

PRESSURE DEPENDENCE OF PHASE SEPARATION IN
BINARY POLYMER BLENDS

Gladys Enuma M'BAMALI

Department of Chemical Engineering
and Chemical Technology
Imperial College
London

Submitted for the Degree of Doctor of Philosophy
of the University of London

June 1989

ABSTRACT

The effects of pressure on the miscibility limits of high molecular weight blends of polystyrene (PS) – poly(vinyl methyl ether)(PVME) have been investigated, by turbidimetry, using a high pressure apparatus designed for operation at pressures up to 3 Kbar and temperatures up to 280°C.

In the molecular weight range studied, this system shows a Lower Critical Solution Temperature (LCST) behaviour.

The phase boundary was raised with an increase in the molecular weight of PVME, with a decrease in the molecular weight of PS, with deuteration and with pressure. The pressure dependence of the LCST, $(\partial T/\partial P)_c$, at the critical composition, was found to be + 0.023 degree atm⁻¹ for hydrogenous PS–PVME blend and + 0.038 degree atm⁻¹ for perdeuterated PS–PVME blend.

The interaction parameters, deduced from measured heats of mixing of the oligomeric mixtures and from Small Angle Neutron Scattering (SANS) measurements of the high molecular weight blends, were found to be favourable for mixing.

The volume contractions on mixing were quantified by density measurements and by the effect of pressure on the cloud point.

Flory's equation of state theory with an entropy correction factor was used to calculate the volume contraction on mixing and the residual thermodynamic quantities.

Computer programs, based on this model, were written for the simulation of the miscibility – temperature – pressure – concentration diagrams, in order to be able to interpret the pressure data using modern thermodynamic theories.

The merits and inherent difficulties of this model were discussed prior to suggestions for improvements, including a need for a completely new model to explain the thermodynamic quantities of blends with specific interactions.

ACKNOWLEDGEMENTS

I gratefully acknowledge the guidance, untiring assistance and constant encouragement of my supervisor, Professor J.S. Higgins.

I would like to thank Dr A Macconachie for her helpful suggestions.

My thanks are also due to:

Ms J. Clarke, for obtaining the SANS data; Dr R Hill for the use of the density gradient column; Drs S. Rostami, P. Musonge and P. Tomlins for useful discussions; the technical staff, especially Mr P. Amrit and Mr S. Roach.

I am grateful to Mrs E. Tustin for patiently typing the manuscript. Finally, I thank my entire family for their understanding, support and encouragement at all times.

CONTENTS

Abstract	i
Acknowledgements	iii
Contents	iv
List of Figures	x
List of Tables	xiv
List of Symbols	xvi
List of Abbreviations	xvii
Chapter 1 Introduction	1
1.1 General	1
1.2 Objectives and scope of work	4
1.3 Layout of the thesis	5
Chapter 2 Theoretical background	6
2.1 General	6
2.2 Thermodynamic theories of binary mixtures	10
2.2.1 Ideal solutions	10
2.2.2 Regular solution (solubility parameter) theory	11
2.2.3 Flory–Huggins 'lattice' theory of polymer solutions	13
2.2.4 Free–volume theories	17
2.2.5 Flory's equation–of–state	20
2.2.6 Application of the 'theory' to cloud point	27
Chapter 3 General background	30
3.1 Binary polymer blends	30
3.2 Phase diagrams	31

3.3	Critical solution phenomenon in binary systems	31
3.4	Preparation of blends	33
3.4.1	Melt mixing	34
3.4.2	Casting from a common solvent or emulsions	34
3.4.3	In situ polymerisation	35
3.5	Miscibility criteria and their determination	37
3.5.1	Optical clarity	37
3.5.2	Glass transition determinations	39
3.6	Infra-red spectroscopy	43
3.7	Microscopy	44
3.8	Fluorescence methods	46
3.9	The present system	46
3.10	Effect of pressure on phase separation temperature of polymer systems	53
3.11	Effect of pressure on miscibility	56
3.12	Effect of pressure on static properties of polymer systems—virial coefficient and chain dimensions	59
3.13	Effect of pressure on the viscosity of polymer systems	61
3.14	Effect of pressure on dynamic properties of polymer systems	61
3.15	The effect of pressure on T_g and dielectric relaxation time of polymer systems	62
Chapter 4 Description of the equipment		63
4.1	The pressure rig	63
4.2	The pressure reactor	67

4.3	The sample loading assembly	71
4.4	The heating system	72
4.5	Instrumentation	75
4.6	Sapphire window housing	76
4.7	Optical alignment	76
4.8	The Pressure line	81
Chapter 5	Experimental	83
5.1	The polymers	83
5.2	Materials	84
5.3	General	86
5.4	Turbidimetry	86
5.5	Experiments on the pressure rig	87
5.5.1	Effect of rate of heating on T_c	89
5.5.2	Effect of initial temperature on T_c	90
5.5.3	Effect of sample thickness on T_c	91
5.5.4	Application of pressure	92
5.6	Light scattering turbidimetry	93
5.6.1	Effect of molecular weight of PS on the phase boundary	95
5.6.2	Effect of molecular weight of PVME on the phase boundary	96
5.7	Heat (enthalpy) of mixing, ΔH_m	97
5.7.1	Experimental	98
5.8	Scanning electron microscopy	99
5.9	Optical microscopy	100
5.10	Differential scanning calorimetry (DSC)	102
5.11	Heating/cooling cycles	102

5.12	Dynamic Mechanical Thermal Analysis (DMTA)	102
5.13	Small Angle Neutron Scattering (SANS)	106
5.13.1	Experimental	108
5.14	Density measurements	111
Chapter 6	Results and discussion	113
6.1	Results of preliminary tests	113
6.2	Effect of molecular weight (of PS) on the LCST of PS–PVME blends	114
6.3	Effect of molecular weight (of PVME) on the miscibility of PS–PVME blends	117
6.4	Temperature dependence of transmitted light intensity under various pressures	119
6.5	The effect of pressure on the LCST phase boundary of PS–PVME blends	120
6.6	Pressure dependence of cloud points at different composition of PS–PVME blends	122
6.7	Effect of molecular weight of perdeuterated PS(PSd) on the cloud point of PSd–PVME blends	128
6.8	Effect of deuteration on the LCST phase boundary of PS–PVME blends	129
6.9	Effect of pressure on the LCST phase boundary of PSd–PVME blends	130
6.10	Pressure dependence of PSd–PVME phase boundary at different blend composition	131
6.11	Heat of mixing, ΔH_m	133
6.12	Density measurements	135
6.13	Small angle neutron scattering (SANS)	137

6.14	The interaction term, X_{12} from ΔH_m	146
6.15	Differential scanning calorimetry	150
6.16	Dynamic mechanical thermal analysis	156
6.17	Scanning electron microscopy	156
6.18	Heat treatment under pressure	157
Chapter 7 Simulation of phase diagrams		167
7.1	General	167
7.2	Evaluation of equation of state parameters	168
7.3	Determination of X_{12} , Q_{12}	171
7.4	Determination of the segmental surface area and chain length ratios	172
7.5	Simulated spinodals	174
7.5.1	Effect of the non-combinatorial entropy parameter, Q_{12}	176
7.5.2	The effect of X_{12}	177
7.5.3	The Effect of $\frac{s_2}{s_1}$ and $\frac{r_2}{r_1}$	179
7.6	The effect of pressure	180
7.6.1	Volume changes on mixing	181
Chapter 8 Concluding Remarks		185
8.1	Problems related to the high pressure rig	185
8.2	Problems related to sample preparation	186
8.3	Conclusions	186
Appendix A		189
Appendix B		204
Appendix C		206
Appendix D		208
Appendix E		210

Appendix F	217
Appendix G	220
Program 'SPIN'	221
Program 'PIDCON'	234
Program 'TURB'	237
References	239

LIST OF FIGURES

Fig. 2.1	Free energy of mixing, ΔG_m , as a function of composition, ϕ , and temperature, T	7
Fig. 2.2	The temperature dependence of the interaction parameter. Schematic representation of contribution to χ_{12}	18
Fig. 3.1	Schematic temperature—composition phase diagram for binary systems	32
Fig. 3.2	A hypothetical phase diagram for two polymers with a common solvent showing a two—phase region	36
Fig. 4.1	The pressure rig	63
Fig. 4.2	The rig and connections	64
Fig. 4.3	Block diagram of the rig	65
Fig. 4.4	The pressure vessel	65a
Fig. 4.5	The sample loading assembly	66
Fig. 4.6	The heating system	67
Fig. 4.7	The pressure reactor	68
Fig. 4.8	Calibration curve of pressure	69
Fig. 4.9	Pressure reactor	70
Fig. 4.10	Side seal assembly	71
Fig. 4.11	End seal assembly	72
Fig. 4.12	Sample loading assembly	73
Fig. 4.13	Sample holder	74
Fig. 4.14	Heating rate	75
Fig. 4.15	Viewing arrangement	77
Fig. 4.16	'Side tube' arrangement	78

Fig. 4.17	Optical alignment	79
Fig. 4.18	Sample orientation	80
Fig. 4.19	Pressure line	82
Fig. 5.1	Transmitted light intensity as a function of temperature	88
Fig. 5.2	Cloud Point Curve from pressure rig	90
Fig. 5.3	Cloud Point Curve from Turbidimeter	91
Fig. 5.4	Applied pressure as a function of time	92
Fig. 5.5	Scattered light intensity as a function of temperature	94
Fig. 5.6	Scattered light intensity as a function of time	96
Fig. 5.7	Calibration curve for distilled water at 28°C	100
Fig. 5.8	Calibration curves for PS/PVME (50/50 wt%) at A 50°C and B 28°C	101
Fig. 5.9	Heating/cooling cycle for a 50% PS blend	103
Fig. 5.10	Schematic relation between various parameters in dynamic mechanical relaxation measurements	104
Fig. 5.11	A SANS spectrometer	110
Fig. 5.12	Calibration of density gradient column	112
Fig. 6.1	Effect of molecular weight of PS on the LCST of PS–PVME blends	115
Fig. 6.2	Effects of molecular weight of PVME on the miscibility of PS–PVME blends	117
Fig. 6.3	Temperature dependence of transmitted light intensity under various pressures	119

Fig. 6.4A	The effect of pressure on the LCST phase boundary of PS–PVME blends	120
Fig. 6.4B	The effect of pressure on the LCST phase boundary of PS–PVME blends	121
Fig. 6.5A	Pressure dependence of cloud points at various compositions	123
Fig. 6.5B	The effect of pressure on the LCST phase boundary of PS–PVME blends	124
Fig. 6.6	Pressure dependence of cloud points on composition of PS–PVME blends	125
Fig. 6.7	Effect of deuteration on the LCST phase boundary of PS–PVME blends	129
Fig. 6.8	Effect of pressure on the LCST phase boundary of PSd–PVME blends	130
Fig. 6.9	Pressure dependence of cloud points on composition of PSd–PVME blends	131
Fig. 6.10	Pressure dependence of cloud points of PSd–PVME blends as a function of composition	132
Fig. 6.11	The scattered intensity from the background	137
Fig. 6.12A	The scattered intensity at various angles	141
Fig. 6.12B	The scattered intensity at various angles	142
Fig. 6.12C	The scattered intensity at various angles	143
Fig. 6.12D	The scattered intensity at various angles	144
Fig. 6.12E	The scattered intensity at various angles	145
Fig. 6.13	Differential scanning calorimeter traces of miscible PS–PVME blends	151

Fig. 6.14	Differential scanning calorimeter traces of phase-separated blends	152
Fig. 6.15	The transition temperature of blends of PS–PVME as a function of PS concentration	155
Fig. 6.16	Dynamic mechanical relaxation curves of miscible blends as a function of composition composition	158
Fig. 6.17	Scanning electron micrographs of a 30% PS blend	160
Fig. 6.18	Transmitted light intensity as a function of time for a 30% PS blend	161
Fig. 6.19	Transmitted light intensity as a function of time under pressure	162
Fig. 6.20	Optical micrographs of a 30% PS blend	163
Fig. 6.21	Optical micrographs of a 50% PS blend	165
Fig. 7.1	Calculated spinodal	175
Fig. 7.2	Effect of Q_{12}	177
Fig. 7.3	Effect of X_{12} on the position of the spinodal curve	178
Fig. 7.4	Effect of X_{12} on the shape of the spinodal curve	179
Fig. 7.5	Effect of S_{21}	180
Fig. 7.6	Effect of r_{21}	183
Fig. 7.7	Effect of pressure	184

LIST OF TABLES

5.1	Polymer origin and characteristics	85
5.2	The coherent scattering lengths of different atoms	107
5.3	Characteristics of samples used for SANS studies	109
5.4	Characteristics of test samples for SANS measurements	110
6.1	Pressure dependence of cloud point on blend composition	126
6.2	Pressure dependence of molecular weight of PS at the critical composition	127
6.3	Effect of molecular weight of PSd on the cloud point of a PSd–PVME blend	128
6.4	Pressure dependence of cloud points of PSd–PVME on blend composition	133
6.5	Data of density and specific volume for PS–PVME blends and for the blend components	135
6.6	Scattered intensity from the samples	139
6.7	Flory–Huggins interaction parameter from SANS measurements	140
6.8	Calculated values of the critical condition for a mixture of two polymers	148
6.9	Values of Flory–Huggins interaction parameter deduced from SANS and from heat of mixing measurements	149

6.10	Effect of composition on temperature of thermal transition of PSH/PVME and PSD/PVME blends cast from toluene	159
7.1	Equation of state parameters for PS and PVME at 50°C	172
7.2	Volume changes on mixing for a 30% blend by various methods as described in the text	182

LIST OF SYMBOLS

ΔH_m	enthalpy of mixing
P	pressure
$\tilde{P}_i$	reduced pressure of species i
P_i^*	hard-core pressure of species i
$\tilde{P}$	reduced pressure of mixture
P^*	hard-core pressure of mixture
Q_{12}	interaction entropy parameter
R	gas constant
r_i	chain length of molecule i
S_i	number of contact sites per segment in species i
T	temperature
$\tilde{T}_i$	reduced temperature of species i
T_i^*	hard-core temperature of species i
$\tilde{T}$	reduced temperature of mixture
T^*	hard-core temperature of mixture
T_g	glass transition temperature
V_1^*	molar hard-core volume of component 1
v_{sp}	specific volume of component i
$\tilde{v}_i$	reduced volume of component i
v_i^*	hard-core volume of component i
$\tilde{v}$	reduced volume of mixture
v^*	hard-core volume of mixture
X_{12}	interactional parameter
χ_{12}	Flory–Huggins interaction parameter
ϕ_i	segment fraction of species i

θ_i	site fraction of species i
$\Delta\mu_1$	chemical potential of component 1
ΔV_m	volume change on mixing
ΔG_m	Gibbs free energy of mixing
ΔS_m	entropy of mixing

ABBREVIATIONS

ABS	acrylonitrile butadiene styrene
SANS	Small Angle Neutron Scattering
PS	polystyrene
PVME	poly(vinyl methyl ether)
PVC	poly vinyl chloride
LCST	Lower Critical Solution Temperature
UCST	Upper Critical Solution Temperature
PPO	poly(phenylene oxide)
DSC	Differential Scanning Calorimeter
DTA	Differential Thermal Analyser
DMA	Dynamic Mechanical Analyser
IR	infra red
FTIR	Fourier Transform infra red
TEM	transmission electron microscope
SEM	scanning electron microscope
CPC	cloud point curve
DMTA	dynamic mechanical thermal analysis
NMR	Nuclear Magnetic Resonance

CHAPTER 1

INTRODUCTION

1.1 General

The increasing demand for the production of polymer materials with 'tailor-made' properties, for engineering and other specialist applications, has initiated in-depth studies in the area of polymer syntheses. In recent years the production of completely new homopolymers which have achieved commercial viability has been small while that of polymer blends and composites has been highly significant. Apart from being a cheaper and easier alternative to expensive and expansive syntheses of new materials, blending offers versatility in terms of both the type and composition of constituents.

In order to utilise this new technology, a fundamental understanding of the phenomena of polymer miscibility is essential. For example, over the past twenty years thermodynamic knowledge has been used to identify a host of homogeneous polymer pairs. The most important quantity needed for such an identification is the free energy (of mixing) of the system, as a function of temperature, composition and molecular weight. Apart from the miscible homogeneous, there are also the phase-separated, heterogeneous blends which comprise the majority of commercial polymer blends, for example, acrylonitrile-butadiene-styrene (ABS) terpolymers. For these, kinetic and morphological studies are useful for the control of phase sizes and adhesion between phases. The composition, thermodynamic coefficients and processing conditions of a blend determine its morphology. It was shown by Yee (1977)

and Van Oene (1978) that the microstructure of a blend has a profound influence on its properties and consequently on its end uses.

It should be noted that a polymer blend does not always provide all the satisfactory properties of a homopolymer. If suitably paired however, each component polymer can still retain most of its individual properties while contributing in a synergistic way to providing new macroscopic properties for the material as a whole.

The effect of temperature and pressure on any system is an important aspect of thermodynamic studies. Temperature has two distinct effects on a system, namely thermal expansion and molecular agitation. It is only by companion studies with pressure that these two effects can be separated so that a comparison may be made with results derived from the usual models which assume constant volume. While pressure effects are transmitted virtually instantaneously, the time scale for any thermal changes are slower because they are dependent on the thermal conductivity of the system. Although the effect of pressure has been extensively studied for gaseous systems, this is not the case for solid and liquid systems. One of the reasons for this is the difficulty in the design of high pressure equipment. The increasing use of high pressure in the polymer industry especially in polymer blend processes, (Chapter 3), demands a better understanding of the effects of pressure on the phase diagrams of polymer blends.

Among the newer techniques, isotopic labelling has become increasingly available in the study of polymer blend miscibility. Small angle neutron scattering (SANS) has been used to measure the physical properties of polymer systems such as single chain dimensions, second virial coefficients, molecular weight, mass diffusion coefficients, local chain configurations and miscibility of polymer blends in the solid state. References are Kirste *et al* (1975); Ballard *et*

al (1976); Schmitt *et al* (1980); Wignall *et al* (1980); Walsh *et al* (1981); Russel and Stein (1982); Warner *et al* (1983); Jelenic *et al* (1984); Hadziioannou and Stein (1984); Maconnachie *et al* (1984). These measurements which use mixtures of two analogues to extract single chain information, assume that isotope-labelled polymers, mainly deuterium-labelled, are physically identical to their hydrogenated analogues or at least differ only negligibly, Yang *et al* (1986). This assumption is largely justified but in some cases however, the properties differ significantly enough to produce measurable isotope effects. The question of deuterium isotope effect has become increasingly important as the use of this technique increases.

Since it was demonstrated, about fifteen years ago, that a blend of hydrogenous polystyrene (PS) and poly(vinyl methyl ether) (PVME) phase-separates on heating and remixes when cooled, this system has been investigated using a number of techniques. It has now taken a prominent post as a model system of thermally induced phase-separation in polymer blends. Surprisingly in its extensive literature, there is only one reported work on the use of high pressure in the study of this blend. No reported studies on the effect of high pressure on (perdeuterated PS)–PVME blend are known to the author. A study on the effect of pressure on the thermodynamic properties of these two blends will further advance the knowledge of this much-studied system. Such a study will also compare the thermodynamic behaviour of hydrogenous and perdeuterated polystyrene.

1.2 Objectives and scope of work

The main objective of the present investigation is to study the pressure dependence of phase separation in binary, high molecular weight polymer blends and to determine quantitatively various thermodynamic coefficients. This work is a contribution to an extensive research programme aimed at the isolation and characterisation of new plastic materials.

In order to achieve the above objectives:

- a number of blends, which varied in composition and in the molecular weight of the components, were prepared from (hydrogenous PS) – PVME and (perdeuterated PS) – PVME.
- high pressure equipment was designed and constructed to study the effect of pressure on the above mentioned blends.
- the heats of mixing of oligomeric mixtures of the system were measured as a function of composition in a batch–type microcalorimeter.
- the interaction parameter of (perdeuterated PS) – PVME blend was measured by SANS, as a function of temperature and composition.
- the densities of the blends were measured as a function of composition in a density gradient column.

From the experimental results, various thermodynamic coefficients were calculated as an input for theoretical simulations of the spinodals. These were made using a modelled equation based on the equation–of–state theory of Flory and his co–workers, so that comparisons could be made between the theoretical spinodals and the experimentally determined phase diagrams.

1.3 Layout of the thesis

The thesis consists broadly of two parts.

The first part consists of eight chapters of which this introductory chapter is the first.

A critical review of the relevant theories is introduced in Chapter 2. In Chapter 3 the general background to the study of polymer blends is presented.

The experimental section begins in Chapter 4 with a description of the pressure rig, followed in Chapter 5 by details of the experimental work carried out.

The results obtained are presented and discussed in Chapter 6.

An account of the simulation of the spinodals is given in Chapter 7.

Chapter 8 is the closing chapter — the major results of Chapter 6 are summarised; various problems encountered during the investigation and their solutions are discussed prior to recommendations for future work.

The second part of the thesis is the Appendices which contain relevant computer programs and derivations of equations, too long to be included in the first part. The Appendices also contain major features of information from elsewhere used in this work.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 General

According to the second law of thermodynamics, the thermodynamic stability of a mixture depends on the sign of ΔG_m , the free energy of mixing, which may be expanded in terms of thermodynamic functions:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.1)$$

ΔH_m and ΔS_m are the enthalpy and entropy changes on mixing, respectively and T is the absolute temperature.

For miscibility to occur between two components 1 and 2, the thermodynamic treatment requires that

$$\Delta G_m \leq 0 \quad (2.2)$$

where
$$\Delta G_m = G_{12} - (G_1 + G_2) \quad (2.3)$$

G_{12} is the free energy of the mixture

G_1 , G_2 are the free energies of the components.

If ΔG_m is negative the mixture is miscible because the free energy of the system is decreased. Although a negative ΔG_m is a necessary requirement for a homogeneous phase, for this phase to be stable against phase separation, the additional requirement that

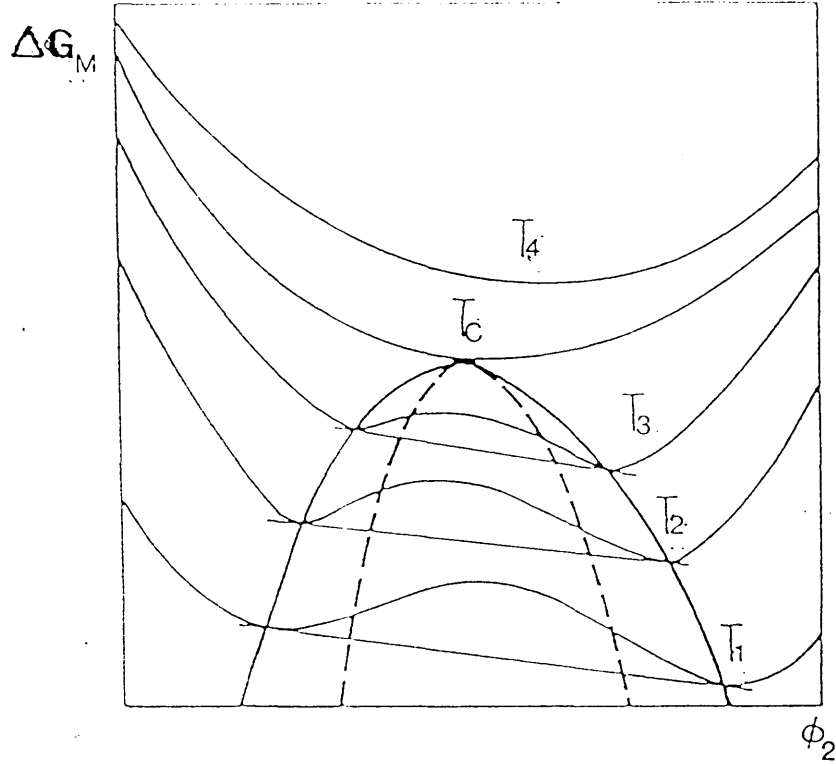


Figure 2.1

Free energy of mixing, ΔG_m , as a function of composition, ϕ ,
and temperature, T

$$\frac{\partial(\Delta G_m)}{\partial \phi_1^2} > 0 \quad (2.4)$$

must also be satisfied (here, ϕ_1 is the volume fraction of either component). This is because the stability of a mixture is also determined by the curvature of ΔG_m , as shown in Fig. 2.1, which is a plot of ΔG_m , as a function of composition at various temperatures. At temperature T_4 the system is miscible in all proportions and the curve is everywhere concave downwards. The system passes through the critical temperature T_c to the partially miscible range $T_1 - T_3$.

Although at these temperatures ΔG_m is still negative the curves are not completely concave. In the central region the mixture can develop a lower free energy by partial separation into two phases. For the system to consist of two phases in equilibrium, the chemical potential (μ) of each component must be equal in both phases,

$$\Delta\mu_1 = \Delta\mu_1' \quad \text{or} \quad \mu_1 = \mu_1' \quad (2.5)$$

where μ_1 and μ_1' are the chemical potentials of component 1 in the two separated phases.

$$\Delta\mu_1 = (\partial\Delta G_m/\partial\phi_2)_{T,P} \quad (2.6)$$

$$\mu_1 = \mu_1^0 + \Delta\mu_1 \quad (2.7)$$

μ_1^0 is the chemical potential of the pure substance at the same temperature and pressure.

This is the condition described by the binodal which separates the stable one-phase region from the region in which two phases coexist in equilibrium.

The spinodal, the locus of points for which the second derivative of the Gibbs free energy of mixing, ΔG_m , equals zero, divides the two-phase region into metastable and unstable portions. The spinodal is defined by

$$[\partial(\Delta\mu_1/RT)/\partial\phi_2]_{T,P} = 0 \quad (2.8)$$

and the critical point by

$$[\partial^2(\Delta\mu_1/RT)/\partial\phi_2^2]_{T,P} = 0 \quad (2.9)$$

Because of the different ways in which the energy state of the homogeneous mixture responds to composition changes, the mechanism of phase separation depends on whether the single phase is metastable or unstable. In the metastable region, $(\partial(\Delta\mu_1/RT)/\partial\phi_2)_{T,P} > 0$ and small fluctuations in volume fraction decay with time. For phase separation to take place, a large composition fluctuation or nucleus is required. Once such a nucleus is formed it can grow by normal diffusion. The composition of the growing phase remains constant during this 'nucleation and growth' process. Although no kinetic model of 'nucleation and growth' exists for polymeric systems, the phenomenon has been observed for polymer blends by both optical, Nishi *et al* (1975) and transmission electron microscopy, McMaster (1974).

Within the unstable region inside the spinodal, $(\partial(\Delta\mu_1/RT)/\partial\phi_2)_{T,P} < 0$ and there is no thermodynamic barrier to phase separation. As a result, small concentration fluctuations can grow with time by a mechanism termed spinodal decomposition. A kinetic treatment of the early stages of the process has been developed by Cahn (1965). Experimental verification of the spinodal decomposition mechanism has been obtained for a number of polymeric systems. The characteristic interconnected phase morphology has been observed for both polymer solutions, van Aartsen (1970), Smolders *et al* (1971) and polymer–polymer blends, McMaster (1974), Nishi *et al* (1975). van Aartsen (1970) successfully predicted the magnitude of the phase spacing for spinodal decomposition in polymer–solvent mixtures, using Cahn's theory together with a Flory–Huggins expression for the free energy of mixing. Finally, Nishi *et al*

(1975) have analysed phase separation in a miscible polymer blend. Their results give direct evidence of the spinodal mechanism: that for short times, the concentrations of the two phases change exponentially with time while only slight changes in the volume fractions of the phases are observed.

2.2 Thermodynamic theories of binary mixtures

Thermodynamic theories as applied to mixtures of small molecules had been well established by the turn of the century. These theories were later modified in order to make them applicable to polymer solutions and mixtures. They provide an expression for the free energy of mixing from which both the miscibility of two components can be predicted and the phase separation of a mixture accounted for, from the view point of thermodynamics. Some of the theories, namely:

- Raoult's Law for ideal solutions
- Hildebrand's 'regular' solution theory
- Flory—Huggins 'lattice' theory
- 'free volume' theories

are briefly reviewed in Sections 2.2.1 to 2.2.4.

2.2.1 Ideal solutions

In the simplest type of mixing where the components of the mixture are chemically similar, for example, benzene and toluene, an ideal mixture is formed in which Raoult's Law is obeyed throughout the composition range. This law states that the partial pressure of each component in the mixture is

proportional to its mole fraction. Hence from the condition for equilibrium between two phases

$$G_1 = kT \ln N_1 \quad \text{and} \quad G_2 = kT \ln N_2 \quad (2.10)$$

The ideal entropy of mixing is given by:

$$\Delta S_m = -k[n_1 \ln N_1 + n_2 \ln N_2] \quad (2.11)$$

where n_1 and n_2 are the number of moles of components 1 and 2 respectively, N_1 , N_2 are their mole fractions and k is Boltzmann's constant.

For ideal mixing

$$\Delta H_m = 0 \quad (2.12)$$

that is, the components mix without any change in energy and since $\Delta S_m > 0$, substituting equations (2.11) – (2.12) into equation (2.1) gives

$$\Delta G_m = -T\Delta S_m \quad (2.13)$$

Consequently spontaneous mixing occurs in all proportions.

2.2.2 Regular solution (solubility parameter) theory

A regular solution is one in which the two kinds of components are distributed randomly but have different interactions with each other in the

mixture. ΔS_m has the ideal value, that is, $\Delta S_m > 0$ but in contrast to the previous theory, ΔH_m is finite, i.e.

$$\Delta H_m > 0 \quad (2.14)$$

It was found that very few liquid mixtures obey Raoult's Law, so Hildebrand and Wood (1933) and Scatchard (1931, 1937) independently derived the following equation

$$\Delta E^m = (N_1 V_1 + N_2 V_2) \left\{ \left[\frac{\Delta E_1^v}{V_1} \right]^{\frac{1}{2}} - \left[\frac{\Delta E_2^v}{V_2} \right]^{\frac{1}{2}} \right\}^2 \phi_1 \phi_2 \quad (2.15)$$

which has formed the basis for the regular solution theory, developed by Hildebrand *et al* (1970).

ΔE^m is the internal energy of mixing, that is, the difference between the energies of the solution and the components and is equivalent to ΔH_m . N_1 and N_2 are the molar fractions and ϕ_1 and ϕ_2 are the volume fractions of the components. V_1 and V_2 are the molar volumes. $\frac{\Delta E^v}{V}$ is the energy of vaporisation per unit volume or the 'cohesive energy density' and is related to the solubility parameter, δ , by

$$\delta = \left[\frac{\Delta E^v}{V} \right]^{\frac{1}{2}} \quad (2.16)$$

Thus
$$\Delta H_m = (N_1 V_1 + N_2 V_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (2.17)$$

The regular solution theory ignores any volume changes on mixing, so while it was able to predict symmetrical phase diagrams it failed to deal with

asymmetric phase diagrams caused by differences in the molar volumes of the components. For this theory, spontaneous mixing occurs in all proportions only when the solubility parameters of both components are equal, leading to $\Delta H_m = 0$ and hence $\Delta G_m < 0$.

2.2.3 Flory–Huggins 'lattice' theory of polymer solutions

Flory (1941, 1942) and Huggins (1941, 1942), working independently, successfully used a rigid 'lattice' model to derive the expression for the ideal entropy of mixing for chemically similar, low molecular weight components. They used the same model to obtain the following expression for the entropy of mixing of polymer solutions

$$\Delta S_m = -k[n_1 \ln \phi_1 + n_2 \ln \phi_2] \quad (2.18)$$

here
$$\phi_1 = \frac{n_1}{n_1 + rn_2}; \quad \phi_2 = \frac{rn_2}{n_1 + rn_2}$$

n_1 is the number of molecules of solvent, n_2 is the number of molecules of polymer, ϕ_1 and ϕ_2 are the volume fractions of the solvent and polymer respectively and r is the degree of polymerisation.

