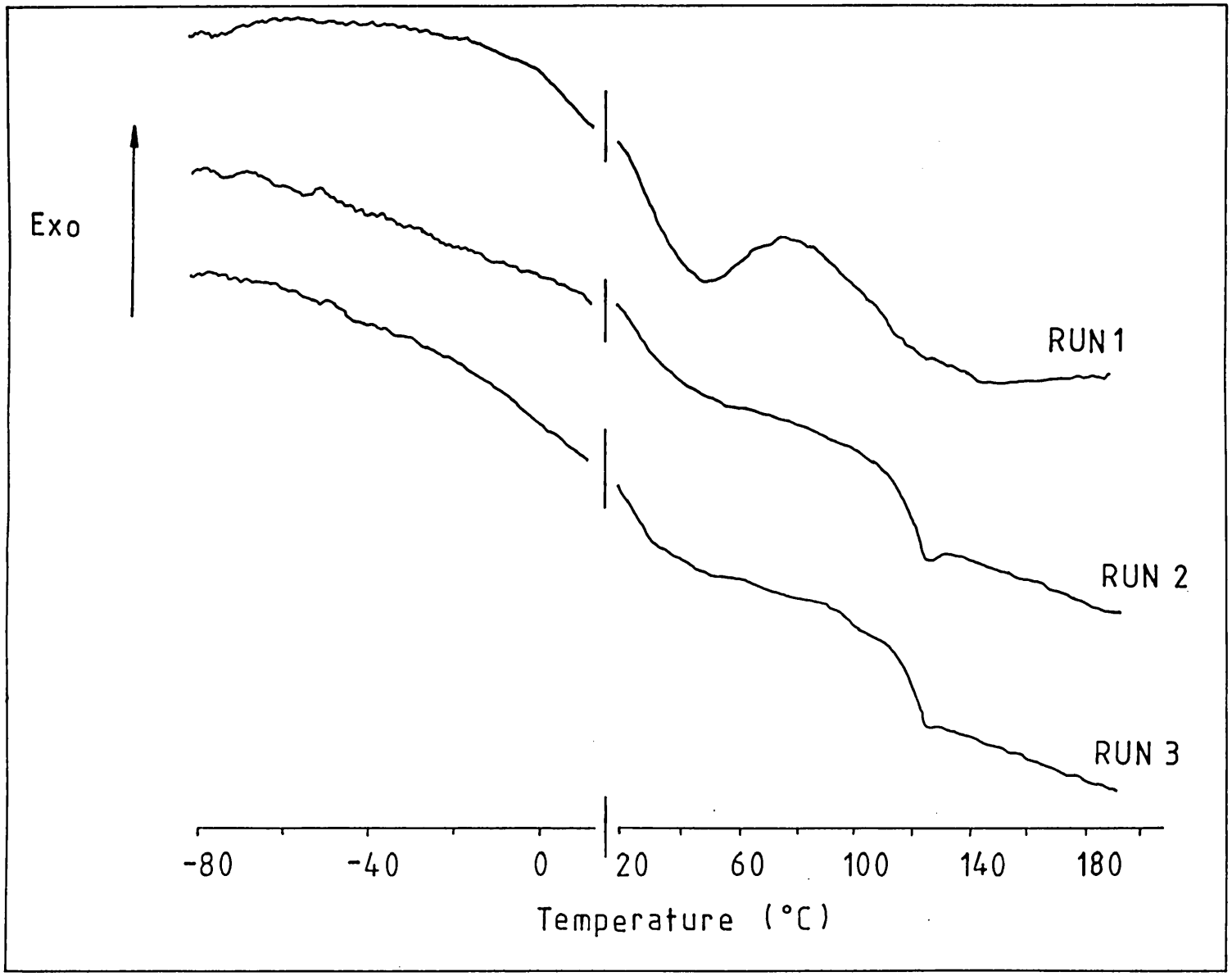


FIG. (5.16):
DSC THERMOGRAMS
FOR PMMA

change was completed.

The first transition was the relaxation of the carbomethoxy side chains of the polymer. The literature value for this process is ~20°C[40] (the relaxation of the aliphatic ester group occurs below ~150°C).

The second transition was the T_g for the sample. Since the PMMA contained a large proportion of syndiotactic links, it was expected that its T_g should have been quite high.

There were no signs of the evaporation of solvent from the sample, which could act as a plasticizer, hence the transition temperatures should have remained in the same regions for the subsequent runs, unless decomposition or other processes had occurred.

Runs (2) and (3) showed the same transitions centred at ~20°C and ~123°C and ~18°C and ~121°C respectively. As expected, no stress relaxation was observed as the sample had attained its new equilibrium after Run (1). No decomposition transitions were observed.

Fig. (5.17) shows the DSC curves for PU3. Run (1) had a slight transition at -67°C corresponding to the T_g of the polyether soft segment. Hence, it was concluded that there was a certain degree of incompatibility between the hard and soft segments of the polyurethane. The transition at ~46°C corresponded to a break down of the H-bonding between the urethane hydrogens and the oxygens of both the soft and hard segments. Melting occurred at ~108°C, followed by decomposition.

Run (2) still contained the soft segment T_g at -76°C. A new melting transition occurred at 20°C. By carrying out DSC measurements for the PTMEG 2000 alone, it was shown that this transition was the melting point for the decomposition products of the polyol after it had been heated to > 200°C. The breaking down of H-bonds still

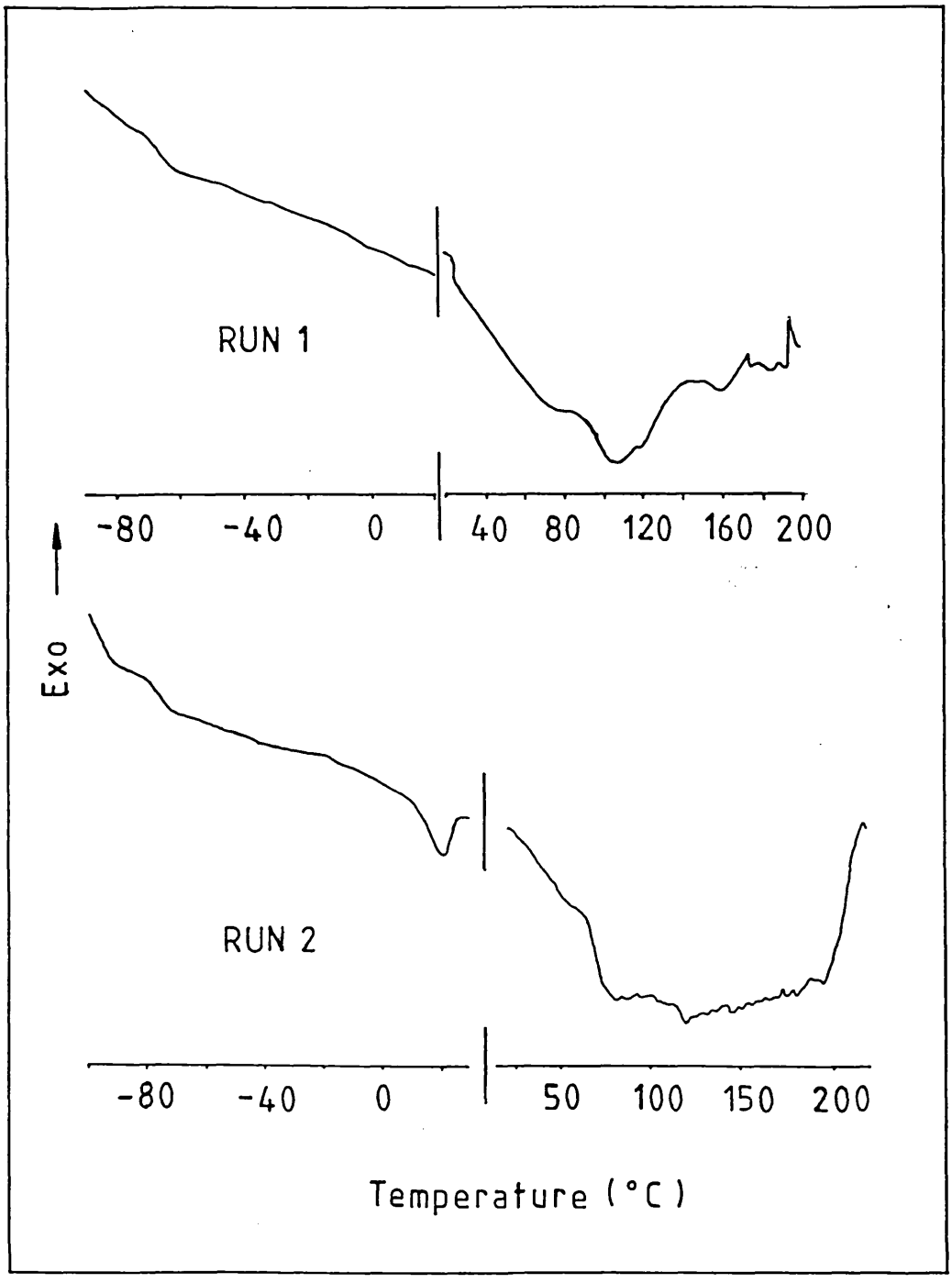


FIG. (5.17): DSC THERMOGRAMS FOR PU3

occurred at 40°C, but the melting transition for the whole polyurethane was carried over a much larger range of temperatures than for Run (1). Further decomposition happened after 200°C.

The DSC curves for P(U3-G-MMA) were very similar to those of PMMA. Fig. (5.18) shows the second run of the sample, which was taken up to 250°C. No polyol T_g was observed due to the low concentration of PU3 in the sample. The T_g of the PMMA occurred at 105°C. The start of the melting transition appeared after 220°C.

(F) STRESS / STRAIN MEASUREMENTS

Table (5.5) shows the results of the stress / strain tests performed on the polymers.

TABLE (5.5): STRESS / STRAIN RESULTS FOR PMMA AND THE POLYMERS BASED ON PU3

SAMPLE	YOUNG'S MODULUS, E ($\times 10^{-8}$ / Pa)	EXTENSION AT BREAK (%)	ULTIMATE STRENGTH ($\times 10^{-7}$ / Pa)
PMMA	5 (±2)	4 (±1)	2 (±1)
PU3	2.0 (±0.4)	5.9 (±0.8)	0.78 (±0.06)
P(U3-G-MMA)-MIX	3.9 (±0.6)	4.8 (±0.6)	1.7 (±0.2)
P(U3-G-MMA)	6 (±1)	3 (±2)	1.5 (±0.2)

Although all of the materials had high values for E and ultimate strength, all had low %-extensions at break. PU3 had a very poor performance compared to polyurethanes based upon MDI (see later results). It would appear that changing from a rigid aromatic diisocyanate to an aliphatic compound disrupts the internal H-bonding and arrangement of the hard segment of the polyurethane. Thus, there

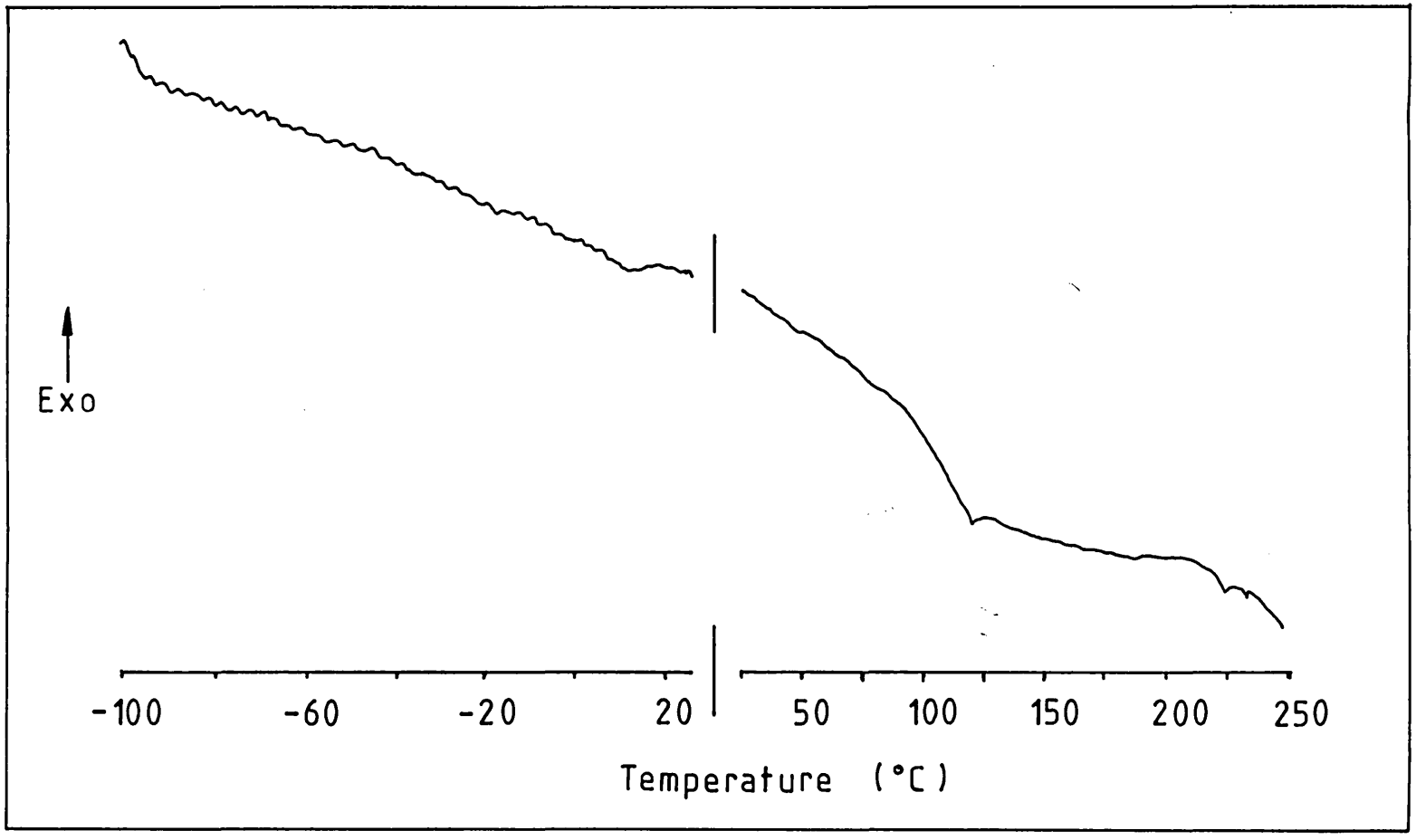


FIG. (5.18) : DSC THERMOGRAM FOR P(U3-G-MMA) (RUN 2)

were weaker physical crosslinks holding the polymer together, and the application of a force caused it to break rather than to stretch. This weakness was also the reason for the low transition temperatures of the DSC measurements for PU3.

ER appeared to be an unsuitable monomer for inclusion in a polyurethane as a site for the grafting of MMA. Certainly grafting to PU2 did not occur, and grafting to PU3 was doubtful. The ER units in the polyurethanes were unreactive towards copolymerisation with MMA probably because they were capable of forming stable allylic radicals instead of undergoing addition reactions with growing PMMA radicals.

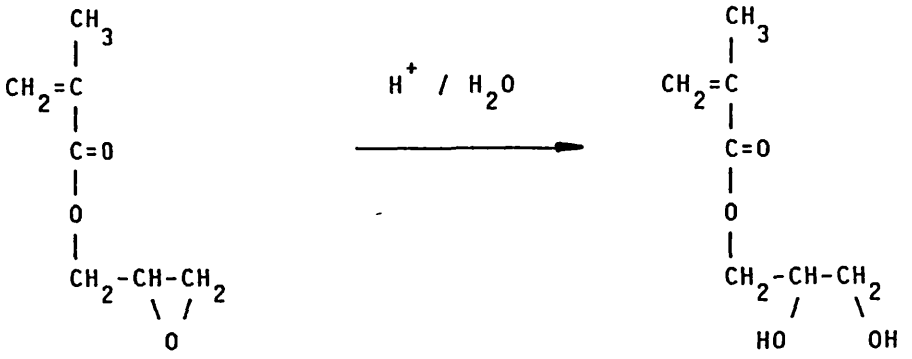
A system consisting of grafted polyurethanes based upon $H_{12}MDI$ would have no apparent benefit to the mechanical properties of the PMMA. Hence, it was decided that other grafting systems deserved investigation.

5.4 ATTEMPTED SYNTHESES OF GLYCERYL MONOMETHACRYLATE (GMM) THROUGH THE HYDROLYSIS OF GLYCIDYL METHACRYLATE (GM)

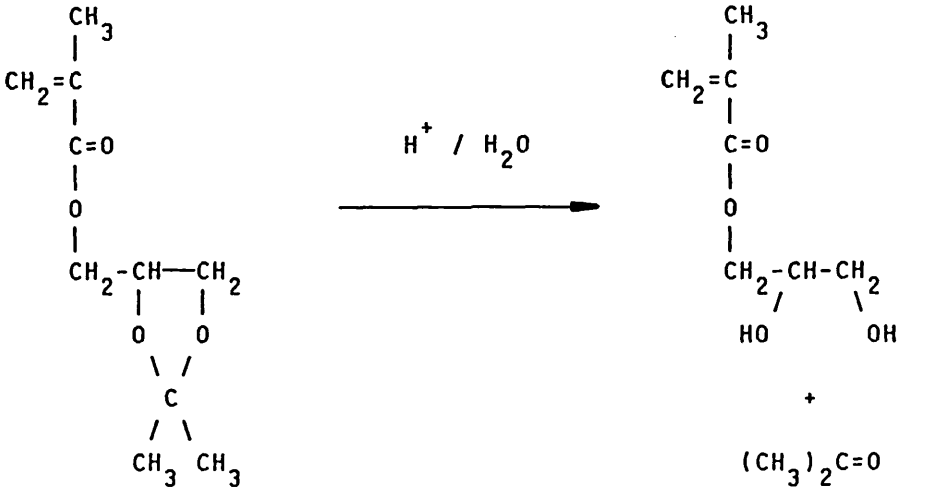
Research into the potential uses of the monomer GMM (2,3-dihydroxypropyl methacrylate) has been restricted so far to the development of biocompatible hydrogels for use as contact lenses, adhesives between metals and bones, and in self-curing dental resins[209]. There has been no apparent work carried out into the use of GMM as a functional chain extender for polyurethanes.

The synthesis of GMM has been performed by several methods:

(A) The hydrolysis of GM or isopropylidene methacrylate[210-214] using dilute acid as the catalyst in order to open the epoxide group, but to prevent the attack of the ester function.

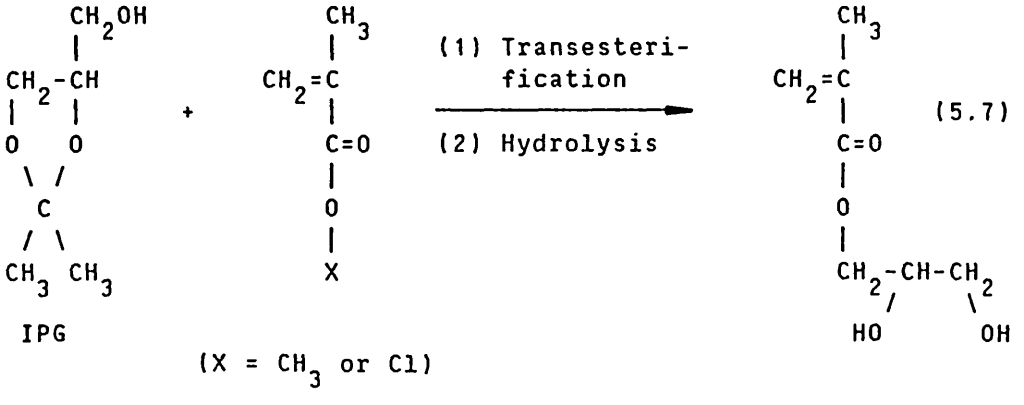


(5.5)



(5.6)

(B) The transesterification of isopropylidene glycerol (IPG) with reactive methacrylic compounds such as MMA or methacryloyl chloride (MAC), followed by the hydrolysis of the acetal group[215,216].



(5.7)

Pang[209] attempted to synthesise GMM by the transesterification reaction between either IPG or glycerol with MMA, MAC, or MAA, but found that the product could not be isolated due to its highly

reactive nature and tendency to readily homopolymerise.

The double bond of GMM is very susceptible to nucleophilic attack due to the inductive effect of the carboxy and hydroxy functions. Also, homopolymerisation is relatively facile, since H-bonding ensures that the monomer units are close together.

GMM is an expensive compound to purchase commercially. Realising its potential as a chain extender for polyurethanes which would introduce pendent reactive groups into the polymer, attempts were made to synthesise GMM through the hydrolysis of GM.

5.4.1 GENERAL EXPERIMENTS

For experiment (1) of section 4.8.1.1, it was obvious that the product was being formed, since the starting material, GM, was immiscible with the water, but, by the end of the reaction, a homogeneous reaction mixture was obtained. Problems were found in isolating the product. Despite loading the crude product with inhibitors, side reactions occurred on distillation, causing the production of gum-like materials. It was decided to follow the hydrolysis reaction by HPLC to see if side reactions were occurring as the main reaction proceeded.

5.4.2 HPLC EXPERIMENTS

HPLC of the samples of the reaction mixture of experiment (1) (section 4.8.2.1) showed that no product had been formed. This was due to insufficient mixing of the reactants.

HPLC of the samples from experiments (2) and (3) (sections 4.8.2.2 and 4.8.2.3) showed that a new material was being formed, as a function of time, which had a lower retention time than the starting material, GM. This was the probably the product GMM, eluting earlier

than GM because of its preference to stay with the polar THF solvent than to interact with the non-polar ODS HPLC column packing. The GM underwent more interactions with the column, and, therefore, had a longer retention time.

Experiments (2) and (3) gave chromatograms with identical values for the retention times of the components of the mixtures. However, the ratio of the peak height for the product compared with the starting material was greater for (2) than for (3), indicating that its rate of reaction was faster. This was due to a larger concentration of water being present in the reaction mixture for (2).

Fig. (5.19) shows a selection of the chromatograms for experiment (3). GM eluted after 162s. The product GMM, which was plainly seen on the chromatograms after a reaction time of 50m, had a peak retention time of 126s.

After 2 days, a sample of the dichloromethane mixture was extracted with water, and HPLC was carried out on the remaining material [fig. (5.19)]. The new peak at 126s had disappeared, whilst the GM peak at 162s remained. This was evidence that the former peak corresponded to the product of the hydrolysis, since GMM was water soluble.

The HPLC experiments showed that the required hydrolysis reaction was occurring, without side reactions. However, the product, GMM, was too reactive to isolate in greater concentrations from the reaction mixtures of the general experiments. As mentioned previously, GMM can readily homopolymerise. Commercially, the monomer is supplied containing 3000ppm of inhibitor in order to prevent homopolymerisation. There are also side reactions which can occur under the hydrolysis conditions. For example, as the concentration of the diol increases, a competitive reaction to the hydration can

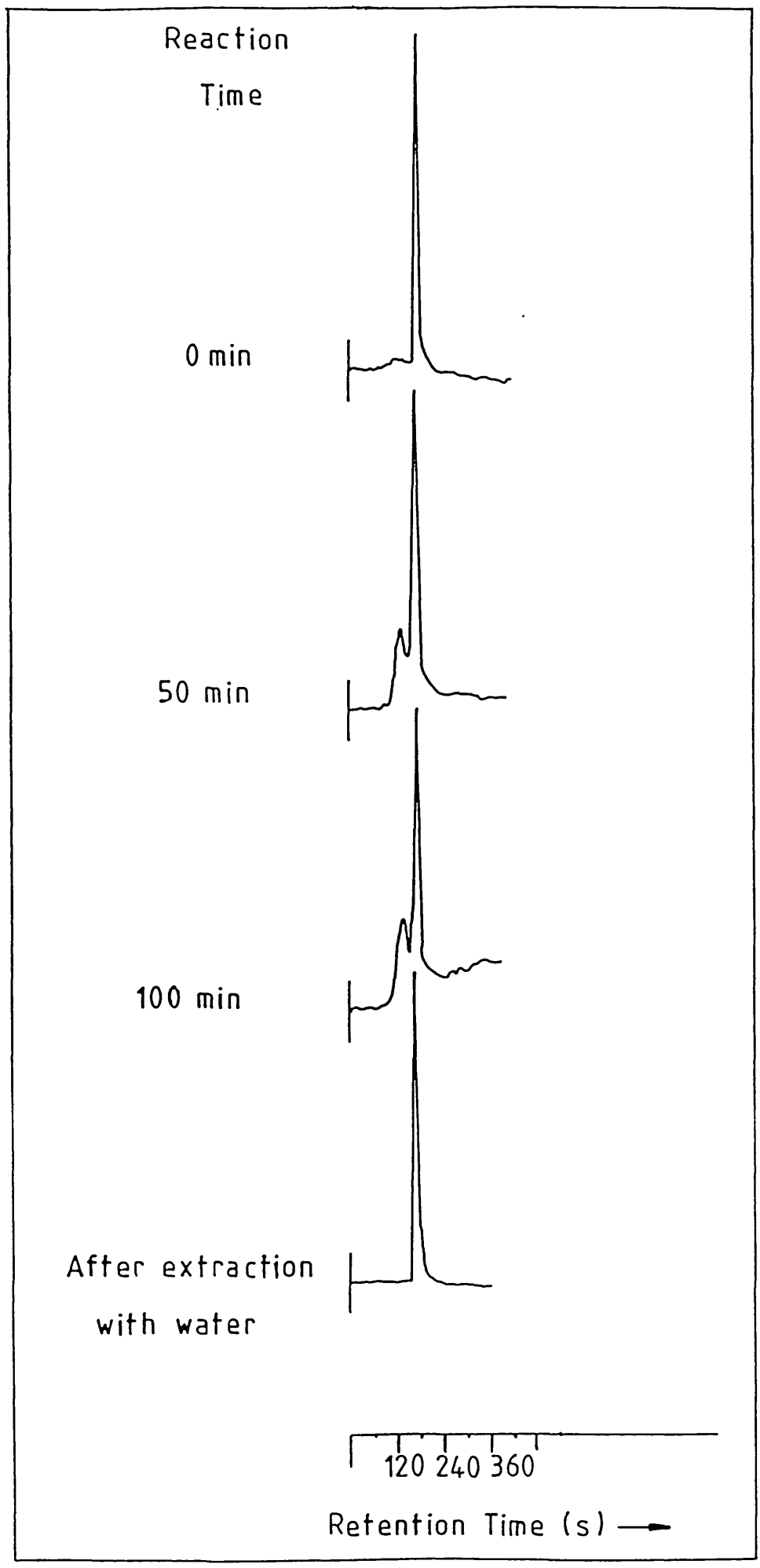
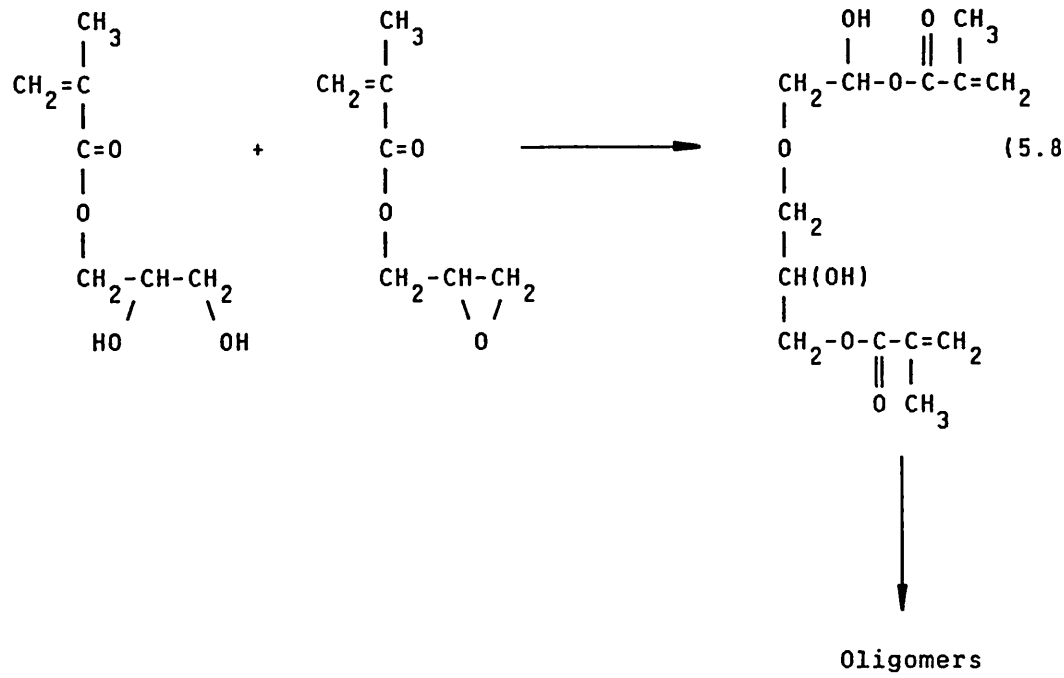


FIG. (5.19): HPLC CHROMATOGRAMS FOR EXPERIMENT (3)

happen, with the GMM acting as a nucleophile and attacking another GM molecule:



As the product still contains several hydroxyl units, the reaction can continue, producing high molecular weight oligomers.

It was decided to abandon the synthesis of the diol GMM, and to concentrate on the production of the polyurethanes prepared from the commercial monomer.

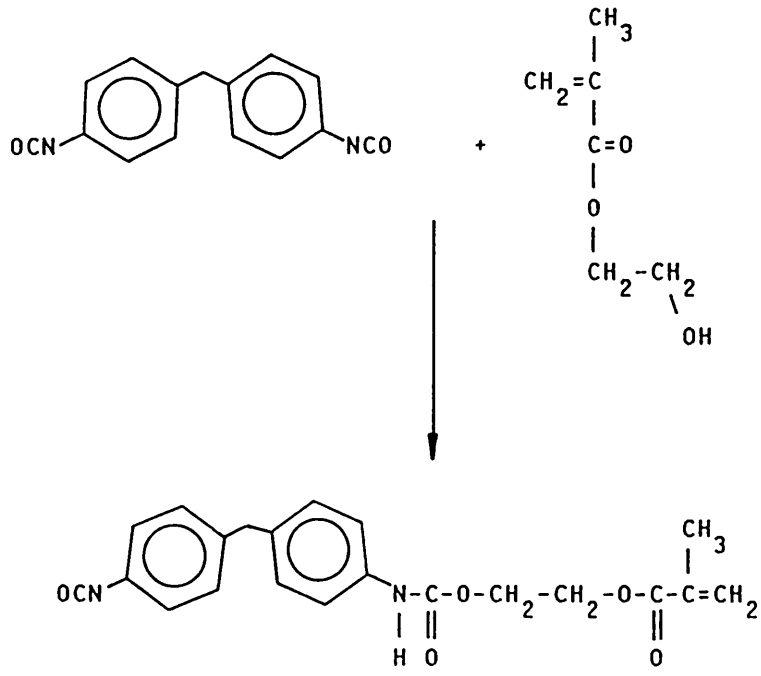
5.5 REACTIONS OF POLYURETHANES CONTAINING MANY METHACRYLATE UNITS (PU4 AND PU7)

5.5.1 REACTIONS OF PU4

5.5.1.1 SYNTHESIS OF PU4

The initial stage of the synthesis of PU4 was the premixing of HEMA with MDI (section 4.6.1). The ratio of the two reactants, 6 : 1, was such that there was an excess of MDI. In theory, therefore, only singly end-capped MDI molecules should have been obtained, which were

dispersed amongst the remainder of the MDI:



(5.9)

(I)

In reality, however, it was expected that a small amount of doubly end-capped compounds would have been formed by the reaction of (I) with another molecule of HEMA.

The presence of the compound (I), which was in effect a mono-isocyanate, would have introduced a degree of stoichiometric imbalance into the reaction mixture for the polyurethane synthesis. This imbalance would have affected the molecular weight of the final polymer. In this case, the number average chain length, x_n, could have been expressed by an extension of the Carother's equation[42]:

$$x_n = \frac{(1 + r)}{(1 + r - 2rp)} \qquad (5.10)$$

where p was the extent of reaction [$p = (N_o - N)/N_o$, N_o being the total number of molecules at time t=0, and N the number of molecules [illegible] at time t], and r was the ratio $N_{AA}/(N_{BB} + 2N_B)$,

where N_{AA} represented the total number of dihydroxy molecules added to the reaction mixture, N_{BB} was the total number of diisocyanate molecules, and N_B was the number of mono-isocyanates present on the addition of the diols.