Equation (2.18) assumes that the system is completely random. This is a good approximation for weakly interacting molecules because strong interactions induce short range order and therefore lower the mixture entropy.

For polymer solutions ΔS_m is small compared to that involving small molecules because there are fewer ways in which the same number of lattice sites can be occupied by polymer segments. The forces between a polymer and a simple molecule are similar to those between pairs of simple molecules. The

heat of interaction between a polymer molecule and its surroundings should vary linearly with the composition . Flory therefore wrote an expression for the heat of mixing of a polymer solution, similar to that used by Scatchard, (1931) for simple molecules

$$\Delta H_m = kT\chi_{12}n_1\phi_2 \quad (2.19)$$

χ_{12} is the Flory–Huggins interaction parameter; it is independent of the concentration and molecular weight of the components.

The free energy of mixing is obtained by a combination of equations (2.18) and (2.19)

$$\Delta G_m = kT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi_{12}) \quad (2.20)$$

Extension of Flory–Huggins theory to polymer–polymer mixtures

The Flory–Huggins equation for the free energy of mixing of a polymer–solvent system was later extended to polymer–polymer systems.

In analogy with equation (2.18) the entropy change of mixing two polymers is given by

$$\Delta S_m = -k(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (2.21)$$

As the molecular weights of the two polymers tend to infinity, n_1 and n_2 tend to zero and ΔS_m tends to zero. For high molecular weight polymers,

$$\Delta S_m \simeq 0 \quad (2.22)$$

Substituting equation (2.22) into equation (2.1),

$$\Delta G_m \simeq \Delta H_m \quad (2.23)$$

Similar to equation (2.19), the enthalpy of mixing of two polymers is

$$\Delta H_m = kT\chi_{12} n_1 r_1 \phi_2 \quad (2.24)$$

The free energy of mixing, ΔG_m , of high molecular weight polymers is therefore determined by the enthalpy of mixing, ΔH_m , since ΔS_m is negligible. A negative ΔH_m , implying an exothermic heat of mixing, is therefore necessary for two high molecular weight polymers to mix spontaneously.

Equation (2.17) suggests that except when $\partial_1 = \partial_2$, ΔH_m must always be positive and so high molecular weight polymers are rarely expected to be miscible. Dowbry and Boyer–Kawenoki, (1947) investigated 73 polymer pairs and confirmed that 90% of them were immiscible.

Flory–Huggins theory was only able to predict miscibility for low molecular weight mixtures (oligomers) which generally show upper critical solution temperature (UCST). This is because these systems mix endothermally (ΔH_m is positive) and ΔS_m is large and positive. An increase in temperature therefore makes ΔG_m more negative and miscibility is improved. Phase-separation occurs on reduction of temperature when $T\Delta S_m$ is offset by the positive value of ΔH_m , equation (2.1).

Although the 'lattice' theory has some merits it also has several disadvantages. It assumes that the interaction parameter is only temperature dependent and fails to account for its concentration, pressure and molecular weight dependence which had been observed in previous studies of polymer

solutions and mixtures. A modified interaction parameter suggested by Tompa (1956) has been extensively used to describe binary mixtures

$$\chi = \chi_1 + \chi_2\phi_2 + \chi_3\phi_2^2 + \dots \quad (2.25)$$

A similar empirical function, g , has also been introduced by Koningsveld and Kleintjens (1971) to replace the interaction parameter

$$g = g_{k,1} + g_{k,2}/T + g_{k,3}T + g_{k,4} \ln T \quad (2.26)$$

$g_{k,i}$ depends on measurable physical quantities such as the heat of mixing and molecular weight. This g function is related to χ_{12} as follows

$$\chi_{12} = g(1 - \phi_2) \frac{\partial g}{\partial \phi_2} \quad (2.27)$$

It has been used, Koningsveld *et al* (1974) when only the second and third terms of equation (2.26) are used to describe the phase boundaries of mixtures. However, no satisfactory molecular interpretations of g exists, Koningsveld *et al* (1974, 1980), Koningsveld and Kleintjens (1977).

The Flory–Huggins theory neither predicts lower critical solution temperature (LCST) nor does it explain all the observed LCST behaviour which is a common feature in high molecular weight polymer mixtures. It does not predict miscible high molecular weight polymer pairs, of which there are now known to be many. A compilation of these miscible polymer blends has been made by Paul and Newman, (1978) and by Olabisi *et al* (1979). The theory, like the previous one, assumes that mixing is entirely random and that there is

no volume change on mixing. By assuming the 'ideal' entropy of mixing, it predicts entropies of dilution that are too positive.

Another shortcoming of the 'lattice' theory was pointed out by Allen *et al* (1960, 1961) who found a bimodality on the cloud point curves of low molecular weight polyisobutene–poly(dimethylsiloxane) mixtures. Koningsveld *et al* (1974) assumed a quadratic dependence of the interaction parameter on concentration, and combined this with equation (2.26) to reproduce the observations of Allen *et al*. In their theoretical simulation a restricted temperature dependence of g was used and polydispersity of the system was ignored. On this basis, Koningsveld *et al* (1974) concluded that the concentration dependence of the interaction parameter can outweigh the effect of the entropy of mixing and this might explain the results of Allen *et al* (1961).

Finally, the theory does not take into account the effect of pressure on the miscibility of mixtures. It was found, Tripathi (1979), that for the oligomeric polystyrene–polybutadiene system, for which positive heats of mixing were measured by Chong (1981), an increase in pressure elevated the cloud point curves to higher temperatures.

However, because of its simplicity and its success in many aspects, at least qualitatively, the Flory–Huggins expression for the free energy of mixing is still often used but generalised to allow the interaction parameter to depend on concentration and other variables.

2.2.4 Free–volume theories

The inadequacies of the last theory have largely been overcome by the 'free volume' theories, whose common factor is the recognition of the dissimilarity in the free volume of the components as a result of their difference

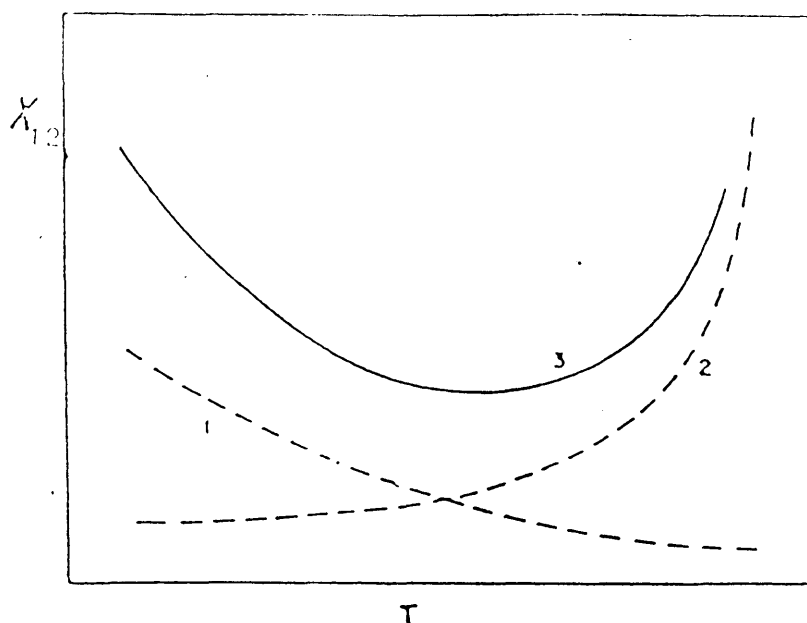


Figure 2.2

The temperature dependence of the interaction parameter.

Schematic representation of contribution to χ_{12}

- Curve 3 total χ_{12} ;
- Curve 2 contribution to χ_{12} due to free volume dissimilarity between the components;
- Curve 1 contribution to χ_{12} due to contact energy dissimilarity between the components.

in size. This difference produces major contributions termed structural or equation-of-state to the thermodynamic mixing functions ΔH_m , ΔS_m , ΔG_m and ΔV_m . During the mixing process, the more expanded component 'condenses' into the denser one so that the total volume change on mixing is negative. This results in a negative contribution to ΔH_m and ΔS_m . These two contributions are often included in a new interaction parameter, X_{12} . X_{12} is therefore made up of the Flory-Huggins interaction parameter, χ_{12} , Equation (2.24) and the negative contributions to ΔH_m and ΔS_m from the 'free volume' effect. While the 'lattice' theory attributes χ_{12} to polymer-polymer interaction alone and predicts it to increase monotonically as the temperature decreases, the

contribution to χ_{12} from the 'free-volume' effect is an increasing function of the temperature (Fig. 2.2). Thus both UCST and LCST are predicted by these theories.

Prigogine and his co-workers (1953, 1955, 1957) first proposed their 'corresponding states' theory, based on the 'cell model' used by Eyring and Hirschfelder (1937). Here each pure component is characterised by three equation of state parameters. V^* , T^* and P^* which may be evaluated from the pure component data, density, thermal expansion coefficient and thermal pressure coefficient (Appendix C). Since then other attempts have also been made to describe the effect of volume changes on polymer mixtures based on the pure components' equation-of-state.

The most widely used of these equations-of-state are the Simha and Somcynsky (SS) hole theory (1969), the lattice fluid theory of Sanchez and Lacombe (SL) (1976) and the Flory, Orwoll and Vrij (FOV) equation, Flory *et al* (1964), Flory (1965), Abe and Flory (1966), Orwoll and Flory (1967), Eichinger and Flory (1968). Of these, the last named has been most extensively applied. The FOV model, henceforth referred to as the Flory's equation-of-state, differs from the cell model in that it uses a partition function which requires a separation of internal and external degrees of freedom.

Although Flory's equation still requires an empirical entropy correction parameter, Q_{12} , to fit detailed behaviour, it has been successfully used to predict the effect of the various contributions to the phase boundaries of hypothetical mixtures, McMaster (1973). It has also been successfully used to simulate the phase boundaries of miscible, high molecular weight polymer blends, Olabisi (1975), Chai *et al* (1983), Rostami and Walsh (1984). The other two theories are still comparatively at the early stages of their development and so lack experimental evidence.

2.2.5 Flory's Equation of State

In deriving this equation, Flory combined some features from the corresponding states theory and the cell models of Prigogine, (1957) while he attempted to correct some of their shortcomings. He therefore treated the intermolecular energy in a more empirical way, following the ideas originally suggested by Hildebrand and Scott (1962). Based on the ideas developed by Tonks (1936), Eyring *et al* (1937), Hirschfelder *et al* (1937) and Rice (1944) for pure liquids, Flory then obtained the free energy directly from the partition function.

The equation of state parameters, P^* , V^* , T^* , which may be evaluated from the pure component data (density, thermal expansion coefficient and thermal pressure coefficient) were used to characterise each pure component while the properties of the mixture were calculated by using an interaction term X_{12} , Flory *et al* (1964, 1965). The combinatorial entropy parts were 'borrowed' from the 'lattice' theory but the terms due to the 'free volume' effect on mixing were derived. Flory's derivation of the 'equation of state' theory is shown in Appendix A. In this section, only an abridged version of the theory is presented.

Since the free energy of mixing, ΔG_m , is related to the partition function, Z by

$$\Delta G_m = kT \ln Z \quad (2.28)$$

Flory first divided N spherical, non-interacting molecules, of a pure component, having $3c$ external degrees of freedom per segment and contained in a volume V ,

into r segments. He then obtained an appropriate partition function Z such that

$$Z = \Omega_c \left[\gamma^{1/3} \left[v^{1/3} - v^{*1/3} \right] \right]^{3Nr} e^{-E_0/kT} \quad (2.29)$$

where

Ω_c is a combinatorial factor which counts the number of ways of mixing

Nr segments, as in the lattice theory

$v = \frac{V}{N}$ is the volume per molecule

v^* , the hard-core volume, is the volume per segment

γ is a purely geometric factor

E_0 is the mean intermolecular energy of a system per molecule which, when only nearest neighbour contacts are important, becomes

$$\begin{aligned} E_0 &= (\text{no of contacts}) \times \frac{\eta}{v} \\ &= -(Nr s\eta/2v) \end{aligned} \quad (2.30)$$

where

$\frac{-\eta}{v}$ is the average interaction energy of a nearest neighbour pair

s is the number of intermolecular contact sites per segment.

Equation (2.30) was further expressed in terms of the reduced parameters

$$\tilde{v} = \frac{v}{v^*}; \quad \tilde{T} = \frac{T}{T^*}; \quad \tilde{P} = \frac{P}{P^*} \quad (2.31)$$

where the hard core parameters are related by the expression

$$P^*v^* = ckT^* \quad (2.32)$$

and
$$T^* = s\eta/2v^* ck \quad (2.33)$$

By substituting v and T from Equation (2.31), Equation (2.29) becomes

$$Z = \text{constant} \left[(\tilde{v}^{1/3} - 1) \right]^{3Nrc} \exp(3Nrc/\tilde{v}\tilde{T}) \quad (2.34)$$

the constant being independent of v and T .

The pure component equation of state was then generated from the partition function by differentiating Equation (2.34) for the pressure of the system, thus

$$P = (kT/Nr) (\partial \ln Z / \partial v)_{T,N} \quad (2.35)$$

On substituting from Equations (2.31) and (2.32), Equation (2.35) becomes

$$\tilde{P} = (\tilde{T}/Nrc) (\partial \ln Z / \partial \tilde{v})_{\tilde{T},N} \quad (2.36)$$

This gives the resulting equation of state for the pure component

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3} / \left[\tilde{v}^{1/3} - 1 \right] - 1/\tilde{T}\tilde{v} \quad (2.37)$$

By making the following assumptions, the theory was adapted to binary mixtures:

- the core volumes of the pure components are additive and the specifications of a segment for each component remains arbitrary. It is therefore convenient to choose segments of equal size so that

$$v_1^* = v_2^* = v^*$$

- the intermolecular energy depends on the surface area of contact between molecules and/or segments since the intermolecular attractions are of short range compared to the molecular diameter of most liquids.

These assumptions have been discussed by Patterson and Delmas (1970).

The pure component parameters could be calculated at a temperature, T and at atmospheric pressure ($\tilde{P} \simeq 0$) from the following relationships

$$\tilde{v}^{1/3} = 1 + \alpha T / (3 + 3\alpha T) \quad (2.38)$$

$$P^* = \gamma T \tilde{v}^2 \quad (2.39)$$

$$\tilde{T} = \left[\tilde{v}^{1/3} - 1 \right] / \tilde{v}^{4/3} \quad (2.40)$$

$$\tilde{T} = \frac{T}{T^*} \quad (2.41)$$

The hard-core pressure P^* and temperature T^* of the mixture are calculated from

$$P^* = P_1^* \phi_1 + P_2^* \phi_2 - \phi_1 \phi_2 X_{12} \quad (2.42)$$

$$T^* = P^* / (\phi_1 P_1^* / T_1^* + \phi_2 P_2^* / T_2^*) \quad (2.43)$$

$\tilde{v}$ can then be found iteratively by using the equation of state

$$\tilde{v}^{1/3} = 1/\{1 - \tilde{T}\tilde{v}/(\tilde{P}\tilde{v}^2 + 1)\} \quad (2.44)$$

The enthalpy change (that is, excess enthalpy) on mixing, which is equal to the energy change on mixing at low pressure is given by

$$\Delta H_m = E_{0_{12}} - (E_{0_1} + E_{0_2}) \quad (2.45)$$

where 1,2 represent the pure components

12 represents the mixture

On further manipulation, Equation (2.45) becomes

$$\Delta H_m = \bar{r}N\tilde{v}^*\{\phi_1P_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \phi_2P_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1}) + \phi_1\theta_2X_{12}/\tilde{v}\} \quad (2.46)$$

The last term in Equation (2.46) is the contribution from contact interactions due to a difference between 1,2 pairs and the mean of 1,1 and 2,2 contact pairs. The terms preceding it are the equation of state terms. Their contribution to the enthalpy change on mixing depends on the reduced volume of the mixture.

X_{12} is related to the Flory–Huggins interaction parameter, χ_{12} , by:

$$\begin{aligned} \chi_{12} = P_1^*V_1^*/RT\phi_2^2\{3\tilde{T}_1 \ln(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1) \\ + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + X_{12}\theta_2^2/P_1^*\tilde{v}\} \end{aligned} \quad (2.47)$$

On substitution and subsequent mathematical manipulation, Eichinger and Flory, (1968), Equation (2.1) becomes

$$\begin{aligned}\Delta G_m = kT(n_1 \ln \phi_1 + n_2 \ln \phi_2) + 3\bar{r}Nv^*\{\phi_1 P_1^* \tilde{T}_1 \ln (\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1) \\ + \phi_2 P_2^* \tilde{T}_2 \ln (\tilde{v}_2^{1/3} - 1)/(\tilde{v}^{1/3} - 1)\} + \bar{r}Nv^*\{(\phi_1 P_1^*(1/\tilde{v}_1 - 1/\tilde{v}) \\ + \phi_2 P_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (\phi_1 \theta_2 X_{12}/\tilde{v})\} \quad (2.48)\end{aligned}$$

The first term is the combinatorial entropy term just as in the Flory–Huggins 'lattice' theory, Equation (2.18). The second term reflects the equation–of–state contributions and the third term represents the enthalpy which contains the interaction contributions (X_{12}).

The "equation–of–state" has been successful in its prediction of lower and upper critical solution phase boundaries for polymer mixtures, negative heats of mixing, interaction parameters and excess volumes of mixing.

Abe and Flory (1965), (1966), Chalal *et al* (1973) found discrepancies between the theoretically predicted and the experimentally determined values of the interaction parameter. The theory had assumed that only contact interactions between nearest neighbour segments contribute to X_{12} which was thus treated as an enthalpy parameter only. These interactions however also affect the entropy and the observed difference was concluded to result from the non–inclusion of the entropy effect. Flory corrected the error by the introduction of a purely entropy correction term, Q_{12} , into the free energy equation of state of the mixture. Q_{12} is represented by its contribution $-\tilde{v}TQ_{12}$

to the total exchange interaction parameter X_{12} which consists of both an entropy and an enthalpy part.

The enthalpy interaction parameter

$$\bar{X}_{12} = X_{12} - \bar{v}Q_{12} \quad (2.49)$$

From the relationship given by Equation (2.49), a positive value of Q_{12} suggests that the entropy of interaction between unlike segments, 1 and 2, is favourable for mixing while a negative value suggests an unfavourable contribution to the mixing. The effect of Q_{12} on the phase boundaries of mixtures will be discussed in Chapter 7.

Despite its weakness, earlier mentioned in Section (2.2.4), Flory's equation-of-state theory has some merits which include:

- the concentration enthalpy and entropy dependence of the interaction parameter are approximated.
- the volume change on mixing is brought within the scope of the treatment.
- the phase diagrams of polymeric systems have been treated more realistically than any other existing theory.
- it is simple to apply when the state parameters of the pure components are known.

For the above reasons, this theory has been applied in the present work, to calculate the interaction parameter and other thermodynamic quantities. It has also been applied for the simulation of the spinodals, which is presented in Chapter 7.

2.2.6 Application of the 'theory' to cloud point

The chemical potential of component 1 in a polymer mixture is given by

$$\begin{aligned}
 \frac{(\partial \Delta G_m / \partial \phi_2)_{T,P}}{RT} &= \Delta \mu_1 / RT \\
 &= \ln \phi_1 + (1 - r_1/r_2) \phi_2 \\
 &+ P_1^* V_1^* / RT \{ 3 \tilde{V}_1 \ln(\tilde{v}_1^{1/3} - 1) / (\tilde{v}^{1/3} - 1) + 1/\tilde{v}_1 - 1/\tilde{v} \\
 &+ \tilde{P}_1(\tilde{v} - \tilde{v}_1) \} + V_1^* X_{12} \theta_2^2 / RT \tilde{v} - V_1^* Q_{12} \theta_2^2 / R
 \end{aligned} \tag{2.50}$$

Applying the spinodal condition

$$(\partial / \partial \phi_2)(\Delta \mu_1 / RT) = 0,$$

this becomes

$$\begin{aligned}
 (\partial / \partial \phi_2)(\Delta \mu_1 / RT) &= 0 = -1/\phi_1 + (1 - r_1/r_2) \\
 &+ P_1^* V_1^* / RT_1^* (-D/\tilde{v} - \tilde{v}^{2/3}) + P_1^* V_1^* D / RT \tilde{v}^2 + P V_1^* D / RT \\
 &+ V_1^* X_{12} 2 \theta_2^2 \theta_1 / RT \tilde{v} \phi_1 \phi_2 - V_1^* X_{12} D \theta_2^2 / RT \tilde{v}^2 \\
 &- V_1^* Q_{12} 2 \theta_2^2 \theta_1 / R \phi_1 \phi_2
 \end{aligned} \tag{2.51}$$

where

$$D = \tilde{\partial \tilde{v}} / \partial \phi_2 \quad (2.52)$$

and

$$\frac{\tilde{\partial \tilde{v}}}{\partial \phi_2} = \frac{\frac{\tilde{\partial \tilde{P}}}{\partial \phi_2} - \frac{\tilde{\partial \tilde{T}}}{\partial \phi_2} \left[\frac{\tilde{P}}{\tilde{T}} + \frac{1}{\tilde{T} \tilde{v}^2} \right]}{\frac{2}{\tilde{v}^3} - \frac{\tilde{T} (3 \tilde{v}^{1/3} - 2)}{3 \tilde{v}^{5/3} (\tilde{v}^{1/3} - 1)^2}} \quad (2.53)$$

with

$$\frac{\tilde{\partial \tilde{P}}}{\partial \phi_2} = \frac{\tilde{P}}{\tilde{P}^*} \left\{ P_1^* - P_2^* - \theta_2 X_{12} \left[1 - \frac{\theta_1}{\theta_2} \right] \right\} \quad (2.54)$$

$$\frac{\tilde{\partial \tilde{T}}}{\partial \phi_2} = \frac{\tilde{T}}{\tilde{P}} \frac{\tilde{\partial \tilde{P}}}{\partial \phi_2} + \frac{P_2^* \tilde{T}_2 - P_1^* \tilde{T}_1}{\tilde{P}^*} \quad (2.55)$$

The effect of the term containing $\tilde{P}_1$ in Equation (2.50) and hence that containing $\tilde{P}$ in Equation (2.51) is small and does not describe the main effect of pressure on the phase diagram which is due to its effect on the expansion coefficients and hence on the reduced volume of the mixture $\tilde{v}$.

In order to solve Equation (2.51) it is necessary to know the following state parameters of the pure components:

- the specific volume, $v_{sp} = \frac{1}{d}$
- the thermal expansion coefficient

$$\alpha = \frac{1}{V \left[\frac{\partial v}{\partial T} \right]_P}$$

- the thermal pressure coefficient

$$\gamma = \left[\frac{\partial P}{\partial T} \right]_V$$

- the surface per unit of core volume ratio, $s = \frac{s_2}{s_1}$
- the interaction terms, X_{12} , Q_{12}

The determination of the above parameters will be shown later, in Chapter 7.

By the use of the determined parameters and Equation (2.51) the spinodal curve can be calculated at any given pressure.

The main assumptions in this treatment are that the equation of state theory in this simplified form can be used with constant values of P^* , T^* and V^* and that the effect of pressure on X_{12} and Q_{12} can be neglected.

CHAPTER 3

GENERAL BACKGROUND

3.1 Binary polymer blends

Binary polymer blends or polyblends are usually understood to be mixtures of two polymers without a lower molecular weight component .

Polymer melts are liquids and so like other liquids, various pairs of polymers might be expected to be miscible. This indeed is the case; however, due to the very high viscosity of polymer systems, the methods of blend preparation and establishment of their miscibility are more tedious; also time scales required to effect separation are much longer than for analogous mixtures involving only small molecules.

Over the years, polymer compatibility and polymer miscibility have often been used synonymously by various workers. To the technologist, interested in the end product, a compatible blend is one which gives a desired or beneficial result irrespective of the number of phases. For example, ABS, a rubber-toughened two-phase system is described as compatible while a single phase blend of PS and poly(phenylene oxide)(PPO) is also compatible. Processability is often used as a criterion for compatibility in commercial productions. In the literature both compatibility and miscibility are generally used synonymously to describe the single phase behaviour of a mixture. Miscibility implies homogeneity on a molecular level and is therefore better defined in thermodynamic terms by the thermodynamic function of the free energy of mixing, which provides an unambiguous criterion for predicting miscibility and a true picture of the equilibrium state of the mixture.

3.2 Phase diagrams

Timmermans (1936) described the phase diagrams of a number of binary systems of simple molecules at atmospheric pressure. Examples of the types of phase diagrams of polymer solutions or blends which appear in the literature are schematically given in Fig. 3.1 (a to d). Polymer solutions for example, PS-acetone, Siow *et al* (1972), cellulose acetate-acetone, Cowie *et al* (1971) have two regions of immiscibility which are bounded by an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST). An interesting variation is the 'hourglass' type which is rare but has been reported with polyoxyethylene-water systems, Malcolm *et al* (1957).

3.3 Critical solution phenomenon in binary systems

Miscible high molecular weight polymer blends generally show an LCST, which has been interpreted by Paul and Newman (1978), Olabisi *et al* (1979) in terms of equation of state or free-volume contributions. Some miscible polymers also exhibit phase separation at low temperatures. This UCST behaviour is rather uncommon and has been observed only when one or both components is an oligomer, Roe and Zin (1980), Zachaius *et al* (1983). The system, PS-polybutadiene was studied by Allen and Yip (1976), a UCST which increased with the molecular weight of either component was reported. A similar observation was made by Friday *et al* (1977) for methoxylated-poly(ethylene oxide)/poly(propylene oxide) systems. In both systems the molecular weight of the components was less than 20,000. It is just possible that for higher molecular weight components these systems may show an LCST behaviour.

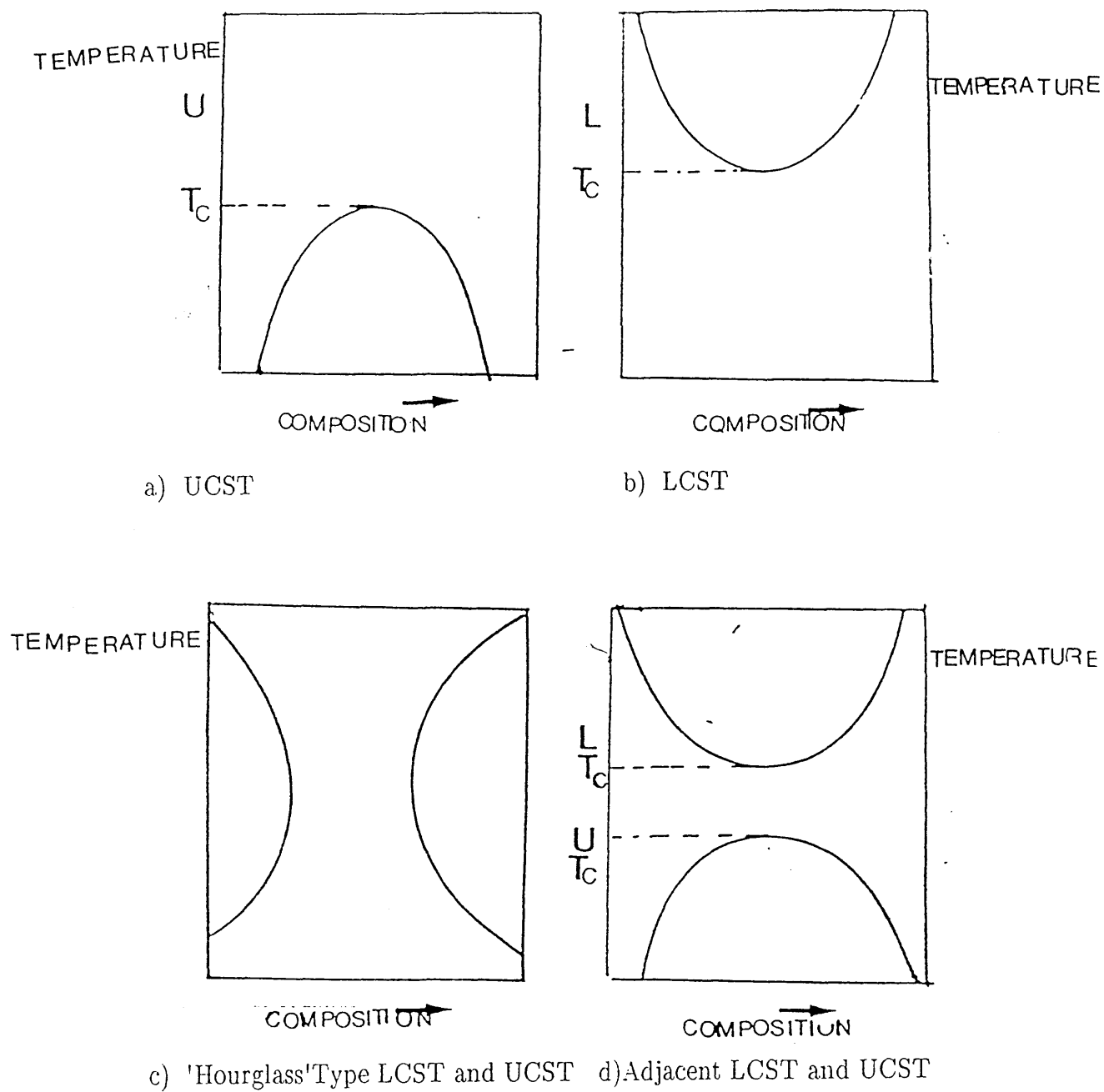


Figure 3.1

Schematic temperature-composition phase diagram for binary systems

Toshiaki Ougizawa *et al* (1985) have recently reported the existence of both a UCST and an LCST behaviour for a mixture of high molar mass polymers. This is an unusual behaviour although McMaster (1973) had predicted the existence of both phase boundaries for miscible high molecular weight polymers which show no net attractive interactions, for example, PS/poly(o - chlorostyrene), Murray *et al* (1985). McMaster suggested that experimental conditions usually prevent the observation of the UCST phase boundary since it would be difficult to detect below the glass transition temperature of the blend.

At high temperatures most polymers start to degrade chemically and this region of the phase diagram may be experimentally inaccessible. On the other hand, because of kinetic considerations, thermodynamic equilibrium is never reached below the glass transition temperature (T_g) of a blend. This is because the molecules are 'frozen-in' in position at T_g . This region of the phase boundary is therefore experimentally inaccessible, if approached via temperature. This 'frozen-in' effect may however be exploited, by 'quenching' a blend into a glassy state to preserve the structured characteristics of a higher temperature, usually for subsequent morphological studies.

3.4 Preparation of blends

The properties and therefore the end uses of a blend largely depend on its preparation. This aims at mixing and bringing the component materials as close as possible, in order to relax any non-equilibrium concentration gradients. Intimate mixing is improved by heat, shear and solvents. Scott (1947) had recognised that two undiluted high molecular weight polymers rarely form a

homogeneous mixture and he deduced the secondary role of solvents on miscibility.

There are three general methods of blend preparation, namely:

3.4.1 Melt mixing

This consists of mechanically mixing the two components in the molten state. High dispersions can be achieved and because no solvents are required the process is simple and the product 'uncontaminated'. However, the high temperatures required to melt them pose serious problems of thermal degradation and thermally induced phase separation of the polymers. It is still the primary commercial blending method where the large amounts of materials used justify the high cost of the equipment such as Banbury mixers and blenders.

3.4.2 Casting from a common solvent or emulsions

This is the simplest laboratory method for obtaining test samples of the blend. This method has been used extensively, Saeki *et al* (1982), Morawetz (1983), Han *et al* (1988). The polymers are dissolved in a common solvent which is subsequently evaporated at a fairly low temperature, leaving a thin film of the blend. Mixing in a common solvent does not however guarantee a homogeneous blend even for miscible polymers. Regions of two-phase coexistence within the polymer/polymer/solvent three component phase diagram can cause the formation of phase separated structures. For example, with poly(vinyl chloride)/poly(ethyl acrylate), no suitable solvents have yet been found to produce homogeneous blends and mixtures can only be prepared

by *in situ* polymerisation, Walsh and Cheng (1984). Although problems associated with high temperatures are eliminated by solvent casting, the difficulty of solvent removal prevents the preparation of thicker shapes and often a common solvent cannot be found for two polymers. Further, some polymers retain some solvents and the residual solvent has an adverse effect on the results of an analysis. Davis and Kwei (1980) found that the nature of the film depends strongly on the solvent and the preparation. Walsh and McKeown (1980) also noted similar problems as well as those of concentration and temperature gradient during the removal of solvent. This effect can sometimes be solved by 'freeze-drying'.

3.4.3 *In situ* polymerisation

When the component polymers are thermally unstable but have a high T_g , miscibility can be enforced at lower temperatures, by reactions between the polymers. For example, *in situ* polymerisation is the polymerisation of one monomer in the presence of another polymer. Although it has many advantages in the preparation of blends it does not guarantee that homogeneous blends can be prepared at all compositions. In the preparation of poly(vinyl chloride)(PVC)/solution chlorinated polyethylene blends, vinyl chloride is only partially miscible with chlorinated polyethylene, Doube and Walsh (1979), which limits the range of compositions prepared by a one-step polymerisation. In the preparation of PVC/poly(butyl acrylate) blends, vinyl chloride is completely miscible with poly(butyl acrylate) but a two-phase region exists within the polymer/polymer/monomer three component phase diagram as shown in Fig. (3.2), Walsh and Cheng (1982). Polymerisation from A to B produces a homogeneous blend whereas from E to H produces a two-phase

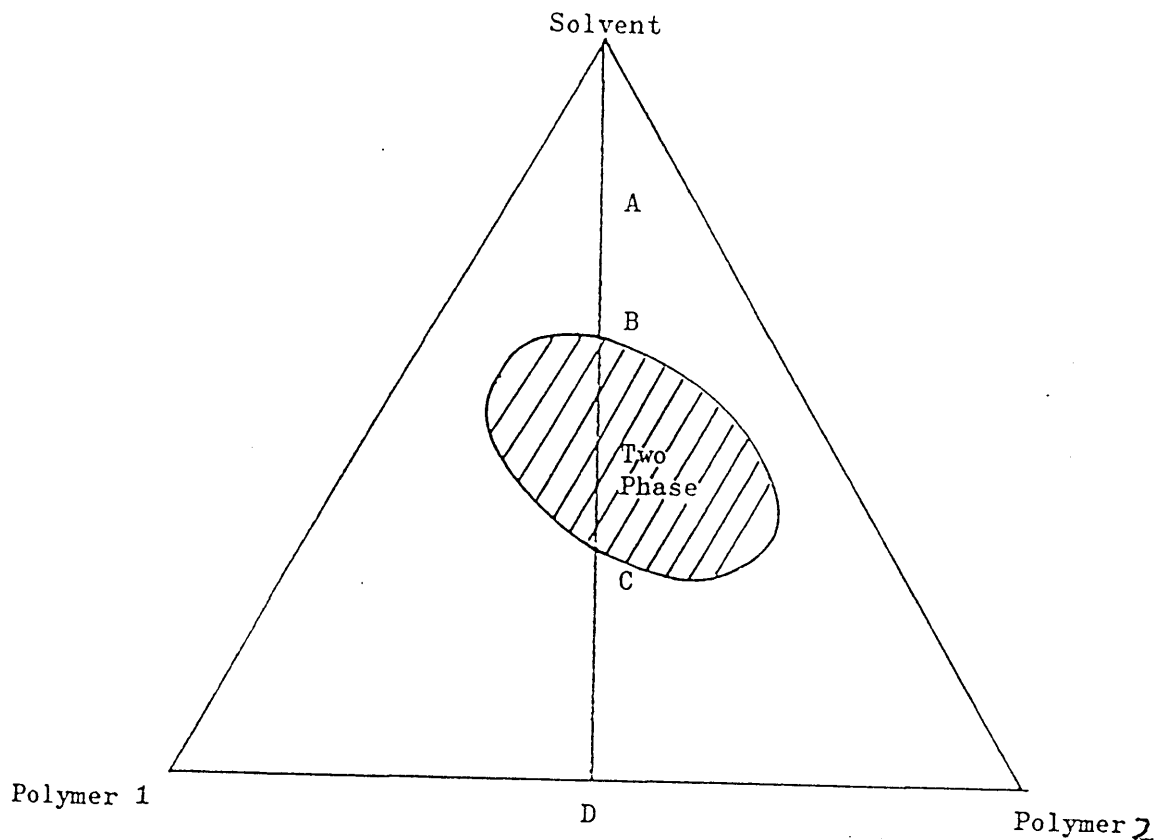


Figure 3.2

A hypothetical phase diagram for two polymers with a common solvent
showing a two-phase region

structure. The polymerisation pathway enters a two-phase region at B and when leaving at C the mixture does not become homogeneous. It is possible to reswell composition B to C and repolymerise to D to produce a homogeneous blend. When phase separation takes place it appears to produce a mixture of relatively pure PVC plus a blend of approximately 50/50 composition. The tie lines are believed to radiate from the apex as shown.

3.5 Miscibility criteria and their determination

Of all the possible binary high molecular weight polymer blends, few are miscible. This is because the combinatorial entropy of mixing of two high molecular weight polymers is very small and much less than that for two low molar mass compounds, Flory (1953). The enthalpy of mixing, on the other hand, is often positive. Therefore dissimilar polymers are only miscible if there are favourable specific interactions which may lead to a negative contribution to the Gibbs free energy of mixing. In most cases however, the molecular origin of the driving force for miscibility is generally not clearly understood. Therefore the search and characterisation of molecular parameters which lower the total free energy, represent important areas of study.

A number of criteria have been employed for the characterisation of polymer miscibility; a review of these has been made by MacKnight *et al* (1978) and Olabisi *et al* (1979). The more important methods are briefly described below.

3.5.1 Optical clarity

A miscible blend is by definition, transparent, indicating optical homogeneity. On phase separation the mixture may turn cloudy or turbid. This change, which can be caused by variations of temperature, pressure or composition of the blend, may vary from almost unnoticeable to a very opaque – white due to the presence in the medium of volume elements of the second phase. The most obvious criterion, therefore, for deciding whether a system is heterogeneous or not is its transparency to light. This criterion, although the simplest, has limitations because light scattering from heterogeneous systems

depends not only on the difference in the refractive indices of the coexisting phases but also on the dimensions of the phase domains. An immiscible blend can appear transparent if the difference in the refractive indices (Δn) of its components satisfies the condition $\Delta n \leq 0.01$, Bohn (1975).

If the dimensions of the dispersed phase are small compared to the wavelength of visible light, ($< 10^{-7}\text{m}$), the amount of scattering will be reduced such that the mixture appears clear. Neutrons or X-rays which have much shorter wavelengths (10^{-9}m) may however be used to overcome this latter problem. It may also be useful in cases where there is no refractive index difference since there may still be an electron density difference (which will result in x-ray 'cloudiness') or a difference in the neutron scattering length density (for a neutron 'cloud point'), Walsh *et al* (1984).

The above situations mentioned earlier have been exploited in the manufacture of optically clear, non-homogeneous blends. For example, immiscible blends of polystyrene and bis phenol - A - polycarbonate with refractive indices of 1.585 and 1.590, respectively, yield transparent films, Rosen, (1967).

The effect of domain size on the film clarity of a miscible LCST blend has been reported by Bank *et al* (1971). As the blend phase - separated, the domain size of the dispersed phase grew larger. At the same time the transparent film changed to a bluish appearance and later became opaque - white. As the size of the separated particles continued to increase, the opacity of the film decreased due to their coalescence. Since miscibility limits for many polymer blends are determined as the temperature at which a given composition becomes cloudy, optical clarity is used to generate phase boundaries. In this case the temperature of the blend is altered at a programmed rate while its clarity is monitored either visually, on a hot stage microscope or by the

measurement of the intensity of the scattered or the transmitted light from the sample. The onset of turbidity is the cloud point; a cloud point curve (cpc) for the blend is generated by measurement of the cloud points for other compositions.

These measurements are usually ambiguous about whether the binodal or the spinodal is being observed. More sophisticated use of the radiations in scattering experiments can in some cases distinguish both loci on the phase diagram, Schwahn *et al* (1987). Generally, nucleation processes are very slow for high molecular weight blends; hence the observed cloud points correspond more to the spinodal. For many high molecular weight polymer blends clarity can be restored on reversal of temperature and this may be proof that phase separation had taken place or that the original clear blend consisted of a single phase. If the sample is heated very fast, however, the phase separation process may lag and cloudiness may not be observed until higher temperatures than the thermodynamic binodal or spinodal. The cloud point may also be difficult to observe if the mobility of the two polymers is not sufficiently high to effect phase separation within a reasonable time.

3.5.2 Glass transition determinations

As a viscous homopolymer is cooled, it changes from a soft elastomer to a rigid glass. This transition occurs at a temperature or over a range of temperatures (due to polydispersity), known as the glass transition temperature, T_g . All polymers exhibit this phenomenon which takes place in their amorphous region. The glass transition temperature is very important because at or in the vicinity of this temperature various physical properties of a blend or homopolymer are altered.

The second common way of determining miscibility limits is to observe the T_g of the systems. For a truly homogeneous system all molecules are in the same environment and only a single, well defined T_g which is a monotonic function of composition is observed. In the heterogeneous system two T_g 's at temperatures identical to those of the pure components will be observed, providing the component polymers themselves have T_g 's differing by about 20°C. The partially miscible system shows a single broad T_g in the one phase region of the phase diagram; this splits into two T_g 's on crossing a phase diagram into the two-phase region. As the blend becomes more segregated, the glass transition temperatures appear increasingly like those of the pure components. The sole use of T_g measurements as a criterion for miscibility in a blend can however be susceptible to error if the ill-defined limits of the measurement techniques are exceeded.

Practical difficulties may also arise, particularly with the Differential Scanning Calorimetry (DSC) if the concentration of one or more of the components falls below approximately 10%, thus reducing its potential detectability. The relationship between detectability and domain size remains unsolved, a consideration which is of particular importance in assessing the degree and miscibility of a system. For example, Matsuo *et al* (1969) observed a single broad loss peak (E'') in blends of poly(vinyl chloride) (PVC) with butadiene – acrylonitrile copolymer although electron micrographs of osmium tetroxide – stained sections indicated domains of about 10nm in size. A related problem is the effect of surface energy on T_g when the domain sizes are small; this can enhance the T_g by as much as 50°C for 6 nm diameter spheres, Couchman (1977).

The concentration dependence of T_g can be described by a number of equations, some of which have empirical origins whilst others are based on free

volume or thermodynamic arguments. The simplest description, based on the rule of mixtures, Nielson, (1978) predicts that the T_g of the blend is given by

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

where w_1 represents the weight fraction of the components and T_{gi} their T_g 's.

This equation is more commonly known in its inverse form as the Fox equation, Fox (1956) which has been successfully used to predict the T_g – composition dependence of several compatible blends, Zakrzewski (1973), Macknight *et al* (1978), Suess *et al* (1987).

A variety of methods exist for determining T_g 's including dielectric relaxation spectroscopy and dilatometry; the latter was used by Akiyama (1972) to study the miscibility of blends of poly vinyl nitrate and poly vinyl acetate. These techniques have been fully described by Ke (1964), Manche *et al* (1972) and Cowie (1973). However, the commonest techniques are based either on calorimetric measurements of heat capacity as a function of temperature or low strain dynamic mechanical measurements of the temperature dependence of the complex modulus. Several recent reviews have been published which describe the applications, methods of data analysis and instrumental capabilities for both mechanical, Read *et al* (to be published), Macknight *et al* (1978), Wetton (1986), and thermal analysis, Richardson (1978), Turi (1981), Fried (1983).

Thermal analysis

Measurements of the temperature dependence of heat capacity (C_p) can be achieved either by Differential Thermal Analysis (DTA) or by its more

quantitative development, DSC, Chiou *et al* (1987). DTA measures the temperature difference between a sample and a reference when both are heated at the same set rate; DSC measures the energy required to maintain a sample and a reference, usually an empty pan, at the same temperature during a programmed heating. Both techniques reflect the changes of enthalpy in a sample.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis comprises a wide variety of techniques such as free vibration and forced non-resonance, some of which have been developed into commercial instruments. Most of these techniques involve monitoring the response of a material to some applied periodic force, either as a function of frequency or temperature, Tagayanagi (1963), Murayama (1986).

Although both thermal analysis and mechanical techniques are used to determine the T_g 's of materials it is often the case that more information about the system can be obtained if they are used in a complementary fashion. However, there are occurrences where this is neither desirable nor practicable. For example, DMA methods require samples in the form of bars, films or fibres, therefore powders can only be studied by DSC or DTA. Limited amounts of sample often preclude the use of mechanical methods in favour of DSC or DTA which can be used to study milligram quantities. The speed at which samples can be heated or cooled in a DSC in a controlled fashion is a necessary requisite if either components are prone to degradation at temperatures near to the phase boundary. DSC-type techniques however, are less sensitive than DMA methods to locating T_g 's. DMA methods also give useful information concerning

more local motion of the chains, for example, side groups which may reflect specific interactions between blend components.

3.6 Infra-red spectroscopy (IR)

IR or vibrational spectroscopy is a method for examining the interactions of different polymers in a blend, using the specific vibrations of the chemical groups. It is thus an attractive technique for establishing miscibility. When properly assigned, the position, intensity and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level. Because intra-chain energy is so much higher than inter-chain non-bonded interactions, spectroscopic features of a single molecule as a result of molecular interaction are generally quite small. Strong interactions such as intermolecular hydrogen bonding are well documented in the literature. In most polymer blends however, small differences in the vibrational spectra are difficult to observe directly and can only be shown in the difference spectra. Fourier transform infra-red (FTIR) spectroscopy has made analysis of chemical mixtures by computer-calculated difference spectra quite convenient and accurate. Several studies have shown that specific spectroscopic features sensitive to changes in miscibility can be observed and these have been used to interpret conformation or environment of polymers when blended.

Coleman and Zarian (1979) studied the FTIR spectrum of poly(ϵ -caprolactone)(PCL) – poly(vinyl chloride)(PVC) blends and observed a band shift to a lower frequency in the C=O absorption of PCL as a function of PVC concentration. The width at half-height of the carbonyl band also varied with PVC composition. These observations indicate the existence of a specific

interaction between the components whose miscibility is due to the interaction. Tabb and Koenig (1975) studied the FTIR spectra of plasticised PVC and suggested that interactions between the carbonyl bands and the carbon—chloride band occur in the amorphous region of this polymer. Coleman *et al* (1977) observed a shift in the C=C stretching frequency of poly (methyl methacrylate)(PMMA) in the presence of poly (vinylidene fluoride)(PVF₂).

3.7 Microscopy

Optical microscopy

Although the transmitted and the phase contrast techniques of optical microscopy require a difference in the refractive indices of the phases, contrast is best obtained in transmission with opaque or coloured samples. With the phase contrast optics, good contrast is obtained with transparent materials. This is because as well as a difference in the refractive indices, contrast also depends on the difference in the geometrical path of the light waves from the components, hence when this technique is available, it is the preferred method .

A hot stage with programmed heating and also a camera can be fitted to an optical microscope in order to study the morphology of the blend; optical micrographs can thus be obtained, at different stages of phase separation.

Electron microscopy

The resolving power of a light microscope is limited by the nature of the light. The minimum spacing, d , which can be resolved by a good microscope is of the order of the wavelength of the radiation source, λ , and is given by:

$$d = \frac{\lambda}{n \sin \theta} \quad (3.1)$$

θ is the angle of acceptance of the lens and n is the difference in the refractive index of the specimen. For better resolution, a larger angle and a shorter wavelength are desirable.

The transmission electron microscope (TEM) has a resolution of 2 to 10 Å. It uses an electron beam source and electrostatic or electromagnetic lenses instead of the glass lenses of optical microscopes. The technique and its application to polymers have been described by Collins *et al* (1973) and Rabek (1980). Other specific applications of electron microscopy are given by McMaster (1975) and Meyer *et al* (1978). It has the advantage that it reveals the geometry of the phase domains as well as the nature, sharp or diffuse, of the phase boundaries.

The method is limited by the sample preparation and the stability of the polymers in the electron beam. Other limitations have been outlined by Christner and Thomas (1977).

Scanning electron microscopy has also been used in the study of blend morphology. A fine beam of electrons is scanned across the surface of the specimen to which a conducting film had previously been applied by evaporation. Secondary or back-scattered electrons or (in the electron microprobe) X-ray photons are emitted when the beam hits the specimen. These are collected to give a signal which is used to modulate the electron beam in a television tube which scans in synchronism with the microscope beam. The resulting image has a great depth of field and a three-dimensional appearance because the microscope beam maintains its small size over the large distance, relative to the specimen. Contrast depends on differences in surface topography or texture.

3.8 Fluorescence methods

Non-radiative energy transfer between appropriately labelled polymers can be used as a criterion of polymer miscibility. In this technique the first polymer is labelled with a fluorescent substituent (the donor) and the second polymer with another fluorescent group (the acceptor) chosen so that the emission spectrum of the donor overlaps the absorption spectrum of the acceptor. It can then be shown that radiant energy supplied to the donor may be transferred to the acceptor over distances of the order of 2–5 nm, so that donor fluorescence intensity, I_D , is enhanced. The ratio I_D/I_A (I_A is the acceptor fluorescence intensity) will therefore decrease to the extent that the two polymeric species are intertwined allowing the donor and acceptor fluorophores to approach one another within a critical distance.

Another fluorescence phenomenon which may be used for the study of polymer miscibility involves excimer formation. An excimer is a complex between an excited and a ground-state fluorophore which involves typically two aromatic residues lying approximately parallel to each other at a spacing of about 3.5 Å. In a polymer carrying closely spaced chromophores of this type, excimers may form either by the interaction of such groups carried by the same chain molecule or different chain molecules. Thus in mixtures of fluorescent and non-fluorescent polymers, excimer emission will be favoured by phase separation.

3.9 The present system, PS–PVME

During the past two decades considerable effort has been expended by the polymer industry to identify miscible polymer pairs. Various techniques

have been used in an attempt to understand both the phase separation behaviour of polymer blends and their associated properties.

Theoretical treatments, for example, Cahn's (1965) concept of spinodal decomposition, was extended by studies on the growth process of the unstable concentration fluctuations involved in the spinodal decomposition mechanism.

As a result an increasing number of publications have been devoted to the miscibility of polymer blends both from an experimental and a theoretical viewpoint.

In a literature search covering the last twenty years, numerous publications dealing in some way with mixtures of polymers were encountered by the author. Rather than try and review this enormous amount of information, this section will be limited to the relevant aspects of miscible high molecular weight blends, in particular, to the present system and to the effects of pressure on polymer systems.

Since Bank *et al* (1971) demonstrated an LCST in PS–PVME blends, there has been a great deal of effort to locate precisely the phase diagrams and the factors which influence their shape and position, Nishi *et al* (1975), Nishi (1977), Nishi (1980), Halary *et al* (1984), Ubrich *et al* (1985). Workers focused their attention on the mechanisms of microphase separation in this blend because high polymer systems suitable for such studies are uncommon. In addition to the thermodynamic constraints pointed out by Olabisi *et al* (1979), it was further observed by Strobl *et al* (1986) that the critical temperature for such a system has to lie above the T_g of the blend and at the same time below the temperature range where rapid chemical decomposition occurs. These workers also observed that among chemically dissimilar polymers, there are only a few pairs in which miscibility can be demonstrated over the whole compositional range. Further, polystyrenes of a variety of molecular weights

are readily obtained, thus making it possible to study the effect of chain length on both the kinetic — Gelles and Frank (1983) and thermodynamic, Ubrich *et al* (1985) — aspects of phase separation in polymer blends. This is an important consideration because most of the 'anomalous' behaviour of polymer systems is a consequence of their high molecular weights. PS–PVME blend also offers versatility in the choice of techniques which include optical and electron microscopy, differential scanning calorimetry, X-ray, light and neutron scattering, nuclear magnetic resonance spectroscopy, vibrational spectroscopy and excimer fluorescence. Both equilibrium and dynamic studies of phase behaviour have been made with this blend so that it has become a 'model' for advancing a fundamental understanding of polymer systems and their materials application. Besides, the unusual miscibility behaviour of this binary mixture is particularly interesting. A number of workers have shown that solvent, molecular weight, composition and temperature can all affect the miscibility of these two polymers, Bank *et al* (1971), McMaster (1973), Kwei *et al* (1977), Davis and Kwei (1980), Reich and Cohen (1981). Bank *et al* (1971) used differential scanning calorimetry and dielectric relaxation studies to investigate the miscibility of this system. They found the phase behaviour to be solvent dependent — an exception to the conclusion reached by Scott (1949). The polymer pair is miscible in all proportions in hydrocarbon solvents such as toluene or xylene but not in chlorinated solvents such as trichloroethylene (TCE) or chloroform. The reason for this unusual solubility behaviour was analysed by Robard and co-workers (1977). Using the gas–liquid–chromatography (GLC) technique, they demonstrated in a conclusive manner that a large difference between the interaction parameters ($\Delta\chi$) of PS–TCE (χ_{12}) and PVME–TCE (χ_{13}) where ($\Delta\chi = \chi_{12} - \chi_{13}$) is responsible for the incomplete miscibility in the ternary solution. Similar conclusions were reached

by other investigators such as Hugelin and Dondos, (1969), Hsu and Prausnitz (1974), Nishi and Kwei (1975) and Aharoni (1978) and Robard *et al* (1978). The general conclusion reached by Bank *et al* (1971) is that for the compositions investigated by them, miscibility is not complete. Further studies by these workers (1972) indicate that the initially single-phase films cast from the appropriate solvents, phase-separates when heated above 125°C. Although all thermally phase-separated samples can be brought back to their original state of miscibility, reversibility of the process depends on such factors as cooling rates and thermal history. The two-phase films cast from the above listed solvents retained two-phase behaviour after thermal treatment consisting of extensive annealing and slow cooling.

Kwei *et al* (1974), Nishi *et al* (1975) and Davis and Kwei (1980) have undertaken detailed investigations to ascertain whether the miscible or the immiscible mixtures represent the thermodynamically preferred state.

Based on density measurements, Kwei *et al* (1974) indicated that miscible PS-PVME films can best be described as microheterogeneous with the different types of polymer molecules extensively mixed but not completely mixed on the segmental level as in random copolymers. This further observation was made because the T_g -composition curve of the blend deviates, especially at high PVME concentrations, from the theoretical predictions made by Fox (1956) which relate T_g to copolymer composition. Vapour sorption techniques allowed further evidence in that the interaction parameter, χ_{12} , was found to be negative in the range 35 – 65% PS, thus satisfying the thermodynamic criteria for miscibility within this range. By means of specific volume and interaction parameter measurements as well as diffusion and nmr spin lattice relaxation time studies, these workers suggested the existence of both a UCST and an LCST behaviour for this blend.

Cowie and Saeki (1981) used ternary solvent₍₁₎/polymer₍₂₎/polymer₍₃₎ system followed by extrapolation to zero solvent — a method developed by them — to locate both a UCST and an LCST for this blend, as earlier suggested by Kwei *et al* (1974). Their phase diagrams show regions of immiscibility above 75°C and below 35°C with a miscible one-phase region in between. This latter region increases as the weight fraction of PS is increased beyond 0.2.

Hourston and Hughes (1978) investigated the dynamic mechanical and sonic velocity behaviour of this blend. They suggested that it consists essentially of a two-phase morphology in which there are regions richer in PS and a completely mixed matrix of PS and PVME. This inhomogeneity is further emphasised by their electron micrograph of a 'miscible' sample containing 40% by weight of PVME; the micrograph clearly shows a two-phase morphology. Theoretical calculations made by these workers show that for this blend incompatibility is predicted over most of the compositional range. These calculations are based on criteria for prediction of miscibility; Scott (1949), Krause (1972) Schneier (1973); McMaster (1973) investigated this system and confirmed the earlier observations made for toluene-cast films. The cloud-point temperature — composition data clearly illustrates it to be an example of an LCST behaviour. Using a modification of Flory's equation-of-state approach to thermodynamics, McMaster confirmed, using this system that an LCST behaviour should generally be anticipated for high molecular weight polymer blends due to differences in the pure component thermal expansion coefficients.

Nishi *et al* (1975) offered evidence of spinodal decomposition by pulsed nmr data which indicates a gradual change in the composition of newly formed phases, whereas phase separation via nucleation and growth leads to discrete phase domains. Hashimoto *et al* (1983) studied the dynamics of its phase

separation and confirmed that the early stages of phase separation in the spinodal decomposition (SD) regimes is in accord with the linear theories of SD originally proposed by Cahn (1965) for small molecules and later extended by de Gennes (1980) for polymers. The later stage of SD is found to deviate from exponential behaviour while in the nucleation and growth (NG) regime, the intensity increases non-exponentially with time.

Recently a new fluorescence method, Halary *et al* (1984), was proposed as a tool for accurate determination of both its spinodal and binodal curves. At about the same time, Yang *et al* (1983), Atkin *et al* (1984) and Halary *et al* (1985) produced evidence from cloud point measurements and from fluorescence and SANS, that the use of perdeuterated polystyrene (PS-d₈) instead of hydrogenous polystyrene (PSH) of identical chain length allows the LCST to rise by about 40°C, thus improving miscibility. Earlier workers, Nishi *et al* (1975) had achieved the same result by cross-linking the blend by UV irradiation. Following Nishi's result, Paul and his coworkers (1978, 1982) concluded that the LCST boundary can generally be moved upwards by making the net interaction between the chains more exothermic. An appealing approach to these workers was the addition of a small amount of comonomer into one of the blend components, Fernandez *et al* (1986), Fowler *et al* (1987), Min and Paul (1987). Kwei *et al* (1985) demonstrated this by incorporating a comonomer having hexafluoroisopropanol units that strongly interact with PVME via hydrogen bonding and by incorporating one into methyl methacrylate where no such interaction is likely, Chien *et al* (1988). Using the PS-PVME system as an example, Min and Paul (1988) provided further illustrations of how cloud point curves can be shifted upwards by use of comonomers. They found that blends of PVME with a styrenic copolymer containing 1% acrylic acid did not phase separate prior to decomposition. It is

possible to elevate the cloud point curve by as much as 100°C using acrylonitrile as the comonomer and by about 60°C using maleic anhydride. A rational choice of a comonomer for this purpose however requires knowledge of both the intermolecular and intramolecular binary interactions among the various monomer residues present. Some attempts had earlier been made by Lu *et al* (1983), Garcia (1984) and Garcia (1984a) to specify precisely the nature of molecular interactions responsible for the miscibility of PS–PVME pair by using FTIR. Although the spectral complexity stood in the way of definite answers, it was proposed that the interaction involves the ether lone-pair electrons of PVME with the benzene ring of PS. Larbi *et al* (1986) tried to cross-check these findings by using quite a different approach based on the location of the phase diagrams of PVME either blended with poly(1-penta-deuterophenyl ethylene)(PS-d₅) or with poly(1-phenyltrideutero-ethylene)(PS-d₃). Their conclusions confirm that the benzene rings of polystyrene are responsible for the interactions with PVME. In addition it was shown that any change in polydispersity of the blend components leads to a shift of the minimum of the phase diagrams, without any modification of the minimum phase separation temperature $(T_{\min})_{\infty}$ which should be observed in the presence of a PS of infinite molecular weight.

The elevation of the cloud point on deuteration of PS was suggested by Yang *et al* (1983) to be due to a solubility parameter difference between hydrogenous (PSH) and perdeuterated – polystyrene (PSD). Strazielle and Benoit (1975) had earlier observed this difference to be – 0.04. Using the relationship proposed by Krause (1978), a difference in interaction parameter, χ_{12} , of 0.01 is estimated for PSH/PVME and PSD/PVME. Although the difference is small, McMaster (1973) had shown that a difference in χ_{12} of 0.05 can, according to the equation-of-state theory, lead to a shift of 130°C in the

LCST. A greater solubility and higher LCST is predicted for the PSD/PVME blend based on these observations. The existence of a volume change on mixing PS and PVME is seen in the data of Kwei *et al* (1974). This volume change, therefore, depends on whether PSH or PSD is blended with PVME.

Hiramatsu *et al* (1983) studied the effect of high pressure on the phase separation behaviour of hydrogenous – PS/PVME blend. They found that with an increase in pressure, the cloud point curves shift to higher temperatures. They also observed that the mechanism of phase separation by both spinodal decomposition and nucleation and growth is slower under high pressure.

Various workers have also observed the effects of pressure on polymer systems. Some of these effects which have been reported in the literature are briefly reviewed in Sections 3.10 – 3.15.

3.10 Effect of pressure on phase separation temperature of polymer systems

Van der Lee (1900) observed that the solubility of the system, phenol – water diminished while its UCST increased with pressure. Since then systematic studies have been carried out by several authors, on the effect of pressure on the critical solution phenomena of simple liquid mixtures, Buchner (1906), Timmermans (1936), polymer mixtures, McMaster (1973) and oligomeric mixtures, Tripathi (1979). As a result of these investigations three possible effects of pressure on various systems have been reported, Timmermans (1900).

- the mutual solubility is reduced while the UCST is increased, for example, the system cyclohexane – aniline, Timmermans (1900).

- the mutual solubility is increased but the UCST is reduced as in the case of hexane – nitrobenzene system, Timmermans (1900).
- both the mutual solubility and the LCST increased as observed with the system (CO₂ – O) – nitrophenol, Timmermans (1900).

In each case, authors have related their results to the volume change on mixing, ΔV_m , and to the heat of mixing, ΔH_m , by the expression for the pressure dependence of the critical solution temperature, Prigogine (1957)

$$(\partial T / \partial P)_c = - (\partial \chi / \partial P)_T / (\partial \chi / \partial T)_P \simeq \frac{T \Delta V_m}{\Delta H_m} \quad (3.1)$$

and

$$\Delta H_m = T \Delta V_m / (\partial T / \partial P)_c \quad (3.2)$$

Therefore the sign of the pressure dependence of the critical solution temperature, $(\partial T / \partial P)_c$, depends on the sign of ΔH_m and on whether the system shows a UCST or an LCST. At a UCST, the mixing is always endothermic, i.e. ΔH_m is positive; the two possibilities are:

$$1. \quad \Delta H_m = \frac{- T \Delta V_m}{- (\partial T / \partial P)_c}$$

If there is a contraction on mixing, $(\partial T / \partial P)_c$ is negative. Therefore an increase in pressure lowers the UCST and miscibility of the blend is improved.

$$2. \quad \Delta H_m = \frac{+ T \Delta V_m}{+ (\partial T / \partial P)_c}$$

Hence if there is expansion on mixing, $(\partial T / \partial P)_c$ is positive and so an increase in pressure raises the UCST and miscibility of the system is reduced.