The ratio of reactants for PU4 were:

MDI	PTMEG 2000	BD	HEMA
12	2	9	2

Therefore, the polymer had a theoretical %-hard block content of 50.5% w/w. If the total number of MDI and HEMA molecules at the start of the synthesis was 12n and 2n respectively, then, after the initial reaction [equation (5.9)] the mixture would have contained 10n molecules of MDI and 2n molecules of the mono-isocyanate (disregarding any other reactions). The total number of dihydroxy molecules then added to this combination was 11n, and the ratio r would have been equal to:

$$r = \frac{11}{14} = 0.79$$

Substituting this value of r into equation (5.10) meant that x_n was equal to:

$$x_n = \frac{1.79}{1.79 - 1.58p}$$

Therefore, if the extent of reaction was 0.99, the value of x_n would have been ~8.

A relatively low temperature and a catalyst was used for the

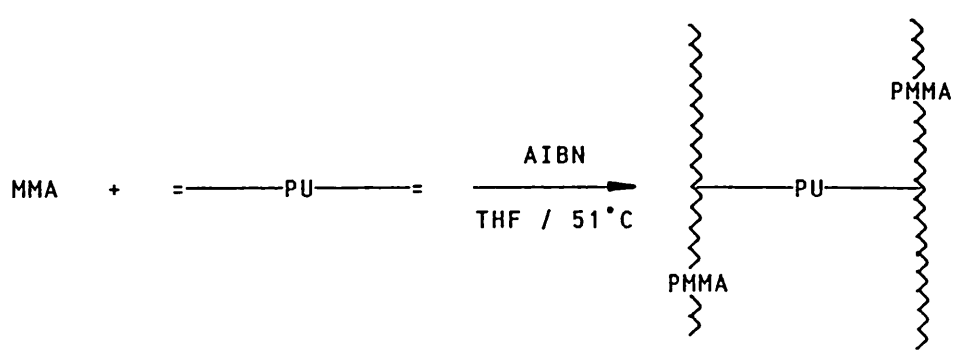
synthesis to prevent a high temperature free-radical polymerisation from occurring during the synthesis. Also, HQ was added as an inhibitor to scavenge any radicals that may have been formed. The inhibitor was water soluble, and would have remained in solution in the water after the precipitation of the polyurethane.

The GPC of PU4 [fig. (5.20)] showed that it had a comparitively broad molecular weight distribution. Small peaks were observed in the low molecular weight region, due to small oligomers resulting from polyurethane molecules that had been terminated by the mono-isocyanate (I) at both ends at an early stage of the reaction.

The ^{1}H-NMR spectrum of PU4 contained two small resonances at $\delta \approx 5.7$ ppm and $\delta \approx 6.1$ ppm corresponding to the protons of the terminal methacrylate groups of the polyurethane molecules. The peaks were too small to determine their splitting pattern.

5.5.1.2 COPOLYMERISATION OF PU4 WITH MMA, P(U4-G-MMA)[1] AND [2]

It was intended that the product of the free-radical copolymerisation reaction of PU4 should have consisted of two PMMA chains linked together by a polyurethane molecule:



(5.11)

However, due to the high reactivity of the PU4 molecules towards copolymerisation with MMA, crosslinked networks were formed for both of the reactions P(U4-G-MMA)[1] and [2].

Fig. (5.20) shows the GPC (UV detector) of the THF solution obtained after the Soxhlet extraction of the products of the reaction

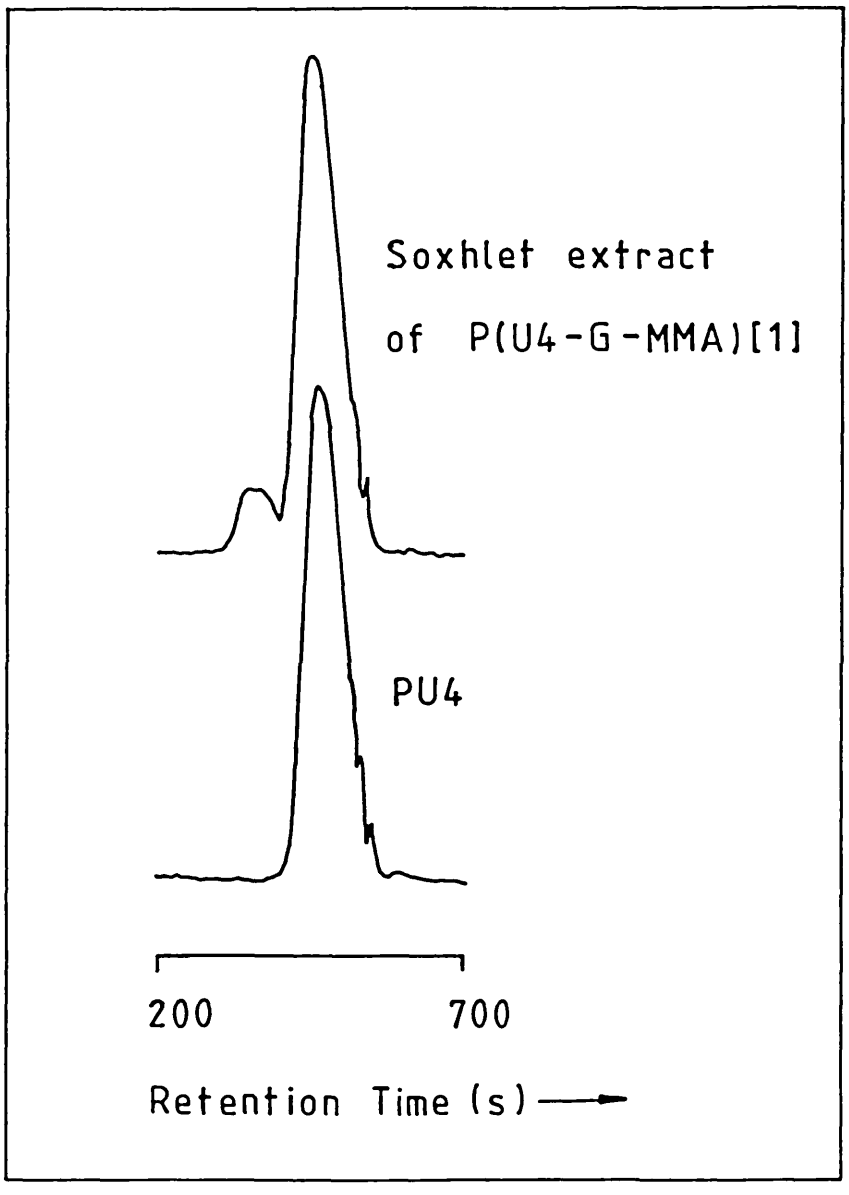


FIG.(5.20): GPC'S OF PU4 AND THE SOXHLET EXTRACT OF P(U4-G-MMA)[1]

P(U4-G-MMA)[1]. There was still some unreacted PU4 present in the products. There was also a new material of a larger molecular size than PU4. Since, the chromatogram was that obtained through the UV detector, it was deduced that this compound contained PU4. It was probably the THF soluble graft copolymer of PU4 and MMA, formed by the copolymerisation of singly end-capped polyurethane molecules.

It was concluded that PU4 was too reactive towards copolymerisation with MMA, and formed gels. It was decided that singly end-capped polyurethane molecules would be better for graft copolymerisation purposes. This was the basis for polyurethanes PU5 and PU6.

5.5.2 REACTIONS OF PU7

5.5.2.1 SYNTHESIS OF PU7

PU7 was chain extended with a mixture of BD and GMM in order to produce a polyurethane molecule containing several pendent methacrylate groups. These unsaturated groups were to act as sites for the grafting of MMA onto the polyurethane. Since MMA readily copolymerises with other methacrylate monomers, it was expected that PU7 would have been more reactive towards the graft copolymerisation reaction than PU2 or PU3.

Again, a low temperature with a catalyst and inhibitor were employed for the polyurethane's synthesis in order to prevent the free-radical polymerisation of the GMM and its step-growth reaction products.

The molar ratios of reactants for PU7 were:

MDI	PTMEG 2000	BD	GMM
11	2	4	5

Therefore, its theoretical %-hard block content was 49.5% w/w.

Fig. (5.21) shows the GPC of PU7 (UV detector).

5.5.2.2 COPOLYMERISATION OF PU7 WITH MMA, P(U7-G-MMA)[1], [2], [3], AND [4]

Reactions P(U7-G-MMA)[1], [2], and [3] (section 4.11) all produced insoluble gels after only two or three hours of reaction. Reaction [4], however, did not contain any gel particles. The reaction was distinguished from the other three by having an initial ratio of 1 : 1 of PU7 to MMA in a relatively dilute solution.

Fig. (5.21) shows the GPC of the products of the reaction P(U7-G-MMA)[4] (UV detector). As well as unreacted PU7, the products contained a new material of a higher molecular size, which was the required graft copolymer. The GPC for the RI detector had an identical shape to that of the UV detector. There was no apparent PMMA homopolymer peak. The PMMA could have been hidden beneath those of the PU7 or the graft copolymer. However, had this been so, then it was expected that the shape of the peaks would not have been quite as identical for the two detectors.

It appeared that the graft copolymerisation of PU7 with MMA followed general copolymerisation rules. Hence, each polymer molecule would have contained PU7 and PMMA, but no PMMA homopolymer would have been formed. Therefore, at the end of the reaction, the products contained the graft copolymer and unreacted PU7 (unreacted MMA was removed on precipitation and drying).

These experiments showed that PU7 was capable of undergoing copolymerisation with MMA, and that the pendent methacrylate groups of the polyurethane were not greatly affected by steric hindrance.

The mechanism of grafting could have occurred by several methods. The shape of the final graft copolymer would have been determined by

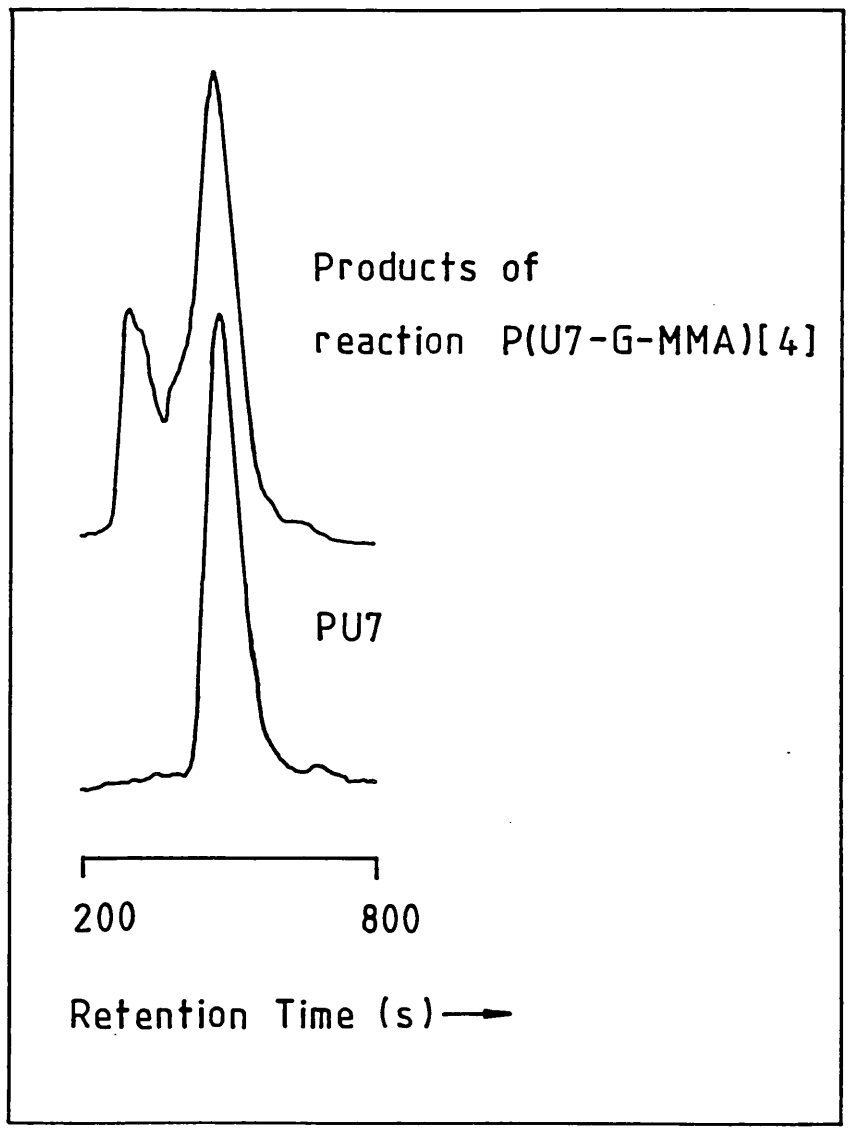
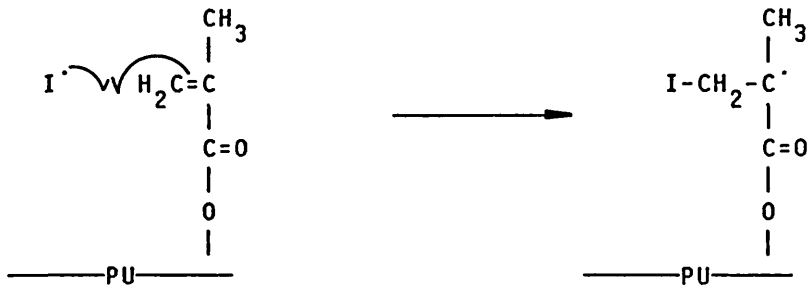


FIG.(5.21): GPC'S OF PU7 AND THE PRODUCTS OF THE REACTION P(U7-G-MMA)[4]

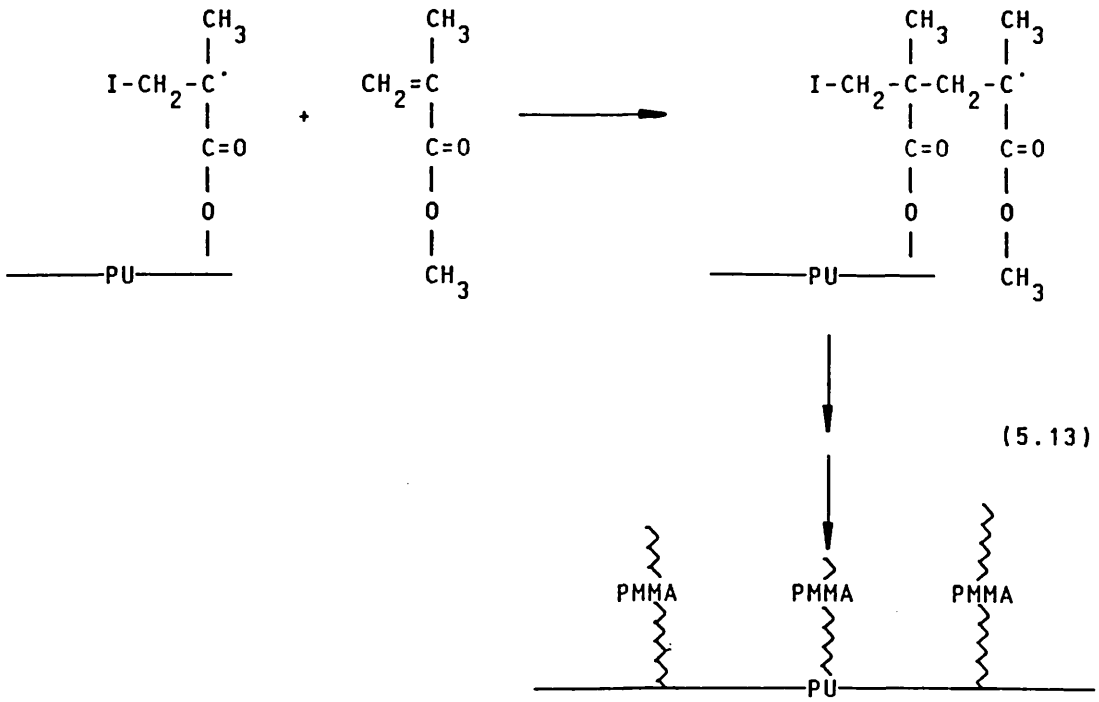
the mechanism.

(A) An initiator fragment ($I^{\cdot}$) could have added to a methacrylate group of PU7, thus forming a macroradical:



(5.12)

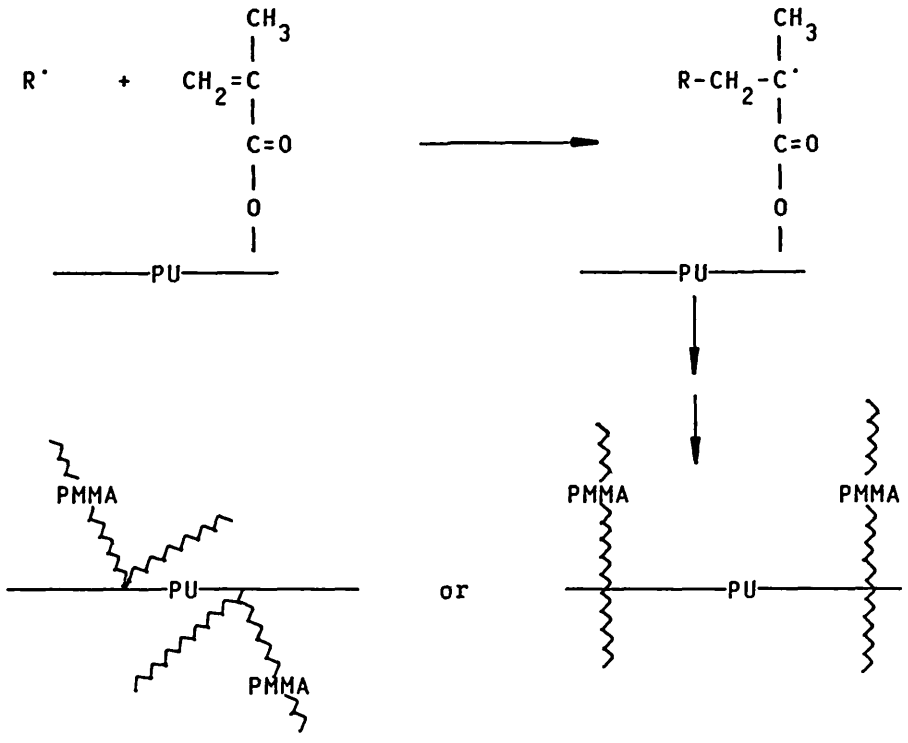
This macroradical would then have interacted with a MMA molecule, and the new radical formed would have continued the reaction to form a comb-like structure, especially if other methacrylate groups on the polyurethane reacted likewise:



(5.13)

(B) The pendent unsaturated groups of PU7 could have been attacked by a PMMA radical ($R^{\cdot}$). The type of macroradical formed would then have

reacted with a MMA molecule and eventually a criss-crossed structure would have been formed:



(5.14)

Crosslinked networks would have been produced if the PMMA radical growing from the polyurethane had interacted with another PU7 molecule, and the reaction was repeated.

The incorporation of GMM into a polyurethane appeared to create an exceptionally good system for the generation of graft copolymers. The high reactivity of the pendent methacrylate groups favoured graft copolymerisation, and the homopolymerisation of MMA was minimised.

However, PU7 was too reactive towards copolymerisation, and gels were formed if the quantity of MMA in the reaction mixture was too high. Hence, another polyurethane was synthesised containing, on average, only one unit of GMM. This was the basis for PU8.

5.6 THE REACTIONS OF THE POLYURETHANES PU5, PU6, AND PU8

5.6.1 THE SYNTHESES OF THE POLYURETHANES

5.6.1.1 SYNTHESIS OF PU5

PU5 was synthesised in a similar fashion to PU4, i.e. the required quantity of HEMA was premixed with the MDI to form the methacrylate terminated monoisocyanate of equation (5.9). Again, there was the possibility of producing the doubly end-capped adduct. However, the molar ratios of reactants for PU5 were:

MDI	PTMEG 2000	BD	HEMA
11	2	9	1

(which produced a polymer with a theoretical %-hard block content of 48.0% w/w). The relative amount of HEMA used was half that used for PU4. The reduced concentration of HEMA would have lowered the possibility of producing the di-methacrylate product.

The presence of the mono-isocyanate would have upset the balance of the reagents for the step-growth polymerisation of the polyurethane. After the reaction between the MDI and HEMA at the start of the polyurethane's synthesis, the relative numbers of molecules of diisocyanate was 10, the mono-isocyanate 1, and the dihydroxy compounds 11. Therefore, the quantity r, for substitution into equation (5.10), would have been equal to:

$$r = \frac{11}{12} = 0.92$$

This meant that x_n was equal to:

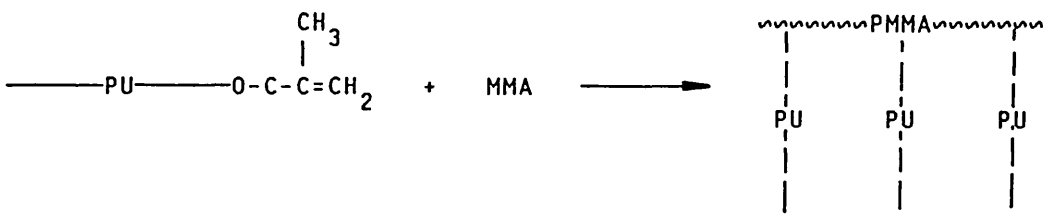
$$x_n = \frac{1.92}{1.92 - 1.83p}$$

Therefore, if the extent of reaction was 0.99, the value of x_n would have been ~18.

Statistically, PU5 would have consisted of 50% singly methacrylate terminated molecules, 25% doubly end-capped molecules, and 25% non-terminated molecules. This meant that at least 25% of the polyurethane used for a graft copolymerisation reaction would remain unreacted.

The existence of the di-functional polyurethane molecules implied the possibilty of gelation occurring during subsequent reactions. It was hoped to reduce the chance of this happening by ensuring that the ratio of PU5 to MMA in the reaction mixture was kept quite low.

The structure of the mono-functional polyurethane molecules was such that they would have copolymerised with MMA to give a comb-like structure composed of a PMMA backbone with PU5 side chains:



(5.15)

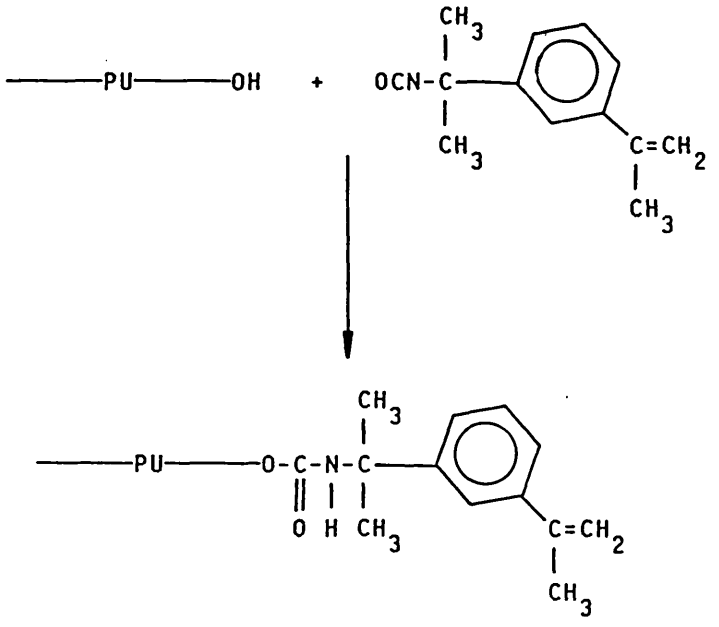
Hence, the polyurethane would be acting as a macromonomer. The graft copolymer was, therefore, a poly(methyl methacrylate-g-urethane), and subsequent copolymers of PU5 were termed P(MMA-G-U5)s.

PU5 was characterised comprehensively, and the results are detailed in later sections of Chapter 5.

5.6.1.2 SYNTHESIS OF PU6

m-TMI was a relatively new, bifunctional monomer containing an

isocyanate group and an α-methyl styrene group. The copolymerisation of MMA with styrene and its derivatives was well documented in the current literature. Therefore, the intention was to create a macromonomer containing a terminal α-methyl styrene unit by reacting a hydroxy terminated polyurethane with m-TMI:



(5.16)

The synthesis of the macromonomer involved initially preparing a polyurethane based on MDI, PTMEG 2000, and BD, the relatively molar ratios of reactants being:

MDI	: PTMEG 2000	: BD
11	2	9

In theory, the ideal polyurethane molecule should have contained an isocyanate group at one end, and a hydroxyl group at the other. In reality, there would have been a statistical distribution of 50% isocyanate / hydroxy terminated molecules, 25% dihydroxy terminated, and 25% diisocyanate terminated. As a result, after the addition of the m-TMI, in the relative molar ratio of 1, there would have been a

statistical distribution of functional polyurethanes produced which was similar to that of PU5. Therefore, there would always have been a certain amount of unreacted polyurethane left at the end of a copolymerisation reaction.

It should be noted that on precipitation into water, any unreacted isocyanate groups would have been converted to amines by the reaction described by the first part of equation (1.7).

The product of the copolymerisation reaction of PU6 with MMA would have generated similar comb-shaped structure as PU5 [equation (5.15)]. Therefore, the copolymers were more correctly termed P(MMA-G-U6)s.

The results of the characterisation of PU6 will be detailed later.

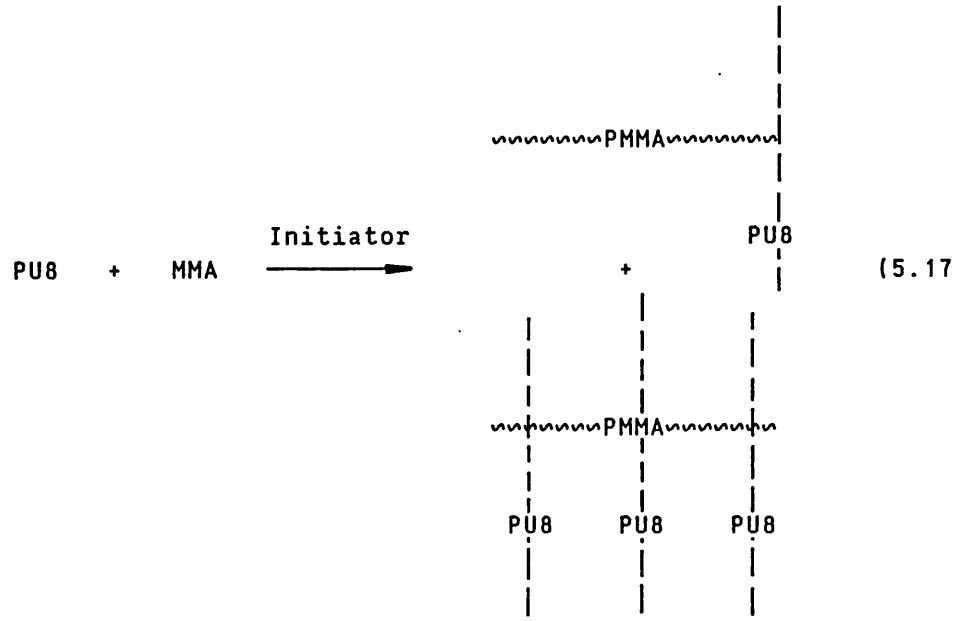
5.6.1.3 SYNTHESIS OF PU8

PU7, the polyurethane containing many units of GMM along its backbone, was so reactive towards copolymerisation with MMA that gels were produced. PU8 was synthesised such that in theory, each molecule should have contained only one unit of GMM. However, in reality, the method of synthesis would have meant that there was a distribution of molecules ranging from those containing no GMM, to those containing several units.

The relative molar ratios of reactants for PU8 were:

MDI	PTMEG 2000	BD	GMM
11	2	8	1

PU8 would have copolymerised with MMA to produce either "T" shaped polymers or criss-crossed polymers in a similar fashion to PU7.



(5.17)

Therefore, it was possible that a particular copolymer molecule could contain several PU8 molecules.

The results of the characterisation of PU8 are detailed later.

5.6.2 ATTEMPTED HOMOPOLYMERISATION OF PU5, PU6, AND PU8

The GPCs of the reaction mixtures for the three polyurethanes indicated that no homopolymerisation had occurred for any of them, as there was no change in their molecular weight distributions.

It was known that the reactive groups of the polyurethanes could homopolymerise under free-radical conditions in their monomeric forms. Therefore, it was deduced that the apparent lack of reactivity of the functional polyurethanes towards homopolymerisation was due to a combination of the low concentration of active sites and steric hindrance.

It was concluded, therefore, that any high molecular weight, polyurethane containing material produced during a copolymerisation reaction would be the required graft copolymer, and that it would not be contaminated with the homopolymer of the polyurethane.

5.6.3 GRAFT COPOLYMERISATION OF PU5, PU6, AND PU8 WITH MMA

For each polyurethane, a series of free-radical graft copolymerisation reactions with MMA were performed. The effects of initiator, initiator concentration, and reaction time were investigated.

5.6.3.1 GRAFT COPOLYMERISATION OF PU5 WITH MMA [P(MMA-G-U5)]

Fig. (5.22) shows the GPCs of PU5 and the unseparated products of its graft copolymerisation reactions with MMA (UV detector).

For each reaction, a new material of a higher molecular size than PU5 was formed. These new polymers were observable by the UV detector, and, therefore, contained PU5. This meant that they were the graft copolymers of PU5 and MMA.

As the concentration of initiator increased, the distinction between the GPC peak of the new material and the unreacted PU5 peak became less obvious. The UV detector's chromatogram for the products P(MMA-G-U5)[4] consisted of one peak only, which was a combination of that for the unreacted polyurethane and the graft copolymer.

The chromatograms obtained from the RI detector consisted of two peaks whose retentions times were such that it was obvious that they corresponded to those obtained by means of the UV detector. Whereas for the UV detector, the unreacted PU5 peak was larger than that for the graft copolymer, for the RI detector, the reverse was true. This was due to contribution of the PMMA part of the graft copolymer to the RI detector's chromatogram.

There was no apparent presence of PMMA homopolymer. This indicated that the reaction had followed the general rules of copolymerisation. Since the concentration of the PU5 macromonomer was very much smaller than that of the MMA present in all of the reaction mixtures, the instantaneous composition of the copolymer could have been expressed

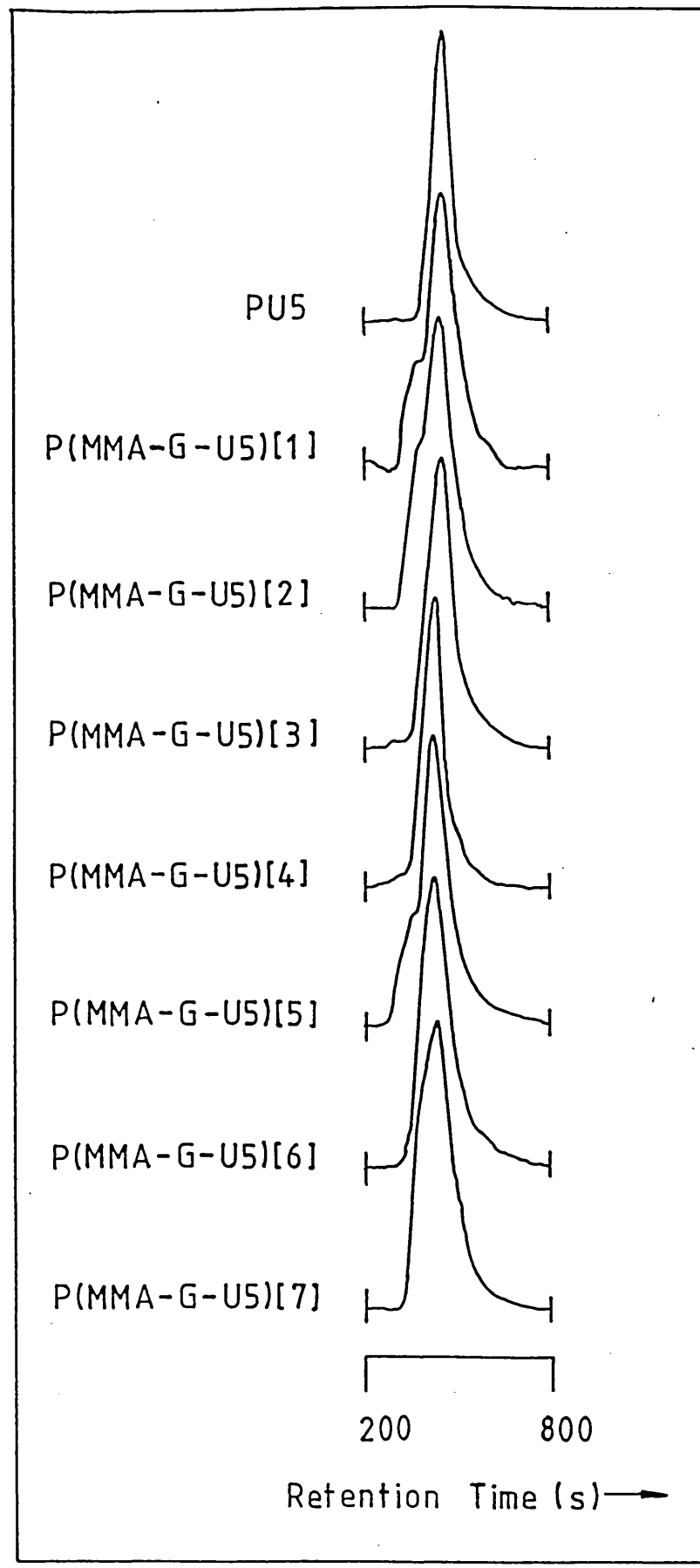


FIG.(5.22): GPC'S OF PU5 AND ITS REACTION PRODUCTS

according to equation (2.38) of Chapter 2:

$$\frac{d[MMA]}{d[PU5]} = r_{MMA} \cdot \frac{[MMA]}{[PU5]} \qquad (5.18)$$

where [PU5] and [MMA] were the concentrations of PU5 and MMA respectively, d[PU5] and d[MMA] were the amounts of PU5 and MMA consumed between times t and (t + dt), and r_{MMA} was the reactivity ratio for MMA, and was equal to:

$$r_{MMA} = \frac{k_{MMA-MMA}}{k_{MMA-PU5}} \qquad (5.19)$$

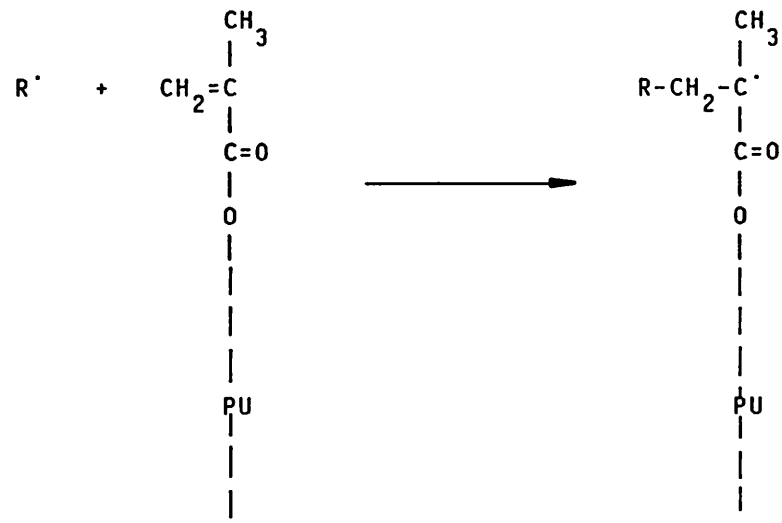
where $k_{MMA-MMA}$ and $k_{MMA-PU5}$ were the rate constants for the addition of PU5 and MMA to the MMA radical.