The effect of pressure at an LCST is just the reverse. In this case mixing is exothermic and the two possibilities are:

$$1. \quad -\Delta H_m = \frac{-T\Delta V_m}{+(\partial T/\partial P)_c}$$

If there is a contraction on mixing, $(\partial T/\partial P)_c$ is positive. Therefore an increase in pressure raises the LCST and miscibility is improved.

$$2. \quad -\Delta H_m = \frac{+T\Delta V_m}{-(\partial T/\partial P)_c}$$

If there is an expansion on mixing, $(\partial T/\partial P)_c$ is negative. Therefore an increase in pressure lowers the LCST and miscibility of the system is reduced.

Whenever there is contraction on mixing, the miscibility of the system generally improves with pressure. On the other hand, miscibility is reduced if the system mixes with an expansion in volume.

For most high molecular weight binary polymer blends, mixing is exothermic and there is contraction in the volume of the system. Therefore pressure is expected to raise the LCST and this should result in an improvement in the miscibility of the system.

The LCST has its origin in a negative non-combinatorial contribution to ΔS_m associated with the difference in the 'free volume' or degree of thermal expansion of the components. Application of pressure decreases this 'free volume' difference. The miscibility of oligomeric systems which show a UCST depends on their large combinatorial entropy. An increase in pressure induces order and reduces the entropy. This decreases the mutual solubility of the system and the UCST is raised.

Saeki *et al* (1975) found that the value of $(\partial T/\partial P)_c$ for PS in cyclohexane (an UCST system) is positive when the molecular weight of PS is 3.7×10^4 but this changes to negative for solutions containing a high molecular weight PS. ($11 - 145 \times 10^4$). Tripathi (1979) also found that an increase in pressure on two UCST systems, (methoxylated poly (ethylene glycol) in methoxylated poly(propylene glycol) and PS in poly(butadiene), decrease their miscibilities. He showed, using the Flory – Huggins model, that χ_{12} values increase with an increase in pressure for the above mentioned systems.

3.11 The effect of pressure on miscibility

The effects of thermodynamic variables on the properties of polymer solutions and blends can be predicted by the 'free volume theories'. A convenient form of this expression, which enables the effects of pressure variation to be monitored has been presented in the literature, Gaeckle and Patterson (1972)

$$\chi_{12}(P,T) = c_1 \left[-\frac{\tilde{U}_1}{\tilde{T}_1} v^2 + \frac{1}{2} \tilde{C}_{P_1} (\tilde{P}_1 \tilde{T}_1) \left\{ \tau + \frac{\tilde{P}_1 \tilde{v}_1^2 \cdot \pi}{\tilde{P}_1 \tilde{v}_1^2 + 1} \right\}^2 \right] \quad (3.3)$$

The equation is written in terms of reduced thermodynamic variables for component 1 (with tilde superscripts) and parameters v^2 , τ and π which characterise differences between the two components. The terms are described as follows:

$\tilde{U}_1$ represents the configurational energy of component q and it is the energy of vaporisation divided by energy reduction parameters.

$3c_1$ is the number of external volume-dependent degrees of freedom of a molecule of component 1.

$$c_1 = P_1^* V_1^* / T_1^{*R} \quad (3.4)$$

$\tilde{C}_{P_1}$ is the reduced configurational heat capacity, equivalent to the temperature derivative of $\bar{U}_1$.

The parameters v^2 , τ and π are defined as follows:

$$v^2 = \left[1 - \left[\frac{\epsilon_{22}}{\epsilon_{11}} \right]^{1/2} \right]^2 = \left[1 - \left[\frac{P_2^*}{P_1^*} \right]^{1/2} \right]^2 \quad (3.5)$$

$$\tau = \left[1 - \left[\frac{T_1^*}{T_2^*} \right] \right] = \left[1 - \left[\frac{c_2/r_2}{c_1/r_2} \right] \right] \quad (3.6)$$

$$\pi = \left[\left[\frac{P_1^*}{P_2^*} \right] - 1 \right] \quad (3.7)$$

ϵ in equation (2.55) is the contact energy, and hence v^2 expresses the difference in the chemical nature of the components.

τ expresses the difference in the degree of thermal expansion of the two components.

π expresses the difference in pressure reduction parameters of the components.

The χ_{12} value calculated from equation (3.3) as a function of pressure can exhibit a wide range of behaviour because of the number of variables and their dependence on pressure, for instance:

— An increase in pressure affects component 1 (the more expanded

component) to a greater extent; therefore τ is decreased. This results in a decrease in χ_{12} and improved miscibility.

- An increase in pressure increases v^2 , the interaction variable. This is unfavorable to mixing because χ_{12} is increased.
- Experimentally, the π coefficient has been found to increase with pressure.
- The reduced volume decreases while the reduced pressure increases with pressure.

The application of pressure has been found to have the most significant effect on χ_{12} at high temperatures where there is a large difference in free volume between the components and in systems where the disparity of intermolecular forces between components is small.

Patterson and Robard (1978) used a combination of the Prigogine and Flory equation-of-state theories to relate the interaction parameter, to two terms interactional and free-volume:

$$\frac{\chi_{12}}{\bar{V}_1^*} = \frac{P_1^*}{RT_1^*} \left[\frac{\bar{v}^{1/3}}{\bar{v}^{1/3}-1} \cdot \frac{X_{12}}{P_1^*} + \left[\frac{4}{3} - \frac{\bar{v}^{1/3}}{3} \right] \cdot \frac{\tau^2}{2} \right] \quad (3.8)$$

interactional
term
free volume
term

where the terms are as defined earlier. Rostami (1983) used the above equation to calculate the effects of temperature and pressure on the LCST system of poly(ethylene – co – vinyl acetate (EVA45) – chlorinated polyethylene (CPE3). He found that an increase in temperature causes the negative interactional term to decrease and the positive free volume term to increase. Application of pressure to this system is expected to reduce $\bar{v}$ and make χ_{12}

more negative. The miscibility of the system therefore increases in a similar manner to that observed by Saeki *et al* (1975, 1976).

3.12 The effect of pressure on static properties of polymer systems – virial coefficient and chain dimensions

The second osmotic virial coefficient, A_2 , is a measure of the miscibility between two components A and B. It reflects the tendency of a segment of polymer A to exclude its neighbours from the volume it occupies, Billmeyer (1971). Thus a large positive A_2 indicates a better affinity between segments of the different components A and B than between like segments of A or B.

The radius of gyration, R_g , is a measure of the average distance of a chain element from the centre of gravity of the coil, Billmeyer (1971). It is also a measure of the miscibility between the components. A large radius of gyration indicates an increase in the interaction between the components and hence enhanced miscibility. The interaction parameter can be calculated from the virial coefficient, A_2 , which is directly obtainable experimentally. Jelenic *et al* (1984).

$$\chi_{12} = \frac{1}{P_1} \left[0.5 - \frac{V_1 M_2^2 A_2}{V_2^2} \right] \quad (3.9)$$

where M_2 is the molecular weight of component 2 and P_1 is the degree of polymerisation of component 1.

χ_{12} and A_2 usually exhibit opposite signs and are almost proportional to each other. Therefore in polymer blends, the usual criterion of miscibility $\chi_{12} < 0$ can be replaced by $A_2 > 0$.

Pressure should have a large effect on parameters such as A_2 and R_g which reflect the interactions between the components especially where the free volume contribution is dominant; these quantities should increase with pressure. This would correspond to a decrease of ΔG_m or to a negative value of ΔV_m . At low temperatures or for UCST, the free volume contribution will be of less importance. The second virial coefficient and the polymer dimensions could decrease with pressure, corresponding to a positive value of ΔV_m .

The second virial coefficient of high molecular weight polystyrene in various solvents, were measured by light scattering as a function of pressure up to 5000 atm. Depending on the system, A_2 is found to increase in magnitude leveling off at high pressures, remains constant independent of pressure or decreases in magnitude, resulting in precipitation, McDonald and Claessor (1973, 1976).

The change in virial coefficient with pressure has been related to the volume of dilution, Schulz and Lechner (1970), thus:

$$\frac{\Delta V_1}{V_1} = C^2 RT \left[- \left[\frac{\partial A_2}{\partial P} \right]_T - x_T A_2 \right] \quad (3.10)$$

where

V_1 is the molar volume of the pure solvent at the experimental temperature and pressure

C is the concentration in weight of polymer per volume of solution and

x_T is the isothermal compressibility: $\left[\frac{1}{V} \right] \left[\frac{\partial V}{\partial P} \right]_T$.

The second term within the bracket in equation (3.10) is usually relatively small. Consequently the volume term and the pressure derivative of the virial coefficient have opposite signs.

A system which has an endothermic heat of mixing or positive volume of dilution would show a negative value for the pressure derivative of the virial coefficient.

3.13 Effect of pressure on the viscosity of polymer systems

For moderate pressures at a given temperature and concentration, Claesson *et al* (1983) found that both the viscosity coefficient, η , and the intrinsic viscosity, $[\eta]$, of PS in toluene increases while the Huggins constant decreases with pressure. Wolf and his co-workers (1979, 1981 and 1982) measured the effect of pressure on solutions of PS in various organic solvents up to 1 Kbar. After an initial increase they observed a sudden decrease in viscosity because of phase separation with increasing pressure. This increase in viscosity which is greater with concentrated solutions is due in part to a closer interaction between the components, brought about by pressure. This results in improved miscibility. This is consistent with the observation (see previous Section) that the second virial coefficient increases gradually with increasing pressure.

3.14 Effect of pressure on dynamic properties of polymer systems

Although a number of reports have appeared in the literature on the effect of pressure on static properties of polymer systems, very little attention has been paid to the pressure dependence of dynamical properties. Roots and Nystrom (1982) studied the pressure dependence of the diffusion coefficient, D , and the hydrodynamic radius, R_{H} , of dilute and semidilute solutions of polystyrene in toluene. The diffusion coefficient was observed to decrease with

pressure. This decrease was however correlated to the change in viscosity of the solution with pressure.

These workers concluded that both the diffusion coefficient, D and the hydrodynamic radius, R_H , are independent of pressure.

3.15 The effect of pressure on glass transition temperature and dielectric relaxation time of polymer systems

In an attempt to clarify the criteria satisfied at the glass transition the effect of pressure on the glass transition temperature of polymer systems has been studied by several workers. O'Reilly (1962) measured the dielectric constant and loss of polyvinyl acetate, as a function of temperature ($25 - 120^\circ\text{C}$), pressure ($0 - 3300$ atm) and frequency ($0.06 - 10$ Kcycles/sec). He found that $\left[\frac{\partial T_g}{\partial P}\right]$ which was identified as the temperature at which ϵ''_{max} occurred at a constant pressure, is 0.022°C/atm . He also found that $\ln \tau_D$ (where τ_D is relaxation time) is linear in the pressure. The pressure dependence of T_g has been found to be positive but its value varies with the type of system, Igonin *et al* (1959), Gilchrist *et al* (1957), Wood (1958), Nolle *et al* (1959), McKinney *et al* (1961).

CHAPTER 4

DESCRIPTION OF THE EQUIPMENT

4.1 The pressure rig

An equipment, the pressure rig (Fig. 4.1) was set up to study the effect of pressure on the phase separation behaviour of miscible, high molecular weight polymer blends. Designed for operation at pressures up to 3 Kbar and temperatures up to 280°C, the rig is equipped with sealed viewing tubes, fitted with sapphire windows through which the sample can be viewed. Fig. (4.2) shows details of the rig. Pressure is transmitted to the sample by silicone oil,

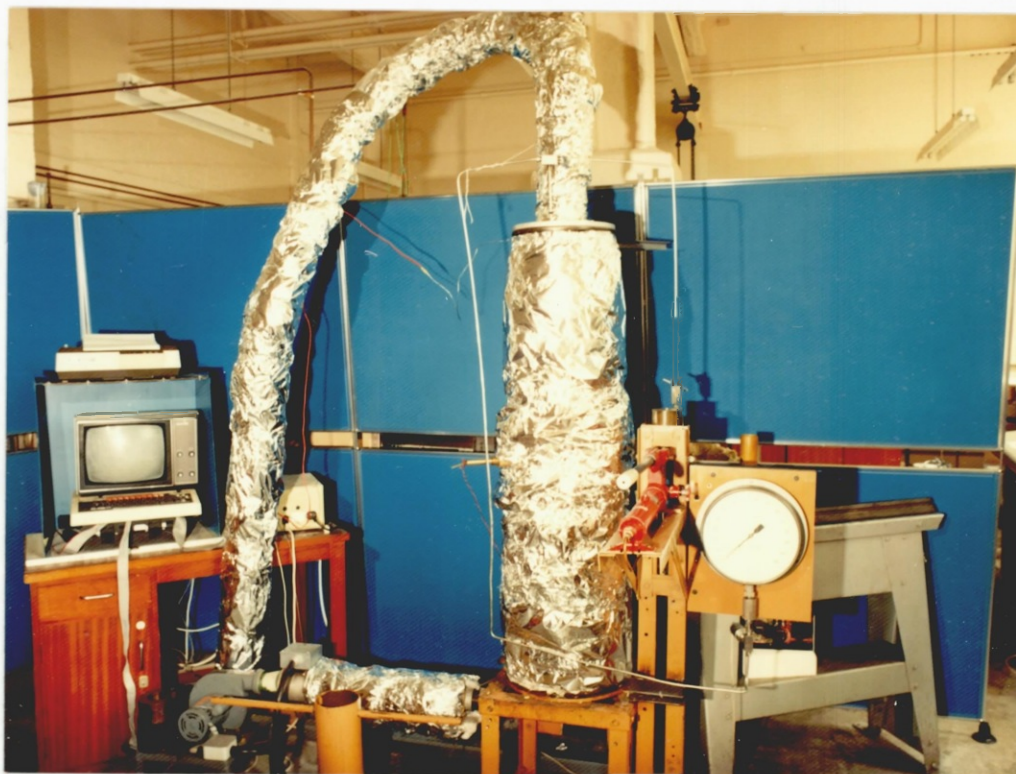


Figure 4.1

The rig

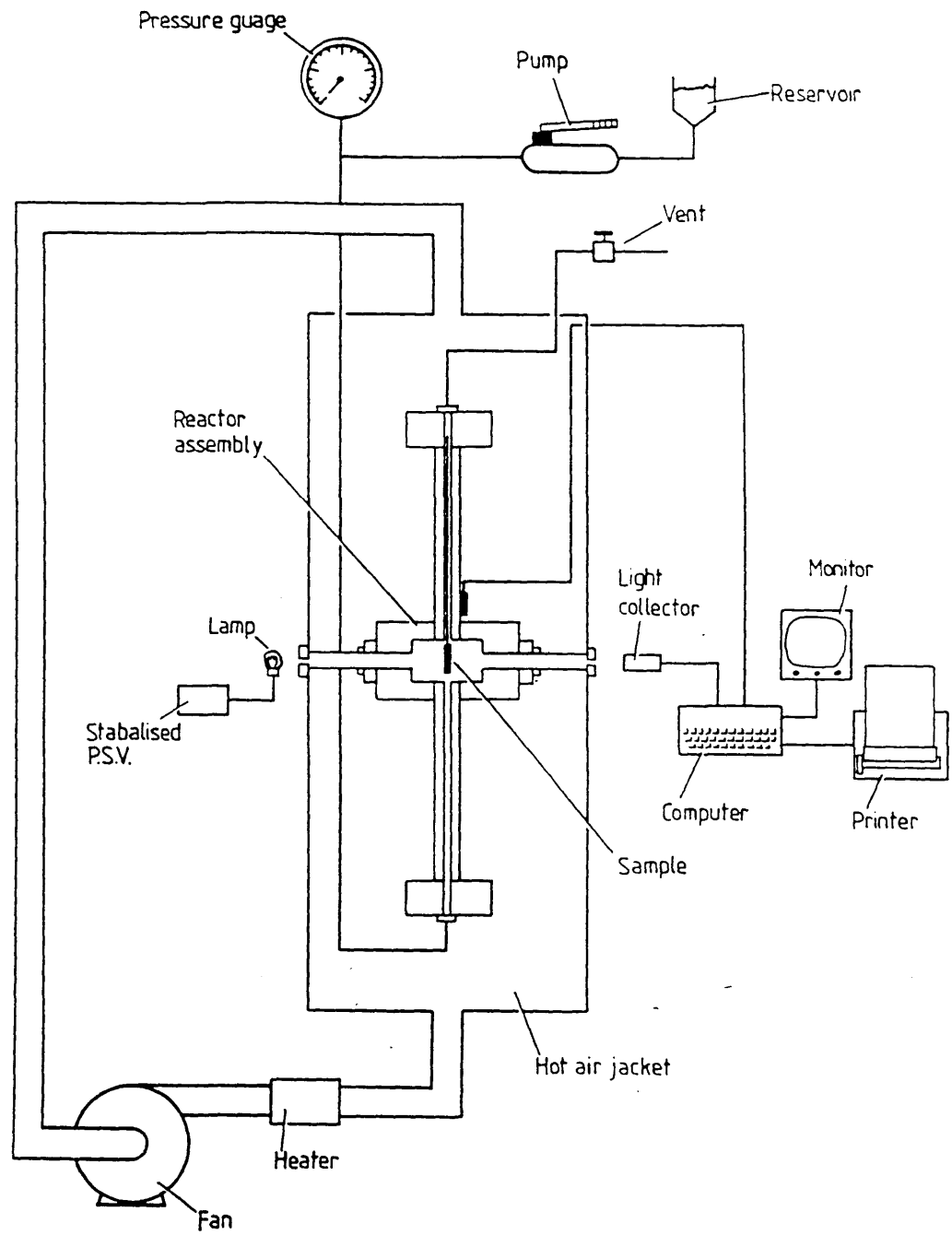


Figure 4.2
The rig and connections

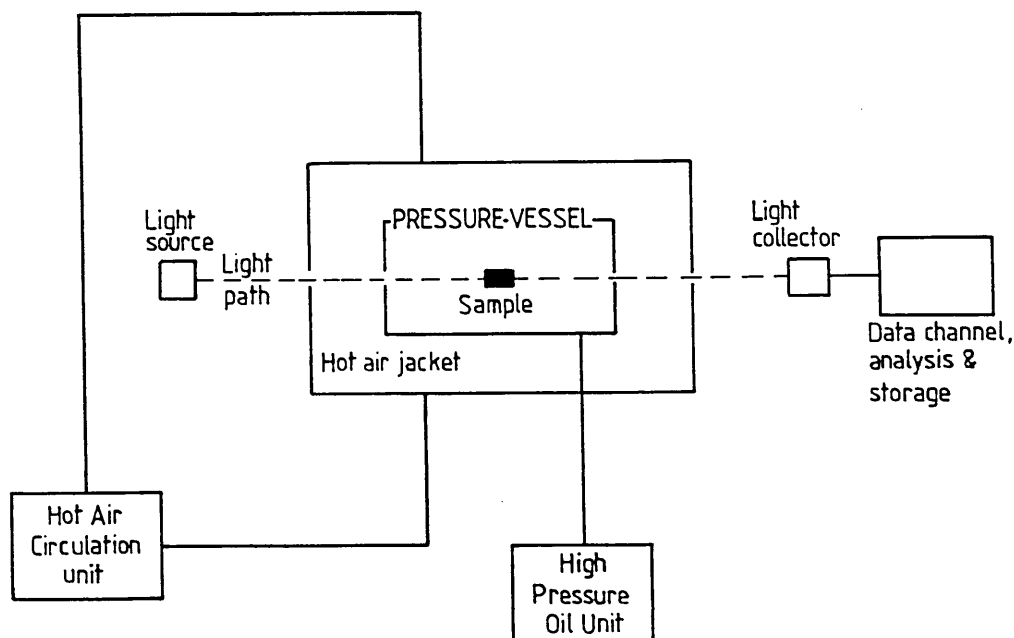


Figure 4.3
Block diagram of the rig

pumped through the pressure line. The temperature of the sample is monitored by a type – K coaxial thermocouple. The intensity of the collimated beam of light, transmitted through the sample, is measured as a function of temperature and pressure by a photodiode. A BBC microcomputer is used for data logging and for driving the temperature ramp at a preset rate. A NEC printer which automatically prints out the data is connected to the microcomputer. Fig. 4.3 is a block diagram of the pressure rig which consists of the following major components:

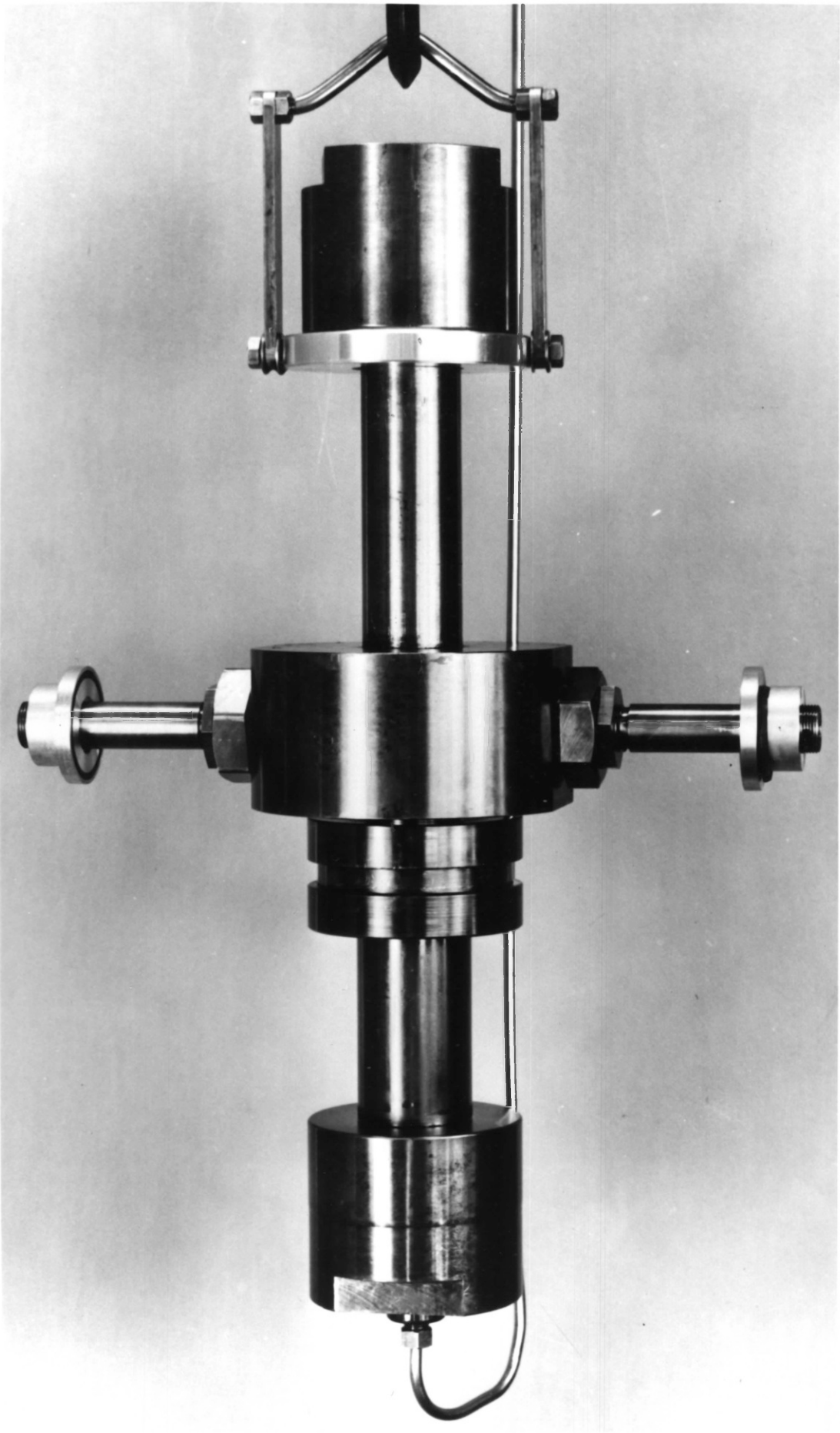


Figure 4.4
The pressure vessel

PRESSURE VESSEL

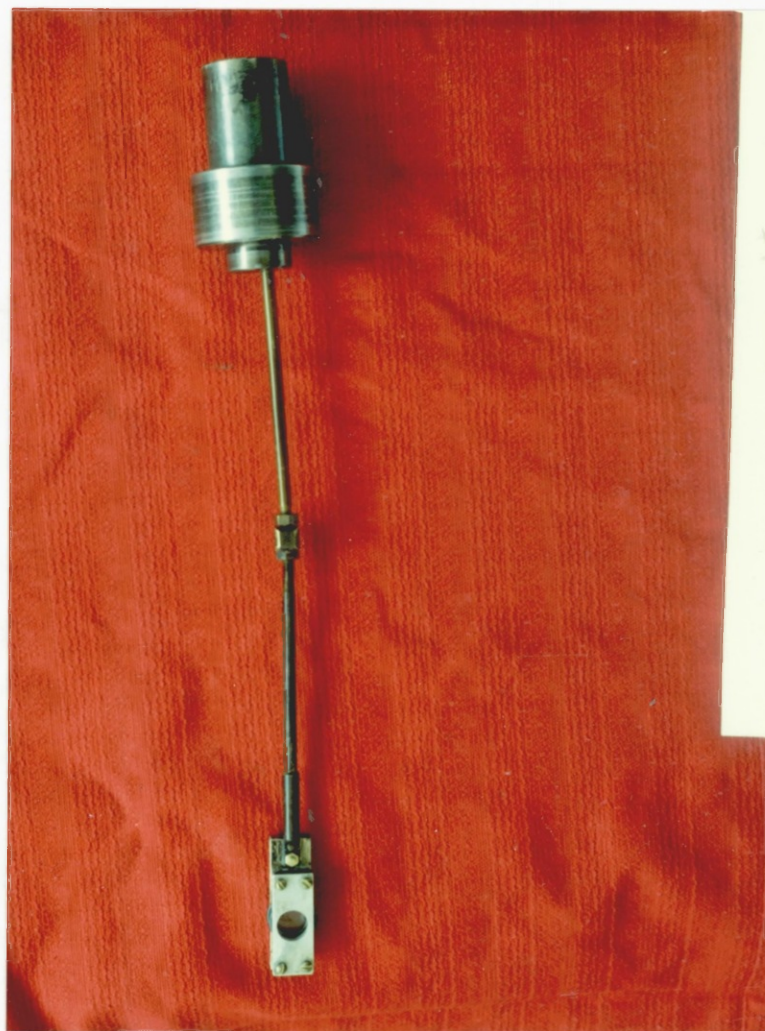


Figure 4.5
The sample loading assembly



Figure 4.6
The heating system

- the pressure reactor (vessel) (Fig. 4.4)
- the sample loading assembly (Fig. 4.5)
- the heating system (Fig. 4.6)

4.2 The pressure reactor

The cylindrical pressure reactor, Fig. (4.7) of dimensions 5.2 cm (OD), 2.3 cm (ID) and 50 cm height, is made of low alloy steel. It has side tubes for sample illumination through sapphire windows. Both ends of the reactor are fitted with identical end – blocks by means of neoprene rubber 'O' ring seals.

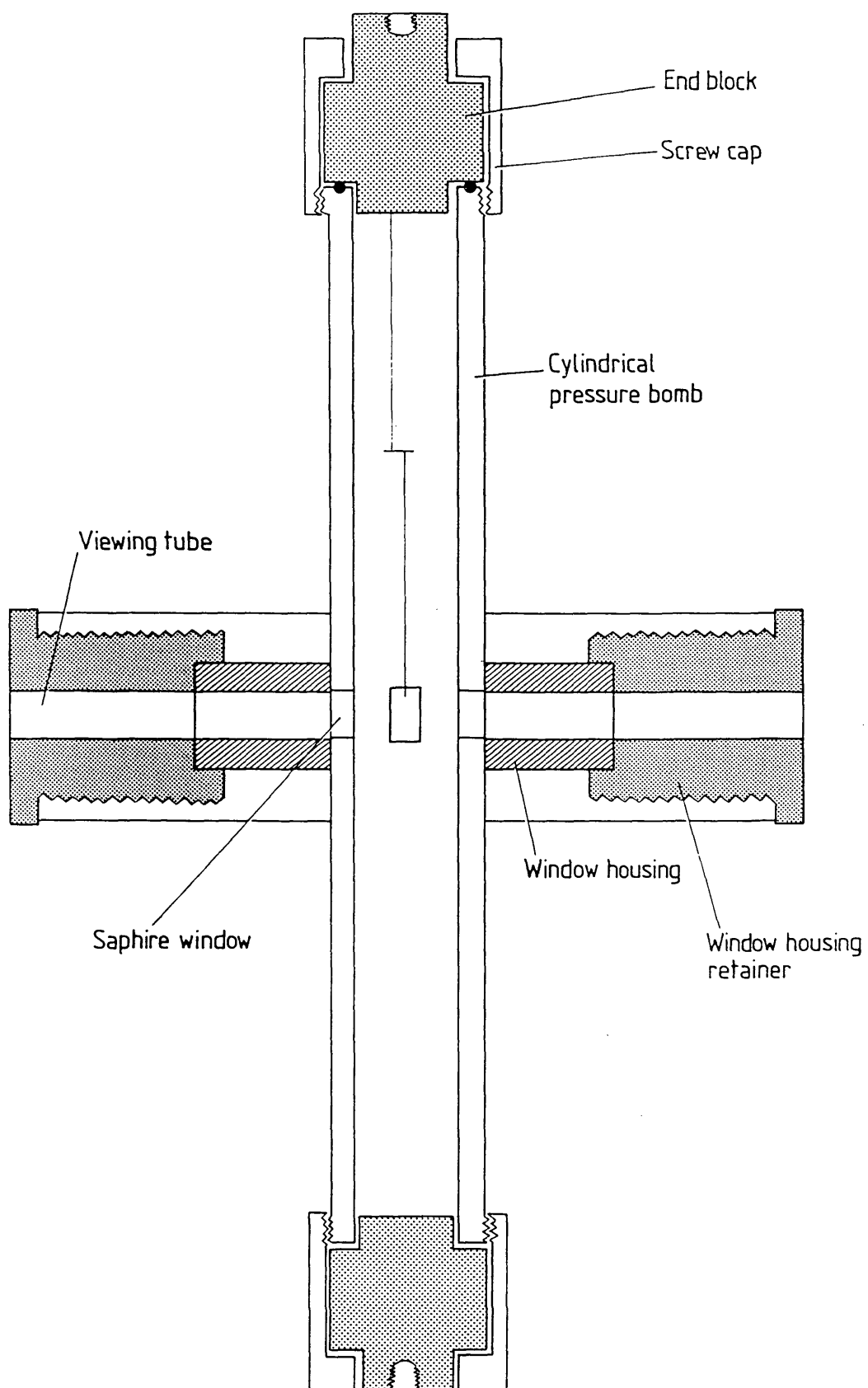


Figure 4.7

The pressure reactor

The end – blocks are retained by screw caps which screw onto the threaded ends of the reactor, thus compressing the 'O' ring seals. The upper surface of the top screw cap is stepped in order to facilitate the seating of a spanner which is used for tightening and releasing the cap. The lower end of the reactor is connected to a pressure gauge and a hydraulic hand pump in a standard tee – piece fitting. An analogue pressure is provided by the 'Budenberg' pressure gauge which can read a maximum of 1500 atm while the voltage from the pressure transducer is digitised prior to its display on the microcomputer. A calibration of the pressure output from the computer against the reading from the pressure gauge is shown in Fig. (4.8). The pump has a capacity of 700 cm³

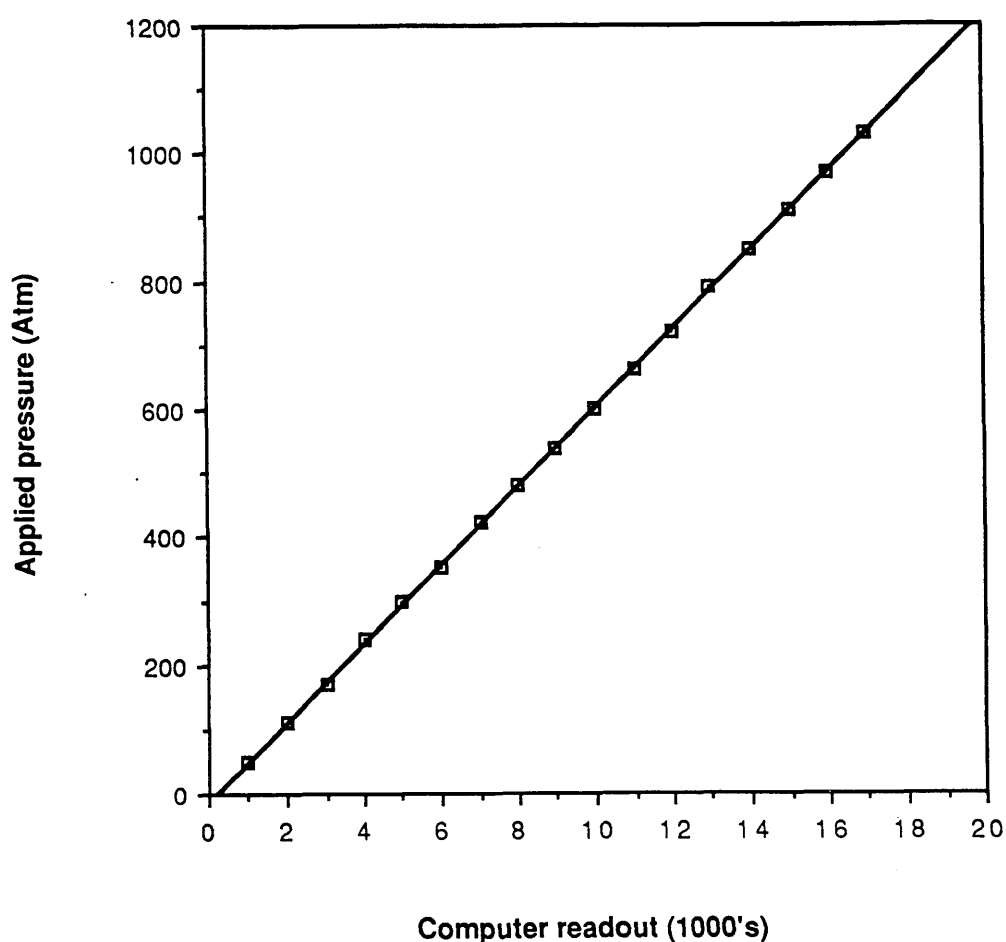


Figure 4.8

Calibration curve of pressure

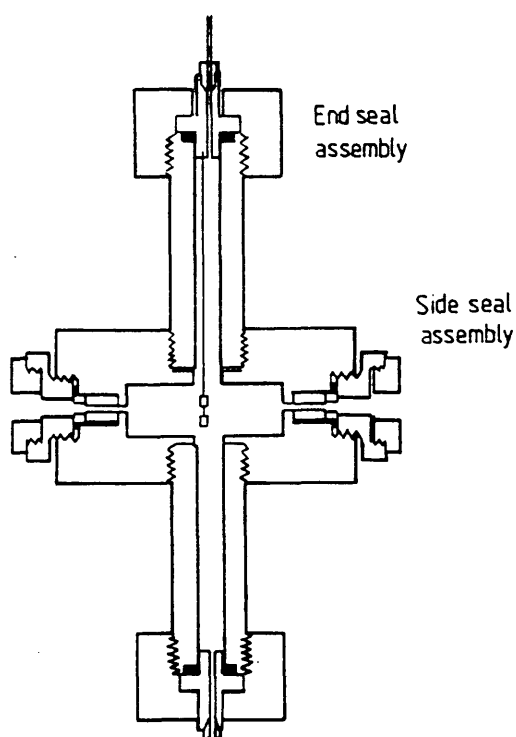


Figure 4.9

Pressure reactor

and it develops pressures up to 3 Kbar. It is connected to a silicone oil reservoir by a (0.6 cm OD) copper tubing. The sapphire windows are retained by copper washers. Fig. (4.9) shows the pressure reactor and the arrangement of the 'seals'. Figs. (4.10) and (4.11) show details of the 'side seal assembly' and the 'end seal assembly' respectively.

The upper end of the reactor like the lower end is connected to a standard AMINCO joint and a high pressure valve. This upper end is mainly used as a vent. The connections to the reactor are carefully made so as to isolate the pressure gauge and the reactor between two standard high pressure

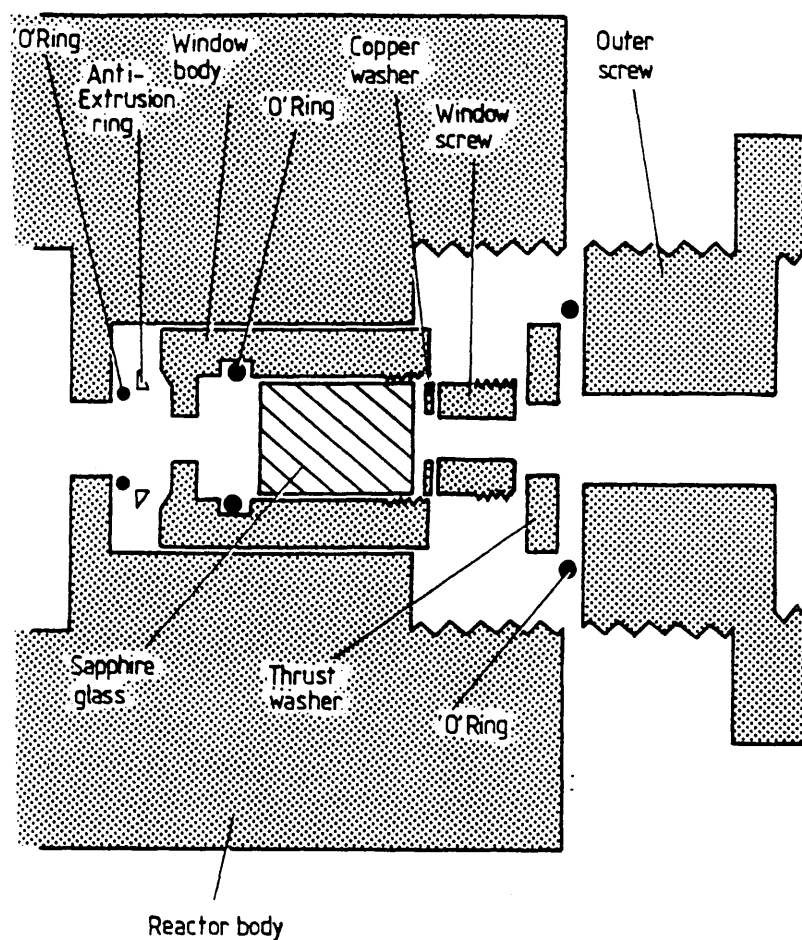


Figure 4.10

Side seal assembly

valves. Standard tubing made of stainless steel (0.64 cm OD and 0.23 ID) is used to connect the different parts of the high pressure reactor.

4.3 The sample loading assembly

The sample loading assembly, Fig. (4.12), consists of a sample holder, Fig. (4.13), mounted on an adjustable support. The latter ensures the correct height for viewing the sample through the sapphire window and viewing tube. The 'assembly' is held in place by a retaining knot.

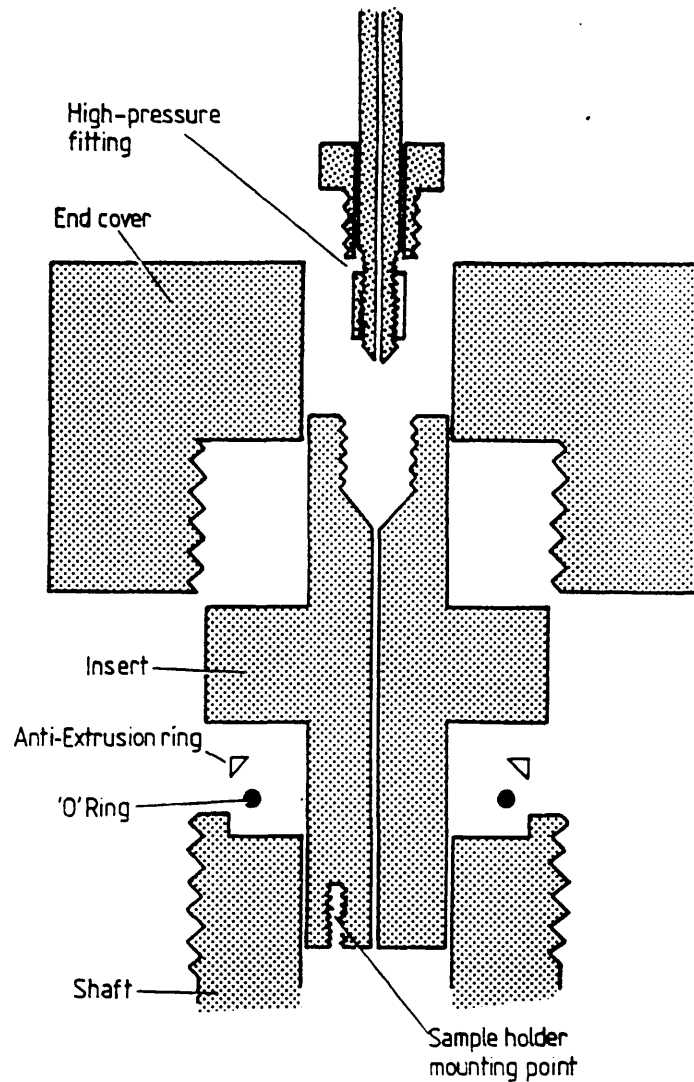


Figure 4.11

End seal assembly

4.4. The heating system

The pressure reactor sits on a hot air jacket, a cylindrical steel tank (25 cm ID, 132 cm high) which serves as a thermostatic air bath. The bath is heated by an 'in - line' process air heater, designed for use with a centrifugal fan. The heater itself has a 9 KW element whose loading is controlled by a 3 - heat switching system connected in parallel. The flow of heat is directed

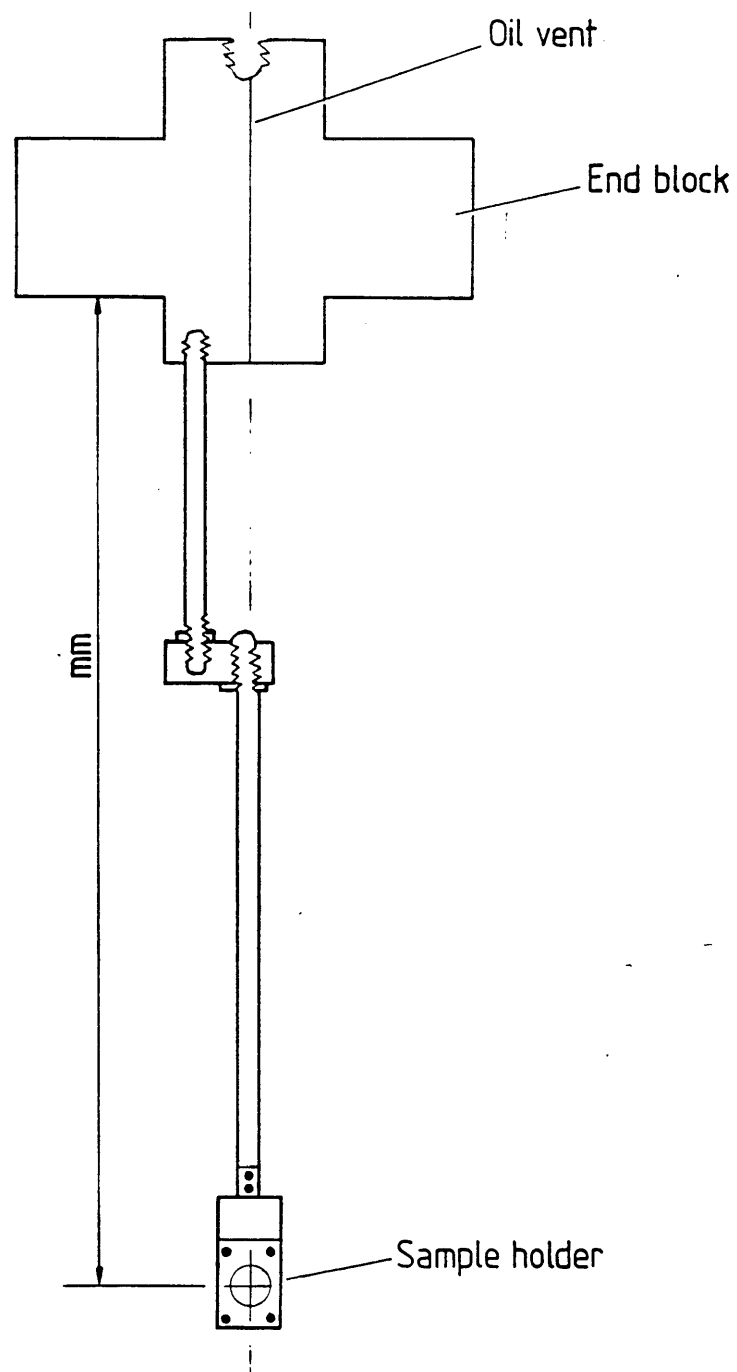
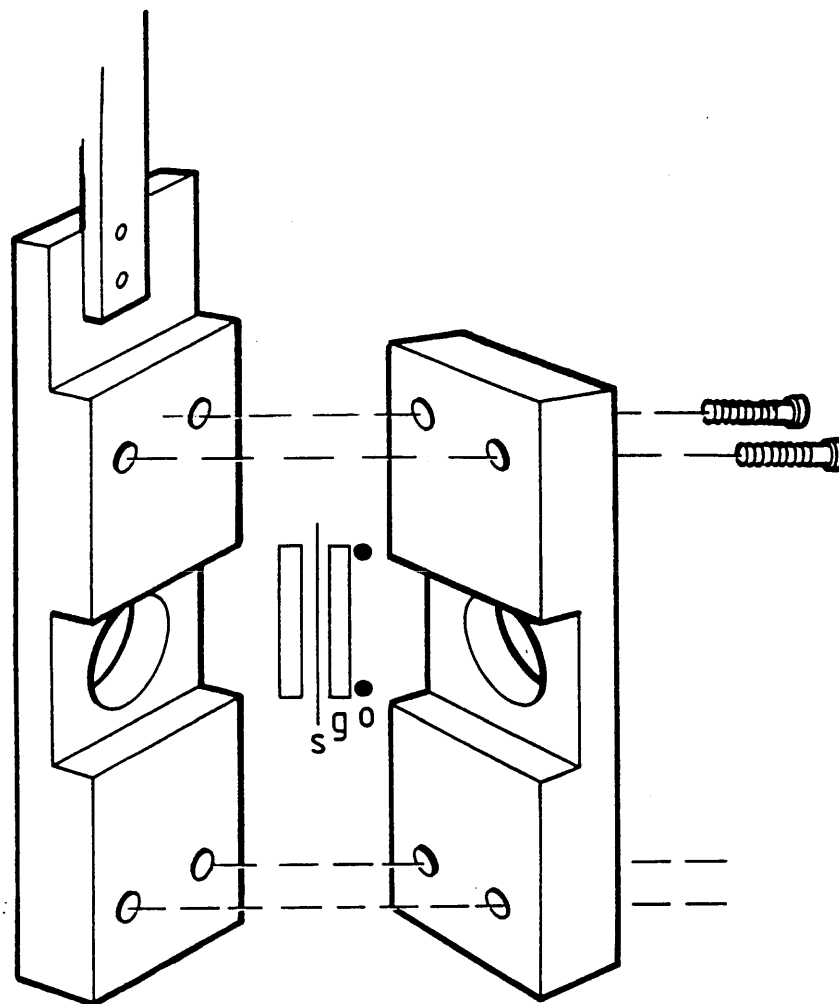


Figure 4.12
Sample loading assembly



s. sample
g. glass plate
o. 'o' ring

Figure 4.13

Sample holder

through a flexible steel hose (3 metres long; 5.1 cm ID) into the air – bath through an air regulating valve. Hot air is thus circulated round the pressure reactor. The equipment is well lagged to prevent heat exchange with the surroundings. The heater is controlled by a proportional – integral –

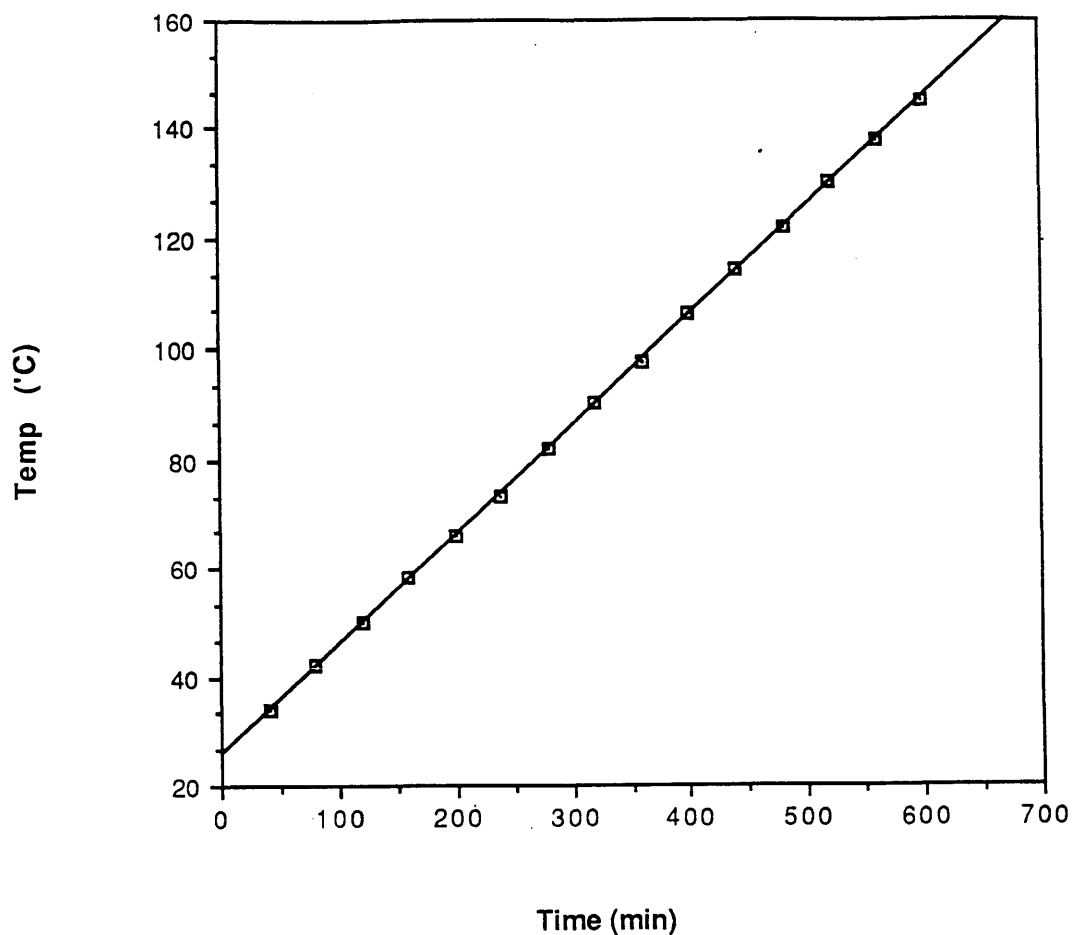


Figure 4.14

Heating rate

differential (PID) controller. The latter has three settings, the proportional factor, the integral factor and the differential factor, which are adjusted to give the best response for the desired rate of heating. Fig. (4.14) shows a controlled experimental heating rate of $0.2^{\circ}\text{C}/\text{minute}$.

4.5 Instrumentation

Experiments on the pressure rig take several hours, hence the need for automation. A BBC microcomputer is used to:

- set up a temperature ramp using a PID control loop

- generate a real time clock
- measure and log the time, temperature, pressure and light intensity
- eliminate storage of redundant data
- collect data on a data file for subsequent processing.

4.6 Sapphire window housing

An adequate sealing of the sapphire windows is most essential for high pressure operation. A special arrangement as shown in Fig. (4.15) has been made to house the windows. The two cylindrical synthetic sapphire windows (1.9 cm diameter and 1.28 cm thickness) with polished parallel faces are mounted diametrically opposite at each end of the viewing tube. They are held in place by copper washers and then pressure — sealed by means of neoprene 'O' rings, as shown in Fig. (4.16). The sapphire windows are finally locked and retained in place with the help of retaining screws.

4.7 Optical alignment

The optical alignment is shown in Fig. (4.17). The sample is illuminated by a collimated beam of light from a 12 volt projector lamp. The beam of light is adjustable for correct viewing height through the guide tube, as shown in Fig. (4.18). The intensity of the light transmitted through the sample is detected by a photodiode set at zero angle to the incident light beam.

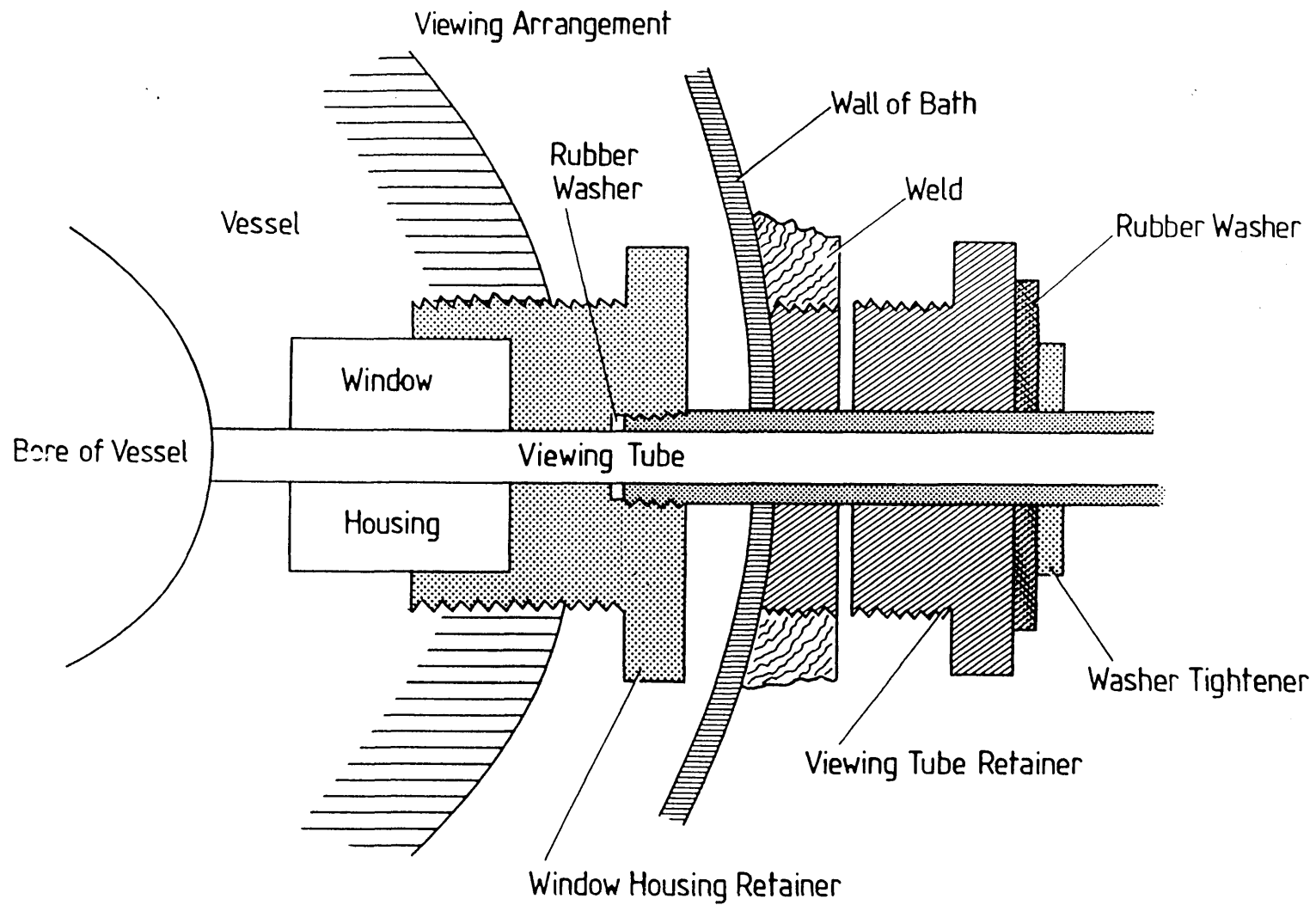


Figure 4.15

Viewing Arrangement

1. Locating nut to pressure vessel
2. Locating tube
3. } Guide tubes, quartz window
4. } incorporated in 3
5. Locating screw
6. Washer retainer
7. Plastic adaptor
8. Rubber washers - need to be replaced frequently

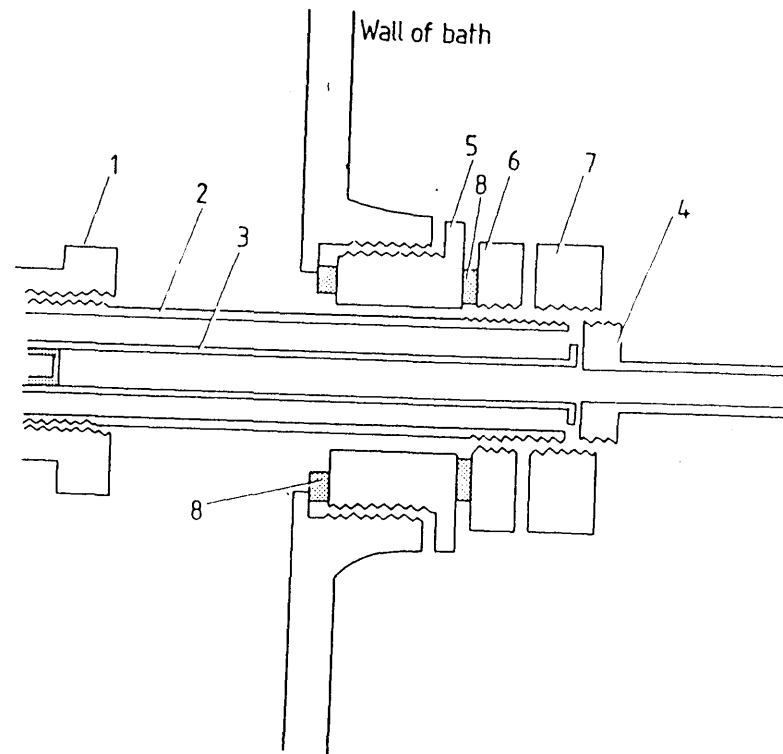


Figure 4.16
'Side tube' arrangement

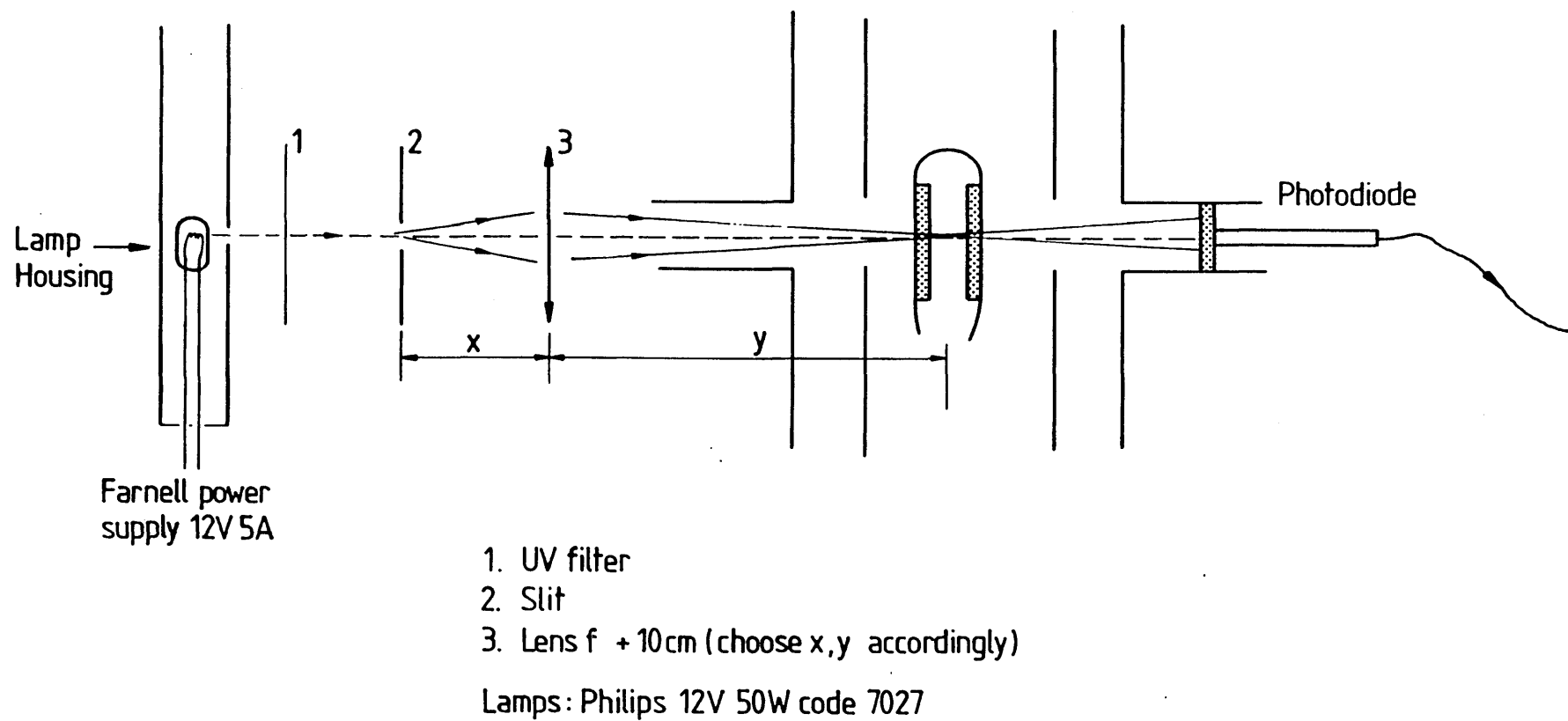


Figure 4.17
Optical alignment

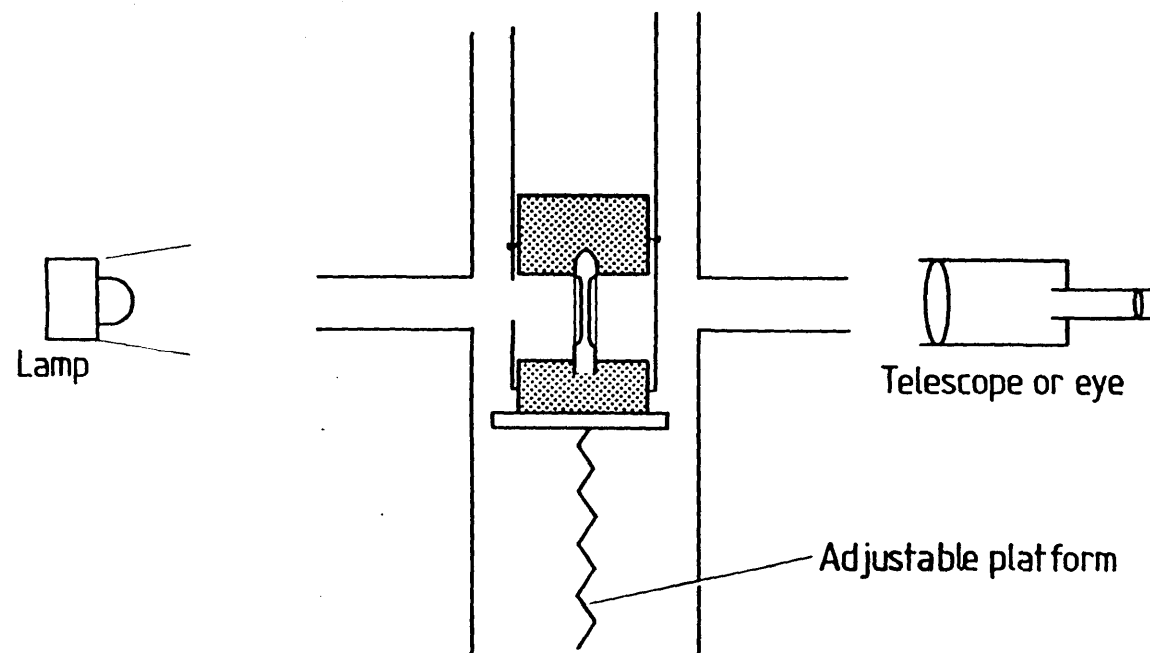


Figure 4.18
Sample orientation

4.8 The pressure line

The pressure line is shown in Fig. (4.19). The optical system is switched on and the sample is viewed. Final adjustment in the position of the sample is made at this stage. The upper cap is replaced and screwed on. The high pressure valve, V_1 , with its fittings is screwed on and remains open. The valve, V_2 , is now open and with the help of the hydraulic pump, silicone oil from the reservoir is pumped into the pressure reactor. Any air present in the vessel and the connecting tube is discharged through the valve, V_1 , and the vent. When there is a continuous flow of oil (indicating the absence of any air bubbles), the valve, V_1 , is closed. The valve, V_2 , remains open and using the hydraulic pump further pressure is applied until the desired pressure is attained. The valve, V_2 , is now closed to isolate the reactor. Usually there will be a slight pressure drop in the first half hour before the system equilibrates.