Equation (5.18) integrated to:

$$r_{MMA} = \frac{\ln\{[MMA]_o/[MMA]\}}{\ln\{[PU5]_o/[PU5]\}} = \frac{\ln(1 - x_{MMA})}{\ln(1 - x_{PU5})} \qquad (5.20)$$

where $[MMA]_o$ and $[PU5]_o$ were the initial concentrations of MMA and PU5 in the reaction mixture, and x_{MMA} and x_{PU5} were the fractional conversions of MMA and PU5 at time t.

The mechanism of grafting would have involved either an initiator fragment or PMMA radical ($R^{\bullet}$) attacking the methacrylate end group of the polyurethane:



(5.21)

This macroradical would then have attacked another MMA molecule, and thus the polymer chain would have been propagated. It was highly improbable that this macroradical would have attacked another PU5 molecule, for the same reasons as to why PU5 did not homopolymerise (section 5.6.2), and due to the relatively higher concentration of MMA molecules.

Disproportionation would probably have been the most dominant termination reaction, as PMMA terminates exclusively by this mechanism above 60°C[42].

The GPC results showed that as the concentration of the initiator increased, the apparent molecular size of the graft copolymer decreased, since the peak retention time of the copolymer increased with increasing initiator concentration. This was as expected because if the free-radical concentration was high, then the probability of radical interaction was high as well, and so short chains were produced. The results of the molecular weight analysis by GPC of the graft copolymers are listed in the characterisation section.

The program of Appendix I was used to calculate the concentration of unreacted polyurethane remaining at the end of each graft copolymerisation reaction. For reactions such as P(MMA-G-U5)[1], it

was relatively straightforward to assess the end of the unreacted PU5 peak and the start of the P(MMA-G-U5) peak (from the UV detector chromatograms).

If the chromatogram resembled that of P(MMA-G-U5)[1] of fig. (5.21), then a perpendicular was dropped from the position of the inflexion of the peak. The area was then calculated from this position to the end of the PU5 peak. This would have given an underestimation of the PU5 peak area. The analysis was run again, but this time the start and end times of the original PU5 chromatogram were input. This would have given an overestimation of the required PU5 peak area. The two results were then averaged. The analysis was then repeated several times to give an approximation of the errors involved, and the concentration of the unreacted PU5 was calculated.

The procedure was more difficult for chromatograms such as those of P(MMA-G-U5)[3], [4], and [6], as there was no clear distinction between the two peaks. The difficulty was overcome by manually superimposing the hard-copy of the original chromatogram of PU5 onto that of the reaction products, and visually assessing the point where the two peaks would have been coalescing. A perpendicular was then dropped from this point, and the time determined. The value was then used to calculate an underestimation of the required area.

The program was then re-run, but this time the start and end times of the original PU5 were input. This gave an overestimate. The two values were then averaged, and the procedure repeated several times to gain an approximation of the errors involved. The unreacted PU5 concentration was then calculated. The accuracy of the results obtained for these types of materials was very low. However, an approximate idea of the general trends was ascertained.

The assumption was then made that all of the PU5 added to the reaction mixture was recovered at the end of the reaction in one form

or another. The yield of graft copolymer and its polyurethane content were then calculated, and the results are shown in table (5.6):

TABLE (5.6): RESULTS FROM THE QUANTITATIVE GPC EXPERIMENTS PERFORMED ON THE CRUDE PRODUCTS OF THE P(MMA-G-U5) REACTIONS

REACTION PRODUCTS P(MMA-G-U5)	CALCULATED %-FREE PU5 IN PRODUCTS (% w/w)	TOTAL YIELD (g)	YIELD OF P(MMA-G-U5) (g)	%-PU5 CONTENT IN P(MMA-G-U5) (% w/w)	%-YIELD OF PMMA (%)
[1]	21.0 (±0.5)	3.12	2.46 (±0.01)	34.1 (±0.6)	40.5 (±0.5)
[2]	11.0 (±0.1)	4.41	3.92 (±0.01)	25.8 (±0.3)	72.8 (±0.5)
[3]	10 (±2)	4.66	4.19 (±0.09)	25 (±2)	80 (±5)
[4]	27.3 (±0.3)	4.60	3.34 (±0.01)	7.2 (±0.3)	77.5 (±0.5)
[5]	21.6 (±0.6)	4.21	3.30 (±0.02)	17.9 (±0.7)	67.8 (±0.9)
[6]	19 (±4)	5.39	4.4 (±0.2)	11 (±5)	98 (±2)
[7]	21.0 (±0.5)	4.94	3.90 (±0.02)	11.8 (±0.6)	86 (±1)

The general trends observed were:

(A) As the concentration of the initiator, AIBN, increased (reactions [1], [2], [3], and [4]), the yield of graft copolymer also went up. However, the %-PU5 content of the graft copolymer decreased.

PU5 seemed to be quite reactive towards copolymerisation with MMA. As the concentration of radicals increased, more PU5 would have been consumed early in the reaction. This would have depleted the amount of active polyurethane in the reaction mixture, and the stoichiometry of the system would have changed. The large excess of MMA compared to active PU5 would have meant that more PMMA would then have been formed within the graft copolymer molecules. Hence, the %-

polyurethane content of the final polymer would have appeared to be less.

Also, a large quantity of radicals increased the possibility of termination reactions. Therefore, there was the chance that initiated macromonomer molecules could have beenannihilated by combination or disproportionation reactions with other radicals before they were included in graft copolymer molecules. Therefore, the amount of PU5 in the graft copolymer with respect to PMMA would have decreased. This was probably the major reason for the very small %-PU content of P(MMA-G-U5)[4].

(B) Comparisons of the reactions involving a change of initiator ([3] and [7]), indicated that there was no apparent initiator effect within the realms of experimental error. Any slight differences in the yields obtained were probably due to differences in the efficiencies of AIBN and BPO.

(C) As the reaction time increased (reactions [1] and [5] and reactions [3] and [6]), the yield of graft copolymers increased, as expected, but the %-PU5 content of the graft copolymer decreased. It appeared, therefore, that as the reactive PU5 molecules were depleted, the stoichiometry of the system changed with time, and the resulting graft copolymers contained more PMMA, due to the higher availablity of MMA molecules. Hence, the graft copolymer had a lower PU5 content than that synthesised over half of the reaction time.

The graft copolymers wee separated from the unreacted PU5 (see later). The graft copolymers and the unseparated products [P(MMA-G-U5)-MIX] were characterised.

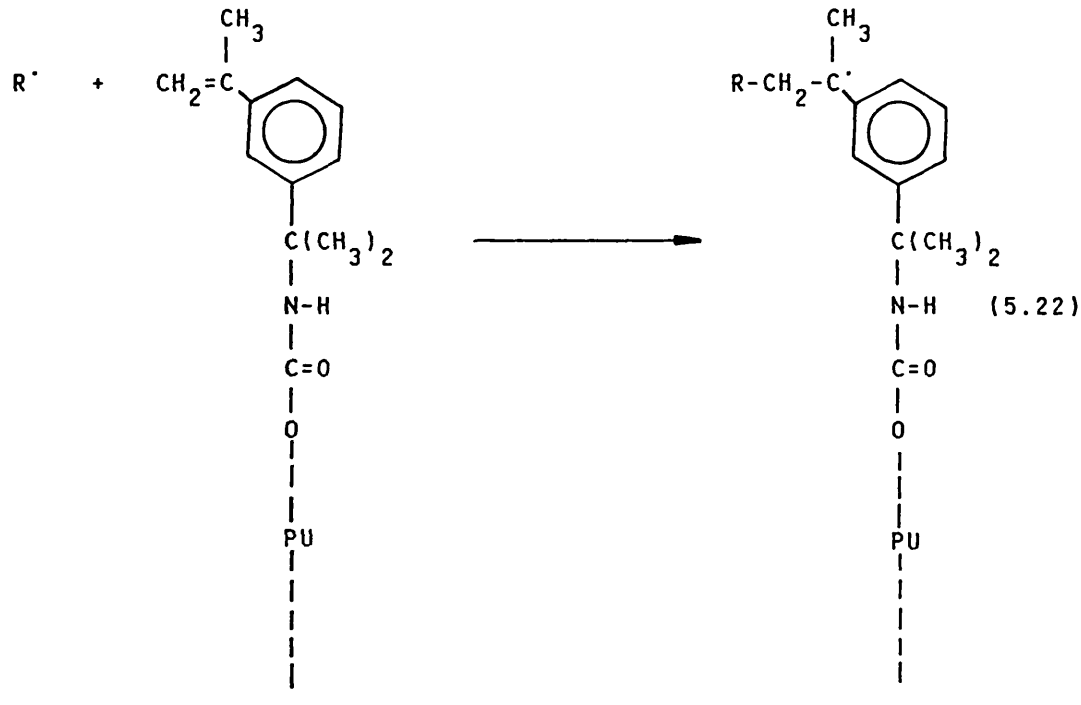
5.6.3.2 GRAFT COPOLYMERISATION OF PU6 WITH MMA [P(MMA-G-U6)]

Fig. (5.23) shows the GPCs of PU6 and the unseparated products of its grafting reactions with MMA (UV detector).

The results obtained showed similar trends to those of PU5. A new material containing PU6 was observed with a higher molecular size than the polyurethane. As the initiator concentration increased, the apparent molecular weight of the graft copolymer decreased. The chromatograms of products synthesised using a large initiator concentration consisted of one peak extending further into the high molecular weight region than the PU6 alone.

Although there was the presence of unreacted PU6, there was no PMMA homopolymer observed. Therefore, the reactions were following general copolymerisation rules, with similar kinetics of reaction as PU5 [equations (5.18) to (5.20)].

The mechanism of grafting would have involved either an initiator fragment or PMMA radical ($R^{\cdot}$) attacking the α-methyl styrene end group of the polyurethane:



(5.22)

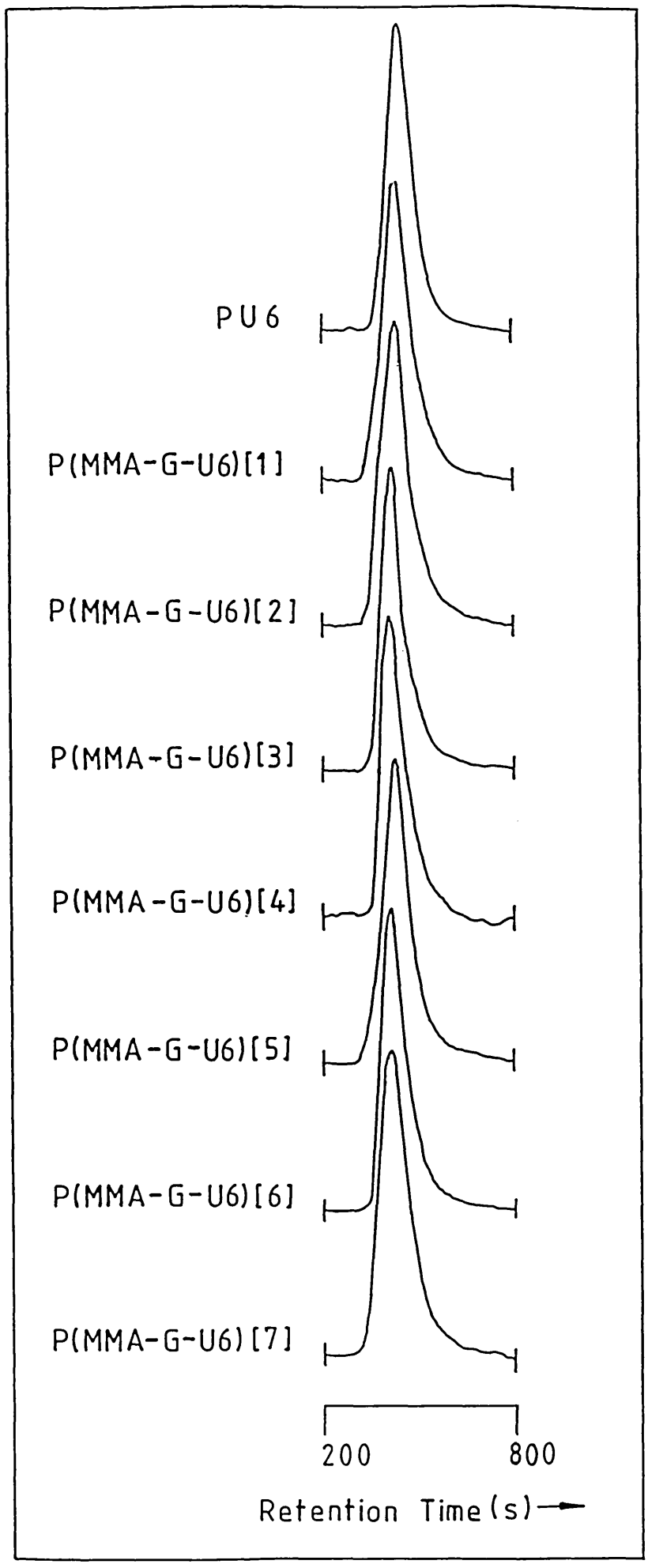


FIG.(5.23): GPC'S OF PU6 AND ITS REACTION PRODUCTS

The polyurethane macroradical would then have attacked another MMA molecule. Again, it would have been highly improbable that the macroradical would have attacked another PU6 molecule.

The program of Appendix I was used to calculate the concentration of the unreacted PU6 remaining at the end of the reactions, following the same procedures as for the products of the reactions of PU5. Again, large inaccuracies were expected for the results of reactions [3], [4], and [6] due to the difficulties in distinguishing between unreacted PU6 and the graft copolymer. The results are listed in table (5.7).

TABLE (5.7): RESULTS FROM THE QUANTITATIVE GPC EXPERIMENTS PERFORMED ON THE CRUDE PRODUCTS OF THE P(MMA-G-U6) REACTIONS

REACTION PRODUCTS P(MMA-G-U6)	CALCULATED %-FREE PU6 IN PRODUCTS (% w/w)	TOTAL YIELD (g)	YIELD OF P(MMA-G-U6) (g)	%-PU6 CONTENT IN P(MMA-G-U6) (% w/w)	%-YIELD OF PMMA (%)
[1]	32.8 (±0.3)	3.68	2.47 (±0.01)	11.7 (±0.4)	54.5 (±0.5)
[2]	24.3 (±0.4)	4.40	3.33 (±0.02)	12.9 (±0.7)	73 (±1)
[3]	21.1 (±0.8)	5.07	4.00 (±0.04)	11 (±1)	89 (±2)
[4]	22.2 (±0.4)	5.42	4.18 (±0.03)	6.2 (±0.8)	98 (±2)
[5]	36.2 (±0.7)	3.66	2.34 (±0.03)	8 (±1)	54.0 (±1.0)
[6]	24.4 (±0.7)	5.09	3.85 (±0.04)	7 (±1)	90 (±2)
[7]	33.0 (±0.3)	3.66	2.45 (±0.01)	11.8 (±0.5)	54.0 (±0.5)

The general trends observed were:

(A) As the initiator concentration increased (reactions [1], [2], [3], and [4]), the yield of graft copolymer increased, but the %-PU6

content of the product remained approximately the same. Therefore, more PU6 underwent reaction as the initiator concentration went up. However, the quantities of PU6 within the graft copolymers were lower than the corresponding PU5 copolymers. This meant that the PU6 molecules were less reactive towards copolymerisation with MMA than PU5.

The effect of increasing the number of radicals within the system caused more PU6 molecules to be converted into macroradicals which were then incorporated into the graft copolymers. The %-PU content of the graft copolymers, therefore, stayed approximately constant because the yield of PMMA also increased.

However, for reaction [4], a decrease in the %-PU content was observed, indicating that the point had been reached where the concentration of PU6 had been depleted so much that the kinetics of the reaction meant that there was a larger increase in the proportion of PMMA in the graft copolymer. Also, termination of the polyurethane macroradicals by, for example, recombination with another radical, could have decreased the amount of PU6 incorporated into the graft copolymer.

(B) A larger yield of PMMA was achieved by using AIBN as the initiator rather than BPO (reactions [3] and [7]). The %-polyurethane contents of the graft copolymers were approximately the same. Again, the discrepancies were probably due to the different efficiencies of the initiators .

(C) Doubling the reaction time (reactions [1] and [5], and [3] and [6]) appeared to have little effect on the composition of the final graft copolymer. Indeed, it seemed that the majority of the reaction had occurred by 24h, and that little more reaction occurred

afterwards.

The graft copolymers were separated from the unreacted PU6 (see later). The graft copolymers and the unseparated products [P(MMA-G-U6)-MIX] were characterised.

5.6.3.2 GRAFT COPOLYMERISATION OF PU8 WITH MMA [P(U8-G-MMA)]

Fig. (5.24) shows the GPCs (UV detector) of PU8 and the crude products of its graft copolymerisations with MMA. A new material was obtained with a higher molecular size than PU8.

Again, the qualitative results indicated that as the initiator concentration increased, the molecular weight of the graft copolymer decreased. Indeed, reaction P(U8-G-MMA)[4] showed no change in the molecular weight distribution of the PU8. Either little or no grafting to the PU8 had occurred.

No PMMA homopolymer was observed, except for reaction [4]. Therefore, PU8 was acting as a macromonomer and undergoing a general copolymerisation reaction with MMA. This meant that the pendent methacrylate unit of the polyurethane was sufficiently exposed so that it could readily undergo reaction.

The program of Appendix I was used to calculate the concentration of unreacted PU8 remaining at the end of the grafting reactions. Again, large inaccuracies were expected for the products that did not appear to have a clear distinction between the graft copolymer and unreacted PU8 peaks. The results are listed in table (5.8):

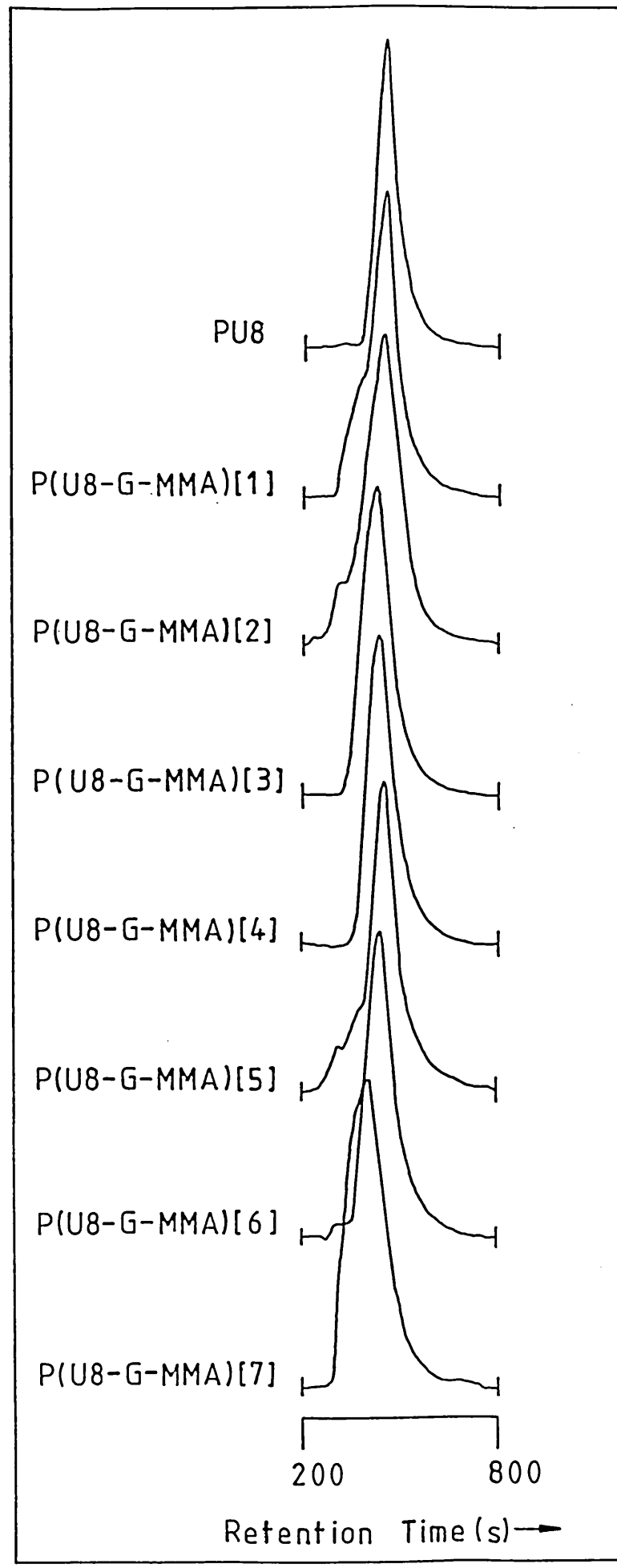


FIG.(5.24): GPC'S OF PU8 AND ITS REACTION PRODUCTS

TABLE (5.8): RESULTS FROM THE QUANTITATIVE GPC EXPERIMENTS PERFORMED ON THE CRUDE PRODUCTS OF THE P(U8-G-MMA) REACTIONS

REACTION PRODUCTS P(U8-G-MMA)	CALCULATED %-FREE PU8 IN PRODUCTS (% w/w)	TOTAL YIELD (g)	YIELD OF P(U8-G-MMA) (g)	%-PU8 CONTENT IN P(U8-G-MMA) (% w/w)	%-YIELD OF PMMA (%)
[1]	19.3 (±0.5)	4.14	3.34 (±0.02)	21.0 (±0.7)	66 (±1)
[2]	25.8 (±0.7)	3.65	2.71 (±0.03)	21 (±1)	54 (±1)
[3]	24.05 (±0.05)	4.08	3.10 (±0.05)	16.7 (±0.3)	64.5 (±0.3)
[4]		No apparent grafting			
[5]	24.1 (±0.9)	3.82	2.90 (±0.04)	20 (±2)	58 (±2)
[6]	22 (±2)	4.65	3.7 (±0.1)	14 (±2)	80 (±5)
[7]	24.0 (±0.4)	4.53	3.44 (±0.02)	11.9 (±0.7)	75.8 (±0.9)

The first point noted was that the yields obtained for the graft copolymers (and, subsequently, the PMMA part of the products) were generally lower than those obtained for PU5 and PU6. It was possible that the reactions were affected by the lower accessibility of the unsaturated group of PU8 compared to the other polyurethanes. The general trends appeared to be:

(A) Increasing the initiator concentration (reactions [1], [2], and [3]) seemed to reduce the quantity of polyurethane within the graft copolymer, and did not increase greatly the yield of PMMA. The grafting reactions were, therefore, slowed down by the inaccessibility of the pendent methacrylate group of the polyurethane, i.e. the PU8 macroradical was so hindered that it had difficulty encountering a MMA molecule. It was probably for this reason that it was impossible for it to approach another PU8 molecule.

Increasing the initiator concentration would have increased the number of initiated molecules, but termination reactions were probably

faster than for the PU8 macroradicals than propagation. Eventually, above a certain initiator concentration, graft copolymerisation would not have occurred (as for reaction [4]).

(B) Changing the initiator from AIBN to BPO (reactions [3] and [7]), appeared to increase the yield of PMMA in the graft copolymer. The Z-PU8 content of the graft copolymer seemed smaller, but this was almost certainly because the relative amount of PMMA produced was larger.

(C) Doubling the reaction time for reaction [1] did not appear to affect the yield or Z-PU8 content of the resulting graft copolymer (reaction [5]). It seemed, therefore, that the reaction was complete by 24h. This could have been due to the low concentration of radicals that were converted into PU8 macroradicals, and which were probably terminated before being able to propagate the chain reaction.

Doubling the reaction time for [3] increased the yield of PMMA in the graft copolymer (reaction [6]), whilst the quantity of polyurethane in the copolymer remained approximately the same. This, again, indicated that the rate of reaction was limited by the accessibilty of the PU8 macroradicals.

The separated graft copolymers and the mixtures of products [P(U8-G-MMA)-MIX] were characterised.

5.7 SEPARATION OF THE GRAFT COPOLYMERS FROM THEIR STARTING MATERIALS

For each of the polyurethanes PU5, PU6, and PU8, at the end of their graft copolymerisation reactions with MMA, a mixture of products was obtained consisting of graft copolymer, unreacted polyurethane, and unreacted MMA. The MMA was removed on precipitation into water and drying in vacuo. However, the removal of the unreacted polyurethane

proved to be a more difficult process. The following sections describe the various techniques tried in order to isolate the final product.

5.7.1 SOLVENT EXTRACTION

5.7.1.1 SOXHLET EXTRACTION USING TOLUENE

Since toluene was a non-solvent for PU5 but was a solvent for PMMA, it was intended to separate the graft copolymers P(MMA-G-U5) from the unreacted PU5 of the crude products by Soxhlet extraction, using toluene as the solvent.

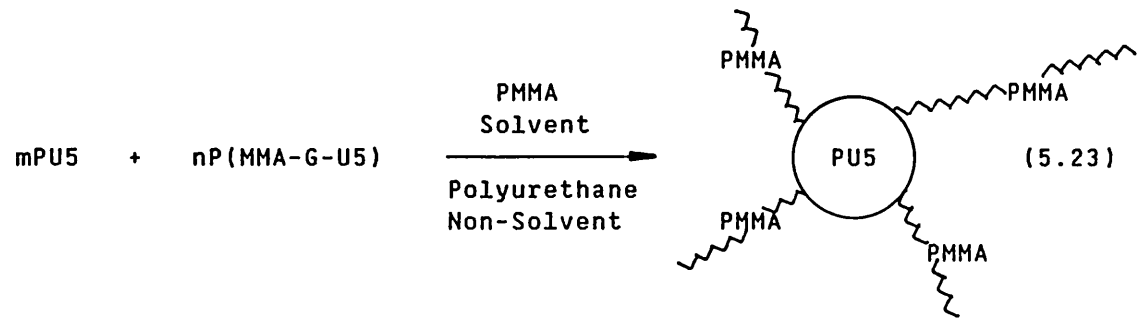
After 16h of extraction, the contents of the thimble were analysed. In certain cases, an insoluble gel had been formed within the thimble under the harsh conditions of the extraction. This could have been caused through the unreacted PU5 molecules containing methacrylate end groups (particularly those which were doubly end-capped) undergoing a free-radical reaction within the thimble, producing a polyurethane network. The reaction could have been induced by the high temperature (> 100°C) and the relatively high concentration of material.

GPC of the thimble residues of those that did not gel showed that they consisted completely of PU5. No degradation of the polyurethane had occurred.

As the toluene extract was reduced in volume by rotary evaporation, a precipitate formed. The precipitate was removed, and the solvent evaporated until no more insoluble material appeared. GPC of the dried precipitate showed that it was predominantly PU5. The GPC of the remaining material in the toluene residue showed that it contained both graft copolymer and unreacted PU5.

It appeared, therefore, that the graft copolymer was enabling PU5 to "dissolve" in solvents with which it would normally have been incompatible. The reason for this was that the graft copolymer was

acting as a surface active agent. In the presence of a polyurethane non-solvent, the P(MMA-G-U5) stabilised the unreacted PU5 by forming micellar structures consisting of a PU5 phase surrounded by PMMA [equation (5.23)].



For micelles to have been produced, the concentration of the surface active species would have had to have been above a certain limit, the "critical micelle concentration" (CMC). Thermodynamically, the enthalpy and entropy of formation of micelles, ΔH_m and ΔS_m respectively, were both positive, i.e. the process was endothermic and entropically unfavourable[217]. Hence, for the micelles to have appeared, either the temperature of the solution would have to have been high, or there would have needed to be sufficient solvent for it to contribute to the entropy of the system (since the solvent molecules could move more freely when the solute molecules were clustered together).

These thermodynamic considerations explain why micelle formation was relatively facile at the high temperature of the Soxhlet extraction. However, on cooling and through the reduction of solvent volume, the micelles collapsed and deposited the PU5, until a stable dispersion was attained.

It was concluded that due to the above reasons, Soxhlet extraction was not the ideal method of isolating the graft copolymers.

5.7.1.2 SIMPLE SOLVENT EXTRACTION

Simple solvent extraction experiments were performed using solvents that were good for PMMA, but poor for PU5, in an attempt to isolate the graft copolymer P(MMA-G-U5) from the unreacted PU5. The experiments differed from the Soxhlet extraction procedures because the temperature of the solvent was kept as low as possible.

(A) USING A THF / CHLOROFORM MIXTURE

No precipitate was formed when chloroform was added to a THF solution of the crude products. Chloroform was a good solvent for PMMA, but a poor one for PU5. It was concluded that as the $CHCl_3$ was added, the graft copolymer molecules were surrounding the PU5 molecules, forming micelles.

The next stage was to attempt the simple solvent extraction from the solid products.

(B) USING TOLUENE

Very little material dissolved when the crude products were stirred in cold toluene. The mixtures were gently warmed to encourage dissolution. After several hours, the polymers that had dissolved were recovered and analysed by GPC. The results showed that, again the PU5 had co-dissolved with the graft copolymer in the form of micelles.

(C) USING ACETONE

The products of the P(MMA-G-U5) reactions formed cloudy suspensions in cold acetone. After centrifugation at -10°C, a precipitate was formed, but the solution still remained milky (characteristic of micellar solutions). GPC showed that the precipitate consisted mainly of PU5. The polymers of the acetone solution, however, still contained graft copolymer and PU5. It was

apparent, therefore, that for acetone, the micelle structures were stable even at very low temperatures.

(D) USING BUTAN-2-OL

Although, a cloudy suspension of the P(MMA-G-U5) reaction products was formed in hot butan-2-ol, the centrifugation or filtration of the mixture was impossible due to the fact that a slight reduction in temperature caused complete precipitation. This system, therefore, was considered unsatisfactory.

It was concluded that simple solvent extraction of the graft copolymer from the PU5 was affected by the same problems as the Soxhlet extraction, and that the micelle formation interferred with the process.

Attempts were made to collapse the micelles produced in the toluene solution by the addition of a non-solvent for both species present. The precipitation was monitored by performing turbidimetric titrations.

5.7.2 TURBIDIMETRIC TITRATIONS

A sample of the products of the reaction P(MMA-G-U5)[5] was modified by means of Soxhlet extraction so as to contain as little free PU5 as possible. Portions of a stock solution of this material were diluted to various concentrations, and the turbidimetric titrations were performed, using methanol as the precipitant (section 4.13.2).

The observed absorbance, A_{obs}, was adjusted to allow for the increase in volume on the addition of each portion of precipitant according to equation (5.24):

$$A_{adj} = A_{obs} \cdot \left[1 + \frac{\Sigma titre}{V_o} \right] \qquad (5.24)$$

where ΣtitrE was the total volume of methanol added up to that point, and V_o was the original volume of solution at the start of the experiment.