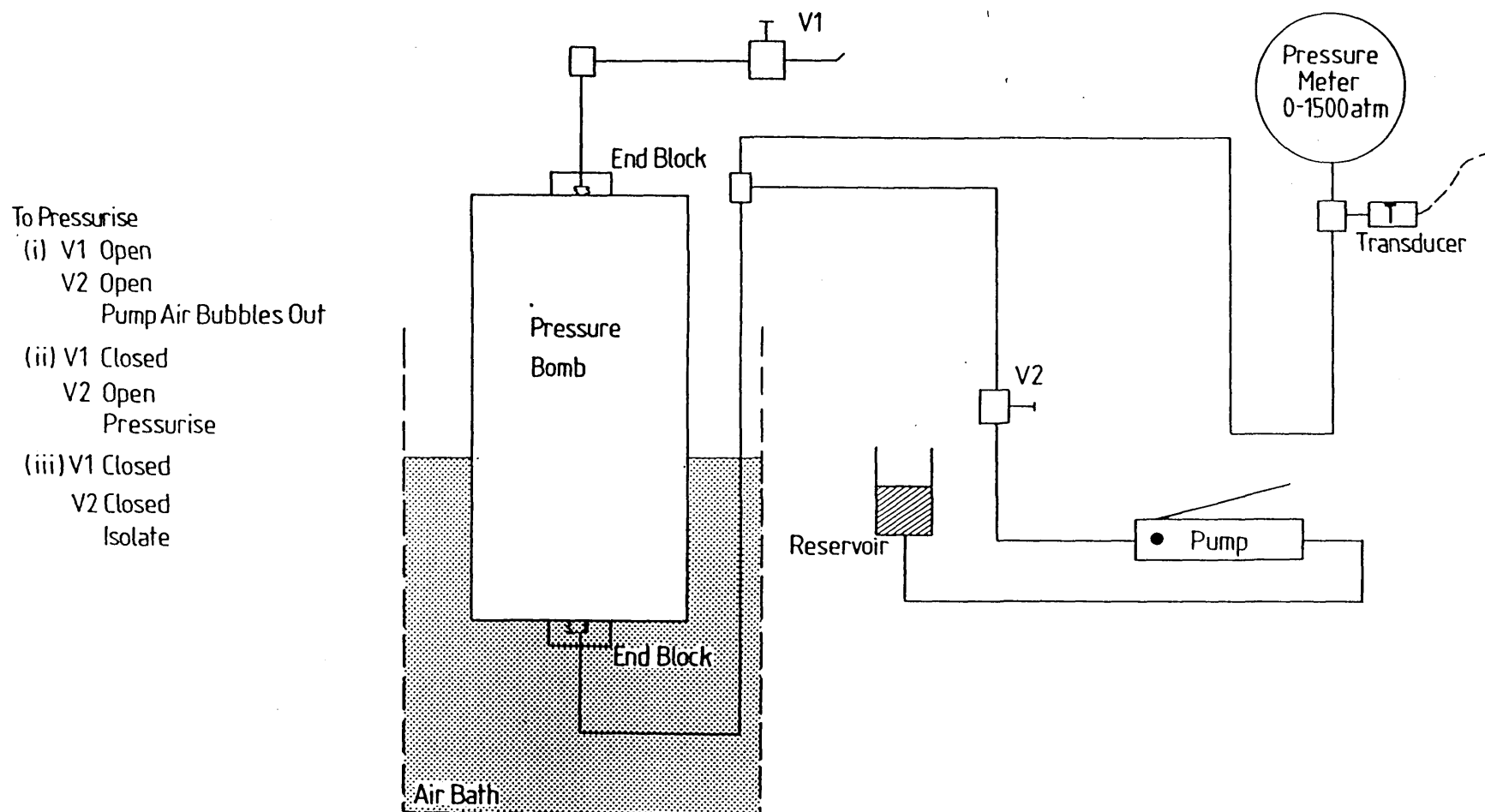


Figure 4.19

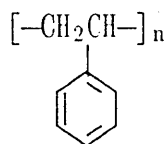
Pressure line

CHAPTER 5

EXPERIMENTAL

5.1 The polymers

Since its first commercial production in 1934, polystyrene



has remained one of the world's highest produced thermoplastics. This is because it combines its low cost with other desirable properties such as hardness, rigidity, transparency and freedom from odour and taste. It has low moisture absorption, good dimensional stability, mouldability, electrical insulation properties and colorability. It also has a reasonable chemical resistance. Its glass transition temperature (T_g) is about 100°C so it is 'glassy' at room temperature (20°C). The principal limitation of the polymer is its brittleness and consequently a number of attempts have been made to modify it for 'improved' impact strength.

The most successful of these attempts has been the use of rubber additives to produce blends of greatly improved toughness. The rubber particles 'bridge' a propagating crack and, because of their higher extensibility, are able to absorb a much larger amount of the energy causing the crack than an equivalent volume of PS. In order to improve its toughness it is necessary that the rubber remains rubbery at any service temperature envisaged for the

blend. A wide range of elastomers have been investigated as possible impact modifier for PS. Poly (vinyl methyl ether), $[-CH_2CHOCH_3]_n$, an elastomer which was first made available in Germany just before 1940, is a water — soluble (cold water), viscous liquid or tacky solid at room temperature. It has a low T_g of -28°C and its main application is in the adhesive and rubber industries.

5.2 Materials

The origin and molecular weight characteristics of the polymer samples used in the present study are given in Table (5.1).

The PS samples are coded PS0 — PS9. PS5 is a commercial sample supplied by BASF. The rest are commercial standards for gel permeation chromatography and are supplied by Polymer Laboratory.

The PVME samples are coded PVME(A — F). NMR study of these samples confirms that they are all atactic polymers. The commercial sample PVME — 1 (Lutonal) supplied by BASF has a broad molecular mass distribution (9.4). Fractionation was carried out to reduce its polydispersity. This was achieved by the use of the lower critical miscibility of aqueous PVME solution.

The procedure of Manson and Arguette (1960) was used for the fractionation. An aqueous PVME solution (2%) was gradually heated until a suitable amount of precipitate was obtained. This was dissolved by reducing the temperature. The precipitation temperature was again approached very slowly. After the first fraction had been taken out (32°C) the procedure was repeated at a slightly higher temperature (34°C). The precipitate was dissolved in methanol and the solution evaporated to dryness under vacuum. This

TABLE 5.1

Polymer Origin and Characteristics

Polymer	Origin	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Source of Data
Hydrogenous Polystyrene				
PS - 0	Polymer Lab.	51,500	Less than 1.04	Supplier
PS - 1	Polymer Lab.	76,500	Less than 1.04	Supplier
PS - 2	Polymer Lab.	95,500	Less than 1.04	Supplier
PS - 3	Polymer Lab.	110,000	Less than 1.04	Supplier
PS - 4	Polymer Lab.	115,000	Less than 1.04	Supplier
PS - 5	BASF	117,000	4	GPC (RAPRA)
PS - 6	Polymer Lab.	195,000	Less than 1.04	Supplier
PS - 7	Polymer Lab.	233,000	Less than 1.04	Supplier
PS - 8	Polymer Lab.	390,000	Less than 1.04	Supplier
PS - 9	Polymer Lab.	500	Less than 1.04	Supplier
PVME - A	(Lutonal) BASF	8,500	3.1	GPC (RAPRA) based on PS standard
PVME - B		8,000	4	Supplier
PVME - C		24,000	4	(by Viscometry)
PVME - D		89,000	4	(by Viscometry)
PVME - E	Polysciences			
PVME - F		1,000	4	Supplier
Deuterated Polystyrene PS - d	Polymer Lab	196,000	less than 1.02	Supplier

fraction $\left[\frac{\bar{M}_w}{\bar{M}_n} = 3.1, \text{ as determined by GPC} \right]$ was used for phase separation studies.

Oligo-PVME - F was kindly supplied by Dr D J Walsh.

PVME - (B-D) were kindly supplied by Dr Adrian Rennie.

PVME - E is a commercial standard supplied by Polysciences.

Deuterated polystyrene, PS-d (1 and 2) are commercial standards for GPC and were supplied by Polymer Laboratories.

Prior to blending, the materials were dried in a vacuum oven at 50°C for 48 hours.

5.3 General

Although several techniques such as DTA, microscopy, dynamic mechanical relaxation and turbidimetry have been developed for measurement of phase boundaries, (see Chapter 3), one of the dominating factors which influences the choice is the rate of phase separation and the size of the separated domains. This is because the measured phase boundary, although in principle an equilibrium thermodynamic property, is often influenced by the kinetics of phase demixing.

For instance phase separation in blends, in which at least one component has a low T_g or a low molecular weight, is fast and the phase domains are large enough to be observed visually by optical microscopy. On the other hand, blends with high T_g components phase separate at a very slow rate to produce small domains which are not readily detectable. PVME has a low T_g (-28°C) and PS is also mobile above its fairly low T_g (100°C). Phase separation in this blend is fast and the domain sizes are large enough to scatter the incident light. At the cloud point, the transparent film becomes turbid so that this transition is easily observed.

5.4 Turbidimetry

A light wave incident on a sample may be transmitted, absorbed or scattered. These phenomena constitute the basis of turbidimetry which has been described by Stein (1978), Olabisi *et al* (1979) and Higgins (1984).

The technique has been used to study the cloud point curves of polymer solutions, Cowie and Saeki (1982); oligomers, Tripathi (1979), Chong (1981) and high molecular weight polymer blends, Reich and Cohen (1981).

While the pressure rig, (Chapter 4) measures the intensity of the transmitted light from the sample, as a function of temperature and pressure, the light scattering turbidimeter, (Section 5.6) measures the scattered light intensity from the sample as a function of temperature.

In the present work, both pieces of equipment were used for the establishment of the cloud point curves of the various blends. The accuracy of each is $\pm 0.05^{\circ}\text{C}$.

5.5 Experiments on the pressure rig

Mixtures of PS and PVME were dissolved in toluene to give 10% solutions of varying composition. Films were cast by placing two drops of the solution on microscope coverslips. The films were dried in an oven, first at room temperature for 24 hours, next at 60°C for 24 hours and finally under vacuum at 60°C for 7 days, for complete removal of the solvent. Control films containing 100% PS, thus treated, showed T_g values characteristic of PS. Film thickness was approximately $100\ \mu\text{m}$.

Two coverslips containing the dried films were sandwiched together and placed between two identical neoprene 'O' rings before being screwed into the sample holder. The microcomputer was programmed to take readings at one minute intervals. The film was heated gradually at an average heating rate of $0.2^{\circ}\text{C min}^{-1}$ at atmospheric pressure.

This rate of heating was used for the determination of the cloud point because the temperature of phase separation of a blend was found (Chapter 6)

to be dependent on its rate of heating. This dependence was more pronounced at a heating rate above $0.2^{\circ}\text{C min}^{-1}$.

The corresponding temperature of the first deflection point was taken as the cloud point temperature. Typical trace of the transmitted intensity as a function of temperature for a 30% PS blend is shown in Fig. (5.1A). A trace of the control experiment in which only the silicone oil was heated is shown in Fig. (5.1B), in this case there was no deflection point.

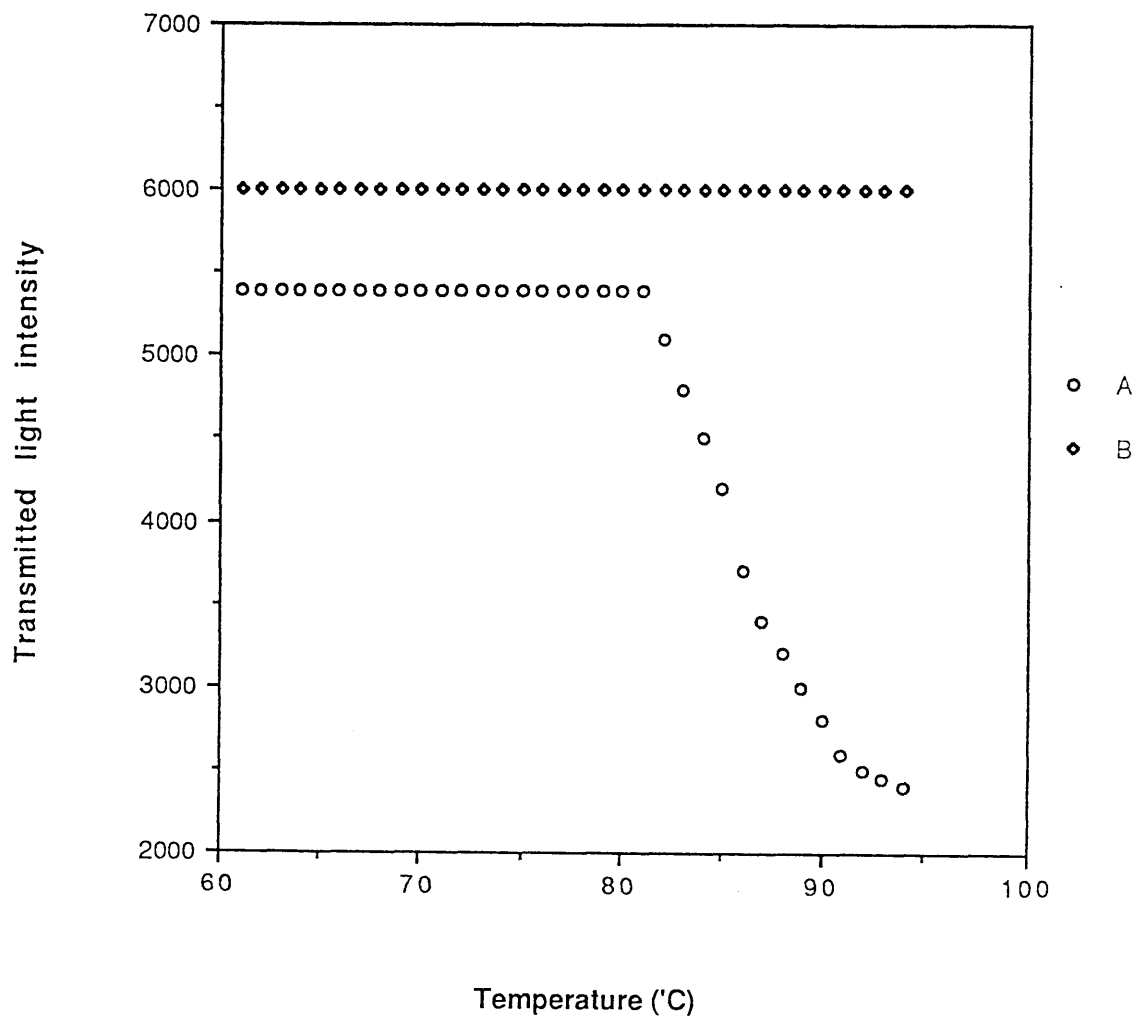


Figure 5.1

Transmitted light intensity as a function of temperature

- A. 30% PS blend
- B. Silicone oil

The procedure was repeated for the whole range of concentrations in order to obtain the cloud point curve of the blend.

Cloud point curves at pressures in the range 100 – 1500 atm. were similarly obtained. Each experiment was repeated twice and the average value was used for processing the data.

It must be pointed out that the silicone oil only acts as a pressure transferring medium and has virtually no effect on the cloud point of the blend. This latter statement was confirmed by:

- sealing the edges of the coverslips in order to prevent any oil from penetrating into the sample. Identical results were obtained both for this sample and for an unsealed one in contact with the transfer oil.
- measurement of the cloud point by light scattering turbidimetry which does not require any pressure transfer oil. The results for experiments using both pieces of equipment at atmospheric pressure are almost identical, Figs. (5.2) and (5.3).

The following investigations, which were carried out on the pressure rig, are briefly described below.

5.5.1 Effect of rate of heating on T_c

Heating rates in the range $0.1^{\circ}\text{C min}^{-1}$ to $10^{\circ}\text{C min}^{-1}$ were varied during the determination of the phase separation temperature of films of a 30% PS blend. Each sample was heated from an initial temperature of 20°C at atmospheric pressure.

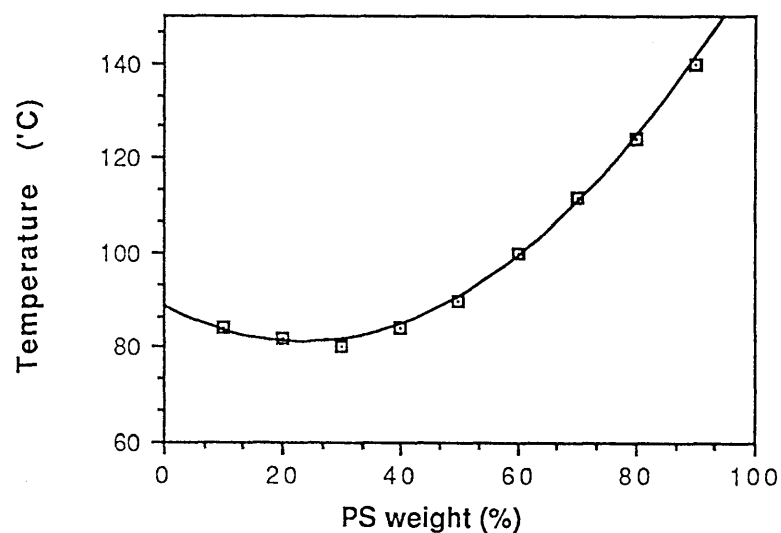


Figure 5.2
CPC from Turbidimeter

5.5.2 Effect of initial temperature on T_c

The effect of initial temperature on the phase separation temperature of a blend was determined at atmospheric pressure by using 100 μm thick films of a 30% PS blend. Each sample was heated at a rate of 0.2°C from an initial temperature in the range 18°C to 30°C.

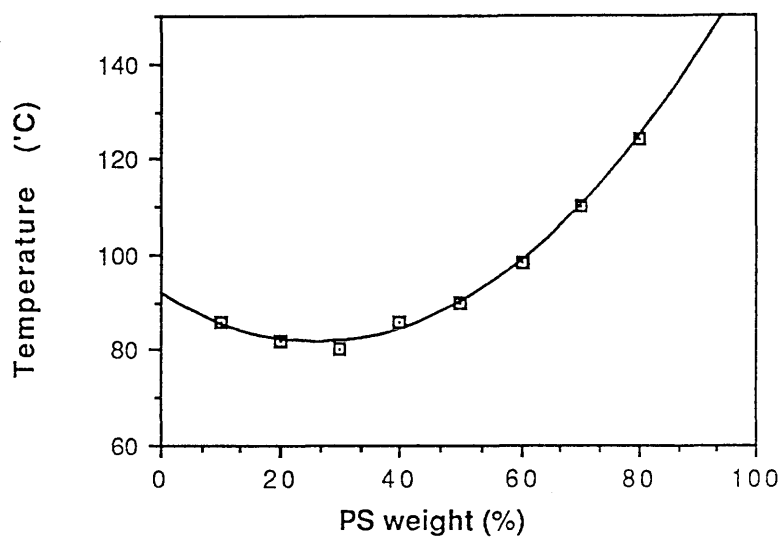


Figure 5.3
CPC from pressure rig

5.5.3 Effect of sample thickness on T_c

Films of various thickness were cast from solutions of a 30% PS blend. The concentration of the solutions were varied in the range 1% to 10%. The cloud points of these films were measured from an initial temperature of 20°C and at a heating rate of 0.2°C min⁻¹.

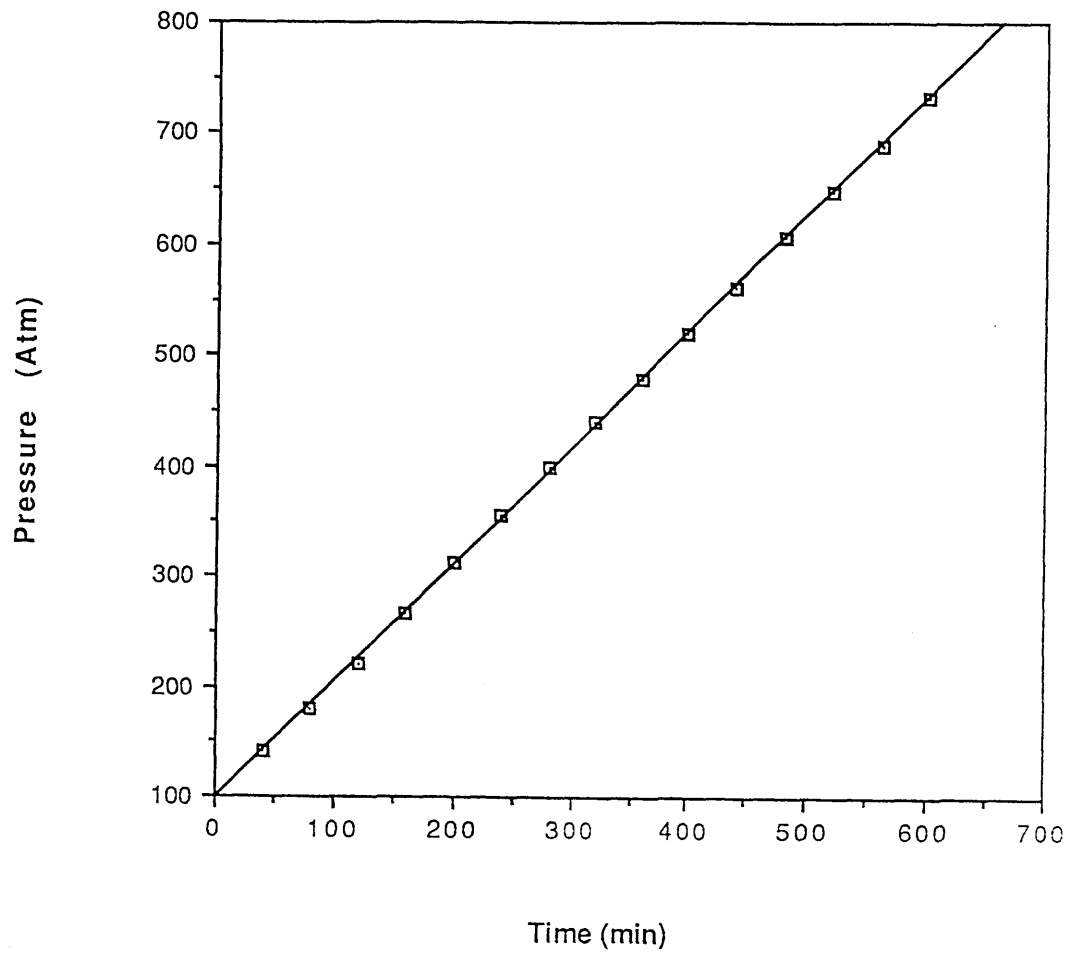


Figure 5.4

Applied pressure as a function of Time

5.5.4 Application of pressure

The pressure of the system increases with its temperature. Pressure can thus be applied by starting from a low value and then allowing it to increase steadily with time, while the system is heated, as shown in Fig. (5.4). The

corresponding pressure at the point of phase separation is taken as the relevant pressure. On the other hand, a constant pressure can be applied and maintained for the duration of the experiment by intermittent opening and closing the valve V_1 , to release excess pressure.

These two methods of application of pressure were compared but for experimental convenience, all the experiments were carried out using the first.

5.5.5 Effect of pressure on the phase separation temperature of binary blends

The effect of pressure on the phase separation temperature of various blends of PSh–PVME and PSd–PVME were studied. The blends varied in the composition and the molecular weight of the components.

5.6 Light scattering turbidimetry

For our investigation, a specially designed, light scattering photometer, described by Chong (1981) was used. The equipment was automated for the present work by the incorporation of a BBC microcomputer to:

- measure and log the temperature, time and intensity at a preset interval,
- eliminate storage of redundant data and
- store data for subsequent processing.

The film (100 μ thick) was supported in a sample holder located in a thermostatically controlled block. Light from a 12 volt tungsten filament lamp was focused on to the sample and the intensity of the light scattered at 45° was measured by a photodiode. The temperature of the block was controlled and programmed to alter at a constant rate by a temperature ramp. The sample

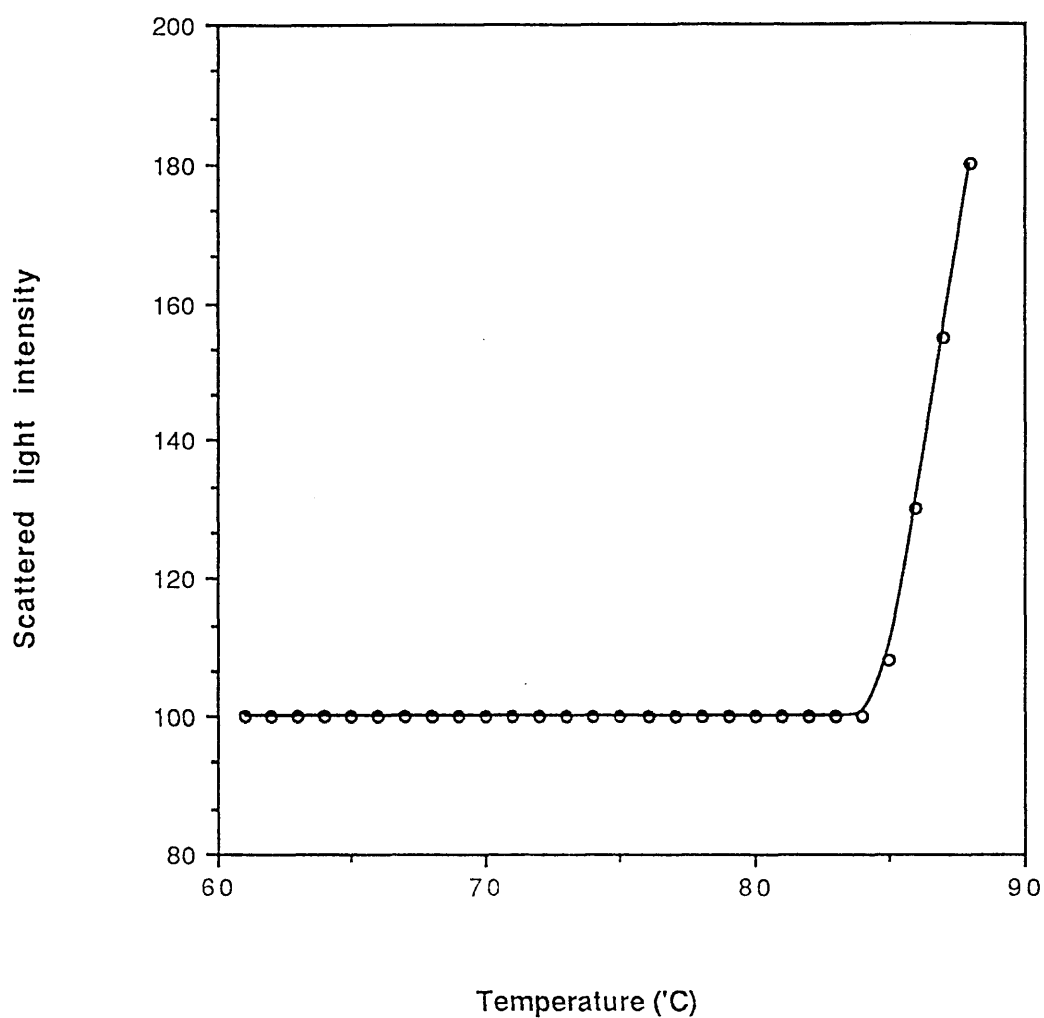


Figure 5.5

Scattered light intensity as a function of temperature

was heated at $0.20^{\circ}\text{C min}^{-1}$ and the microcomputer was programmed to take readings at one minute intervals. A plot of scattered light intensity against temperature was obtained. At the cloud point the intensity increased rapidly and the corresponding temperature of the point of intersection of the two tangents which reflect the trends of intensity before and after phase separation, was taken as the cloud point, as shown in Fig. (5.5). Each measurement was repeated twice and the phase boundary for the blend was generated. The accuracy of the phase boundary is estimated as $\pm 0.20^{\circ}\text{C}$.

In order to determine whether a blend was undergoing phase separation or merely domain ripening, the scattering intensity at an angle of 45° was observed as a function of time. This is equivalent to the light scattering invariant, at a fixed angle, as defined by Koberstein *et al* (1979).

$$Q_{LS} = \int_0^\infty R \underline{h} \, d\underline{h} \quad (5.1)$$

where R is the Rayleigh ratio and

$$\underline{h} = \frac{4\pi}{\lambda \sin \frac{\theta}{2}} \text{ is the scattering vector.}$$

In the spinodal decomposition or nucleation and growth mechanisms of phase separation, Q_{LS} increases with time, whereas in the domain ripening mechanism it remains constant with time. Fig. (5.6) shows the continuous increases in scattering intensities with time for a 20% PS blend. The figure shows an increase in the intensity of the light scattered at temperatures above the cloud point and a constant value below this point. These observations show that the phase separation mechanism is not by domain ripening and they also provide an alternative method of finding the cloud point of the blends.

The investigations carried out with the light scattering turbidimeter are outlined in the following section.

5.6.1 Effect of molecular weight of PS on the phase boundary

The molecular weight of PS was varied in the range 51,500 to 390,000 while that of PVME was kept constant. The phase boundaries of these various blends were determined at a heating rate of $0.2^\circ\text{C min}^{-1}$.

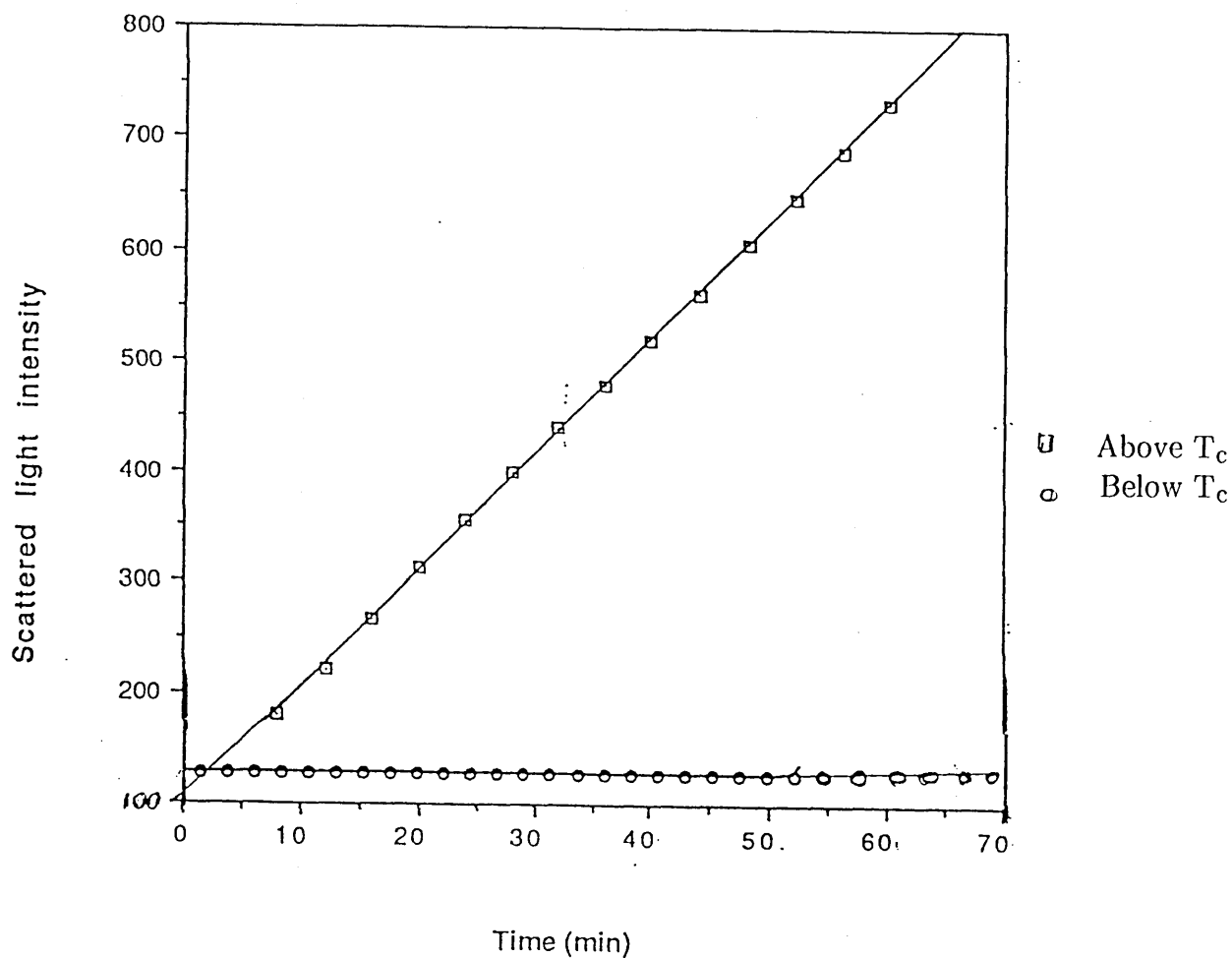


Figure 5.6
Scattered light intensity as a function of time

5.6.2 Effect of molecular weight of PVME on the phase boundary

The molecular weight of PVME was varied in the range 8,000 to 99,000 while that of PS, 115,000, was kept constant. The cloud points of the blends were determined at a heating rate of $0.2^{\circ}\text{C min}^{-1}$ and their phase boundaries were generated.

5.7. Heat (enthalpy) of mixing, ΔH_m

Evaluation of the heat of mixing is essential for the prediction of polymer miscibility and also for the simulation of the spinodal curve. Patterson (1968) showed that the heat of mixing changes sign in the region corresponding to two phases. Cruz *et al* (1979) demonstrated that two polymers with a negative heat of mixing are likely to be miscible.

Efforts have been made by a number of workers to determine the heat of mixing of polymers. Weeks *et al* (1977) reported substantial errors in the calculation, made by Tager *et al* (1975), of the heat of mixing of solid polymers by the use of Hess' Law. Natansohn (1985) measured the heat of mixing of a PS – PVME blend by observing demixing in the DSC. An unsuccessful attempt was made by the author to obtain the heat of mixing of a 50% PS blend by this method. Perhaps our DSC is not sensitive enough to detect the heat of demixing.

Experimental values of the heat of mixing are usually obtained by direct calorimetric measurements with the components, at a constant pressure. Allen *et al* (1960), Cooper and Booth (1977) successfully used this method to obtain the heat of mixing of oligomeric mixtures. Enthalpic interactions are primarily determined by intermolecular interactions between neighbours. Since it is almost impossible to directly measure the change in enthalpy associated with mixing two polymers, much of the quantitative correlation work has involved measurement of heat of mixing of low molecular weight liquids which have chemical structures similar to those of the polymers of interest. While this technique has proved useful in many studies, Cruz *et al* (1979), Harris *et al* (1984), Woo *et al* (1985), Rostami and Walsh (1985), Cheng and Walsh (1985), its success depends on how closely the selected analogue actually simulate the

interactions of the polymers. It is also often difficult to find liquid molecules which are structurally identical to the polymer repeat units of interest.

This problem can in principle be resolved by using a group contribution – based, thermodynamic model to obtain characteristic interaction parameters for structural groups which are common to both the liquids and the polymers. Barlow *et al* (1988) have discussed the results of such a model, used by Lai *et al* (1988) for predicting polymer – polymer miscibility.

In our heat of mixing experiments, oligomeric mixtures of the two components were used. As far as is known to the author, this is the first reported measurement of its kind for this system.

The oligo – PVME has a molecular weight of 1000 while the molecular weight of oligo – PS is 500. Both oligomers are viscous liquids at room temperature (20°C).

5.7.1 Experimental

The heats of mixing were measured using a modified NBS batch – type heat conduction calorimeter which depends on the measurement of a temperature change. It consists of a calorimeter compartment or cell surrounded by a heat flow device which in turn is surrounded by a heat sink (or block). The heat sink is kept at a constant temperature by two constant temperature jackets. The heat flow device consists of multiple-junction, serially connected thermocouples (thermoelectric cells) between an inner face in good contact with the calorimeter cell and an outer face in good contact with the heat sink. Details of the calorimeter have been given by Chong, (1981). The equipment has an accuracy of ± 0.02 J/g as determined by an acid – base reaction. The viscosity of the oligomers, however, made mixing difficult and an

error of ± 0.1 J/g may be more appropriate for this system. The equipment was calibrated electrically, using a 77 ohm resistor immersed in a 50/50 w/w % mixture of the oligomers. The current, I , was fed into the resistor R for time, t . The chart recorder showed a peak whose area, A , was proportional to the heat Q , generated by the resistor. By varying the time, t , a plot of Q vs A was obtained, hence the calibration constant was calculated by

$$F = Q/A \quad (5.2)$$

Figs. (5.7) and (5.8) show examples of the calibrations, first in distilled water and then in the mixture at 28°C and at 50°C.

The stability of the temperature of the equipment was within 0.001°C. The total weight of the two components was 1.0 gm. The samples were kept at the experimental temperature for about 6 hours before the mixing. The heat of mixing measurements were carried out only at one temperature, 50°C, due to the limited quantity of the samples.

5.8 Scanning electron microscopy

A 30% hydrogenous polystyrene (PSh) and a 30% perdeuterated polystyrene (PSd) blend with PVME were studied by both optical and scanning electron microscopy. Scanning electron micrographs of these blends, at the different stages of phase — separation were taken.

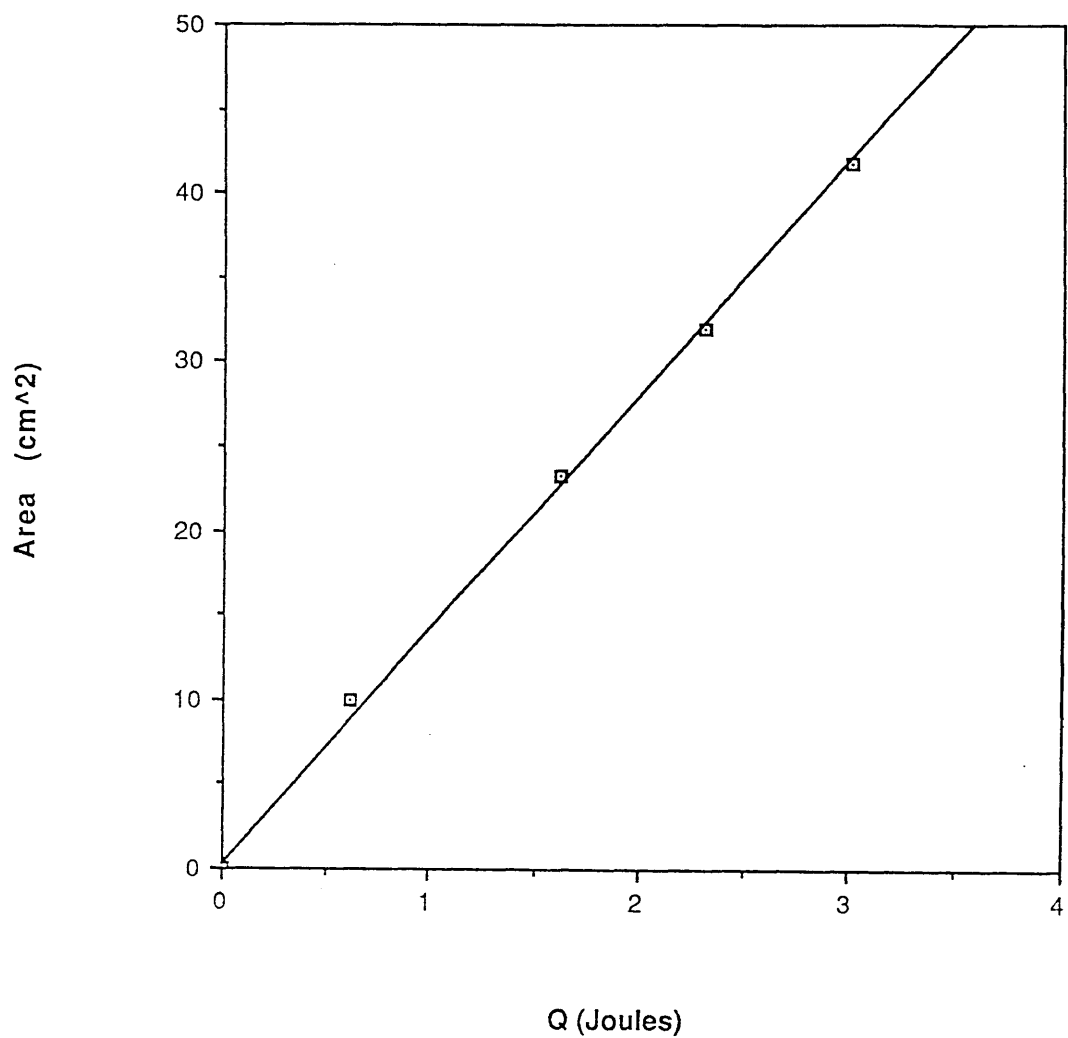


Figure 5.7

Calibration curve for distilled water at 28°C

5.9 Optical microscopy

Morphological observations using a camera-equipped optical microscope were made on a 30% PSh (critical composition) and a 50% PSh blend. These samples phase – separate by 'spinodal' decomposition and 'nucleation and growth', respectively.

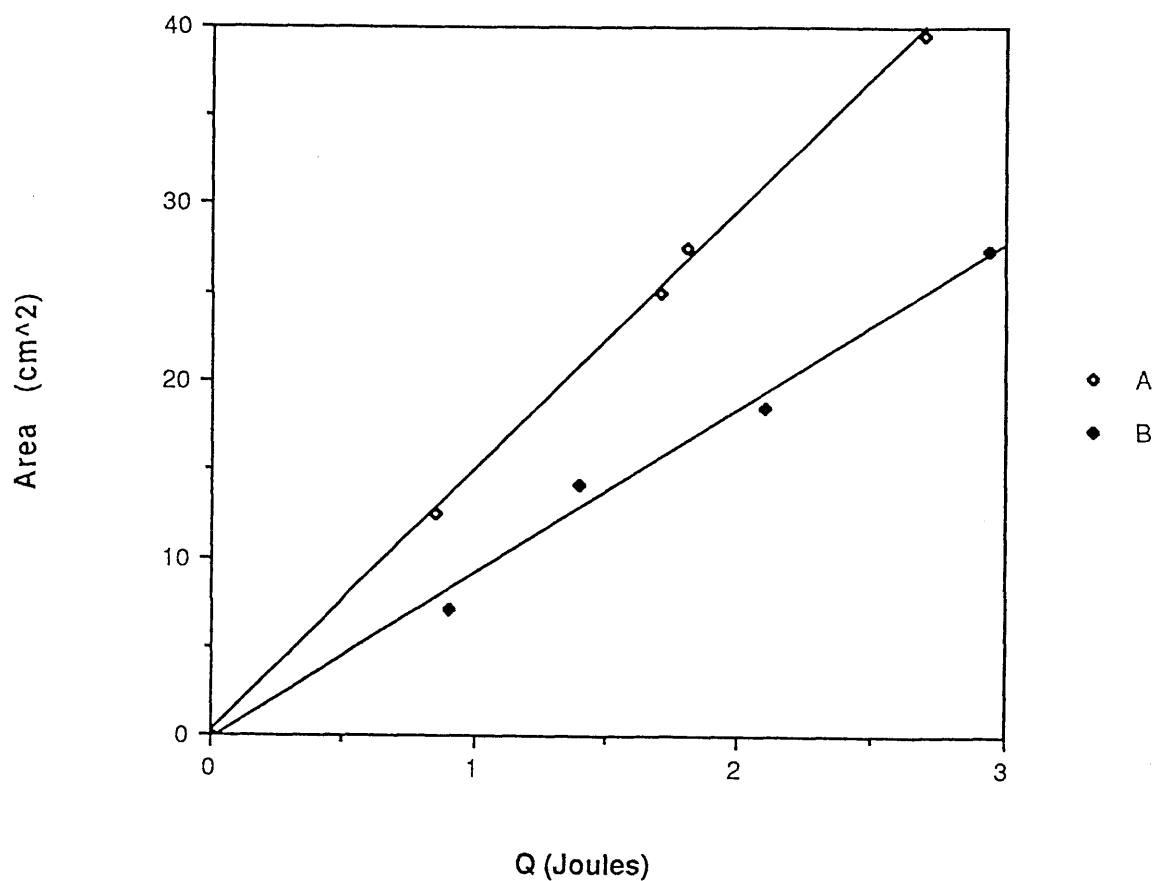


Figure 5.8

Calibration curves for PS/PVME (50/50 wt%) at A 50°C and B 28°C

The sample was heated at a given pressure up to a temperature below its cloud point at $0.2^{\circ}\text{C min}^{-1}$ and then heated at $2^{\circ}\text{C min}^{-1}$ to a temperature 20°C higher than its cloud point. The time dependence of the transmitted light intensity, as a function of pressure and composition was determined. Micrographs of samples, 'quenched' at different stages of the phase – separation were taken.

5.10 Differential scanning calorimetry (DSC)

The DSC measurements were carried out in a Perkin – Elmer DSC1, with a cell at a sensitivity of $0.2 \text{ mcal sec}^{-1}$ and a heating rate of $20^{\circ}\text{C min}^{-1}$. The samples were scanned between -25°C and 110°C . The heat flow as a result of a power difference between a sample ($\sim 10 \text{ mg}$) in an aluminium pan and a similar empty pan was recorded. DSC traces were obtained for miscible clear films and for cloudy, phase – separated films of PSd – PVME and PSh – PVME blends. These blends varied in the composition of the components.

5.11 Heating/cooling cycles

A thermally phase – separated sample when cooled to below its cloud point, usually regains its clarity. A 50% PSh sample was subjected to a heating/cooling cycle, as shown in Fig. (5.9). Although the sample regained clarity, Fig. (5.9) shows that a certain amount of turbidity was still retained. DSC traces of the sample 'quenched' at points A, B, C, D and E were obtained, and these confirm the observation of Fig. (5.9).

5.12 Dynamic Mechanical Thermal Analysis (DMTA)

The mechanical responses, stress – relaxation and creep, of long chain molecules at their glass transition temperature, T_g , are viscoelastic and time – dependent. Stress relaxation is defined as the decrease in the force (stress) required to sustain the deformation under constant strain. Creep responds to progressive increase in strain over a long period under a constant stress.

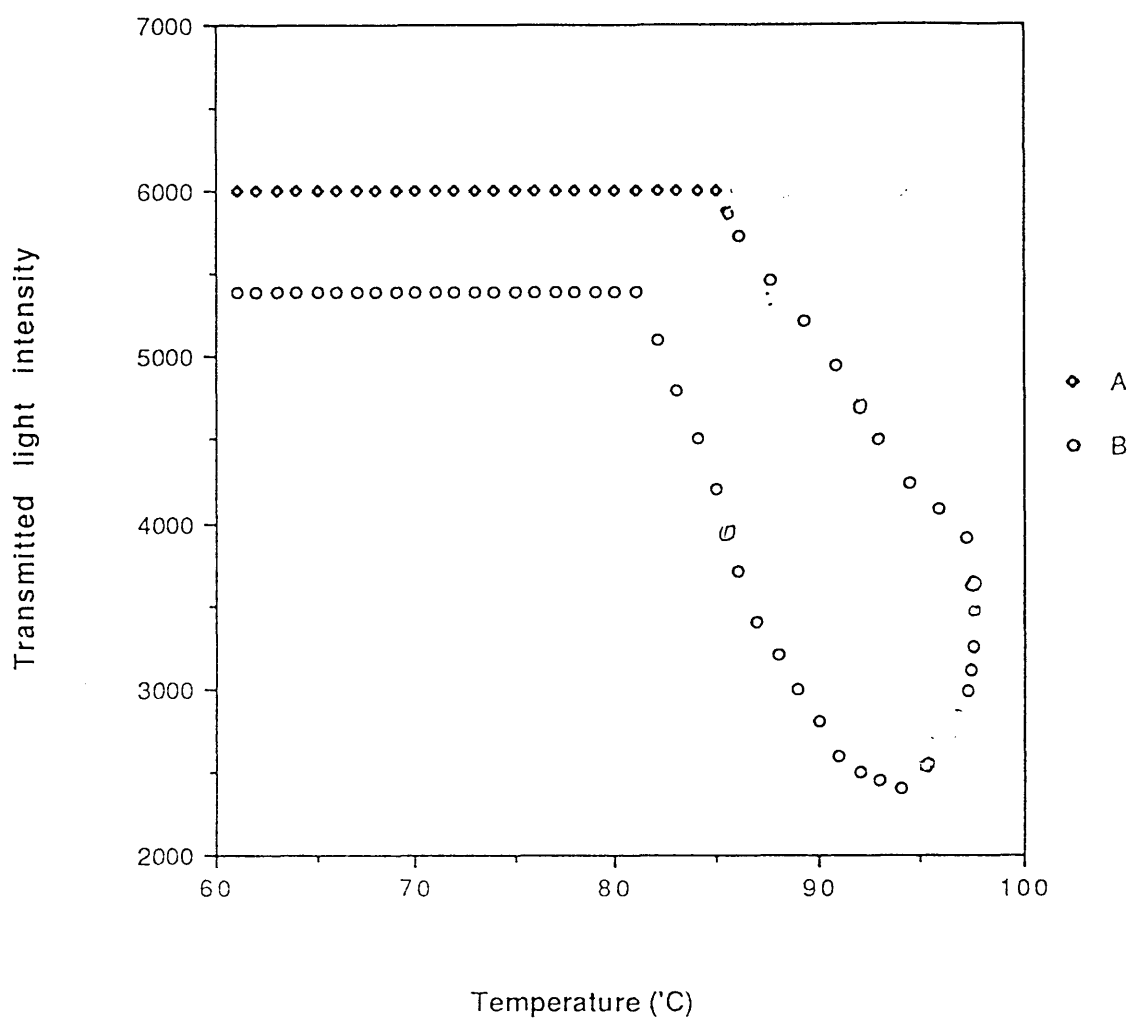


Figure 5.9

Heating/cooling cycle for a 50% PS blend: A heating and B cooling

If a sinusoidal strain, ϵ , is applied to a viscoelastic material at a frequency, ω , and with a small amplitude, the stress will also vary sinusoidally but will be out of phase with the strain by a phase angle, δ , as shown in Fig. (5.10). A phase lag results from the time required for molecular

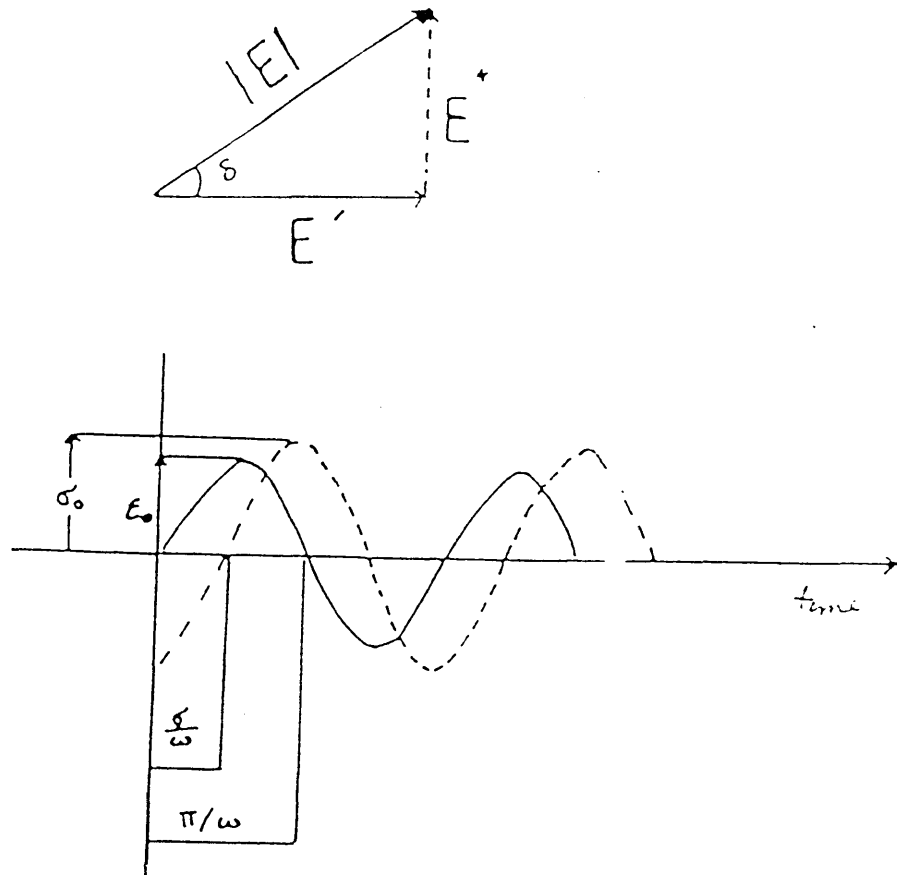


Figure 5.10

Schematic relation between various parameters in dynamic mechanical relaxation measurements

rearrangement associated with the relaxation. The stress, σ , and strain, ϵ , are expressed by:

$$\sigma = \sigma_0 \sin(\omega t + \delta); \quad \epsilon = \epsilon_0 \sin \omega t \quad (5.3)$$

where ω is the angular frequency
 δ is the phase angle
 ϵ_0 and σ_0 are the maximum strain and stress respectively.
 On expansion,

$$\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad (5.4)$$

The stress can hence be resolved into two components:

$\sigma_0 \cos \delta$, which is in $-$ phase with the strain and is related to the stored elastic energy and $\sigma_0 \sin \delta$, which is out of phase. Modulus $\left[\frac{\text{stress}}{\text{strain}} \right]$ can thus be separated into in $-$ phase (real) and out $-$ of $-$ phase (imaginary) components, i.e.

$$E' = \frac{\sigma_0}{\epsilon_0} \cos \delta \text{ and } E'' = \frac{\sigma_0}{\epsilon_0} \sin \delta \quad (5.5)$$

where E' is the storage modulus and E'' is the loss modulus.

The energy loss per cycle or damping in the system can be measured from the "loss tangent", $\tan \delta$, defined by:

$$\tan \delta = \frac{E''}{E'} = \frac{1}{\tau \omega} \quad (5.6)$$

where τ is the relaxation time.

A maximum in $\tan \delta$ marks the onset of main chain segmental motion which corresponds to the glass transition. The ratio $\frac{E''}{E'}$ is the dissipation factor.

The dynamic mechanical measurements were carried out using a 'Dynamic Mechanical Thermal Analyser', (Model PL – DMTA, Polymer Laboratories LTD., UK) at a constant oscillating frequency of 1 Hz on x4 strain

setting, which corresponds to 62.5 μm peak displacement $\left[\text{strain} = \frac{\text{displacement}}{\text{length}} \right]$. This strain setting controls the transducer amplifier gain and the applied existing force.

A strip of the sample, (20 x 5 x 0.3 mm), was firmly clamped in the apparatus and subjected to a sinusoidal force applied to its midpoint. A temperature range of -20 to 200°C was scanned at a $20^\circ\text{C min}^{-1}$ heating rate. A plot of loss tangent, δ and $\log E'$ against temperature was recorded.

5.13 Small Angle Neutron Scattering (SANS)

The availability of SANS techniques in recent years has initiated many new research projects in the area of homopolymers and polymer blends. A number of recent articles on details of neutron scattering experiments and theory, as applied to polymer systems, have appeared in the literature; Richards (1980); Sperling (1984); Higgins and Macconnachie (1985). While the technique can be used to observe the miscibility limits in the equivalent of a cloud point measurement, the cost of neutrons and the relative inaccessibility of neutron sources have confined its uses to problems where it provides a unique advantage. It is used for instance:

- in the study of the structure and dynamics of amorphous polymers since information about the crystalline state may be obtained by X-ray diffraction and other conventional spectroscopic techniques.
- in the study of molecular conformation of labelled chains in the single phase and the interactions between them.
- when the domain dimensions of separated phases are closer to neutron than light wavelength.

Table 5.2

The coherent scattering lengths of different atoms

Atom	Nucleus	$b \times 10^{-15} \text{m}$
Hydrogen	^1H	- 3.740
Deuterium	^2H	6.674
Carbon	^{12}C	6.648
Oxygen	^{16}O	5.830
Nitrogen	^{14}N	9.36

In these studies deuterated polymer molecules are substituted for some of the usual hydrogen-containing molecules as a means of selective labelling. Such substitution relies on the fact that the neutron scattering lengths of deuterium and hydrogen are very different, (Table 5.2), while the difference in other physical and chemical properties between the deuterated and hydrogenated counterparts is negligibly small. Scattering measurements from assemblies of atoms consist of coherent and incoherent scattering. The latter is isotropic and produces a background effect that must be subtracted from the measured total scattering in order to determine the intensity of the coherent scattering which provides the structural information about the material. The methods of subtraction of the scattering background have been discussed in detail by Maconnachie and Richards, (1978).

For a two-component polymer blend, an expression for the scattered intensity, $I(q)$, at any angle, which depends on the Flory–Huggins interaction parameter, χ_{12} , can be obtained by the use of the random-phase approximation technique, as introduced by de Gennes (1979).

Warner *et al* (1983) derived a general expression for a sample containing volume fraction ϕ_1 and ϕ_2 of two polymers, where the type 1 segment is deuterated. The expression can be manipulated in several ways to extract different parameters.

At zero angle, for instance, the scattered intensity can be expressed by:

$$I(0) = \frac{(d - \beta b)^2 / V_1}{[(\phi_1 N_1)^{-1} + \beta(\phi_2 N_2)^{-1} - 2\chi_{12}]} \quad 5.7$$

where

χ_{12} is the interaction parameter,

d and b are scattering lengths per monomer unit, of monomer 1 and monomer 2 respectively,

V_1 is the molar volume of one repeat unit of polymer 1,

$\beta = \left[\frac{V_1}{V_2} \right]$ is the relative volume of monomer 1 and monomer 2,

ϕ_1 and ϕ_2 are the volume fractions of the polymers and

N_1 and N_2 are the degrees of polymerisation.

In the present study, the expression has been used to obtain the binary interaction parameter, χ_{12} , for a deuterated–PS/PVME system.

5.13.1 Experimental

The characteristics of the deuterated–PS (compound 1) and hydrogenated PVME (compound 2) are listed in Table (5.3).

Table 5.3

Characteristics of samples used for SANS studies

Polymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Molar Volume ($\text{cm}^3 \text{ mol}^{-1}$)	N_1	N_2
Deuterated-PS	196,000	1.02	100.54	3438	
Hydrogenous- PVME	99,000	2.3	55.47		3414

The neutron scattering samples were prepared from the above listed polymers by solution casting from toluene, as earlier described in section (5.1). The cast films were cut, stacked between aluminium foils and then 'pressed' between two stainless steel plates at 100°C, into discs of 19 mm diameter and varied thickness, as shown in Table (5.4).

The discs were mounted in brass cells and coded, based on the weight percentage of PSd. All the specimens were thoroughly dried in a vacuum at 80°C for sixteen hours. SANS experiments were carried out at the 'listed' temperatures, on the D17 spectrometer of the Institut Max von Laue Langevin, Grenoble, France. A SANS spectrometer at the Institut is shown in Fig. (5.11).

Table 5.4 Characteristics of test samples

Run number	Sample code	Wt % PS-d	Temperature °C	Sample thickness ± 0.01 mm mm
6597	D70	70	50	0.764
6594	D70	70	71.2	0.764
6632	D70	70	Room Temp (~20)	0.764
6593	D30	30	50	0.6
6607	D30	30	30	0.6
6608	Background			1.4

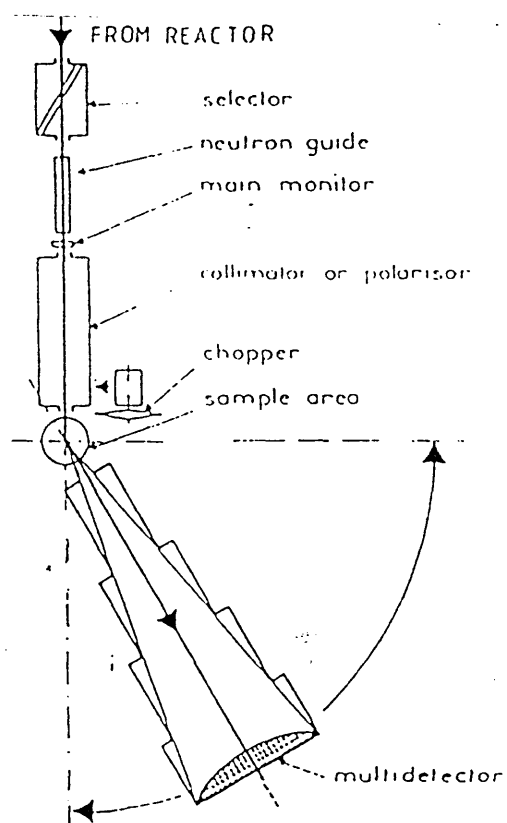


Figure 5.11

A SANS spectrometer

5.14 Density Measurements

The density of the films of the pure components and of their different blend compositions were measured in a density gradient column at 35°C.