A graph of adjusted absorbance versus the volume of methanol added was plotted for each titration. An inflexion in the curve was expected, which would have indicated the point between the precipitation of the graft copolymer and that of the PU5. However, fig. (5.25) shows the graphical results obtained for titration 4.13.2.7. This result was typical for all of the titrations carried out, i.e. no distinctions between the precipitation of the graft copolymer and the unreacted PU5 were observed.

As non-solvent was added to the toluene solution, any micelles present should have collapsed releasing the PU5. Therefore, the unreacted PU5, being insoluble in both the toluene and the methanol, was precipitated along with the higher fractions of the graft copolymer. As a result, all species precipitated continuously.

The next stage was to add non-solvent to a solution of the crude products in a good solvent for all of the species present. This was the basis of the following fractional precipitations.

5.7.3 FRACTIONAL PRECIPITATIONS

Bulk fractionation was performed using various solvent / non-solvent combinations (section 4.13.3). It was expected that the graft copolymer should have precipitated first due to its larger molecular size and weight compared to the polyurethane. It was also hoped that the presence of non-solvent should have prevented any formation of

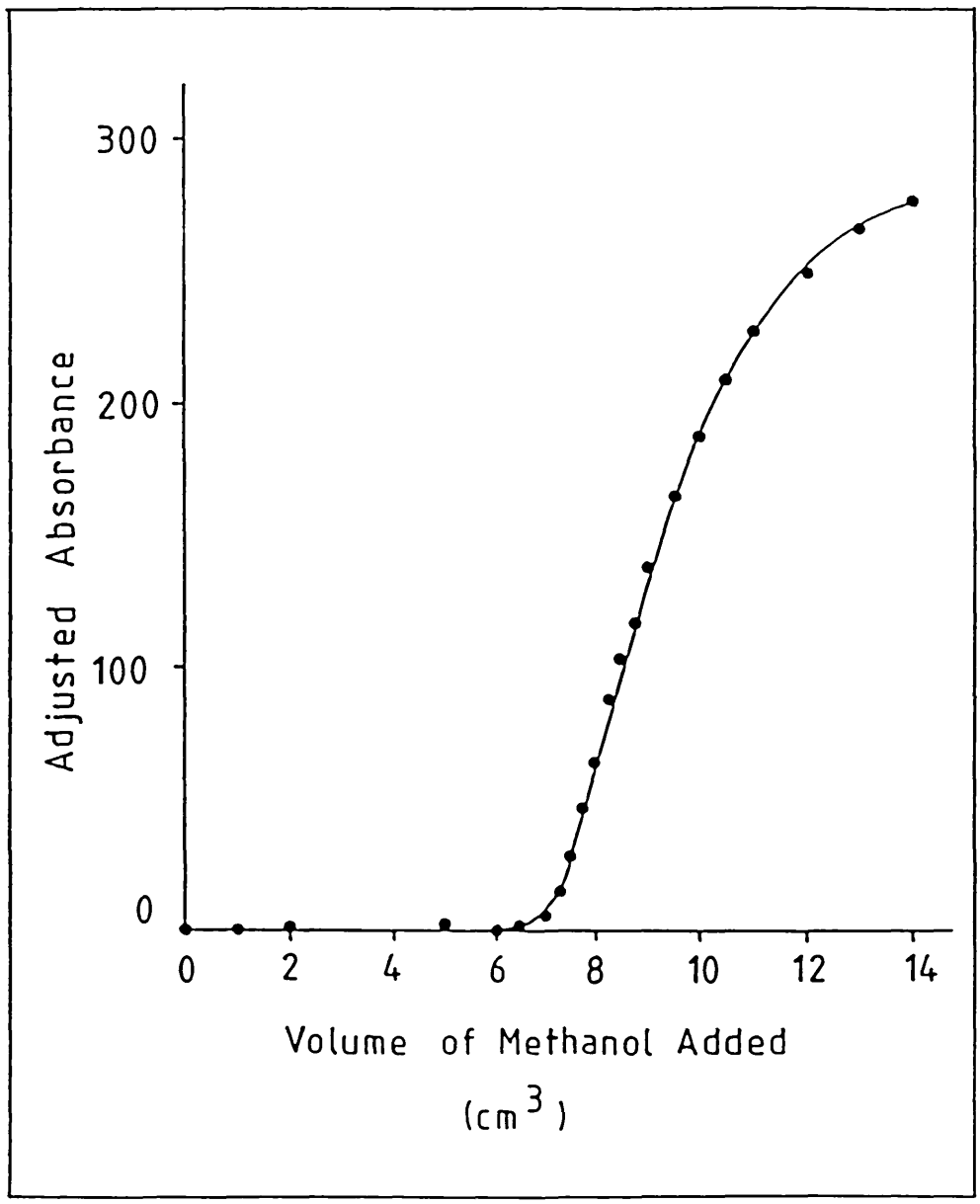


FIG.(5.25): GRAPHICAL RESULTS FOR THE TURBIDIMETRIC TITRATION 4.13.2.7

micelles during the experiments.

However, GPCs of the various fractions obtained for each system indicated that although the graft copolymer was fractionated into components of different molecular weights, a certain quantity of PU5 persisted in precipitating with each fraction. This indicated that even in a good solvent for each component of the mixture, a degree of association occurred between the PU5 of the graft copolymer and the free PU5, probably as a consequence of intermolecular H-bonding. Hence, upon fractionation, the "associated" PU5 precipitated with the relevant fraction of the graft copolymer.

This association was broken down during GPC due to the high dilution factor. Thus the separated components of the mixture were detected.

More evidence of this intermolecular attraction was attained from the rheology experiments carried out. The results of these are detailed in a later section.

It became obvious that fractional precipitation was unable to separate the required graft copolymers from the mixtures of products. Absorption column chromatography was tried in an attempt to exploit the solubility differences of the two polymers and their different interactions with a silica column.

5.7.4 ADSORPTION COLUMN CHROMATOGRAPHY

It was expected that the interaction of the PU5 with the silica of the column would have been different to that of the graft copolymer. By using various solvent combinations, it was hoped that a separation would be achieved. TLC experiments showed that when using solvents such as THF and acetone, both of the species in the mixture moved up the plate at the same rate. Benzene, DMF, and ethyl acetate, however, appeared to encourage separation. These were then utilised

with the adsorption column.

However, once again, GPC of the fractions obtained for each solvent showed that free PU5 was still eluting with the graft copolymer. It was concluded that the intermolecular association was stronger than the interaction of the graft copolymer or the PU5 with the silica column.

It was finally realised that the only technique used so far that had succeeded in separating the two polymers in the reaction products was GPC. Unfortunately, analytical-GPC only used minute quantities of material. Nevertheless, Prep-GPC enabled several milligrams of polymer to be isolated.

5.7.5 PREP-GPC

5.7.5.1 USING THE WATERS EQUIPMENT

The Waters equipment was used in its recycle mode in order to ascertain the number of components present in several samples of crude products. After several cycles, the chromatograms showed that for each sample analysed, the peaks obtained broadened and eventually split into two distinct parts. This was further evidence that the products contained only graft copolymer and unreacted polyurethane.

The Waters equipment was then used in its collection mode to isolate the graft copolymers from the unreacted polyurethane. Analytical-GPC was used to ascertain which fractions to combine, and which to discard.

So as to remove all of the free polyurethane, the middle fractions were discarded. As a result, the graft copolymers had higher molecular weight distributions than expected due to the absence of their lower fractions.

Eventually, the Waters apparatus was superseded by the Altex

equipment.

5.7.5.2 USING THE ALTEX EQUIPMENT

The Altex equipment had several advantages over the Waters apparatus as it was linked to a computer integrator, enabled better control of the solvent flowrate, and had the RI detector in series with the column instead of in parallel.

A typical run took approximately 45 minutes to complete. Injection of 2.5cm^3 of a 10% w/w solution yielded ~50mg of graft copolymer. The procedure was repeated 6 or 7 times in order to isolate enough polymer to form a free standing film of a suitable thickness for mechanical testing.

Samples of all of the graft copolymers were isolated by this technique. Characterisation of the polymers was then carried out.

5.8 CHARACTERISATION OF THE GRAFT COPOLYMERS OF PU5, PU6, AND PU8

5.8.1 MOLECULAR WEIGHT ANALYSIS

5.8.1.1 GRAFT COPOLYMERS OF PU5

After separation from the unreacted polyurethane, estimations of the molecular weight averages for PU5 and its graft copolymers with MMA were ascertained by analytical GPC methods. The results are listed in table (5.9). The values for each detector were treated separately.

TABLE (5.9): MOLECULAR WEIGHT AVERAGES FOR PU5 AND THE GRAFT COPOLYMERS P(MMA-G-U5) AS EVALUATED BY GPC (WITH RESPECT TO PS STANDARDS)

SAMPLE	UV DETECTOR		RI DETECTOR	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
PU5	15 000	37 000	14 500	34 000
P(MMA-G-U5)				
[1]	408 500	83 993 000	374 300	1 695 600
[2]	161 500	8 314 000	158 000	8 875 000
[3]	52 500	449 000	78 000	474 000
[4]	75 500	555 500	88 000	220 500
[5]	182 500	14 515 000	234 000	13 425 000
[6]	89 000	5 626 000	88 000	406 000
[7]	147 000	1 545 000	109 000	1 289 000

It should be noted that the results were a representation of the true values, and, therefore, were quoted to the nearest whole hundred. This was because:

(A) Separation by GPC depended upon molecular size rather than molecular weight. Therefore, since a comb-shaped graft copolymer appeared to be smaller than its linear analogue due to its compact shape, its molecular weight would have seemed to be lower.

(B) The GPC was calibrated with linear PS standards. Since the interactions of the PS with the column would have been different to those of other polymers, inaccuracies would have developed when using the PS calibration to calculate the molecular weight averages of other materials.

(C) The lower fractions of the graft copolymers were lost on

isolation. Therefore, the averages were biased towards the higher molecular weights.

The results do, however, indicate several features. As the concentration of initiator in the reaction mixture increased (reactions [1] to [4]), the apparent molecular weight decreased.

Changing the initiator from AIBN to BPO (reactions [3] and [7]) increased the molecular weight of the graft copolymer produced. The discrepancy may have been due to the differences in the efficiencies or decomposition rate constants of the two initiators.

As expected, increasing the reaction time (reactions [1] and [5] and [3] and [6]) did not greatly affect the molecular weight of the polymers.

The polydispersities ($\bar{M}_w/\bar{M}_n$) of the graft copolymers were very high. These probably came about because the graft copolymers contained the polyurethane prepolymer which itself had a broad molecular weight distribution.

By combining the results of table (5.9) with those of the Z-PU5 contents of the graft copolymers [table (5.6)], an assessment of the average number of PU5 branches per graft copolymer molecule was made. The results are shown in table (5.10).

TABLE (5.10): ESTIMATION OF THE AVERAGE NUMBER OF PU5 BRANCHES PER GRAFT COPOLYMER MOLECULE FOR P(MMA-G-U5)

P(MMA-G-U5)	%-PU5 CONTENT (%)	NUMBER OF BRANCHES (UV DETECTOR)	NUMBER OF BRANCHES (RI DETECTOR)
[1]	34.1 (±0.6)	9.3	8.8
[2]	25.8 (±0.3)	2.7	2.8
[3]	25 (±2)	0.9	1.3
[4]	7.2 (±0.3)	0.4	0.4
[5]	17.9 (±0.7)	2.2	2.8
[6]	11 (±5)	0.7	0.7
[7]	11.8 (±0.6)	1.2	0.9

5.8.1.2 GRAFT COPOLYMERS OF PU6

Molecular weight analysis by analytical GPC was performed for the graft copolymers of PU6. The results were affected by the same factors as PU5, and are listed in table (5.11).

TABLE (5.11): MOLECULAR WEIGHT AVERAGES FOR PU6 AND THE GRAFT COPOLYMERS P(MMA-G-U6) AS DETERMINED BY GPC (WITH RESPECT TO PS STANDARDS)

SAMPLE	UV DETECTOR		RI DETECTOR	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
PU6	13 400	49 500	27 300	59 900
P(MMA-G-U6)				
[1]	106 500	51 192 100	309 900	4 651 700
[2]	84 000	3 285 500	129 000	4 042 000
[3]	52 000	234 500	55 000	244 000
[4]	30 500	849 000	73 000	281 000
[5]	103 000	2 117 400	239 000	2 750 650
[6]	30 500	101 500	37 500	96 000
[7]	104 000	1 624 500	97 500	1 126 000

Similar trends were observed as for the graft copolymers of PU5.

The results were combined with those of table (5.7) in order to estimate the number of branches per graft copolymer molecule [table (5.12)].

TABLE (5.12): ESTIMATION OF THE AVERAGE NUMBER OF PU6 BRANCHES PER GRAFT COPOLYMER MOLECULE FOR P(MMA-G-U6)

P(MMA-G-U6)	%-PU6 CONTENT (%)	NUMBER OF BRANCHES (UV DETECTOR)	NUMBER OF BRANCHES (RI DETECTOR)
[1]	11.7 (±0.4)	0.9	1.3
[2]	12.9 (±0.7)	0.8	0.6
[3]	11 (±1)	0.4	0.2
[4]	6.2 (±0.8)	0.1	0.2
[5]	8 (±1)	0.6	0.7
[6]	7 (±1)	0.2	0.1
[7]	11.8 (±0.5)	0.9	0.4

5.8.1.3 GRAFT COPOLYMERS OF PU8

The results from the molecular weight analysis by GPC of the graft copolymers of PU8 are shown in table (5.13).

TABLE (5.13): MOLECULAR WEIGHT AVERAGES FOR PU8 AND THE GRAFT COPOLYMERS P(U8-G-MMA) AS EVALUATED BY GPC (WITH RESPECT TO PS STANDARDS)

SAMPLE	UV DETECTOR		RI DETECTOR	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
PU8	15 700	72 000	21 800	70 000
P(U8-G-MMA)				
[1]	156 000	33 636 500	279 000	43 570 000
[2]	130 000	11 425 000	166 000	12 989 500
[3]	41 500	454 000	86 500	414 500
[4]	No Apparent Grafting			
[5]	125 000	27 832 000	172 500	18 669 000
[6]	40 000	232 000	61 900	156 300
[7]	121 000	3 464 000	120 000	2 851 300

Again, the observed trends were similar to those for PU5. Table (5.14) lists the estimates of the average number of branches per graft copolymer molecule, ascertained by combining the results of tables (5.8) and (5.13).

TABLE (5.14): ESTIMATION OF THE AVERAGE NUMBER OF PU8 BRANCHES PER GRAFT COPOLYMER MOLECULE FOR P(U8-G-MMA)

P(U8-G-MMA)	%-PU8 CONTENT (%)	NUMBER OF BRANCHES (UV DETECTOR)	NUMBER OF BRANCHES (RI DETECTOR)
[1]	21.0 (±0.7)	2.1	2.7
[2]	21 (±1)	1.7	1.6
[3]	16.7 (±0.3)	0.4	0.7
[5]	20.0 (±0.2)	1.6	1.6
[6]	14 (±2)	0.4	0.4
[7]	11.9 (±0.7)	0.9	0.7

5.8.2 MICROANALYSIS RESULTS

Microanalysis was performed for each polyurethane and samples [1], [2], and [3] for each set of graft copolymers. From the values obtained for the %-N content of the materials, the %-polyurethane content of the graft copolymers were calculated using equation (5.4). The results are listed in table (5.15).

TABLE (5.15): %-POLYURETHANE CONTENTS OF THE GRAFT COPOLYMERS OF PU5, PU6, AND PU8 AS OBTAINED FROM THE MICROANALYSIS RESULTS

SAMPLE	%-N CONTENT (% w/w)	CALCULATED %-POLYURETHANE CONTENT (% w/w)	%-POLYURETHANE BY GPC METHODS (% w/w)
PU5	4.00		
P(MMA-G-U5)			
[1]	0.82	20.5	34.1 (±0.6)
[2]	0.94	23.5	25.8 (±0.3)
[3]	0.91	22.8	25 (±2)
PU6	4.21		
P(MMA-G-U6)			
[1]	1.20	28.5	11.7 (±0.4)
[2]	0.86	20.4	12.9 (±0.7)
[3]	1.35	32.1	11 (±1)
PU8	4.04		
P(U8-G-MMA)			
[1]	0.93	23.0	21.0 (±0.7)
[2]	0.97	24.0	21 (±1)
[3]	1.31	32.4	16.7 (±0.3)

The results corresponded poorly with those obtained by GPC

methods. It was considered that the GPC results were more accurate due to the errors that would have been entailed in measuring such small values of %-N content of the polymers.

5.8.3 SPECTROSCOPIC ANALYSIS

IR spectroscopy, ^{1}H-NMR, and ^{13}C-NMR were carried out on PU5, PU6, PU8, and selected graft copolymers.

5.8.3.1 IR SPECTROSCOPY

The IR spectra for the polyurethanes PU5, PU6, and PU8, were virtually identical. No individual absorptions were observed for the unsaturated functional groups present due to their low concentrations with respect to the other functions present.

The IR spectra for the graft copolymers were also identical, and were combinations of those of the corresponding polyurethane and PMMA [fig. (5.8)]. Consequently, the "fingerprint" regions around 1000 - 1400cm^{-1} were poorly defined. Fig. (5.26) shows the IR spectra for PU8 and P(U8-G-MMA)[3], which were typical of all respective polymers.

5.8.3.2 ^{1}H-NMR

Figures (5.27) to (5.29) show the ^{1}H-NMR spectra for solutions of PU5, PU6, PU8, and their respective graft copolymers in d_6-DMSO.

In general, the spectra for the polyurethanes were identical. The urethane hydrogen resonance appeared at δ = 9.5ppm, and a small amount of urea showed at δ = 8.5ppm.

The aromatic hydrogens of the MDI units had their characteristic resonance centred at δ = 7.2ppm. The collection of resonances between δ = 1 to 4.5ppm corresponded to those of the polyether and chain extender protons.

For each polyurethane. however, small peaks were observed for the

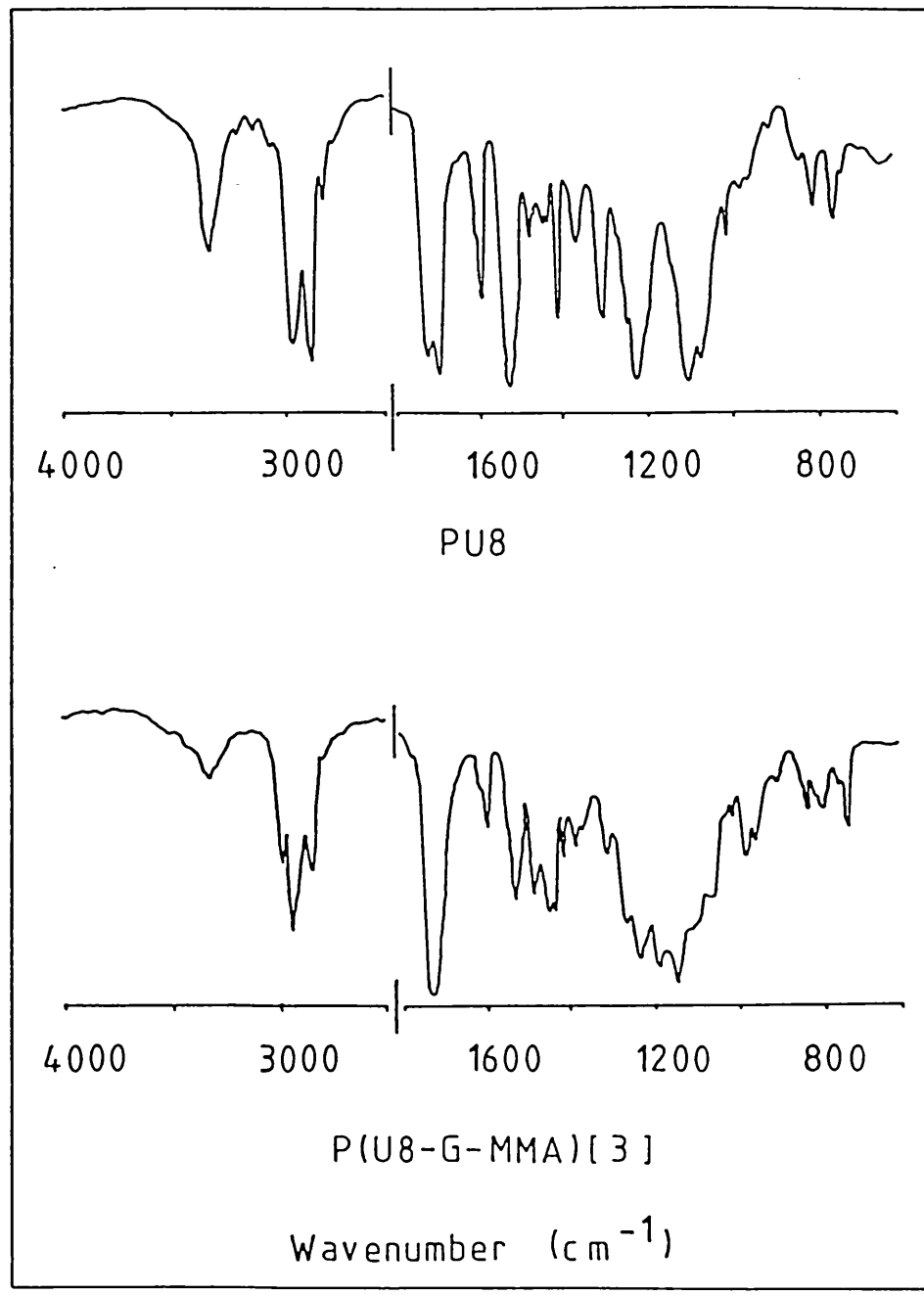


FIG.(5.26): IR SPECTRA OF PU8 AND P(U8-G-MMA)[3]

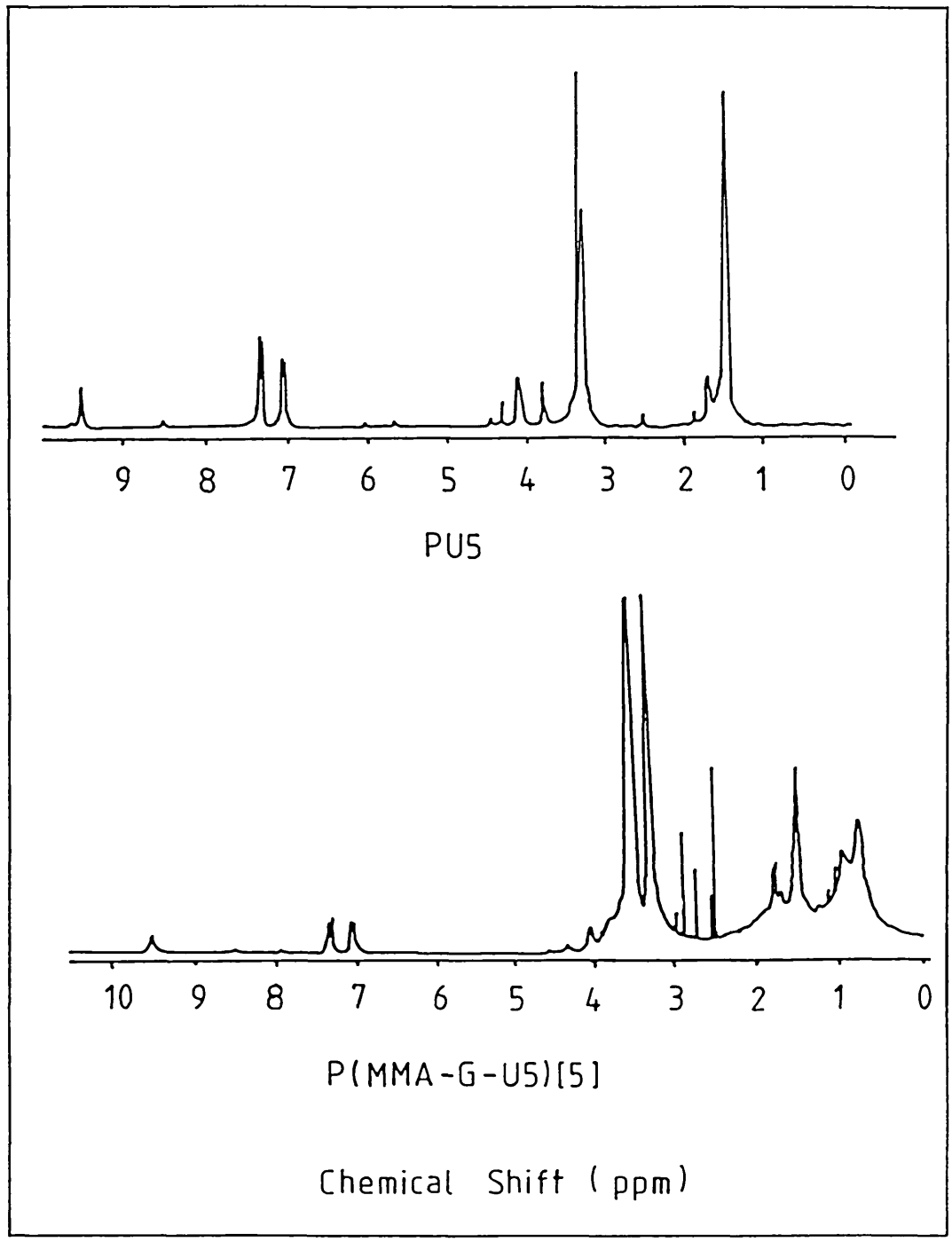


FIG.(5.27): ^{1}H-NMR SPECTRA OF PU5 AND P(MMA-G-U5)[5]

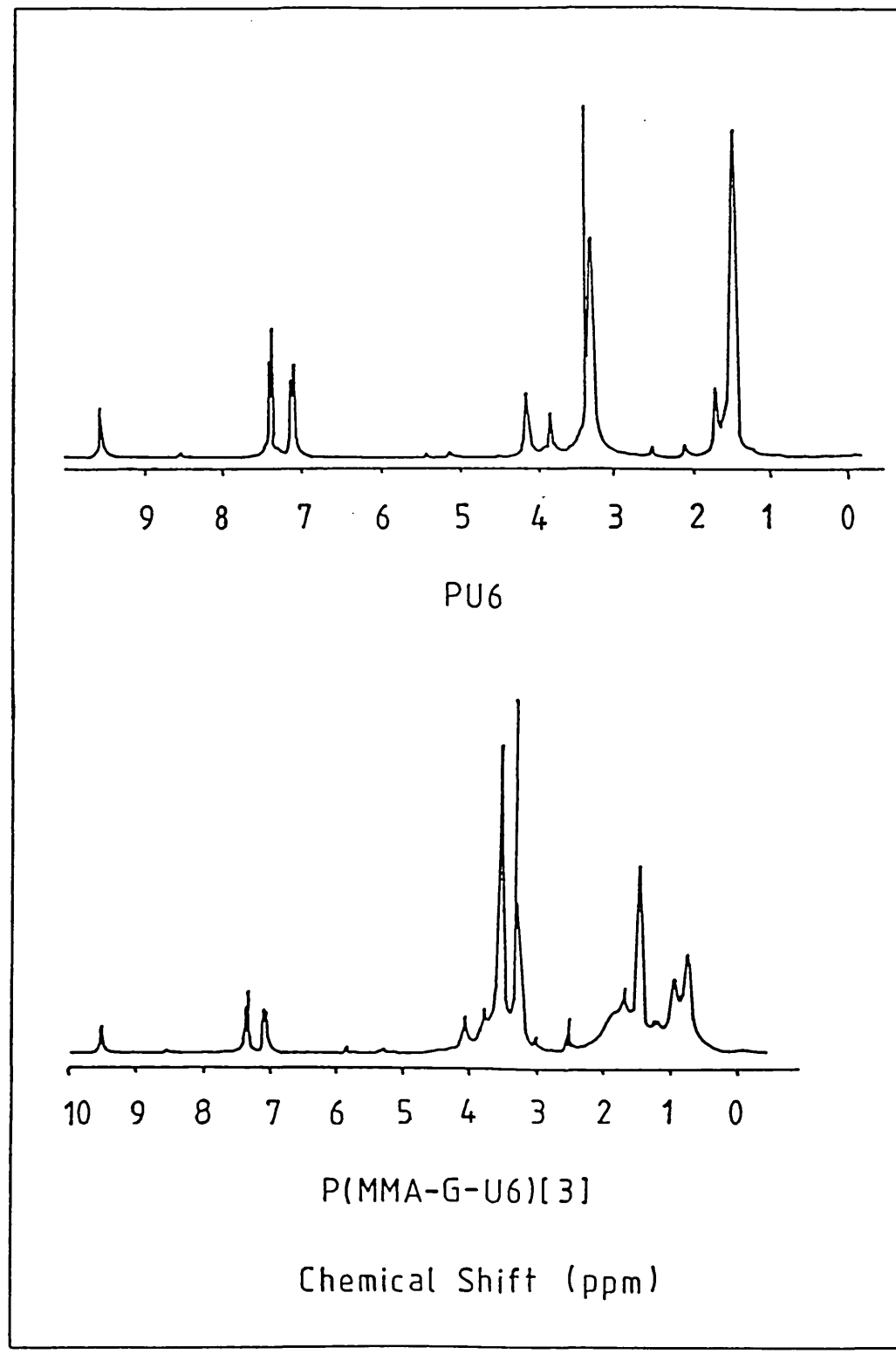


FIG.(5.28): ^{1}H-NMR SPECTRA OF PU6 AND P(MMA-G-U6)[3]

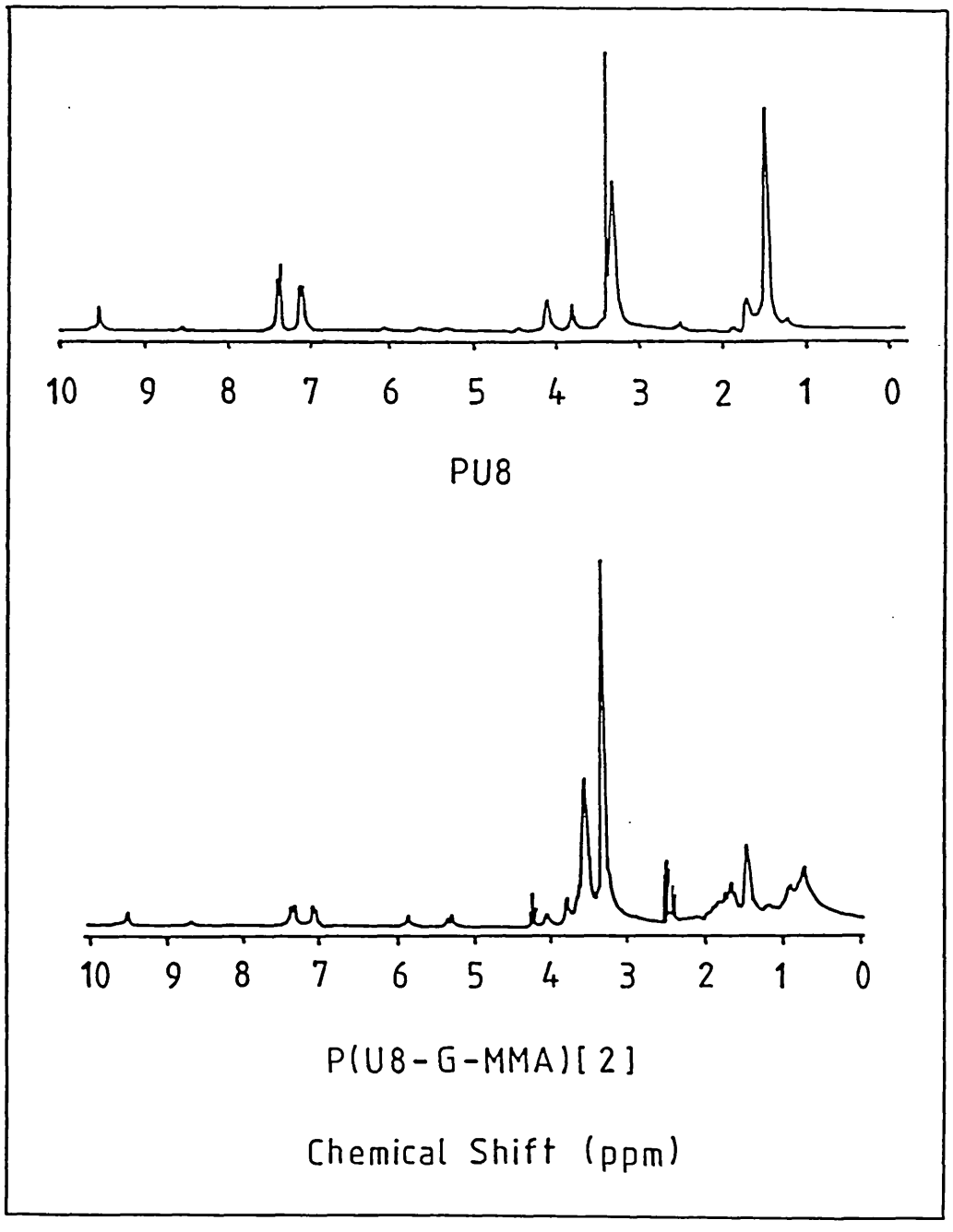


FIG.(5.29): ^{1}H-NMR SPECTRA OF PU8 AND P(U8-G-MMA)[2]

hydrogens of the functional unsaturated groups in the δ ~ 5 to 6ppm region.

For PU5 and PU8 (both containing methacrylate-type unsaturation), small resonances appeared at δ ≈ 5.7ppm and δ ≈ 6.1ppm. These corresponded to the two non-equivalent alkenic hydrogens. For the monomer MMA, in $CDCl_3$, these resonances are at 5.55 and 6.11ppm[207], and are complicated by long range coupling to the methyl group of the adjacent carbon atom.

For PU6 (containing the α-methyl styrene unit), small peaks were observed at δ ≈ 5.1 and δ ≈ 5.4ppm, corresponding to the two hydrogens on the carbon atom which was beta to the phenyl group. For the monomer styrene, in CCl_4, these resonances are at 5.1 and 5.6ppm[207].

The ^{1}H-NMR spectra for the graft copolymers seemed to be a combination of the PMMA spectrum [fig. (5.11)] and the corresponding polyurethane spectrum. The region between δ ~ 0 to 5ppm was extremely complicated by the mixture of resonances. However, the aromatic hydrogens of the MDI units and the urethane groups gave distinctive peaks.

5.8.3.3 ^{13}C-NMR

The ^{13}C-NMR spectra for PU5, PU6, and PU8 were identical, as were those of their corresponding graft copolymers. Fig. (5.30) shows the spectra for PU6 and P(MMA-G-U6)[3], which were typical for all of the respective polymers. The technique was not sensitive enough to detect the resonances of the carbon atoms of the functional unsaturated groups of the polyurethanes.

Table (5.16) lists the various groups assigned to the resonances observed for the polyurethanes [according to table (1.2)].

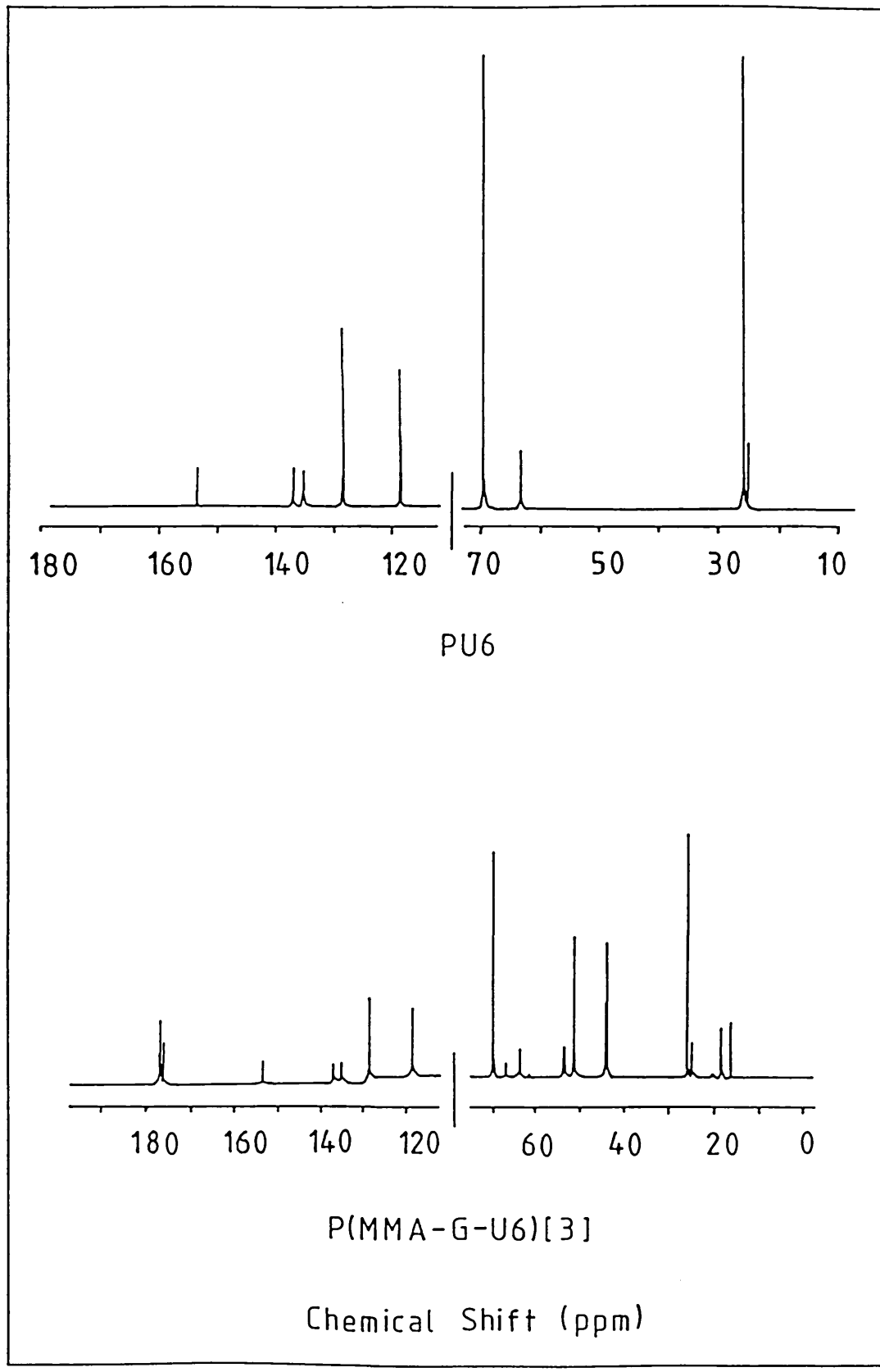
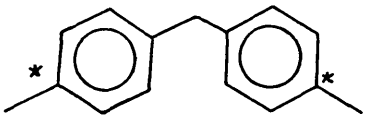
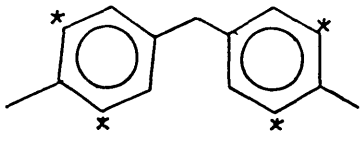
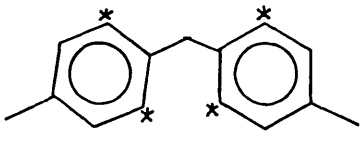
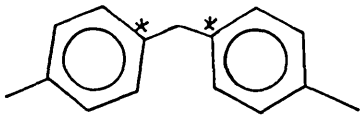


FIG.(5.30): ^{13}C-NMR SPECTRA OF PU6 AND P(MMA-G-U6)[3]

TABLE (5.16): ^{13}C-NMR CHEMICAL SHIFTS OBSERVED FOR THE CARBON ATOMS OF THE GROUPS PRESENT IN PU5, PU6, AND PU8

CHEMICAL SHIFT (ppm)	FUNCTIONAL GROUP
25	$-O-CH_2-\overset{*}{C}H_2-\overset{*}{C}H_2-CH_2-O-$ (BD and PTMEG 2000)
63	$-O-\underset{\underset{O}{\vert}}{C}-\underset{\underset{H}{\vert}}{N}-Ph-\overset{*}{C}H_2-Ph-\underset{\underset{H}{\vert}}{N}-\underset{\underset{O}{\vert}}{C}-O-$
69	$-O-\overset{*}{C}H_2-CH_2-CH_2-\overset{*}{C}H_2-O-$ (BD and PTMEG 2000)
118	
128	
135	
137	
153	C=O (Urethane)

The ^{13}C-NMR spectra for the graft copolymers were combinations of those of the corresponding polyurethane and PMMA [fig. (5.14)]. The tacticity of the PMMA part of the graft copolymer was observable, and appeared to be predominantly syndiotactic.

5.9 THERMAL AND MECHANICAL PROPERTIES OF THE GRAFT COPOLYMERS AND THEIR BLENDS WITH UNREACTED POLYURETHANE

5.9.1 DSC STUDIES

DSC was performed on several samples of the polyurethanes PU5, PU6, and PU8, their respective graft copolymers, and their blends of graft copolymers with unreacted polyurethane (i.e. the crude reaction products). The trends observed showed no differences from one polyurethane system to another. As examples, therefore, figures (5.31) and (5.32) show the DSC thermograms for PU8 and P(U8-G-MMA)[1] respectively.

For the polyurethanes, three runs were carried out on the same sample. The first two ran between -100 and 200°C, and the third from -100 to 250°C. Run (1) showed a transition between -80 to -50°C (centred at -65°C) which corresponded to the T_g of the polyether soft segment of the polyurethane. The fact that this was perceived indicated that there was a certain degree of phase separation between the hard and soft segments of the polymers.

A slight and broad transition was observed between 30 to 80°C, detectable as a change in gradient. This probably corresponded to the break down of the ordering of the hard segment. It was followed by a broad melting transition which started at ~150°C and peaked at ~175°C. The broadness of the transitions was reflection of the polydispersity of the polyurethanes.

Run (2) also contained the polyether transition at -65°C. However, a strong melting transition occurred at 20°C. This

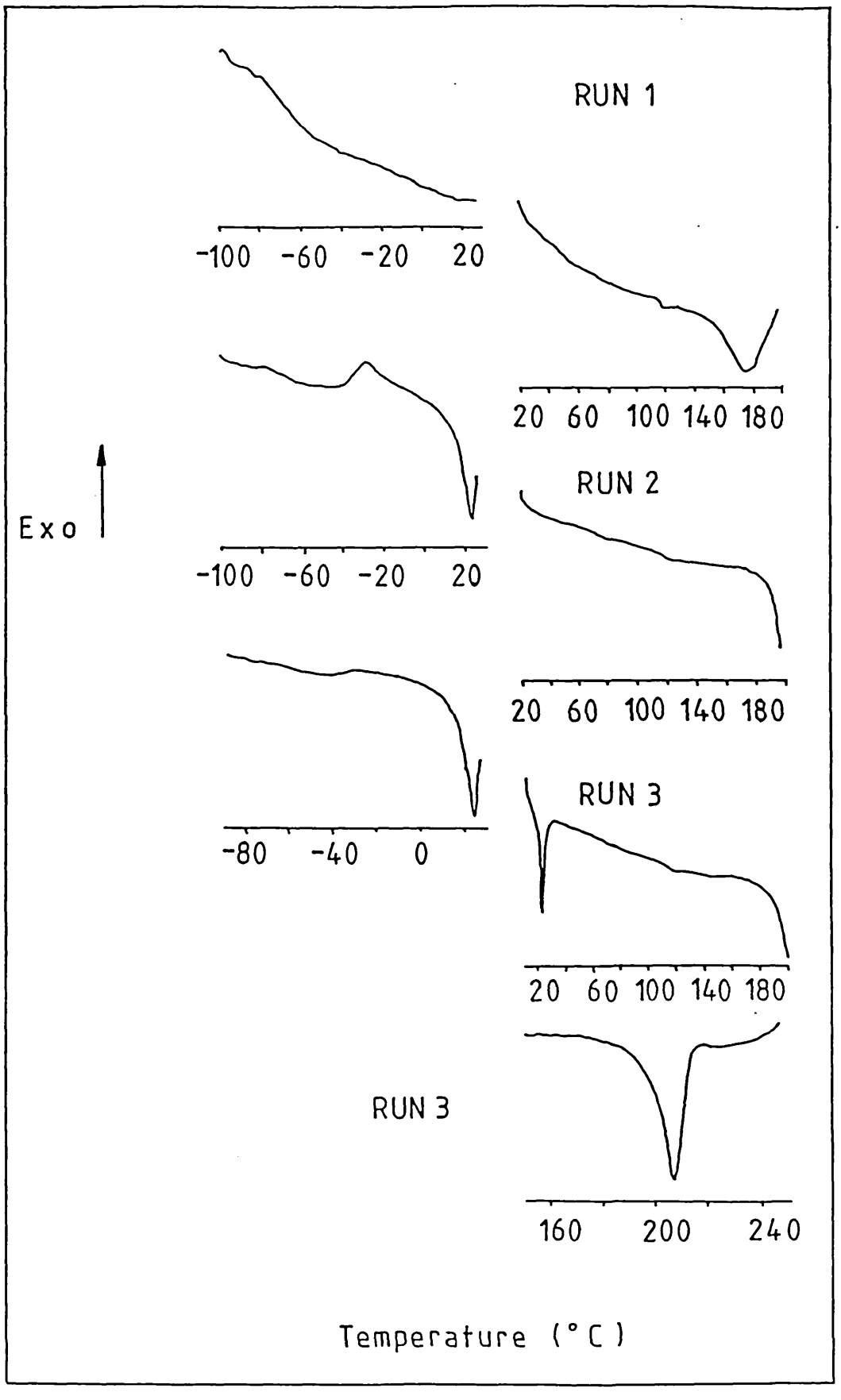


FIG.(5.31): DSC THERMOGRAMS FOR PU8

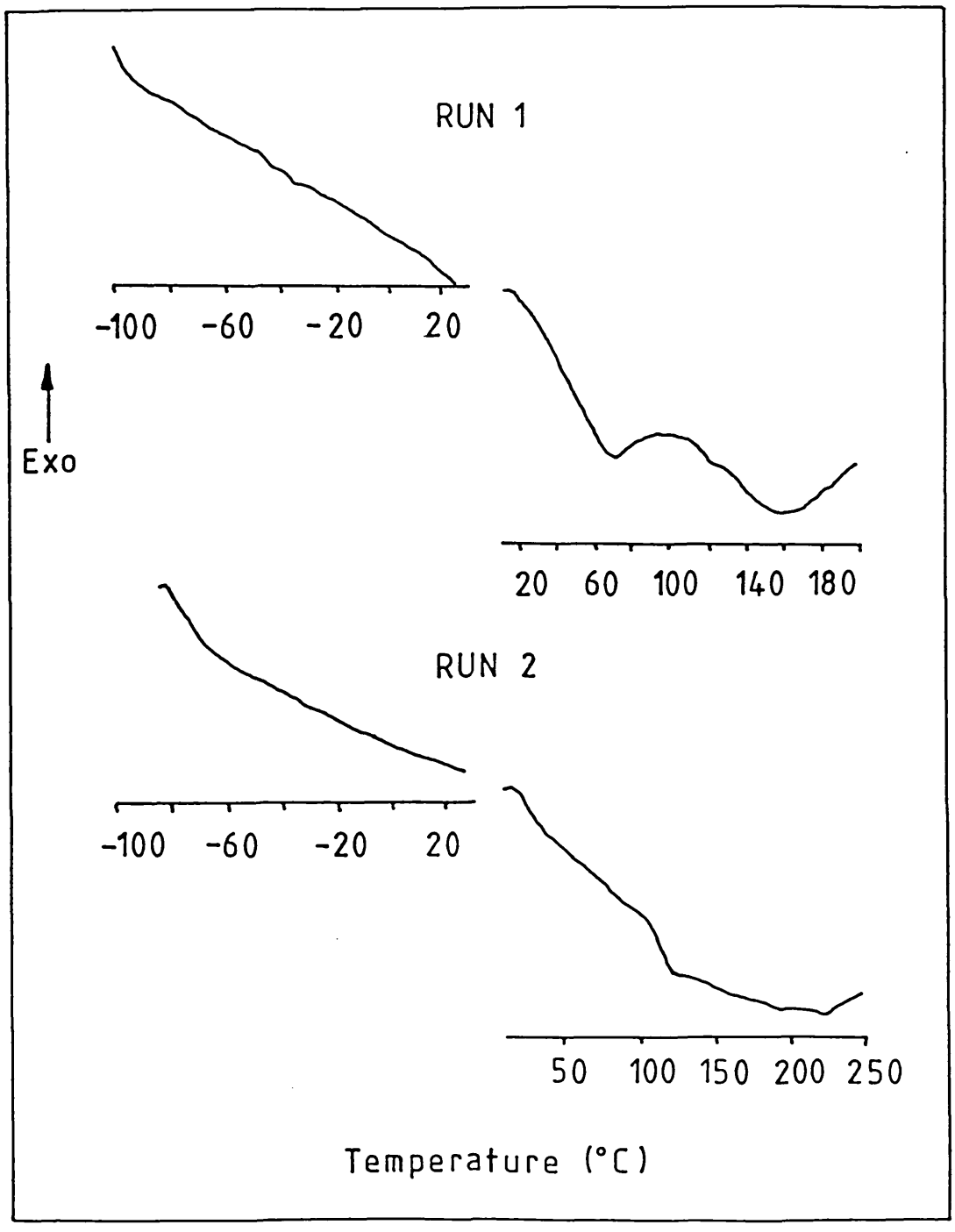


FIG.(5.32): DSC THERMOGRAMS FOR P(U8-G-MMA)[1]

corresponded well to the T_m of PTMEG 2000 homopolymer. The disruption of the hard segment occurred over a larger range of temperatures (~30 to 110°C) and was flatter than previously. A sharper melting transition occurred after ~185°C.

Run (3) showed all of the same features as run (2), with the T_m of the polyurethane peaking at 208°C, and a decomposition exotherm occurring after 240°C.

The GPC of samples of the polyurethanes after DSC showed changes in their molecular weight distributions. The polymers were more biased towards the low molecular weight regions. Hence, some form of decomposition was occurring.

The GPC of a sample of the PTMEG 2000 homopolymer after DSC up to 200°C also indicated that a small amount of decomposition had occurred within the polymer.

It seemed, therefore, that the soft segment of the polyurethane underwent decomposition into various fragments above the temperature of 150°C. These fragments crystallised upon cooling, and had a melting point similar to that of the polyether glycol homopolymer.

Annealing also disrupted the H-bonding of the hard segments of the polyurethanes. Hence, the endotherm corresponding to the hard segment T_g broadened.

Decomposition of the urethane linkages occurred after 240°C. The urethane groups would have converted back to the hydroxyl and isocyanate group from which it had been formed.

Two DSC analyses were performed on each sample of graft copolymer film from -100 to 200°C and -100 to 250°C respectively.

Run (1) had no transition belonging to the polyether of the polyurethane. This indicated that the aggregation of the polyurethane soft segments to form their own domains within the graft copolymers

was restricted. This was probably due to the "dilution" of the polyurethane within the graft copolymer by the PMMA. Therefore, it was concluded that a one-phase system existed.

Two endothermic transitions occurred between 10 to 70°C and 100 to 150°C. Both showed the signs of stress-relaxation.

The first transition consisted of two curves of different gradients, the point of inflexion being at ~30°C. The initial transition was probably the relaxation of the carbomethoxy side groups of the PMMA homopolymer [fig. (5.16)]. The second part of the transition was considered to be due to an interaction between the two polymeric species present in the graft copolymers. A similar endotherm was recorded by Akcelrud and Gomes[187] for their graft copolymers, which consisted of a PMMA backbone with polyurethane side chains based on PPG and TDI.

The endotherm centred at ~125°C was the T_g of the PMMA segments. The high temperature of the transition was another indication that the polymer was predominantly syndiotactic in structure.

However, it appeared that after heat treatment, the sample underwent rearrangements, and for run (2) an endotherm was observed, centred at ~-70°C, which was probably the T_g of the polyurethane soft segment. This also followed the observations of Akcelrud and Gomes[187] who found that for a polyurethane content below 20%, the T_g of their polyurethane soft segment was not seen until the graft copolymer had been heat treated.

An endotherm was seen centred at ~25°C, with no apparent stress relaxation. This was the relaxation of the side groups of the PMMA. The continuation of this transition as observed during run (1) was not visible. This again supported the view that the graft copolymer had undergone rearrangements and that the phase mixing between the polymers present had been eliminated by the heat treatment of run (1).

The T_g of the PMMA part of the graft copolymer appeared as an exotherm centred at ~112°C. The beginnings of a decomposition exotherm occurred at ~225°C.

The GPC chromatograms for the graft copolymers after the DSC experiments showed that decomposition of the polymers had occurred. The process could have involved either the breaking down of the polyurethane or the depolymerisation of the PMMA.

5.9.2 STRESS / STRAIN TESTS

Table (5.17) lists the results obtained for the stress / strain tests performed on samples of PMMA, PU5, PU6, PU8 and their respective graft copolymers, and the blends of the graft copolymers with unreacted polyurethane.

The films cast of all of the mixtures of products were opaque, indicating that there was a degree of phase separation within the blends. The mixtures of the graft copolymers labelled [3] formed very brittle films which could not hold together long enough in order to carry out mechanical tests.

The films of the pure graft copolymers were usually clear or slightly cloudy. However, occasionally white films were produced. Re-casting formed a clear film, indicating that the whiteness was caused during the drying of the film.

Necking occurred for certain samples, particularly in the case of the blends of unreacted polyurethane and graft copolymer. During the process, the materials underwent "stress-whitening". As the sample was being drawn out, the molecules within the polymer would have re-orientated. This re-alignment affected the refractive index of the material, causing it to have appeared as white. For the samples that underwent necking, values of ultimate strength are quoted at the yield point and at the point of break.

TABLE (5.17): STRESS / STRAIN RESULTS

SAMPLE	YOUNG'S MODULUS ($E \times 10^{-8}$/Pa)	ULTIMATE STRENGTH ($\times 10^{-7}$/Pa)	BREAKING STRAIN (%)
PMMA	5 (±2)	2 (±1)	4.0 (±0.8)
PU5	0.24 (±0.04)	0.36 (±0.02)	100 (±15)
PU6	0.27 (±0.06)	0.47 (±0.07)	320 (±10)
PU8	0.16 (±0.05)	0.34 (±0.02)	110 (±30)
P(MMA-G-U5)			
[1]-MIX	5 (±2)	1.7 (±0.1) [at yield] 0.8 (±0.4) [at break]	28 (±2)
[1]	2.8 (±0.4)	0.77 (±0.05)	3.9 (±0.6)
[2]-MIX	2.9 (±0.2)	1.2 (±0.2) [at yield] 0.94 (±0.06) [at break]	14 (±4)
[2]	6 (±1)	1.8 (±0.5)	3.5 (±0.2)
[3]	3.5 (±0.3)	0.5 (±0.1)	1.4 (±0.4)
[7]-MIX	4.3 (±0.4)	1.6 (±0.1) [at yield] 1.11 (±0.08) [at break]	12.7 (±0.7)
[7]	6.3 (±0.4)	1.8 (±0.1)	4.4 (±0.1)
P(MMA-G-U6)			
[1]-MIX	4.4 (±0.3)	1.75 (±0.07) [at yield] 0.57 (±0.04) [at break]	26 (±4)
[1]	3.7 (±0.9)	1.3 (±0.2) [at yield] 1.0 (±0.2) [at break]	18 (±2)
[2]-MIX	4.2 (±0.6)	1.4 (±0.6) [at yield] 0.6 (±0.1) [at break]	23 (±6)
[2]	2.0 (±0.7)	0.7 (±0.2)	6 (±1)

SAMPLE	YOUNG'S MODULUS ($E \times 10^{-8}$/Pa)	ULTIMATE STRENGTH ($\times 10^{-7}$/Pa)	BREAKING STRAIN (%)
[3]	3.4 (±0.5)	1.3 (±0.2)	6.0 (±0.1)
[7]-MIX	3.6 (±0.3)	1.5 (±0.1) [at yield] 1.1 (±0.2) [at break]	25 (±3)
[7]	5 (±2)	1.9 (±0.4)	15.2 (±0.3)
P(U8-G-MMA)			
[1]-MIX	2.9 (±0.8)	0.91 (±0.07) [at yield] 0.4 (±0.2) [at break]	12 (±2)
[1]	3.2 (±0.7)	1.5 (±0.3) [at yield] 0.7 (±0.4) [at break]	33 (±3)
[2]-MIX	3.9 (±0.3)	1.7 (±0.1) [at yield] 1.0 (±0.2) [at break]	10 (±2)
[2]	1.9 (±0.7)	0.9 (±0.3)	9 (±2)
[3]	3.3 (±0.7)	1.1 (±0.2)	6 (±1)
[7]-MIX	6.1 (±0.3)	1.68 (±0.02) [at yield] 1.0 (±0.1) [at break]	45 (±2)
[7]	4.1 (±0.4)	1.7 (±0.2) [at yield] 1.2 (±0.1) [at break]	17.3 (±0.5)

The PU5 and PU6 polymers exhibited similar trends. The results for these materials showed qualitatively that:

(A) For the pure graft copolymers:

E	≈	PMMA homopolymer
	>	Corresponding polyurethane
Ultimate strength	<	PMMA homopolymer
	>	Corresponding polyurethane
Breaking strain	>	PMMA homopolymer
	<<	Corresponding polyurethane

The stress / strain results for the graft copolymers of PU5 showed only very slight differences with changes in molecular weight. Polymers with $\bar{M}_n$ in the region of 150,000 (by GPC methods) had the best overall results (products [2] and [7]).

For the graft copolymers of PU6, those with a $\bar{M}_n$ of ~100,000 (products [1] and [7]) had better tensile qualities than their lower molecular weight analogues.

Although their values of ultimate strength and E were approximately equal, the breaking strains for P(MMA-G-U6) polymers were greater than their PU5 counterparts. This may have been a reflection of the ideal %-polyurethane content of the graft copolymers which produced a material with the best tensile properties. The graft copolymers of PU6 all contained ~12% polyurethane by weight [according to GPC methods, table (5.7)], whereas those of PU5 contained 12 - 34%

polyurethane [table (5.6)].

Therefore, for PU5 and PU6, it was concluded that the best tensile properties for the graft copolymer alone were achieved with a polymer of $\bar{M}_n$ around 100,000 to 200,000 (by GPC methods), and a polyurethane content between 10 - 20% w/w.

(B) For the unseparated products:

E	≈	PMMA homopolymer
	>	Corresponding polyurethane
	≈	Corresponding graft copolymer

The samples yielded and the stress decreased with increasing strain before breaking. However:

Maximum stress	≈	PMMA homopolymer
	>	Corresponding polyurethane
	≈	Corresponding graft copolymer
Breaking strain	>	PMMA homopolymer
	<	Corresponding polyurethane
	>	Corresponding graft copolymer

In general, it again appeared that a combination of a relatively high molecular weight graft copolymer ($\bar{M}_n$ ~150,000) and a polyurethane content between 10 - 20% w/w for the graft copolymer gave a better performance. In fact, the mixtures of products that produced stable films ([1], [2], and [7]) performed better than their corresponding pure graft copolymers, in as much as the breaking strains were much larger for the blends (reflecting the larger content of elastomeric

polyurethane), whilst E and the ultimate strength remained approximately the same.

It appeared, therefore, that these sort of systems produced graft copolymers capable of producing stabilised blends with free polyurethane provided that the molecular weights of the graft copolymers were sufficiently high enough, and that their %-polyurethane contents were constrained within certain limits.

The polymers of PU8 showed similar tendencies to those of PU5 and PU6. This time, however, both the pure graft copolymers and the blends had larger breaking strains than the sample of PMMA homopolymer (although they were considerably less than that of PU8 alone).

Although E and the ultimate strength were only slightly affected by molecular weight, the breaking strain was highest, again, for polymers with a GPC $\bar{M}_n$ between 100,000 and 150,000.

The greater extensibilities of the PU8 polymers compared to those of PU5 and PU6, particularly with respect to the pure graft copolymers, could be due to the different shapes of the polymers. PU8 could form the criss-crossed shaped materials of equation (5.17). The copolymer molecules may have packed together more closely than those of PU5 and PU6 because of their more compact form. The denser packing of the molecules would have made them more difficult to separate under stress. Hence, the overall polymer would stretch further, under the influence of the polyurethane chains, before breaking apart.

5.9.3 IMPACT TESTS

Since the impact test equipment required a certain minimum quantity of polymer, in the form of a film, in order to produce meaningful results, the materials tested were the blends of graft copolymer with unreacted polyurethane only. Table (5.18) lists the

TABLE (5.18): RESULTS OF THE IMPACT TESTS

SAMPLE	IMPACT VELOCITY ($m\ s^{-1}$)	SECANT MODULUS ($x\ 10^{-8}$/Pa)	ULTIMATE STRENGTH (PEAK STRESS) ($x\ 10^{-7}$/Pa)	BREAKING STRAIN (%)
PMMA	0.44 (±0.04)	3.74 (±0.06)	0.45 (±0.04)	1.19 (±0.07)
P(MMA-G-U5)				
[1]-MIX	0.42 (±0.01)	8.0 (±0.7)	2.3 (±0.2)	2.8 (±0.3)
[2]-MIX	0.427 (±0.004)	4.1 (±0.5)	0.35 (±0.07)	0.8 (±0.1)
[7]-MIX	0.403 (±0.007)	1.0 (±0.2)	0.14 (±0.04)	1.4 (±0.1)
P(MMA-G-U6)				
[1]-MIX	0.416 (±0.008)	7.3 (±0.2)	2.8 (±0.1)	3.86 (±0.01)
[2]-MIX	0.425 (±0.008)	7.7 (±0.1)	2.53 (±0.03)	3.3 (±0.1)
[7]-MIX	0.43 (±0.01)	6.0 (±0.6)	0.53 (±0.01)	0.9 (±0.1)
P(U8-G-MMA)				
[1]-MIX	0.417 (±0.001)	7.7 (±0.6)	2.86 (±0.05)	3.7 (±0.4)
[2]-MIX	0.427 (±0.006)	6.1 (±0.3)	1.3 (±0.3)	2.0 (±0.4)
[7]-MIX	0.428 (±0.004)	2.3 (±0.2)	0.33 (±0.04)	1.45 (±0.05)

results obtained.

For the majority of the materials, the results were better than those for the sample of PMMA homopolymer. Again, a combination of a relatively high molecular weight graft copolymer with a %-polyurethane content between 10 - 20% w/w gave the best performance.

5.10 RHEOLOGICAL PROPERTIES OF THE GRAFT COPOLYMERS AND THEIR BLENDS WITH UNREACTED POLYURETHANE

It was found that the minimum concentration of polymer in solution in DMF, in order to produce meaningful results for the tests performed, was 20% w/v. Therefore, since only small quantities of the pure graft copolymers could be isolated at one time by Prep-GPC, the samples whose rheological properties were investigated were the blends of the graft copolymers of PU5, PU6, and PU8 with their unreacted polyurethane, the pure graft copolymers of PU6, separate solutions of PU6 and PMMA, and a 1:1 blend of PU6 and PMMA.

Chapter 3 describes the theory governing the various properties studied.

5.10.1 VISCOMETRY TESTS

For the viscometry tests, values of the viscosity, η, and shear stress, σ_s, were measured for each sample for a series of different shear rates, $\dot{\gamma}$. Readings were made initially with the shear rate gradually increasing. The measurements were then repeated with the shear rate decreasing to see if any time dependent effects were to be seen. If thixotropy or rheopexy did not occur, the value of η or σ_s for a particular shear rate was taken to be the average of the two readings.

Figures (5.33) to (5.37) show the results of the viscometry tests for each sample.

Fig. (5.33) is a graph of σ_s versus $\dot{\gamma}$ for the solutions of PMMA homopolymer, the 1:1 PU6 / PMMA blend, and PU6. Each sample showed a linear dependency of σ_s with $\dot{\gamma}$, and as a result, their values of η were constant over that range of shear rates. Therefore, each sample was behaving as a Newtonian liquid. The values of η varied from 0.55Pa s (for the solution of PU6) to 2.9Pa s (for the solution of PMMA). This was a reflection of the molecular weight differences of the polymers, as the polyurethane had a $\bar{M}_n$ of ~20,000, and the sample of PMMA had an $\bar{M}_n$ of ~100,000 (by GPC methods). The blend had an intermediate viscosity, since it was a mixture of the low and high molecular weight polymers.

The linear plots of σ_s versus $\dot{\gamma}$ and the constant value of η indicated that there was no apparent clustering of the polymer molecules in solution into aggregates that could have been broken down into smaller units by the application of shear.

Fig. (5.34) shows the results of the viscometry tests for a selection of the pure graft copolymers of PU6. Samples [1] and [2] did not show linear dependency of σ_s with $\dot{\gamma}$. Also, their viscosities were not constant, but decreased with increasing $\dot{\gamma}$. Therefore, the materials were exhibiting pseudoplasticity.

GPC analysis was carried out on the samples after the tests to check that the decrease in viscosity was not due to the degradation of the molecules in smaller fragments. No apparent degradation had occurred. This indicated that the polymer molecules were clustering together at low shear rates. Therefore, the apparent viscosity was abnormally high because the sample contained large particles. However, at high shear rates, the aggregates were broken down, the particles in

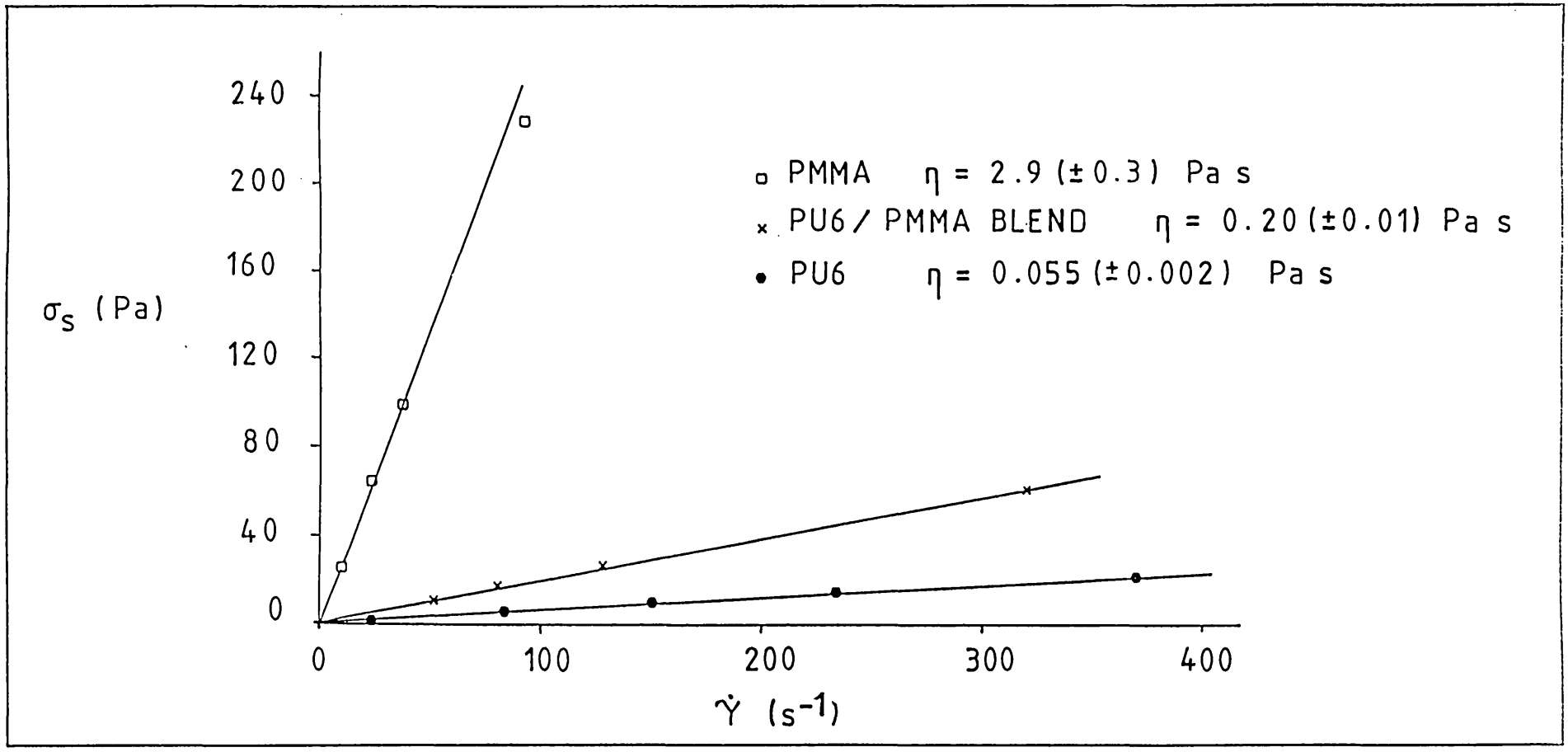


FIG. (5.33): GRAPH OF σ_s VERSUS $\dot{\gamma}$ FOR THE 20% w/v DMF SOLUTIONS OF PMMA, 1:1 w/w BLEND OF PU6 AND PMMA, AND PU6

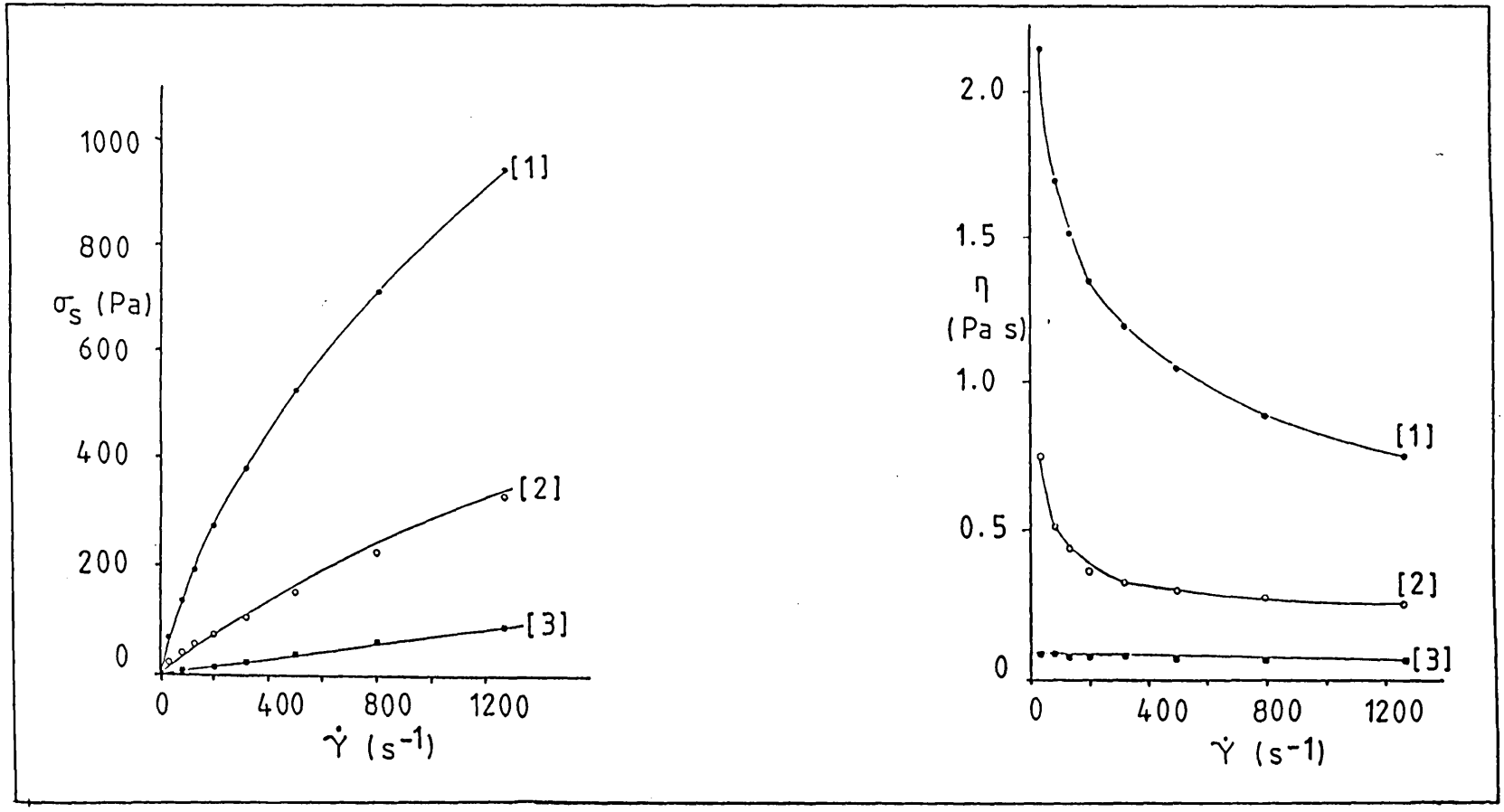


FIG.(5.34): GRAPHS OF σ_s AND η VERSUS $\dot{\gamma}$ FOR THE GRAFT COPOLYMERS OF PU6: P(MMA-G-U6)[1], [2], AND [3]

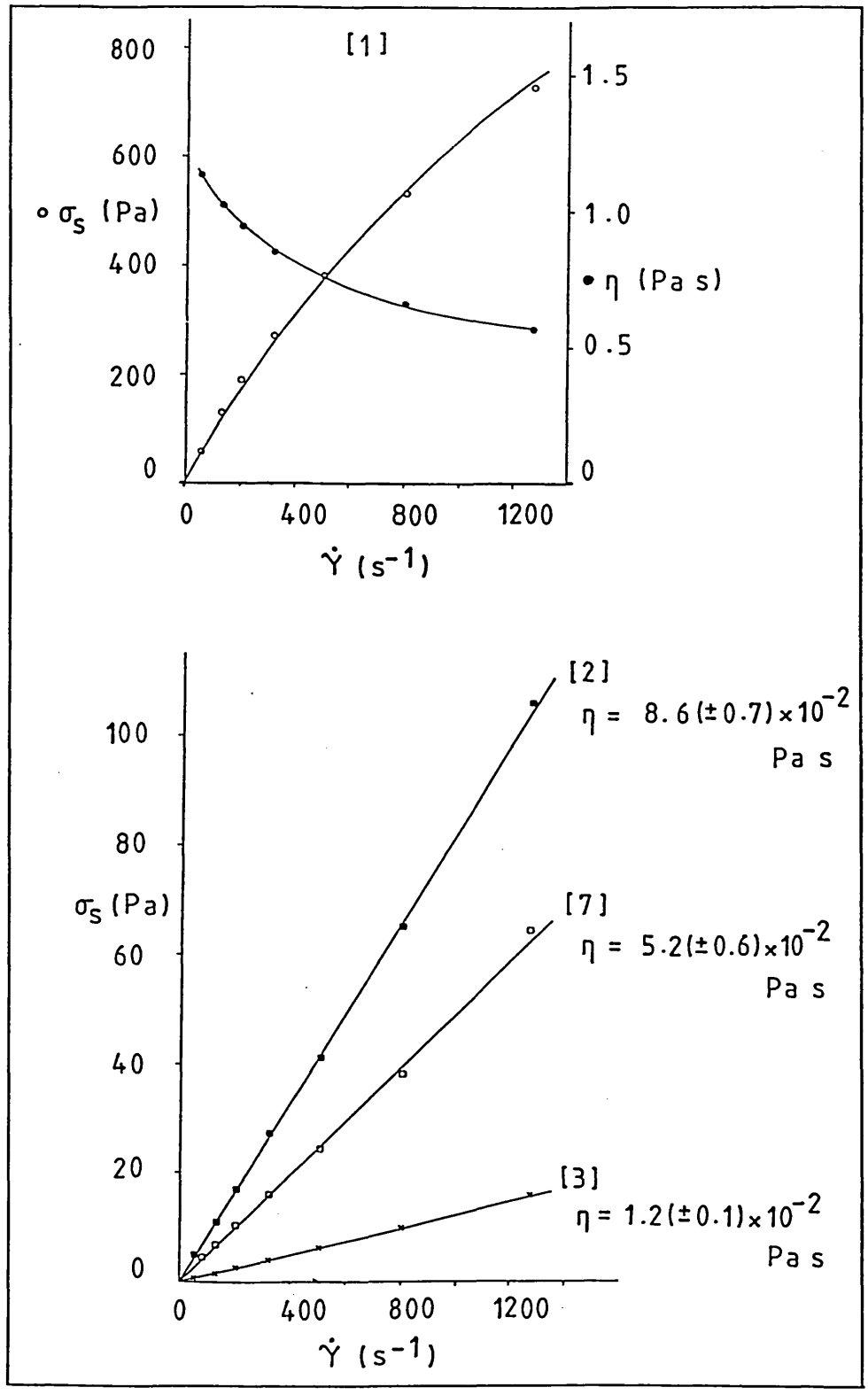


FIG.(5.35): GRAPHICAL RESULTS OF THE VISCOMETRY TESTS PERFORMED ON THE SOLUTIONS OF P(MMA-G-U5)-MIX [1],[2],[3], & [7]

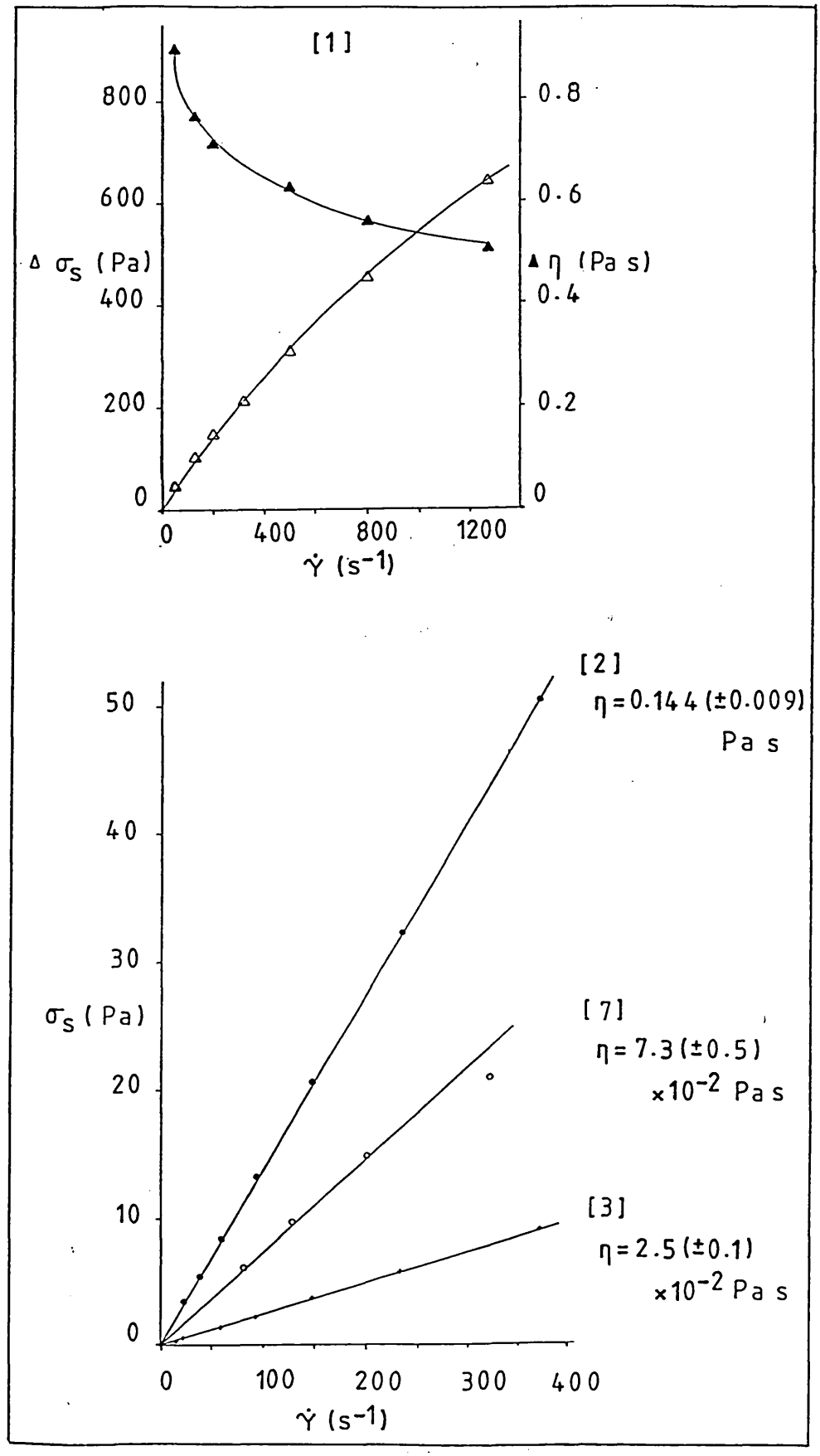


FIG. (5.36): GRAPHICAL RESULTS OF THE VISCOMETRY TESTS PERFORMED ON THE SOLUTIONS OF P(MMA-G-U6)-MIX[1], [2], [3], & [7]

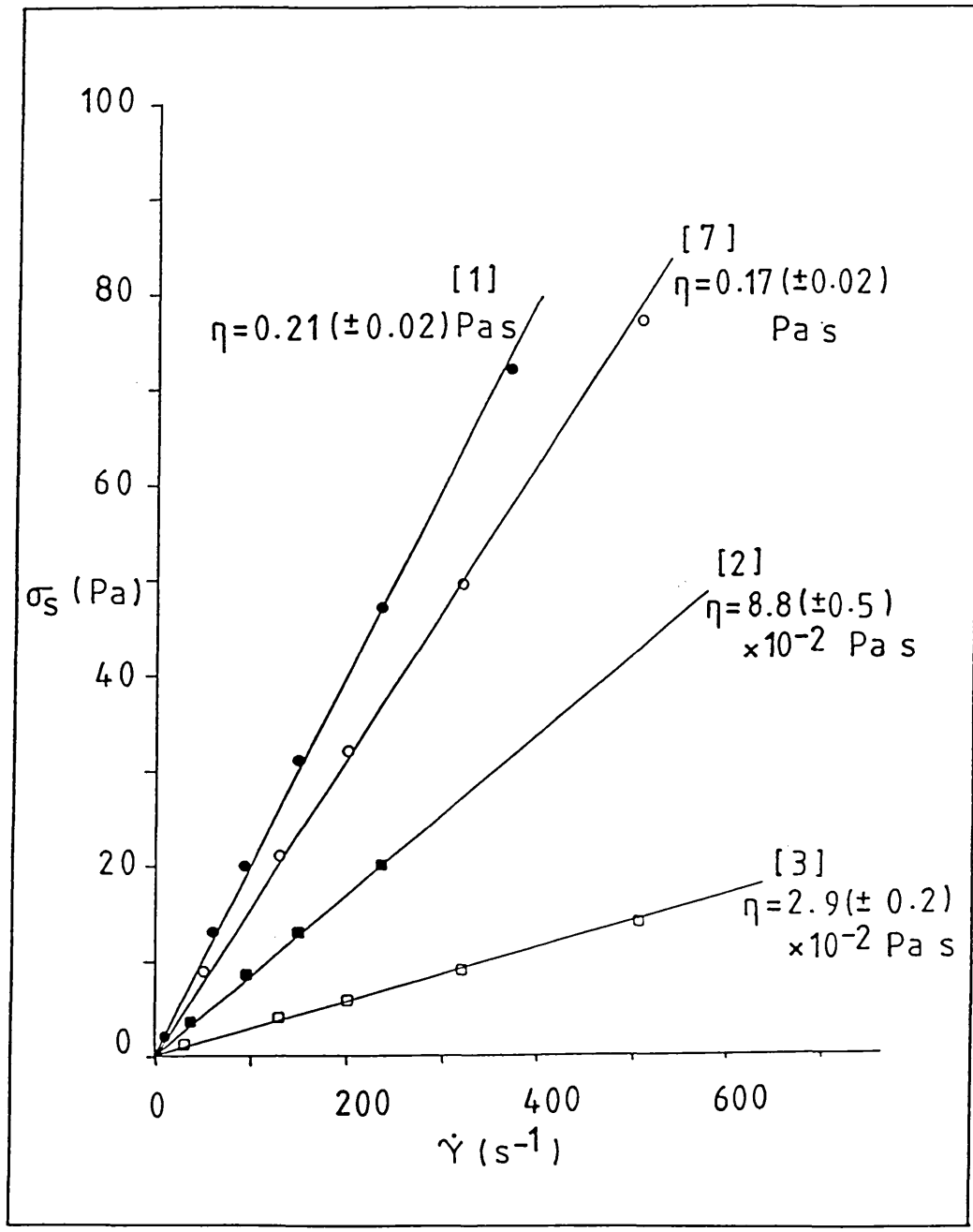


FIG.(5.37): GRAPHICAL RESULTS OF THE VISCOMETRY TESTS PERFORMED ON THE SOLUTIONS OF P(U8-G-MMA)-MIX[1],[2],[3], & [7]

the solution "appeared" to be smaller, and the viscosity decreased.

The clusters of molecules, therefore, probably consisted of groups of graft copolymer molecules held together either by frictional forces (i.e. the molecules could not "slip" over one another with ease) or by intermolecular attractions (e.g. intermolecular H-bonding between polyurethane hard segments).

For an individual shear rate, the values of σ_s and η decreased from samples [1] to [3]. This, again, was due to the corresponding decrease in molecular weight for each material.

Sample [3] appeared to have a constant viscosity and linear dependency of σ_s with $\dot{\gamma}$. This may have been due to the lack of aggregation of molecules with the solution, since sample [3] had a lower molecular size and less polyurethane chains per molecule. Hence the molecules would have suffered less frictional forces. However, it was also probable that the sensitivity of the equipment was too low to observe any pseudoplastic effects for the sample.

Figures (5.35) to (5.37) show the results of the viscometry tests for the blends of samples [1], [2], [3], and [7] of the graft copolymers and unreacted polyurethane for PU5, PU6, and PU8.

Those of PU5 and PU6 showed similar trends. Samples P(MMA-G-U5)[1]-MIX and P(MMA-G-U6)[1]-MIX showed pseudoplastic tendencies, whereas the other samples had linear dependencies for η and σ_s with $\dot{\gamma}$.

This indicated that for the relatively high molecular weight graft copolymer blends of PU5 and PU6, aggregation of the molecules occurred in the solutions, despite the fact that DMF was a good solvent for all of the species present. As the shear rate increased, the aggregates were broken down and the apparent η decreased. Again, the clustering of the molecules could have been due to intermolecular H-bonding between molecules of free polyurethane and the polyurethane

of the graft copolymers, or due to frictional forces hindering the movement of molecules over one another.

These results correlated well with the experimental observations for the attempted separation of P(MMA-G-U5) graft copolymers from the unreacted PU5 by fractional precipitation (section 5.7.3). The fact that a certain quantity of unreacted PU5 precipitated with each fraction obtained indicated that even in a good solvent, such as THF, the graft copolymer and the free polyurethane molecules were entangled together. Hence, separation was not achieved by these means.

The lower molecular weight graft copolymers, samples [2]-MIX, [3]-MIX, and [7]-MIX, did not appear to exhibit pseudoplastic behaviour. This was probaly due to their lower molecular weights compared to sample [1]-MIX. Less clustering of the molecules would have occurred, and intermolecular frictional forces would have been smaller. Hence, the solute had more freedom to move about in the solution. Also, since the values of η and σ_s measured were quite small, it was possible that the sensitivity of the apparatus would not have registered small deviations from linearity.

The measured viscosities and shear stresses for the PU6 blends were smaller than those for the corresponding pure graft copolymers. This was due to the presence of the free PU6 in the blends, which lowered the molecular weight averages of the samples compared to the solutions of the pure graft copolymers of the same concentration.

The samples of the blends of PU8, however, showed no pseudoplastic effects. It appeared, therefore, that no aggregation of molecules or high frictional forces between molecules occurred in the solutions. Alternatively, any aggregates formed were stable under the shear rate ranges used. However, on the basis of the results for PU5 and PU6, this latter hypothesis was unlikely.

The observations, therefore, may have been due to the difference in the general shape of the PU8 graft copolymers, which were of a more compact size than those of PU5 and PU6 (particularly for the criss-crossed form of graft copolymer). In solution, the restrictions imposed on the polyurethane part of the copolymer would have created difficulties in the polymers surrounding free PU8 molecules. Also, intermolecular frictional forces would have been reduced.

On the basis of these observations, it was possible that the graft copolymers of PU8 could have isolated by fractional precipitation.

Pseudoplastic behaviour is a beneficial property for the formulation of a surface coating. It would mean that under the influence of a high rate of shear (by the action, say, of a spray gun) the paint would behave as a low viscosity liquid. However, when subjected to a low rate of shear (for instance, when left to dry) the coating would act as a high viscosity material and would, therefore, be less likely to drip off its substrate.

It appeared that the relatively high molecular weight graft copolymers, of the shape of those for PU5 and PU6, tended towards ideal rheological behaviour for use as a paint.

5.10.2 DYNAMIC (OSCILLATION) TESTS

The oscillation tests were performed on fresh samples of the solutions used for the viscometry tests. Values of the phase angle, δ, the storage modulus, G', the loss modulus, G'', the complex modulus, G^* [related to G' and G'' by equations (3.28) and (3.29) of Chapter 3], and the dynamic viscosity, η', were measured for a series of different frequencies of oscillation.

Figures (5.38) to (5.40) show the graphical results obtained for samples [1], [2], and [3] of the pure graft copolymers of PU6.

For each sample, G'' was much greater than G', indicating that each solution was behaving as a viscous liquid. More energy was being lost per cycle than was being stored.

Actual values of the moduli, for a particular frequency, decreased from sample [1] to [3], again due to the molecular weight differences of the solutes.

The dynamic viscosity, η', declined with increasing frequency for each sample, but to a lesser extent from [1] to [3]. Since the samples showed pseudoplastic behaviour during the viscometry tests, η' did not tend to exactly the same values of η for the sample at low frequencies. However, they were of similar magnitudes.

The value of δ was high for each sample [therefore, so was tan(δ)]. Since tan(δ) was a measure of the energy lost compared to the energy stored per cycle, this was again an indication that the solutions were behaving as viscous liquids. For samples [1] and [2], δ gradually decreased with increasing frequency. For sample [3], however, δ remained constant at a value of ~86°. Again this was probably due to the lower molecular weight averages of [3] compared to [1] and [2].

The results for the other samples investigated are described in tabular form in table (5.19).

In general, samples which showed constant values of η and linear dependency of σ_s with $\dot{\gamma}$, for the viscometry tests, showed constant values of η'. These were approximately equal to η. The blend of PU6 with PMMA homopolymer was an exception, however, with η' being slightly greater than η.

η' decreased with increasing frequency for samples P(MMA-G-

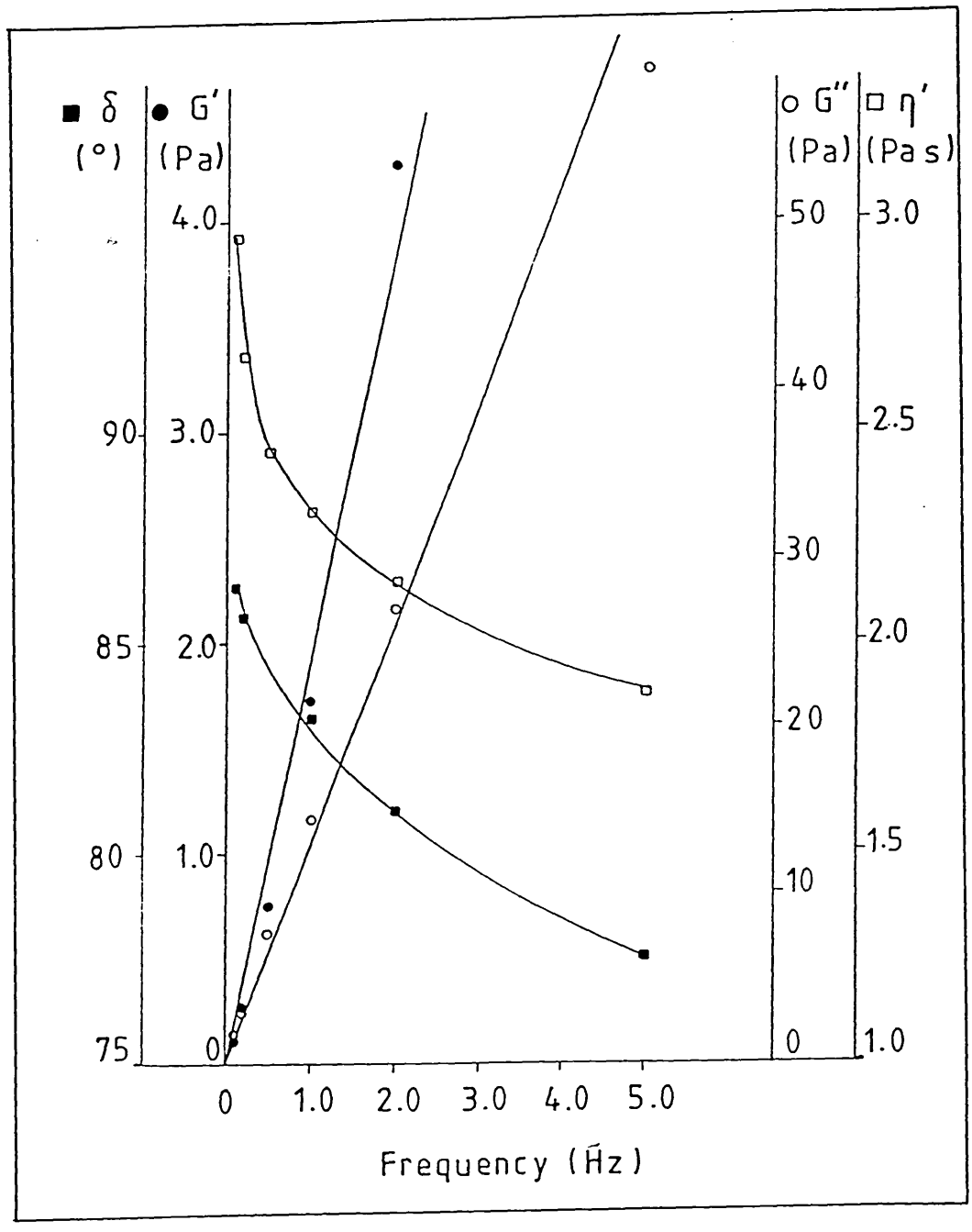


FIG.(5.38): GRAPHICAL RESULTS OF THE OSCILLATION TESTS PERFORMED ON THE SOLUTION OF P(MMA-G-U6)[1]

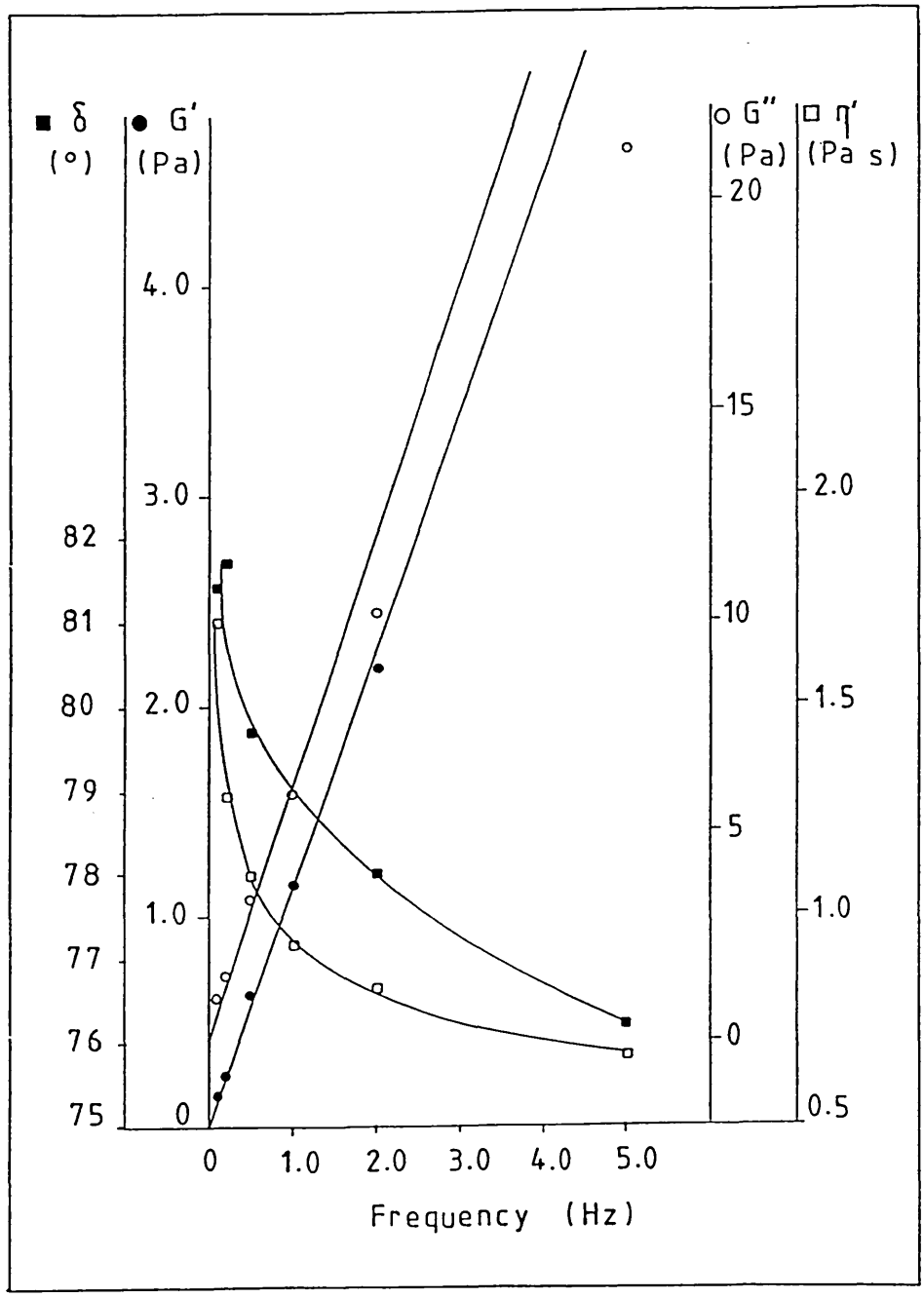


FIG.(5.39): GRAPHICAL RESULTS OF THE OSCILLATION TESTS PERFORMED ON THE SOLUTION OF P(MMA-G-U6)[2]

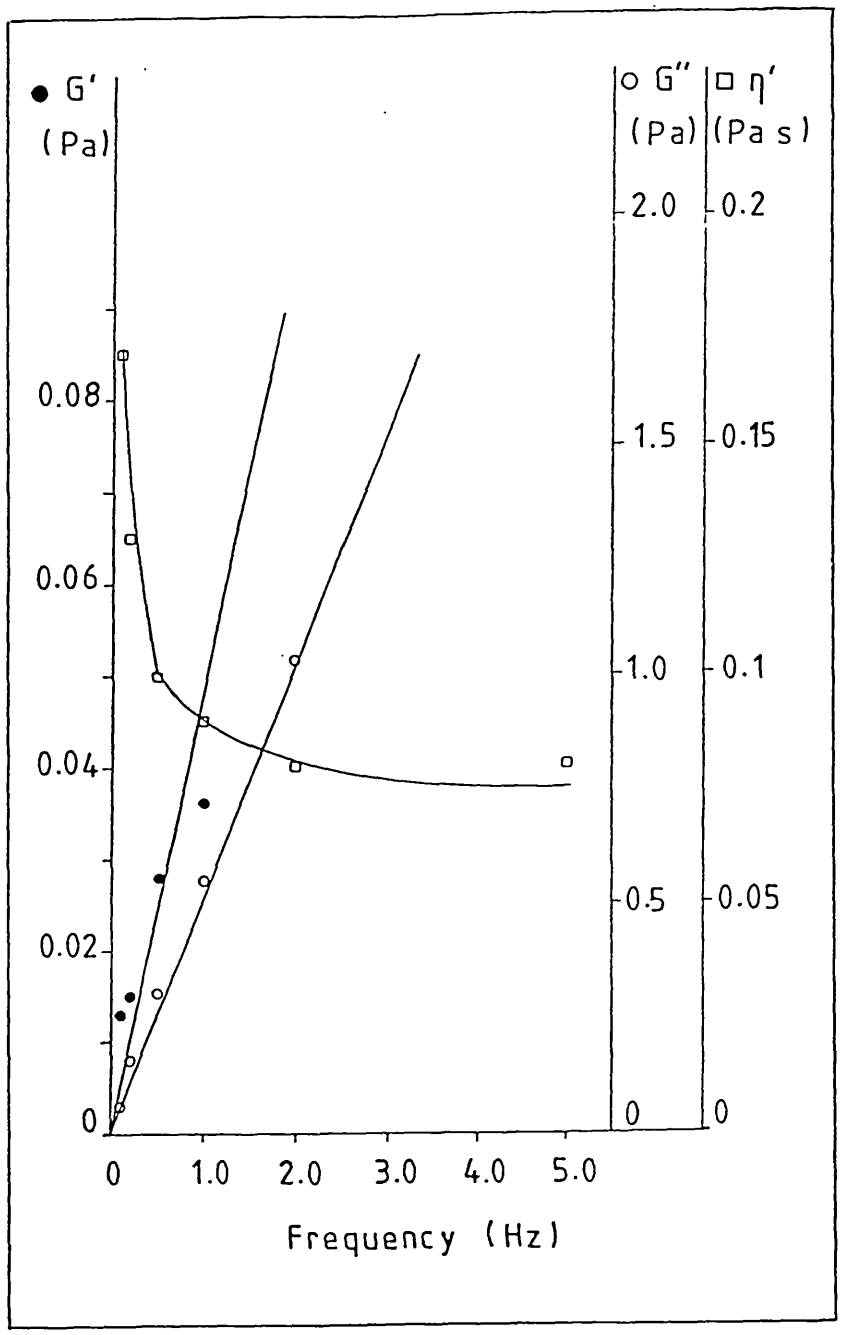


FIG.(5.40): GRAPHICAL RESULTS OF THE OSCILLATION TESTS PERFORMED ON THE SOLUTION OF P(MMA-G-U6)[3]

TABLE (5.19): RESULTS OF THE OSCILLATION TESTS ON THE 20% w/v DMF SOLUTIONS OF PMMA, PU6, PU6 / PMMA BLEND, AND THE MIXTURES OF GRAFT COPOLYMERS WITH UNREACTED POLYURETHANES

SAMPLE	FREQUENCY RANGE (Hz)	δ (°)	G' (Pa)	G'' (Pa)	η' (Pa s)
PMMA	0.05-10.0	84 (±6)	0.05 (±0.04)-51 (±1)	1.0 (±0.2)-161 (±1)	3.1 (±0.5)
PU6	0.5-10.0	80 (±8)	0.019 (±0.002)-0.97 (±0.06)	0.25 (±0.02)-3.7 (±0.2)	0.07 (±0.02)
PU6 / PMMA BLEND	0.05-10.0	84 (±3)	0.08 (±0.01)-1.5 (±0.6)	0.7 (±0.3)-14 (±3)	2 (±1)
P(MMA-G-U5)					
[1]-MIX	0.1-5.0	72.6 (±0.9)-58.05 (±0.05)	5.0 (±0.5)-106.5 (±0.5)	15.7 (±0.9) 171	26 (±2)-5.44 (±0.01)
[2]-MIX	0.1-5.0	89 (±1)	0.002 (±0.001)-0.18 (±0.02)	0.09 (±0.01)-3.99 (±0.02)	0.14 (±0.02)
[3]-MIX	0.2-5.0	80 (±10)	0.0061 (±0.0002) - 0.03 (±0.01)	0.010 (±0.005) - 0.375 (±0.006)	0.011 (±0.007)
[7]-MIX	0.1-5.0	86 (±4)	0.008 (±0.002) - 0.04 (±0.02)	0.053 (±0.009) - 1.82 (±0.01)	0.08 (±0.02)
P(MMA-G-U6)					
[1]-MIX	0.2-10.0	82 (±7)	0.06 (±0.02)-12.5 (±0.4)	1.23 (±0.04) - 46.7 (±0.3)	0.98 (±0.04) 0.744 (±0.005)
[2]-MIX	0.2-10.0	86 (±4)	0.06 (±0.06)-0.9 (±0.2)	0.2 (±0.02) - 10.9 (±0.3)	0.17 (±0.02)

SAMPLE	FREQUENCY RANGE (Hz)	δ (°)	G' (Pa)	G'' (Pa)	η' (Pa s)
[3]-MIX	0.2-10.0	70 (±20)	0.013 (±0.002)-0.9 (±0.2)	0.3 (±0.01) - 0.99 (±0.03)	0.04 (±0.03)
[7]-MIX	0.2-5.0	89 (±1)	0.005 (±0.001) - 0.06 (±0.02)	0.116 (±0.003) - 2.915 (± 0.005)	0.091 (±0.003)
P(U8-G-MMA)					
[1]-MIX	0.2-10.0	84 (±6)	0.038 (±0.006) - 3.06 (±0.01)	0.40 (±0.01) - 17.2 (±0.2)	0.30 (±0.03)
[2]-MIX	0.1-10.0	80 (±10)	0.004 (±0.001) - 1.28 (±0.04)	0.0610 (±0.0005) - 6.26 (±0.09)	0.10 (±0.05)
[3]-MIX	0.05-5.00	30 (±5)-76 (±3)	0.22 (±0.03)-0.20 (±0.04)	0.12 (±0.01) - 0.76 (±0.01)	0.39 (±0.04) - 0.0240 (±0.0001)
[7]-MIX	0.01-5.0	87 (±7)	0.020-0.13 (±0.02)	0.113 (±0.008) - 5.06 (±0.05)	0.18 (±0.02)

U5)[1]-MIX, P(MMA-G-U6)[1]-MIX, and P(U8-G-MMA)[3]-MIX (although the values of η' for this sample were very low). However, the value of η' for P(U8-G-MMA)[3]-MIX was almost equal to η, its steady flow viscosity, at low frequencies.

All solutions acted as viscous liquids, i.e. $G'' > G'$ and δ was high ($\sim 90°$). The moduli were smaller with decreasing molecular weight of graft copolymer. Also, the moduli were smaller for the mixtures of polymers compared to the pure graft copolymers.

In conclusion, the rheology experiments showed that:

(A) In 20% w/v solutions, the graft copolymers, and their blends with free polyurethane behaved as viscous liquids.

(B) The relatively high molecular graft copolymers of PU5 and PU6 showed pseudoplasticity, which is a favourable quality for paint formulation.

(C) A certain degree of association occurred between the high molecular weight graft copolymers of PU5 and PU6 and the unreacted polyurethane in solution in a good solvent for all species.

(D) Intermolecular frictional forces could have affected the rheological properties of the relatively high molecular weight graft copolymers and their blends.

(E) The graft copolymers and blends of PU8 did not show pseudoplasticity. Therefore, changing the shape of the graft copolymers also affected their rheological behaviour.

(F) Values of moduli and viscosities were molecular weight dependent.

5.11 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) was performed on gold-coated samples of polyurethanes, graft copolymers, and blends of graft copolymer with free polyurethane. SEM surveyed the surface of the gold-modified samples.

Fig. (5.41) shows the electron micrograph for PU8, which was typical for all of the polyurethanes based upon MDI. At the magnifications available, the polymer surface appeared to be featureless, i.e. no separate hard or soft segment domains were observed. The white spots on the micrograph corresponded to contaminating particles that were being charged up by the electron beam.

Samples of PMMA were analysed. However, these were rapidly damaged by the heating effect of the electron beam.

Figures (5.42) and (5.43) show the micrographs for sample P(MMA-G-U5)[1]-MIX and P(MMA-G-U5)[3]-MIX respectively. Quite obviously, there was a certain degree of phase separation occurring in each sample. Fig. (5.42) has been dramatically enlarged, hence it has a particularly grainy appearance.

Samples [1]-MIX and [3]-MIX were distinguished because they contained different molecular weight graft copolymers. Sample [1]-MIX had a micrograph consisting of a channelled arrangement. The structure probably consisted of a PMMA phase and a PU5 phase consisting of unreacted polyurethane and that belonging to the graft copolymer.

Sample [3]-MIX, however, appeared to have circular depressions

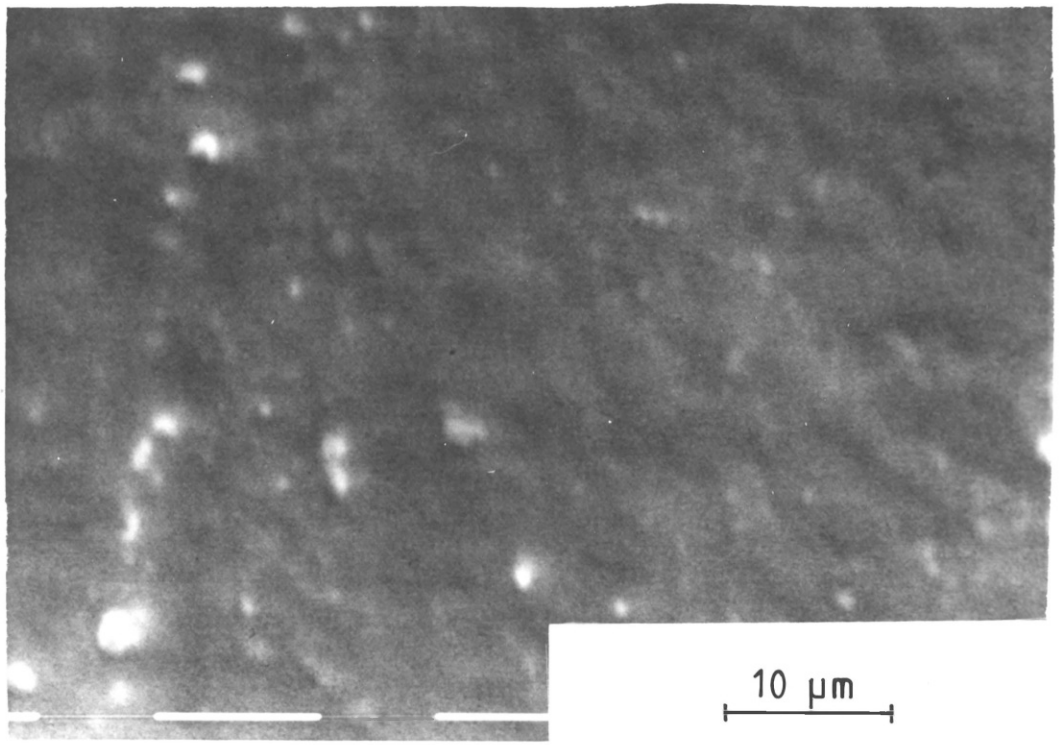


FIG.(5.41): SEM OF PU8

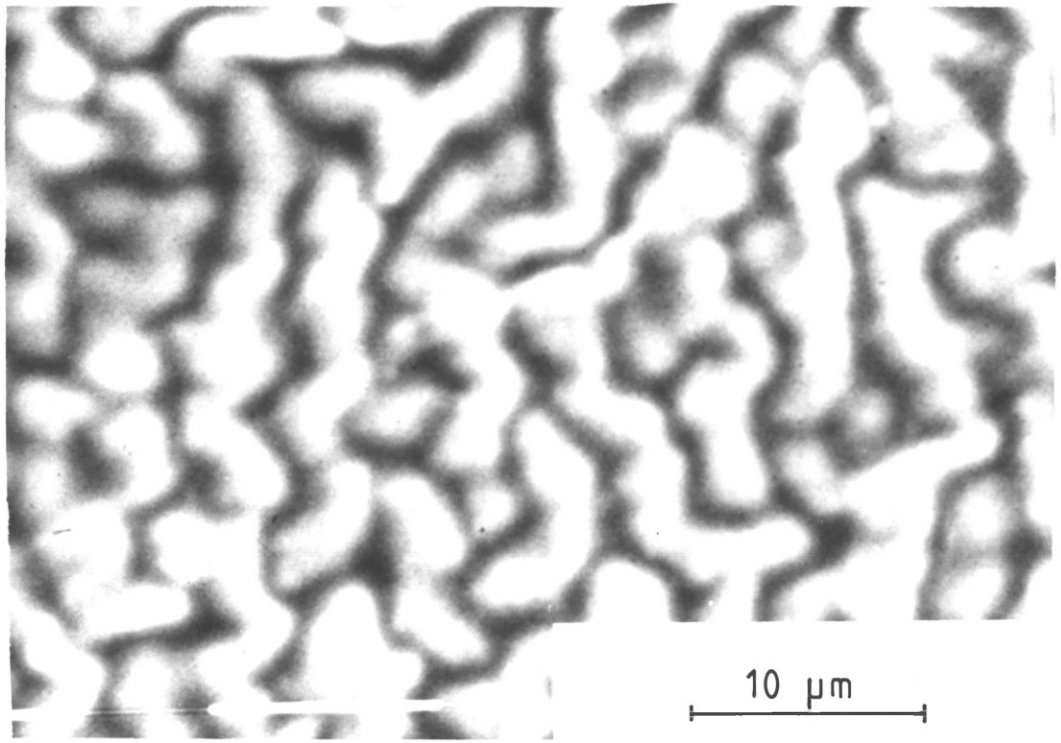


FIG.(5.42): SEM OF P(MMA-G-U5)[1]-MIX

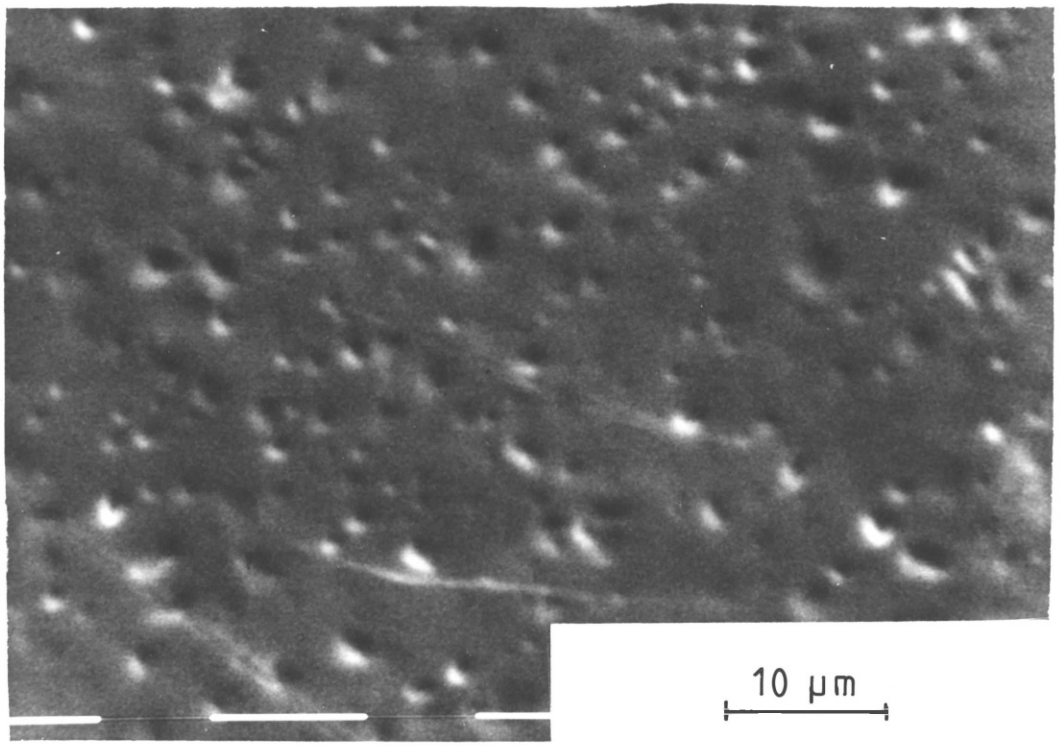


FIG.(5.43): SEM OF P(MMA-G-U5)[3]-MIX

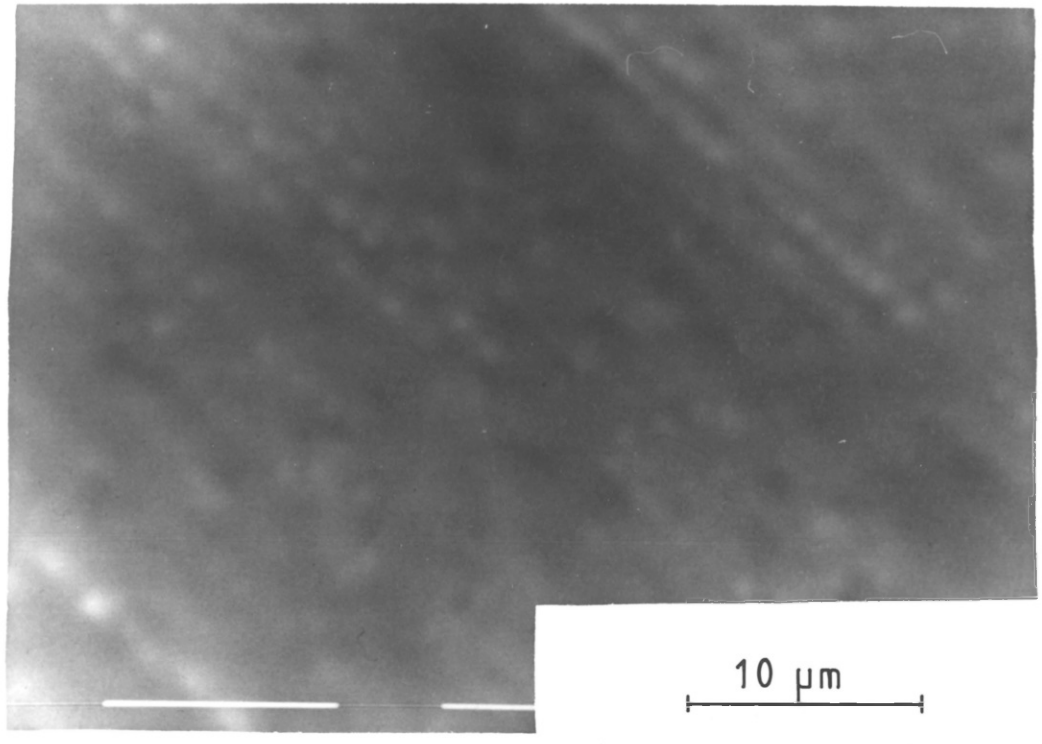


FIG. (5.44): SEM OF P(U8-G-MMA)[3]

dispersed amongst an otherwise featureless phase. It was probable that these were domains of unreacted PU5 dispersed amongst the graft copolymer. This sample was very brittle, whereas sample [1]-MIX had very good tensile properties. The difference in structure, therefore, determined the strength of the film. It seemed that small patches of free polyurethane dispersed within the film created discontinuities which weakened the material. Having a series of interconnecting channels, however, strengthened the film.

Similar micrographs were obtained for other samples of the blends of graft copolymers with unreacted polyurethane.

Fig. (5.44) shows the electron micrograph of the pure graft copolymer P(U8-G-MMA)[3]. This micrograph had to photographed very quickly as the sample underwent dramatic changes under the influence of the electron beam. Overall, the surface of the graft copolymer appeared to be featureless. However, black spots rapidly grew on the surface of the film (the start of these black spots can be seen faintly on the micrograph).

This phenomenon could have been due to two processes. DSC experiments (section 5.9.1) showed that after the graft copolymers had been annealed, re-arrangements had occurred within the sample, causing some phase separation to develop between the polyurethane and PMMA phases. It was possible that this was the process that was observed as the electron beam heated the sample of graft copolymer.

Alternatively, since PMMA homopolymer degraded quite dramatically under the influence of the beam, it was also possible that the black spots were an indication of the film damaging.

This effect was also observed for other samples of graft copolymer.

5.12 EFFECT OF STORAGE OF THE GRAFT COPOLYMERS

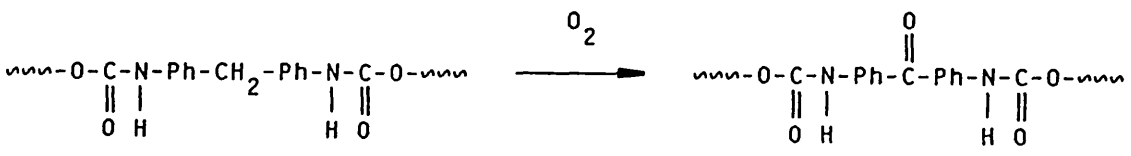
As explained in section 4.15 of Chapter 4, each polymer sample was stored in a protective container, in the dark, at 4°C.

However, a set of experiments were performed on six samples of the unseparated products of the reactions P(MMA-G-U5)[1], P(MMA-G-U6)[2], and P(U8-G-MMA)[6]. The samples were left under the conditions described in table (4.15) for exactly 6 months. After this time, the physical appearance of the polymers was assessed. GPC was carried out on each sample.

For the samples labelled [A] (i.e. samples that had been kept in the dark, but in the presence of air), a definite discolouration had occurred. The polymers had changed from white to light brown in colour. GPC, however, indicated that there had been no degradation.

The samples labelled [B] (i.e. samples that had been left exposed to light in the absence of air) were still white in colour, and GPC showed that no decomposition of these samples had occurred.

It appeared, therefore, that the samples were very stable when exposed to light, but were affected by air. It was probable that the polyurethane part of the samples was oxidised by the oxygen present in the air. Polyurethanes based upon MDI are prone to discolouration on exposure to air for long periods of time, whereas samples of PMMA are very stable under the same conditions. Oxidation of the polyurethanes occurs at the central methylene groups of the MDI units:



(5.25)

This oxidation process causes the polyurethanes to turn light brown in colour.

It was advantageous, therefore, to store all of the polymers in sealed containers below room temperature.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

Graft copolymerisation is a method of chemically combining two or more polymers in such a way that a material is produced with enhanced properties. The initial aim of this research project was to form the graft copolymers of an elastomeric, segmented polyurethane and PMMA. The intention was that the final product was to have a mixture of the favourable physical properties of the constituent polymers, and was to act as an interfacial agent, enabling free polyurethane to form a stable blend with PMMA homopolymer.

The grafting of various monomers onto polyurethanes has been achieved previously by many methods (see Chapter 2). Graft copolymerisation by means of free-radical attack of an active unsaturated group introduced into the polyurethane was used in this research project. This way was chosen because other workers had used this method with success, and the synthetic procedures required were very straightforward.

Consideration of the results obtained led to the following deductions:

(A) From the results of the synthetic methods chosen for the graft copolymerisation reactions, the inclusion of an active unsaturated group into the polyurethane was necessary for grafting to occur.

(B) Polyurethanes based on MDI and containing units of ER were unreactive towards graft copolymerisation with MMA. Substitution of the MDI with H_{12}MDI may have permitted a very small amount of grafting to have occurred. However, this was inconclusive, and the physical

properties of the final polymers were relatively poor. Hence, research into these systems was discontinued.

(C) Polyurethanes containing on average more than one methacrylate unit per molecule (PU4 and PU7) were too reactive towards graft copolymerisation with MMA, and produced crosslinked gels, unless the experimental conditions were very carefully controlled. As gels were to be avoided, the remainder of the research work involved the investigation into the properties of polyurethanes containing on average only one reactive unsaturated unit per molecule.

(D) Polyurethane macromonomers, such as PU5 and PU6, have proven to be a convenient means of producing graft copolymers of polyurethanes and MMA. Under the reaction conditions used, no PMMA homopolymer was produced. Hence, at the end of the reactions, only unreacted polyurethane and graft copolymer remained. Unreacted MMA was removed by drying the products in vacuo.

However, isolation of the graft copolymer proved to be very difficult. Eventually, preparative-GPC provided the means of achieving the required separation. However, this meant that only minute quantities of graft copolymer could be isolated at one time.

Polyurethanes terminated with methacrylate groups formed graft copolymers of a higher %-polyurethane content than the corresponding polyurethanes terminated with α-methyl styrene groups.

Mechanical tests showed that a relatively high molecular weight graft copolymer ($\bar{M}_n \sim 100,000 - 200,000$) with a %-polyurethane content of ~10 - 20% w/w gave the most desirable results. Tests performed on the unseparated reaction products indicated that the blends containing the high molecular weight graft copolymer had larger breaking strains than the corresponding pure graft copolymer, whilst still retaining

relatively high values of moduli and ultimate strengths.

Rheology tests carried out on the DMF solutions of the blends and the pure graft copolymers showed that pseudoplasticity was observed for the high molecular weight materials.

In conclusion, therefore, the higher the molecular weight of the graft copolymer, the better the mechanical properties (i.e. relatively high values of modulus, ultimate strength, and breaking strain), and the more ideal its rheological properties for use as a paint.

(E) Lower yields of PMMA were obtained for the grafting reactions involving PU8, compared to those of PU5 and PU6. However, the %-polyurethane contents of the final graft copolymers were relatively high.

Again, no PMMA homopolymer was formed unless the initiator concentration in the reaction mixture was so high as to inhibit the production of graft copolymer. This meant that PU8 was behaving as a special type of macromonomer, with its unit of unsaturation being dispersed along the polymer backbone.

The mechanical properties of the graft copolymers and blends of PU8 were good in comparison to those of PU5 and PU6. However, the rheology experiments indicated that the solutions of the PU8 polymers did not show pseudoplastic behaviour.

6.2 FUTURE WORK

The research work carried out for this thesis showed that graft copolymers with MMA could be produced from polyurethane macromonomers containing on average one unit of unsaturation. The reactive unit had to be capable of copolymerisation with MMA in its monomeric form.

The synthesis of these macromonomers was an extension of the general step-growth solution polymerisation of polyurethanes. As a

result, the final polymer contained a distribution of doubly end-capped, singly end-capped, and non-end-capped molecules.

Future work should concentrate on the development of polyurethane macromonomers of the structures of PU5 and PU6 which contain only one terminal unsaturated end group per molecule. The production of this type of macromonomer may involve the use of a chemical support from which the polyurethane molecule would be grown. The polyurethane could then be terminated with the unsaturated group whilst still attached to the support. Otherwise, it could be terminated with an inert function, and then chemically released from the support to yield an active end group capable of undergoing further reaction.

An alternative method of producing the singly end-capped polyurethane macromonomers could be by exploiting the reactivity differences between various groups and the isocyanate group. This was used by Hudecek et al.[139,140] [see Chapter 2, section 2.2.1.3 (D)] and their work with polyester-urethanes.

Due to the difficulties encountered in isolating the graft copolymers and time considerations, characterisation tests were limited to the crude reaction products and the pure graft copolymers. It would be interesting, however, to see the effect of adding known quanitities of PMMA homopolymer to the above materials. It is hoped that the addition of PMMA homopolymer would reduce the opacity of the mixtures of products.

The results of the rheology tests indicated that there was a certain degree of aggregration of free polyurethane molecules with the graft copolymer molecules, even in solvents that were good for both polymeric species. If the solubility properties of the polyurethane were altered, it may be possible to effect a separation of the graft

copolymer from the free polyurethane by solvent extraction techniques. A polyurethane is required which is soluble in a non-solvent for PMMA. All solvents for the polyurethanes of this project were also solvents for PMMA.

GMM has proved to be a highly reactive monomer for inclusion into polyurethanes. Previous research into this compound has been very limited. Hence, its potential usefulness in polymer science has yet to be exploited. The monomer is not only invaluable in polyurethane chemistry, but can also be used to produce other functional polymers, such as polyesters.

Chapter 2 of this thesis described a selection of the various methods of producing graft copolymers. Investigations into the production of graft copolymers of polyurethanes and MMA using extensions of the other techniques discussed should be carried out. Thus, the development of polymers with enhanced properties will be continued.

APPENDIX I

PROGRAM TO CALCULATE THE AREA UNDER A PEAK OF A GPC CHROMATOGRAM BETWEEN TWO SPECIFIED POINTS

The following program was written for use with the TRIVECTOR TRILAB 2000 computer integrator, operating TRIVECTOR BASIC Version 6.45. The program was designed to analyse chromatograms that were either present in the computer's memory, or stored on 5.25" floppy disc. The program gave the user sets of instructions, and recognised when unreasonable data had been input.

After recognition of the sample, the program required the start and end times of the peak whose area was to be calculated. The portion of the chromatogram between these points was then split into smaller areas which were one data point in width (e.g. if the sampling rate was one data point per second, then the smaller areas were the equivalent of 1s in width). These areas were then considered to be trapeziums, and their individual areas calculated (by the rules of geometry, the area of a trapezium is half the sum of the parallel sides, multiplied by the perpendicular distance between them).

The area of the peak was then taken to be sum of the areas of the individual trapeziums. The program allowed a hardcopy of the required area to be printed.

```
10  REM *PROGRAM TO CALCULATE THE AREA OF A PEAK USING THE
        TRAPEZOIDAL RULE*
20  REM *WRITTEN 11th March 1987*
30  ----------------------------------------------------------------
40  PRINT "**********DETERMINATION OF THE AREA OF A PEAK**********"
50  DIM Y(100)
60  M=0, M1=0, M2=0, M3=0, N=0, S=0, S1=0, S2=0, S3=0, S4=0, V1=0,
    V2=0, E1=0, R=0
70  H=0, H1=0, H2=0, H4=0, H5=0, L=0, L1=0, K=0, K1=0, K2=0, Q=0
80  INPUT ("ENTER SAMPLE AREA CHANNEL AND NUMBER ")A$
```

```
 90  GOSUB 1000
100  GOSUB 2000
110  IF M1=1 THEN GOTO 100
120  IF M(1)=77 THEN GOTO 150
130  IF M(1)=68 THEN GOSUB 3000
140  REM *FIND SAMPLE AREA AND READ DATA*
150  OPEN IN#,GPCA,STORE,RAN,A$
160  SAMPLE #GPCA,Z1,B1$,B2$,C1,Z2,Z3,Z4,C2,Z5,Z6,Z7,S1,Z8,Z9
170  IF M(1)=77 THEN PRINT B2$
180  INPUT (ENTER START AND END TIMES OF PEAK ")V1,V2
190  IF V1>=V2 THEN PRINT "START TIME IS GREATER THAN END TIME!"
200  IF V1>=V2 GOTO 180
210  E=((V1/C1)-Z8)
220  RESTORE #GPCA,E
230  REM *CONVERT SAMPLING RATE FROM MS TO S*
240  C1=C1/100
250  REM *DATA COLLECTED FOR INDIVIDUAL TRAPEZIUMS AND THE AREA OF THE
          PEAK CALCULATED*
260  FOR I=0 TO C2 STEP C1
270  E1=E1+C1
280  INPUT #GPCA,Y(E1)
290  NEXT I
300  FOR J=V1 TO (V2-C1) STEP C1
310  R=(((Y(J)+Y(J+C1))/2)*C1)+R
320  NEXT J
330  REM *ALLOWANCES MADE FOR BASELINE*
340  IF Y(V1)>=Y(V2) THEN R=R-((V2-V1)*Y(V2))
350  IF Y(V2)>Y(V1) THEN R=R-((V2-V1)*Y(V1))
360  PRINT "THE REQUIRED ARE IS ";R
370  INPUT ("IS HARDCOPY REQUIRED (Y/N)? ")S$
380  GOSUB 4000
390  IF S4=1 THEN GOTO 370
400  IF S(1)=89 THEN GOSUB 5000
410  INPUT ("IS THERE ANOTHER AREA TO CALCULATE (Y/N)? "K$
420  CHANGE K$ TO K
430  IF K(1)=89 THEN CLOSE GPCA
440  IF K(1)=89 THEN GOTO 80
450  IF K(1)=78 THEN GOTO 500
460  IF K(1)<>89 THEN K1=1
470  IF K(1)<>78 THEN K2=1
480  IF (K1+K2)=2 THEN PRINT "ENTER YES OR NO ONLY!"
490  GOTO 410
500  END
510  ----------------------------------------------------------------
1000 REM *CHECK THAT SAMPLE AREA IS VALID*
1010 H$=SUBSTR$(A$,1,1)
1020 CHANGE H$ TO H
1030 IF H(1)<>65 THEN H1=1
1040 IF H(1)<>66 THEN H2=1
1050 IF H(1)<>67 THEN H3=1
1060 IF H(1)<>68 THEN H4=1
1070 H5=(H1+H2+H3+H4)
1080 IF H5=4 THEN PRINT "INVALID SAMPLE AREA CHANNEL"
1090 IF H5=4 THEN GOTO 80
1100 Q=LEN(A$)
1110 L$=SUBSTR$(A$,2,(Q-1))
1120 L=VAL(L$)
1130 IF L<001 THEN L1=1
1140 IF L>999 THEN L1=1
1150 IF L1=1 THEN PRINT "INVALID SAMPLE NUMBER"
```

```
1160  IF L1=1 THEN GOTO 80
1170  RETURN
1180  ------------------------------------------------------------
2000  REM *CHECK WHETHER SAMPLE IS ON DISC OR IN MEMORY*
2010  INPUT ("ENTER 'M' IF SAMPLE IS IN MEMORY OR 'D' IF IT IS STORED
      ON DISC ")M$;
2020  CHANGE M$ TO M
2030  IF M(1)<>77 THEN M2=1
2040  IF M(1)<>68 THEN M3=1
2050  IF (M2+M3)=2 THEN M1=1
2060  IF M(1)=77 THEN M1=0
2070  IF M(1)=68 THEN M1=0
2080  IF M1=1 THEN PRINT "ENTER 'M' OR 'D' ONLY!"
2090  RETURN
2100  ------------------------------------------------------------
3000  REM *OPENS FILE FROM DISC*
3010  INPUT ("PLACE APPROPRIATE DISC IN DRIVE 1 THEN PRESS '*' ")R$
3020  CHANGE R$ TO N
3030  IF N(1)<>42 THEN PRINT "PRESS '*' ONLY!"
3040  IF N(1)<>42 THEN GOTO 3010
3050  IF N(1)=42 THE D$="Z1:"
3060  P$=D$&A$
3070  F$="0"
3080  CALL SLOAD,F$,P$
3090  RETURN
3100  ------------------------------------------------------------
4000  REM *CHECK FOR HARDCOPY*
4010  CHANGE S$ TO S
4020  IF S(1)<>89 THEN S2=1
4030  IF S(1)<>78 THEN S3=1
4040  IF (S2+S3)=2 THEN S4=1
4050  IF S(1)=89 THEN S4=0
4060  IF S(1)=78 THEN S4=0
4070  IF S4=1 THEN PRINT "ENTER YES OR NO ONLY!"
4080  RETURN
4090  ------------------------------------------------------------
5000  REM *TO GIVE HARDCOPY*
5010  DEVICE 1
5020  PRINT "THE AREA OF SAMPLE ";A$;B$;" BETWEEN THE LIMITS ";V1;"
      AND ";V2;" IS ";R
5030  DEVICE 0
5040  RETURN
5050  ------------------------------------------------------------
```

APPENDIX II

PROGRAM TO CALCULATE THE SECANT MODULUS, BREAKING STRAIN, AND BREAKING STRESS OF SAMPLES THAT WERE SUBJECTED TO IMPACT TESTS, USING THE RAW DATA OBTAINED FROM THE IMPACT TESTER

The following program was used to calculate the results for the impact tests performed described in Chapter 4. It has been written for operation on a BBC Model B microcomputer.

```
 10  REM *PROGRAM TO CALCULATE SECANT MODULUS AND BREAKING STRESS AND
          STRAIN FROM THE RAW IMPACT TESTER DATA*
 20  REM *CREATE VARIABLES*
 30  S$="": PD=0: PF=0: B=10: D=0: T=0: E=0: P=0: SS=0: SS2=0: SN=0:
     MD=0: MD2=0
 40  REM *INPUT DATA*
 50  INPUT "SAMPLE NAME ",S$
 60  INPUT "ENTER PEAK DISPLACEMENT, PD (mm) "PD
 70  INPUT "ENTER PEAK FORCE, PF (N) "PF
 80  INPUT "ENTER SAMPLE DEPTH (mm) "D
 90  REM *CALCULATE TAN(X)*
100  T=(28.7+PD)/20
110  REM *CALCULATE EXTENSION RATIO*
120  E=(4/7)*SQR(1+T^2)
130  REM *CALCULATE STRAIN*
140  SN=E-1
150  REM *CALCULATE % EXTENSION*
160  P=(E-1)*100
170  REM *CALCULATE STRESS IN N/mm^2*
180  SS=(PF*SQR(1+T^2))/(2*B*D*T)
190  REM *CONVERT STRESS INTO N/m^2*
200  SS2=SS*1000000
210  REM *CALCULATE SECANT MODULUS IN N/mm^2*
220  MD=SS/SN
230  REM *CONVERT SECANT MODULUS INTO N/m^2*
240  MD2=MD*1000000
250  REM *PRINT RESULTS*
260  VDU2
270  PRINT "FOR SAMPLE: ";S$
280  PRINT "BREAKING STRAIN= ";SN
290  PRINT "% EXTENSION ON BREAKING= ";P
300  PRINT "BREAKING STRESS= ";SS;" N/mm^2"
310  PRINT "BREAKING STRESS= ";SS2;" N/m^2"
320  PRINT "SECANT MODULUS= ";MD;" N/mm^2"
330  PRINT "SECANT MODULUS= ";MD2;" N/m^2"
340  PRINT
350  VDU3
360  STOP
```

REFERENCES

1 BAYER, O., Angew. Chem. A59, 275, (1947)

2 BAYER, O., RINKE, H., SIEFKEN, W., ORTHNER, L., SCHILD, H., DE 728,981 (1937)

3 SAUNDERS, J.H., FRISCH, K.C., "Polyurethanes: Chemistry and Technology Part 1: Chemistry", Vol. XVI of the series "High Polymers", John Wiley & Sons (1962)

4 WOODS, G., "The ICI Polyurethanes Book", published jointly by ICI Polyurethanes and John Wiley & Sons (1987)

5 SAUNDERS, K.J., "Organic Polymer Chemistry", Chapter 14, Chapman and Hall Ltd. (1973)

6 HEPBURN, C., "Polyurethane Elastomers", Applied Science Publishers Ltd. (1982)

7 REDMAN, R.P., "Developments in Polyurethane Elastomers", Chapter 3 of "Developments in Polyurethane-1", Ed. BUIST, J.M., Applied Science Publishers Ltd. (1978)

8 ADIBI, K., PhD Thesis, University of London (1979)

9 EGBOH, H.S., PhD Thesis, University of London (1982)

10 BUTLER, C., PhD Thesis, University of London (1987)

11 UNION CARBIDE, US 3,523,924 (1970)

12 WALSH, D.J., "Newer Synthetic Routes to Isocyanates and Urethanes", Chapter 2 of "Developments in Polyurethane-1", Ed. BUIST, J.M., Applied Science Publishers Ltd. (1978)

13 LYMAN, D.J., J.Polym.Sci. 45, 49, (1960)

14 WURTZ, A., Ann. 71, 326, (1849)

15 FRISCH, K.C., KRESTA, J.E., WONGKAMOLSECH, K., University of Detroit, Unpublished Data (From the technical data manual for Isocyanato-ethyl methacrylate, published by Dow Chemical, USA.)

16 ARNOLD, R.G., NELSON, J.A., VERBANC, J.J., Chem.Revs. 57, 47, (1957)

17 PETROVIC, Z.S., BUDINSKI-SIMENDIC, J., Rubber Chem.Tech. 58, 685, (1985)

18 SHEARD, E., Chem.Tech. 298, (1973)

19 PECHHOLD, E., PRUCKMAYER, G., Rubber Chem.Tech. 55, 76, (1982)

20 PETROVIC, Z.S., BUDINSKI-SIMENDIC, J., Rubber Chem.Tech. 58, 701, (1985)

21 TAKAHARA, A., TASHITA, J., KOYIYAMA, T., TAKAYANGI, M.,

MACKNIGHT, W.J., Polymer 26, 978, (1985)

22 YILGOR, I., McGRATH, J.E., J.Appl.Polym.Sci. 30, 1733, (1985)

23 SATO, M., J.Am.Chem.Soc. 82, 3893, (1960)

24 HOSTETTLER, F., COX, E.F., Rubber World 140, 87, (1959)

25 SEYMOUR, R.W., ESTES, G.M., COOPER, S.L., Macromol. 3, 579, (1970)

26 BONART, R., MORBITZER, L., MULLER, E.H., J.Macromol.Sci.-Phys. 9, 447, (1974)

27 KAMPF, G., "Characterisation of Plastics by Physical Methods", Hanser (1986)

28 SUMI, M., CHOKKI, Y., NAKAI, Y., NAKABAYASHI, M., KANZAWA, T., Makromol.Chem. 78, 146, (1964)

29 DELIDES, C., PETHRICK, R.A., CUNLIFFE, A.V., KLEIN, P.G., Polymer 22, 1205, (1981)

30 GRANT, D.M., PAUL, E.G., J.Am.Chem.Soc. 86, 2984, (1964)

31 GRANT, D.M., LITCHAM, W.M., J.Am.Chem.Soc. 90, 1400, (1968)

32 MILLER, J.A., LIN, S.B., HWANG, K.K.S., WU, K.S., GIBSON, P.E., COOPER, S.L., Macromol. 18, 32, (1985)

33 GIBSON, P.E., VALLANCE, M.A., COOPER, S.L., "Morphology and Properties of Polyurethane Block Copolymers", Chapter 6 of "Developments in Block Copolymers-1", Ed. GOODMAN, I., Applied Science Publishers (1982)

34 ALLEGREZZA, A.E.Jr., SEYMOUR, R.W., NG, H.N., COOPER, S.L., Polymer 15, 433, (1974)

35 SEYMOUR, R.W., COOPER, S.L., Macromol. 6, 48, (1973)

36 MACKNIGHT, W.J., YANG, M., KAJIYAMA, T., Polym.Prepr. 9, 860, (1968)

37 HUH, D.S., COOPER, S.L., Polym.Eng.Sci. 11, 369, (1971)

38 SAMUELS, S.L., WILKES, G.L., J.Polym.Sci. C43, 149, (1973)

39 NG, H.N., ALLEGREZZA, A.E., SEYMOUR, R.W., COOPER, S.L., Polymer 14, 255, (1973)

40 BILLMEYER, F.W.Jr., "Textbook of Polymer Science" 3rd Edition, John Wiley and Sons (1984)

41 WINDING, C.C., HIATT, G.D., "Polymeric Materials", McGraw-Hill (1961)

42 COWIE, J.M.G., "Polymers: Chemistry and Physics of Modern Materials", International Textbook Co. Ltd. (1973)

43 BENDIT, E.G., J.Macromol.Sci.-Phys. B17, 129, (1980)

44 SEYMOUR, R.W., ALLEGREZZA, A.E.Jr., COOPER, S.L., Macromol. 6, 896, (1973)

45 SEYMOUR, R.W., COOPER, S.L., Rubber Chem.Tech. 47, 19, (1974)

46 FU, B., MACKNIGHT, W.J., SCHNEIDER, N.S., Rubber Chem. Tech. 59, 896, (1986)

47 PETROVIC, Z.S., FERGUSON, J., Hem.Ind. 32, 531, (1978)

48 KOUTSKY, J.A., HIEN, N.V., COOPER, S.L., J.Polym.Sci. B8, 353, (1970)

49 SCHNEIDER, N.S., DESPER, C.R., ILLINGER, J.L., KING, A.O., BARR, D., J.Macromol.Sci.-Phys. B11, 527, (1975)

50 PAUL, S., "Surface Coatings: Science and Technology", Wiley (1985)

51 SAUNDERS, K.J., "Organic Polymer Chemistry", Chapman and Hall (1973)

52 BOLKER, H.I., "Natural and Synthetic Polymers - An Introduction", Marcel Dekker Inc. (NY) (1974)

53 KLEIN, D.H., JPT, 42(545), 335, (1970)

54 EDWARDS, W.M., Chapter 9 of "Technology of Paints, Varnishes, and Lacquers", Ed. MARTENS, R., Book Corp. (1968)

55 WAKEMAN, R.L., "The Chemistry of Commercial Plastics", Reinhold Publishing Corp. (NY) (1947)

56 SLOMIN, I.Ya., LYUBIMOV, A.N., "The NMR of Polymers", Plenum Press (NY) (1970)

57 LEVY, G.C., J.Am.Chem.Soc. 95, 6117, (1973)

58 LYERLA, J.R.Jr., HONKAWA, T.T., JOHNSON, D.E., J.Am.Chem. Soc. 99, 2463, (1973)

59 INOUE, Y., KONNO, T., CHUJO, R., NISHOKA, A., Makromol.Chem. 178, 213, (1977)

60 FOX, T.G., GARRETT, B., GOODE, W., GRATCH, S., KINCAID, J., SPELL, A., STROUPE, J., J.Am.Chem.Soc. 80, 1768, (1958)

61 HUMMEL, D.O., "Infra-red Spectra of Polymers in the Medium and Long Wavelength Regions", Interscience Publishers (1966)

62 BOVEY, F.A., J.Polym.Sci. 46, 59, (1960)

63 FOX, T.G., SCHINEKO, H.W., Polymer 3, 575, (1962)

64 BAWN, C.E.H., LEDWITH, A., Quarterly Rev. 16, 361, (1962)

65 BUTLER, K., THOMAS, R.R., TYLER, G.J., J.Polym.Sci. 48, 357, (1960)

66 SCHUERCH, C., Ann.Rev.Phys.Chem. 13, 195, (1962)

67 FOX, T.G., GOODE, W., GRATCH, S., HUGGETT, C., KINCAID, J., SPELL, A., STOUPE, J., J.Polym.Sci. 31, 173, (1958)

68 MILLER, R.G.J., MILLS, B., SMALL, P., TURNER-JONES, A., WOOD, D., Chem.Ind. 1958, 1323

69 BAUMANN, U., SCHREIBER, H., TESSMAR, K., Makromol.Chem. 36, 81, (1960)

70 KOROTKOV, A.A., MITSENGENDLER, C.P., KRASULINA, V.N., VOLKOVA, L.A., Polym.Sci.USSR 1, 506, (1960)

71 HUMMEL, D., BUSSE, A., "Far IR Spectra of Polymers and Resins and Their Analytical Use", International Symposium on Far IR Spectroscopy, Cincinnati, Ohio (Aug. 1962)

72 SHETTER, J.A., J.Polym.Sci. B1, 209, (1963)

73 KARASZ, F.E., MACKNIGHT, W.J., Macromol. 1, 537, (1968)

74 YOON, D.Y., FLORY, P.J., Polymer 16, 645, (1975)

75 BYWATER, S., TOPOROWSKI, P.M., Polymer 13, 94, (1972)

76 FERNANDEZ-MARTIN, F., FERNANDEZ-PIEROCA, I., HORTA, A., J.Polym.Sci., Polym.Phys. 19, 1353, (1981)

77 FOX, T.G., Bull.Am.Phys.Soc. 1, 123, (1956)

78 BAZUIN, C.G., EISENBERG, A., Ind.Eng.Chem.Prod.Res.Dev. 20, 271, (1981)

79 SOLOMON, D.H., "The Chemistry of Organic Film Formers", R.E. Krieger Pub. Co. (NY) (1977)

80 PAUL, S., Prog.Org.Coat. 5(1), 79, (1977)

81 GRIFFITH, R.K., J.Appl.Polym.Sci. 12, 1939, (1968)

82 GRIFFITH, R.K., ZORSKA, R., J.Appl.Polym.Sci. 13, 1159, (1969)

83 DJOMO, H., MORIN, A., DAMYANIDU, M., MEYER, G., Polymer 24, 65, (1983)

84 CERESA, R.J., "Block and Graft Copolymers", Butterworths (1962)

85 HAM, G.E., "Copolymerization", Volume XVIII of "High Polymers", Interscience Pub. (1964)

86 FLORY, P.J., J.Am.Chem.Soc. 59, 241, (1937)

87 SMETS, G., ROOVERS, J., VAN HUMBEEK, W., J.Appl.Polym.Sci. 5, 149, (1961)

88 BEVINGTON, J.C., MELVILLE, H.W., TAYLOR, R.P., J.Polym.Sci. 12, 449, (1954)

89 BEVINGTON, J.C., MELVILLE, H.W., TAYLOR, R.P., J.Polym.Sci. 14, 463, (1954)

90 CERESA, R.J., "Block and Graft Copolymerization" Vol. 1, Wiley (1973)

91 ANBAZHAGAN, K., REDDI, C.R., JOSEPH, K.T., Leather Sci. 30, 56, (1983)

92 ANBAZHAGAN, K., REDDY, C.R., JOSEPH, K.T., J.Appl.Polym.Sci 30, 391, (1985)

93 KURYLA, W.C., CRITCHFIELD, F.E., PLATT, L.W., STAMBERGER, P. J.Cellular Plast. 2, 84, (1966)

94 ALLEN, G., BOWDEN, M.J., LEWIS, G., BLUNDELL, D.J., JEFFS, G.M. Polymer 15, 13, (1974)

95 MORIMOTO, A., KITAGAWA, Y., ITO, J., ASAGAWA, T., JP 48/31288 (1973)

96 KURIYAMA, S., NAKAJIMA, S., KOYAMA, T., MURATA, T., JP 61/200116 (1986)

97 KATAYAMA, S., NOMURA, S., KISHI, K., TSUTSUMI, J., JIN, K., JP 54/90287 (1979)

98 BRYDON, A., CAMERON, G.G., Prog.Polym.Sci. 4, 209, (1975)

99 BEVINGTON, J.C., J.Chem.Soc. 3707, (1954)

100 VAN DER HOFF, B.M.E., Appl.Polym.Symposia 7, 21, (1968)

101 WETTON, R.E., MOORE, J.D., FOX, B.E., Makromol.Chem. 132, 135, (1970)

102 MANARESI, P., PASSALACQUA, V., SIMONAZZI, T., Chimica Ind.Milano 51, 351, (1969)

103 SMETS, G., SCHMETS, J., Bull.Soc.Chim.Belg. 62, 358, (1953)

104 EGBOH, S.H.O., J.Macromol.Sci.-Chem. A19, 1041, (1983)

105 EGBOH, S.H., Die Angew.Makromol.Chem. 117, 95, (1983)

106 EGBOH, S.H., GEORGE, M.H., BARRIE, J.A., WALSH, D.J., Makromol. Chem. 184, 725, (1983)

107 EGBOH, H.S., GEORGE, M.H., BARRIE, J.A., WALSH, D.J., J.Polym. Sci. A20, 2879, (1982)

108 GUJRAL, A.S., PhD Thesis, University of London (1984)

109 DAVISON, I.R., Unpublished Results, Dept. of Chemistry, Imperial College, London (Dec. 1985)

110 BEACHELL, H.C., PETERSON-BUCK, J.C., J.Polym.Sci. A7, 1873, (1969)

111 BEACHELL, H.C., BLUMSTEIN, R., PETERSON, J.C., J.Polym.Sci. C22, 569, (1969)

112 HITACHI LTD., JP 57/61019 (1982)

113 TOYODA GOSEI CO. LTD. JP 57/21470 (1982)

114 KURIYAMA, K., ICHIHARA, M., MISAIZU, I., KASHIWAMURA, M., JP 61/115917 (1986)

115 TAKAI, T., JP 62/25113 (1987)

116 YAMASHITA, Y., J.Appl.Polym.Sci. 36, 193, (1981)

117 REMPP, P., FRANTA, E., Adv.Polym.Sci. 58, 1, (1984)

118 REMPP, P., LUTZ, P., MASSON, P., CHAUMONT, P., FRANTA, E., Makromol.Chem.Suppl. 13, 47, (1985)

119 WAACK, R., DORAN, M.A., Polymer 2, 365, (1961)

120 WAACK, R., US 3,235,626 (1966)

121 WAACK, R., DORAN, M.A., J.Org.Chem. 32, 3395, (1967)

122 ANDERSON, B.C., ANDREWS, G.D., ARTHUR, P.Jr., JACOBSON, H.W., MELBY, L.R., PLAYTIS, A.J., SHARKEY, W.H., Macromol. 14, 1599, (1981)

123 QUIRK, R.P., CHIEN, W.C., Makromol.Chem. 183, 2071, (1982)

124 SPACH, G., LEVY, M., SZWARC, M., J.Chem.Soc. 1962, 355

125 BURGESS, F.J., CUNLIFFE, A.V., RICHARDS, D.H., THOMPSON, D., Polymer 19, 334, (1978)

126 ASAMI, R., TAKAKI, M., 27th IUPAC Symp. on Macromols., Strasbourg (1981), Preprints I, p. 270

127 KATZ, D., ZEWI, I.G., J.Polym.Sci. A16, 597, (1978)

128 KENNEDY, J.P., Polym.J. 12, 609, (1980)

129 KENNEDY, J.P., 5th Int. Symp. on Cationic Polym., Kyoto (1980), Preprints p. 6

130 KENNEDY, J.P., SMITH, R.A., ACS Polym.Prepr. 20, 316, (1979)

131 KENNEDY, J.P., FRISCH, K.Jr., IUPAC Symp. on Macromols., Firenze (1980), Preprints II p. 162

132 BROSSE, J.C., BAUNIER, M., LEGEAY, G., Makromol.Chem. 182, 3457, (1981)

133 BROSSE, J.C., BAUNIER, M., LEGEAY, G., Makromol.Chem. 183, 303, (1982)

134 GILLMAN, K.F., SENOGLES, E., Polym.Lett. 5, 477, (1967)

135 CHUJO, Y., TATSUDA, T., YAMASHITA, Y., Polym.Bull. 8, 239, (1982)

136 YAMASHITA, Y., CHUJO, Y., KOBAYASHI, H., KAWAKAMI, Y., Polym. Bull. 5, 361, (1981)

137 BAMFORD, C.H., WHITE, E.F.T., Trans.Faraday Soc. 52, 716, (1956)

138 CACIOLI, P., HAWTHORNE, D.G., LASLETT, R.L., RIZZARDO, E., SOLOMON, D.H., J.Macromol.Sci.-Chem. A23, 839, (1986)

139 HUDECEK, S., SPEVACEK, J., HUDECKOVA, I., Prepr. Short Contrib. - Bratislava IUPAC Int. Conf. Modif. Polym., 5th, Vol. 1, 159-63, Slov. Akad. Vied., Ustav. Polym. Bratislava, Czech. (1979)

140 HUDECEK, S., SPEVACEK, J., HUDECKOVA, I., MIKESOVA, J., Polym. Bull. 3, 143, (1980)

141 HUDECEK, S., HUDECKOVA, I., CEFELIN, P., Izv.Akad.Nauk.Kaz. SSR, Ser.Khim. (5), 53, (1981)

142 HUDECKOVA, I., CEFELIN, P., HUDECEK, S., GB 2,099,437 (1982)

143 HUDECEK, S., HUDECKOVA, I., CEFELIN, P., US 4,584,354 (1986)

144 HUDECEK, S., HUDECKOVA, I., OTOUPALOVA, J., CEFELIN, P., DE 3,602,512 (1986)

145 HAYES, M., Third Year Undergraduate Research Exercise Report, Dept. of Chem., Imperial College, London (1986)

146 THEODORE, A.N., CHATTA, M.S., J.Coat.Technol. 57(721), 67, (1985)

147 MASLYUK, A.F., SOPINA, I.M., RUDNEVA, S.P., BELOV, I.B., Plast. Massy (8), 10, (1978)

148 SOROKIN, M.F., SHODE, L.G., ONOSOVA, L.A., GUSEVA, O.F., Deposited Doc. VINITI 1836, (1979)

149 METZ, D.T., MESROBIAN, R.B., J.Polym.Sci. 16, 345, (1955)

150 MANSOUR, O.Y., NAGATY, A., Prog.Polym.Sci. 11, 91, (1985)

151 SMETS, G., POOT, A., MULLIER, M., BEX, J.P., J.Polym.Sci. 34, 287, (1959)

152 POOT, A., Thesis, University of Louvain (1958)

153 SUN, Y.H., QIU, K.Y., FENG, X.D., Polym.Commun.(Beijing), 1983(2), 81

154 FENG, X.D., VOONG, S.T., SUN, Y.H., QIU, K.Y., Makromol.Chem. 186, 1533, (1985)

155 HUANG, Z., CHEN, H., YANG, G., Shiyou Huagong 15, 725, (1986)

156 VALENTINE, L., CHAPMAN, B., Results reported at IUPAC Macromolecular Symp., Milan - Turin (1954), Ric. Sci. (1955), 25 Supplement 278

157 SIMIONESCU, C.I., COMANITA, E., PASTRAVANU, M., DUMITRIU, S., Prog.Polym.Sci. 12, 1, (1986)

158 LENKA, S., NAYAK, P.L., J.Macromol.Sci.-Revs.Macromol. Chem.and Phys. C25, 157, (1985)

159 GHOSH, D., GHOSH, T.K., J.Macromol.Sci.(Chem.) A17, 847, (1982)

160 RATNER, B.D., BALISKY, T., HOFFMAN, A.S., J.Bioeng. 1, 115, (1977)

161 FENG, X.D., SUN, Y.H., QIU, K.Y., Macromol. 18, 2105, (1985)

162 OGURA, T., JP 50/34629 (1975)

163 BAMFORD, C.H., "Organometallic Derivatives of Transition Metals as Initiators of Free-Radical Polymerisation", Chapter 3 of "Reactivity, Mechanism, and Structure in Polymer Chemistry", Eds. JENKINS, A.D., LEDWITH, A., Wiley (1974)

164 BAMFORD, C.H., MIDDLETON, I.P., Eur.Polym.J. 19(10/11), 1027, (1983)

165 SKRABA, W.J., LYNN, J.W., Adv.Chem.Ser. 66, 214, (1967)

166 CHAPIRO, A., J.Polym.Sci. 29, 321, (1958)

167 HAYAKAWA, K., YAMAKITA, H., J.Appl.Polym.Sci. 21, 665, (1977)

168 SHARMA, C.P., NAIR, A.K., J.Colloid and Interf.Sci. 104, 277, (1985)

169 JANSEN, B., ELLINGHORST, G., Radiat.Phys.Chem. 18, 1195, (1981)

170 JANSEN, B., Polym.Sci.Technol.(Plenum), 23(Polym.Med.), 287, (1983)

171 JANSEN, B., Adv.Biomater. 5(Biomater.Biomech.1983),415, (1984)

172 JANSEN, B., LUDWICKA, A., STORZ, L.W., Radiat.Phys.Chem. 25, 529, (1985)

173 EGBOH, S.H., GEORGE, M.H., BARRIE, J.A., Polymer 25, 1157, (1984)

174 PARRY, A., "Anionic Polymerisation", Chapter 11 of "Reactivity, Mechanism, and Structure in Polymer Chemistry", Eds. JENKINS, A.D., LEDWITH, A., Wiley (1974)

175 FINAZ, G., GALLOT, Y., PARROD, J., REMPP, P., J.Polym.Sci. 58, 1363, (1962)

176 HAAS, H.C., KAMATH, P.M., SCHULER, N.W., J.Polym.Sci. 24, 85, (1957)

177 KAMATH, P.M., HAAS, H.C., J.Polym.Sci. 24, 143, (1957)

178 KOCKELBERGH, G., SMETS, G., J.Polym.Sci. 33, 227, (1958)

179 JONES, M.H., Canad.J.Chem. 34, 948, (1956)

180 GUILLET, J.E., NORRISH, R.G.W., Nature (Lond.) 173, 625, (1954)

181 GUILLET, J.E., NORRISH, R.G.W., IUPAC Macromolecular Symp. Milan - Turin (1954), Ric. Sci. 25, Supplement, 250, (1955)

182 GUILLET, J.E., NORRISH, R.G.W., Proc.Roy.Soc. A 233, 172, (1955)

183 MILLER, M.L., Canad.J.Chem. 36, 303, (1958)

184 CRAUBNER, H., J.Polym.Sci. A18, 2011, (1980)

185 CRAUBNER, H., J.Polym.Sci. A20, 1935, (1982)

186 KAWAGUCHI, T., ITOI, K., JP 48/17553 (1973)

187 AKCELRUD, L., GOMES, A.S., J.Polym.Sci. A24, 2831, (1986)

188 AKCELRUD, L., GOMES, A.S., J.Polym.Sci. A24, 2845, (1986)

189 CAMPBELL, D.S., LOEBER, D.E., TINKER, A.J., Polymer 19, 1106, (1978)

190 CAMPBELL, D.S., LOEBER, D.E., TINKER, A.J., Polymer 20, 393, (1979)

191 MENDIS, L.P., PEMAWANSA, K.P.W., HETTIARACHCHI, S., Polymer 18, 100, (1977)

192 MARK, M.F., GAYLORD, N.G., BIKALES, N.M., (Eds), "Encyclopedia of Polymer Science and Technology: Plastics, Resins, Rubbers, Fibers" Vol. 2, Amino Resins to Casein, Wiley, (1965)

193 YANAGITA, M., KAWABE, H., SHINOHAR, K., TAKAMATSU, T., Sci. Papers Inst.Phys.Chem.Res.(Tokyo) 56, 218, (1962)

194 PAYAK, J., Chem.in Brit. 23, 122, (1987)

195 TURNER, G.P.A., "Introduction to Paint Chemistry", 2nd Edn., Chapman and Hall (1980)

196 MORGANS, W.M., "Outlines of Paint Technology", Vol. 2, 2nd Edn., Charles Griffin and Co. Ltd. (1984)

197 MORGANS, W.M., "Outlines of Paint Technology", Vol. 1, 2nd Edn., Charles Griffin and Co. Ltd. (1982)

198 PATTON, T.C., "Paint Flow and Pigment Dispersion", Wiley NY (1979)

199 FERRY, J.D., "Viscoelastic Properties of Polymers", 2nd Edn., Wiley (1970)

200 LENK, J.D., "Polymer Rheology", Applied Science Publishers Ltd. (1978)

201 FOX, T.G., GRATCH, S., LOSHAEK, S., "Viscosity Relationships for Polymers in Bulk and in Concentrated Solution", Chapter 12 of "Rheology - Theory and Applications", Vol. 1, Ed. EIRICH, F.R. Academic Press (1956)

202 WILLIAMS, M.L., LANDEL, R.F., FERRY, J.D., J.Am.Chem.Soc. 77, 3701, (1955)

203 BISSINGER, W.E., FREDENBERG, R.H., KADESCH, R.G., KUNG, F., LANGSTON, J.H., STEVENS, H.C., STRAIN, F., J.Am.Chem.Soc. 69, 2955, (1947)

204 MANN, F.G., SAUNDERS, B.C., "Practical Organic Chemistry" 4th Edn., Longmans (1960), p. 48

205 WATERS ASSOCIATES, Manual for the Prep-LC/System 500

206 KEMP, W., "Qualitative Organic Analysis", Revised Edn., McGraw and Hill (1979)

207 SIMONS, W.W., ZANGER, M., "The Sadtler Guide to the NMR Spectra of Polymers", Sadtler Research Laboratories Inc. (1973)

208 LEVY, G.C., LICHTER, R.L., NELSON, G.L., "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd Edn., p. 196, Wiley (1980)

209 PANG, S., Third Year Undergraduate Research Exercise Report, Department of Chemistry, Imperial College, London (1987)

210 GEGONIS, D.E., CHEN, C.M., ANDRADE, J.D., Polym.Prepr., Am.Chem.Soc.,Div.Polym.Chem. 16, 349, (1975)

211 REFOJO, M.F., J.Appl.Polym.Sci. 9, 3161, (1965)

212 HILD, G., Makromol.Chem. 177, 1945, (1976)

213 BEINERT, G., HILD, G., REMPP, P., Makromol.Chem. 175, 2069, (1974)

214 MACRET, M., HILD, G., Polymer 23, 81, (1982)

215 SOUTIF, J.C., OUCHATAR, L., COUVERT, D., BROSSE, J.C., Makromol.Chem. 187, 561, (1986)

216 DESCHENAUX, R., STILLE, J.K., J.Org.Chem. 50, 2299, (1985)

217 ATKINS, P.W., "Physical Chemistry", 2nd Edn., Oxford University Press (1982)