Experimental

A density gradient column containing a solution of sucrose in distilled water was prepared, such that the density of the solution was in the range 1.030 and 1.070; details of the preparation of the density gradient columns are contained in the manual by Davenport Ltd (1972). The temperature of the column was maintained by a thermostat.

Suitable 'floats' within the range of the gradient column were selected and cleaned in diethyl ether to remove any grease. They were gently dropped into the gradient column, one by one, with the aid of tweezers. Care was taken to prevent air bubbles from adhering to the 'floats'.

The column was covered and the floats left for 24 hours to reach equilibrium. At the end of this period, they were checked for air bubbles. a calibration graph of the height of the float (with the aid of the scale on the tube and measured from the centre of the float) and its density was drawn, Fig. (5.12).

Two specimens were cut from each sample, using a very sharp razor blade. The cut edges were 'clean' and free from voids. The shapes of the specimens were such that they could be identified and also their centre could be easily determined. The specimens were 'cleaned' with diethyl ether and gently dropped into the column. The rubber cap on the tube was replaced to prevent any contamination of the liquid. The samples were left for four hours to

equilibrate. The centre of their volume positions was determined with the scale and their density ascertained.

The experimental errors of the densities measured are estimated to be $\pm 0.00049 \text{ g cm}^{-3}$.

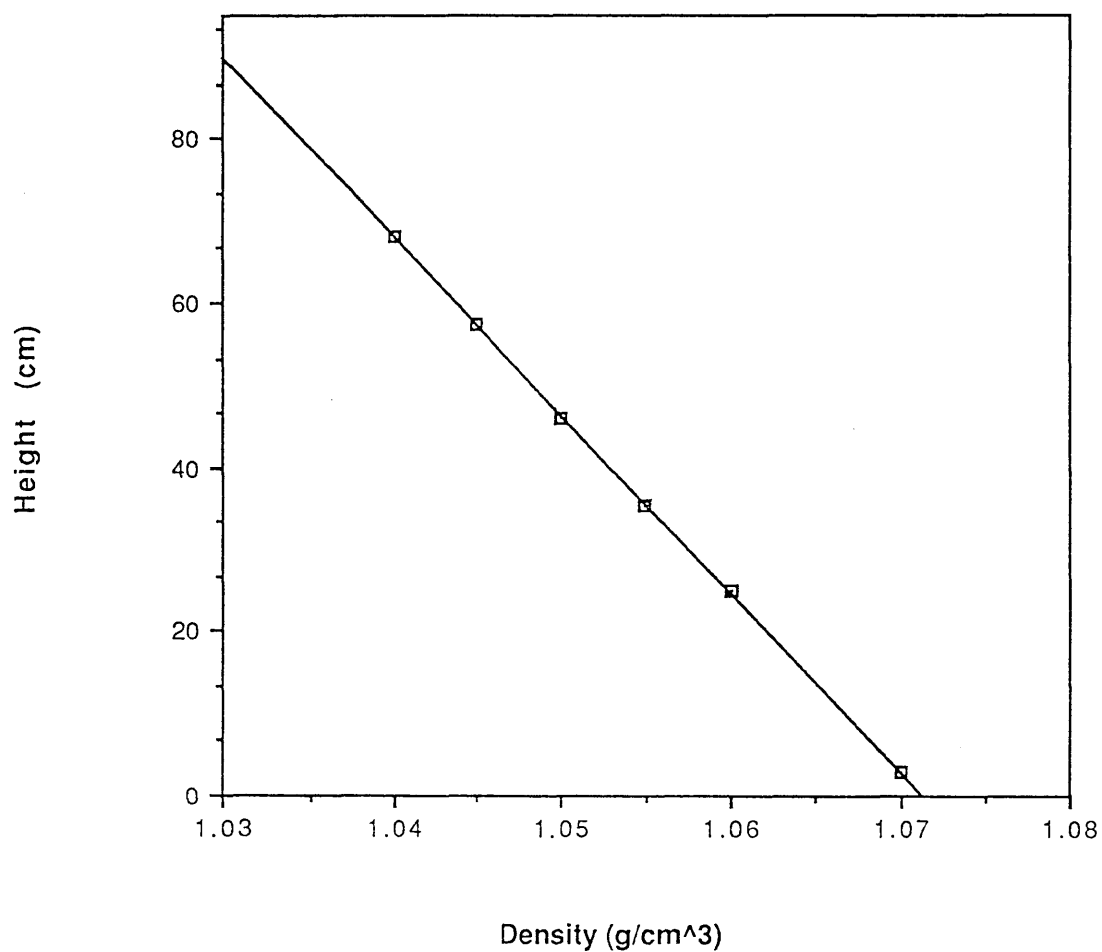


Figure 5.12
Calibration of density gradient column

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Results of preliminary tests

Prior to the determination of the cloud point of the blends, preliminary tests were carried out, as described in Section (5.1) to investigate the effect on the cloud point of:

- initial temperature
- film thickness
- rate of heating

Effect of initial temperature

Varying the initial temperature within the range 18°C to 30°C did not affect the cloud point of the sample. For consistency, all the samples were heated from 20°C.

Effect of film thickness

The cloud point was not affected by the variation in the sample thickness. The intensity of the scattered light, however, increased with the thickness of the film. All the samples used for cloud point determination are prepared from 10% toluene solutions.

Effect of rate of heating

It was found that the cloud point temperature depends on the rate of heating: the higher the rate, the higher the cloud point. The rate of heating was varied in the range 0.1 and 5°C/min., while the increase in the cloud point was about 4°.

A heating rate of 0.2°C/min. is used for all the determinations.

Accuracy

The experimental error in the determination of the cloud points by this technique (turbidimetry) is $\pm 1^\circ\text{C}$ for this system due to the sharp cloud points caused by the high mobility in this system.

6.2 Effect of molecular weight (of PS) on the LCST of PS–PVME blends

PVME–A (from Table 5.1) was blended with monodisperse PS whose molecular weight varied in the range 50,000 to 390,000. The resultant cloud point curves, determined at atmospheric pressure, are shown in Fig. (6.1).

The effect of increasing the molecular weight of PS is to lower the phase boundary of the PS–PVME blend. This is expected since the combinatorial entropy term in the free energy of mixing decreases with an increase in the molecular weight of either component, as suggested by Equation (2.21). Using a modified version of Flory's equation-of-state theory, McMaster computed that the mutual solubility of two polymers decreases as the molecular weight of either is increased. Nishi and Kwei (1975) confirmed the above theoretical predictions by determining the cloud point curves for blends of PVME and monodisperse PS of varying molecular weight. Their cloud point curves shift strongly to lower temperatures with an increase in the molecular weight of PS. Patterson (1982) used 'entropic stabilisation' to quantitatively verify this effect. He applied the Flory–Huggins expression for the ΔS_m associated with mixing N_1 moles of component 1 with N_2 moles of component 2:

$$\frac{\Delta S_m}{R} = -[N_1 \ln \phi_1 + N_2 \ln \phi_2] \quad (6.1)$$

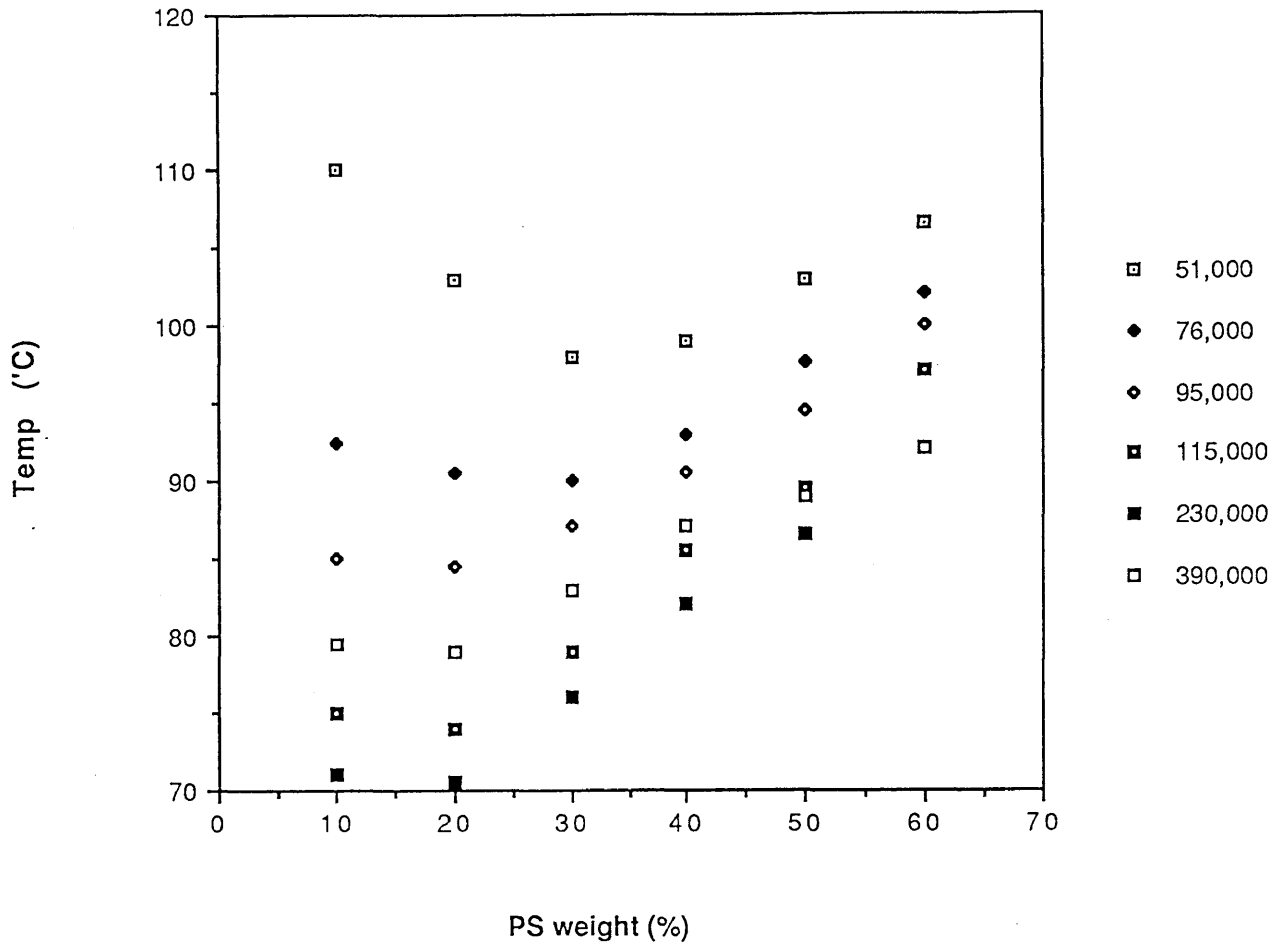


Figure 6.1

Effect of molecular weight of PS on the LCST of PS–PVME blends

where R is the gas constant and ϕ_i are the volume fractions of the components in the blend. Since $\phi_1 < 1$, ΔS_m is positive, as required for 'entropic stabilisation' of the blend. On transforming the above equation to give the combinatorial ΔS_m per volume, V , of blend, it becomes

$$\Delta S_m/RV = - \left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2} \right] \quad (6.2)$$

with V_i = the molar volumes of the pure components.

As the molecular weight of component 2 is increased, V_2 is also increased and the second term of Equation (6.1) is reduced in importance, finally disappearing as $V_2 \rightarrow \infty$ for a polymer of infinite molecular weight. Thus as the molecular weight of either component is increased the entropic stabilisation of a blend is decreased and phase separation is made easier.

Fig. (6.1) shows that the shift in the position of the curves reverses for PS having molecular weight of 390,000. Nishi and Kwei (1975) observed this unusual reversal phenomenon for PS having molecular weight above 110,000 and attributed it to chain entanglement. For PS, the critical chain length for the formation of entanglement is about 300 to 500 ($M_w \simeq 30,000$ to $50,000$), Fox and Flory, (1954); Beng and Fox, (1968); Porter and Johnson, (1968). For PVME the entanglement chain length is not known but it is probably about 300 ($M_w \simeq 17,000$) or less because the chain is more flexible. The two polymers are mixed well in toluene and there should be many molecular entanglements between PS and PVME molecules as solvent evaporates. After evaporation of toluene the entanglement between different chains can be preserved and can act as a hindrance to phase separation at high temperatures although separation is favoured on thermodynamic grounds.

Based on the above reasoning, a very slow heating rate of 0.2°C per minute (fifty times slower than that of Nishi and Kwei, 1975) has been used in this investigation in order to allow enough time for chain disentanglement prior to phase separation. The effect has been observed not in the range quoted by the above workers but for a much higher molecular weight. This observation implies that the phenomenon is a non-equilibrium, time-dependent effect.

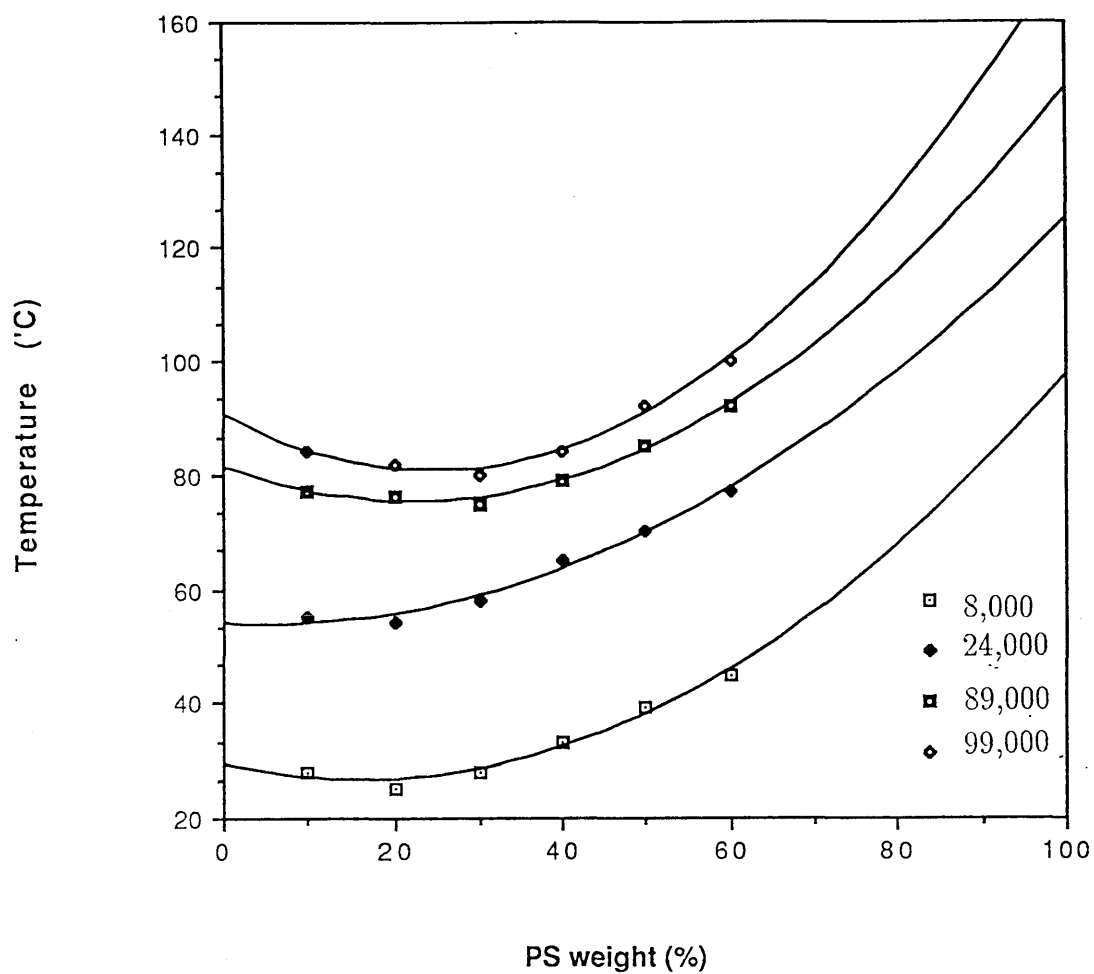


Figure 6.2
Effect of mol.wt. (of PVME) on the
miscibility of PS-PVME blends

6.3 Effect of molecular weight of PVME on the miscibility of PS-PVME blends

Monodisperse polystyrene of molecular weight 110,000 was blended with PVME, the molecular weight of which ranged from 8,000 to 99,000. The result, Fig. (6.2) shows that the LCST is raised with an increase in the molecular weight of PVME.

The observed experimental result is contrary to theoretical prediction. It should be noted however, that the molecular weight effects are accounted for in the theory, in terms of chain length effects for monodisperse, unbranched polymers; all the PVME samples used in the present investigation are polydisperse. Their molecular weight and polydispersity are indicated in Table (5.1).

Previous investigations on the molecular weight effects in this system have concentrated on varying the molecular weight of PS while that of PVME remained constant. This may be due to the comparatively easier access to monodisperse PS of different molecular weight. The effect on the phase boundary of varying the molecular weight of PVME has not previously been demonstrated, consequently no previous suggestions have been made in the literature to explain this observation. It is suggested that this unusual behaviour is due to an unfavourable contribution to the thermodynamic excess functions of mixing.

Schneider and Brekner (1985) observed the flow behaviour of this blend and noted that its mobility is dependent on the more flexible PVME chain. Taking into account the interaction between the components of this blend, it may be assumed that a lower molecular weight PVME will adapt closer to the PS chain, thereby introducing less free volume. As the temperature is raised, however, the mobility of the chain-ends of PVME will contribute to an enlargement of the free volume of the blend, an effect which is unfavourable to miscibility. The lower the molecular weight of PVME, the higher the number of chain-ends and hence the greater the unfavourable contribution which leads to phase separation.

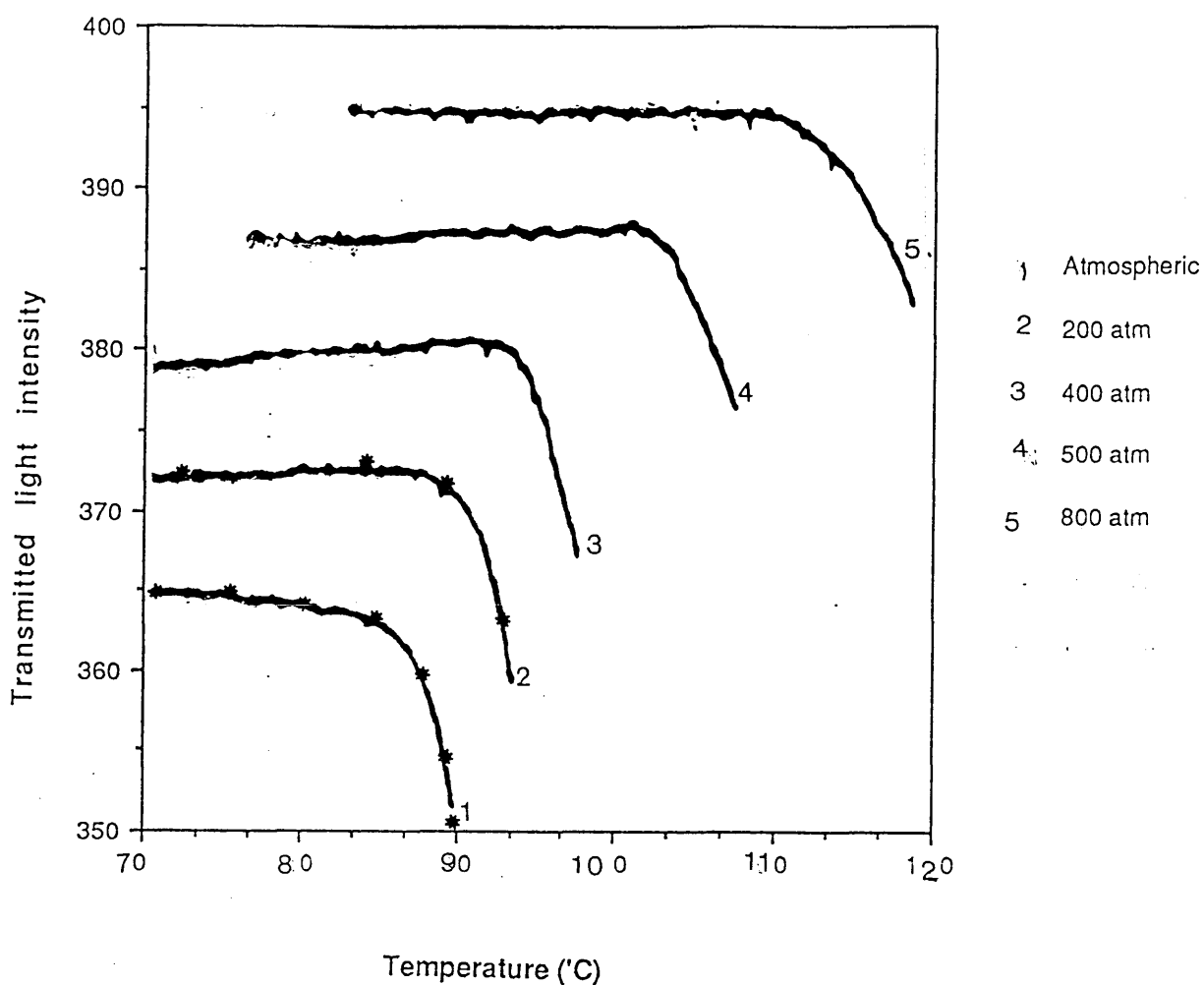


Figure 6.3

Temperature dependence of transimitted light intensity under various pressures

6.4 Temperature dependence of transmitted light intensity under various pressures

At a given pressure, the decrease in light intensity transmitted through an 'LCST' blend is a function of temperature. The effect of pressure on the temperature dependence of the transmitted light intensity through a 50% blend of PS-3 and PVME-E (whose characteristics are given in Table (5.1)) is shown in Fig. (6.3). It is seen that the cloud point increases while the decrease in light intensity becomes less 'pronounced' with an increase in pressure.

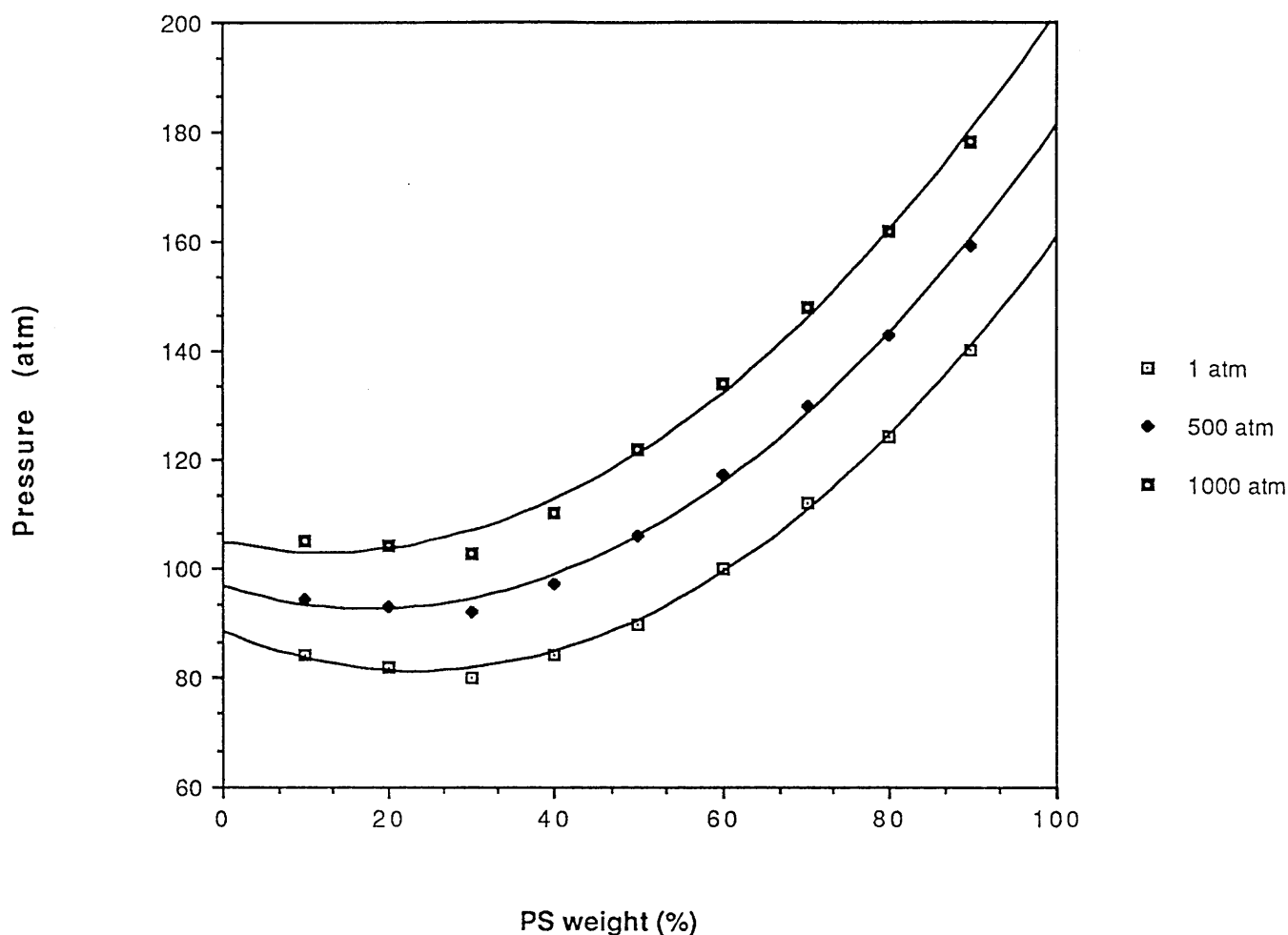


Figure 6.4 A

The effect of pressure on the LCST phase boundary of PS–PVME blends

6.5 The effect of pressure on the LCST phase boundary of PS–PVME blends

The effect of pressure on the cloud point curves (cpc) of blends of PS–PVME was investigated. Fig. (6.4)(A and B) shows the cpc of blends of PS–3 and PVME–E both at atmospheric pressure and at other higher pressures, as indicated. This result is typical of those obtained using blends of PS and PVME whose molecular weight characteristics are different from the above–mentioned samples.

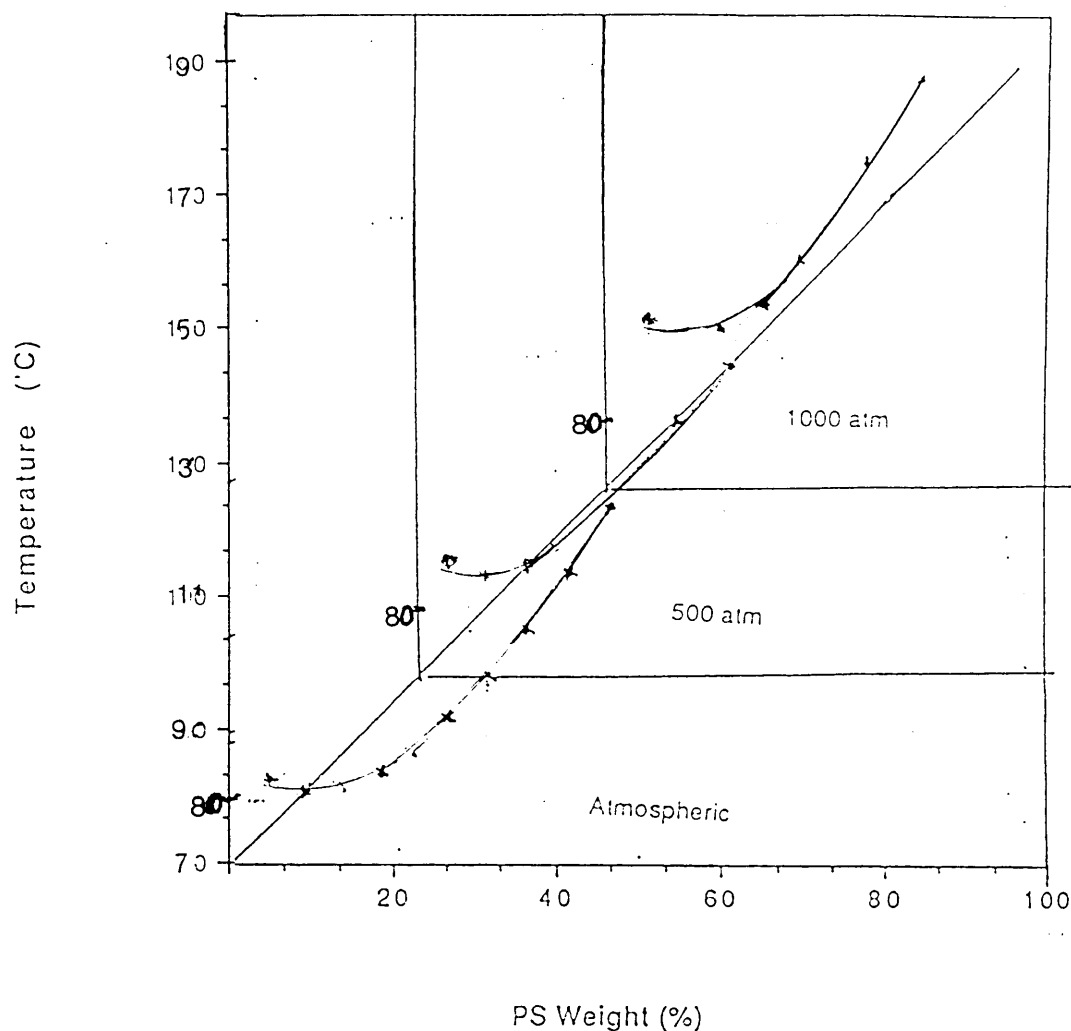


Figure 6.4 B

The effect of pressure on the LCST phase boundary of PS-PVME blends

It is found that although their LCST profiles (i.e. having a minimum) are retained, the cloud point curves shift to higher temperatures with an increase in pressure. The results indicate that the miscibility gap of PS-PVME blends is increased on the application of pressure. This is in accord with theoretical predictions based on the 'free volume' theories, as suggested by Equation (3.3). High molecular weight polymers mix with a contraction in

their free volumes; this brings the molecules of the system closer together introducing a negative contribution (net contraction) in ΔV_m , which also results in negative contributions in ΔH_m and ΔS_m .

LCST occurs because of the difference in the degree of thermal expansion of the two components which leads to an increase in the free volume difference and phase separation.

The effect of pressure is to reduce this difference and thus improve miscibility. The application of pressure has been found to have the greatest effect at high temperatures where there is a large difference in free volume between the components.

6.6 Pressure dependence of cloud points at different composition of PS–PVME blends

The pressure dependence of the cloud points obtained from the results of Fig. (6.4) is shown in Fig. (6.5)(A and B). For every blend composition, the cloud points increase linearly with pressure. Allen and Baker (1965) and Saeki *et al* (1976) also observed a linear pressure dependence on the LCST of their polymer–solvent systems.

The pressure dependence is found to vary with composition and is highest for the 90% PS blend. Because of this variation with composition, it is expected that the shape of the cloud point curve changes with pressure.

Table (6.1) and Fig. (6.6) show the pressure dependence for the blend of polymers of indicated molecular weight, as a function of composition. The pressure dependence at the critical composition is $0.023^{\circ}\text{C}/\text{atm} \pm 0.002^{\circ}\text{C}/\text{atm}$. For the molecular weight studied by them, Hiramatsu *et al* (1983) obtained a value of $0.03^{\circ}\text{C}/\text{atm}$. for the critical composition.

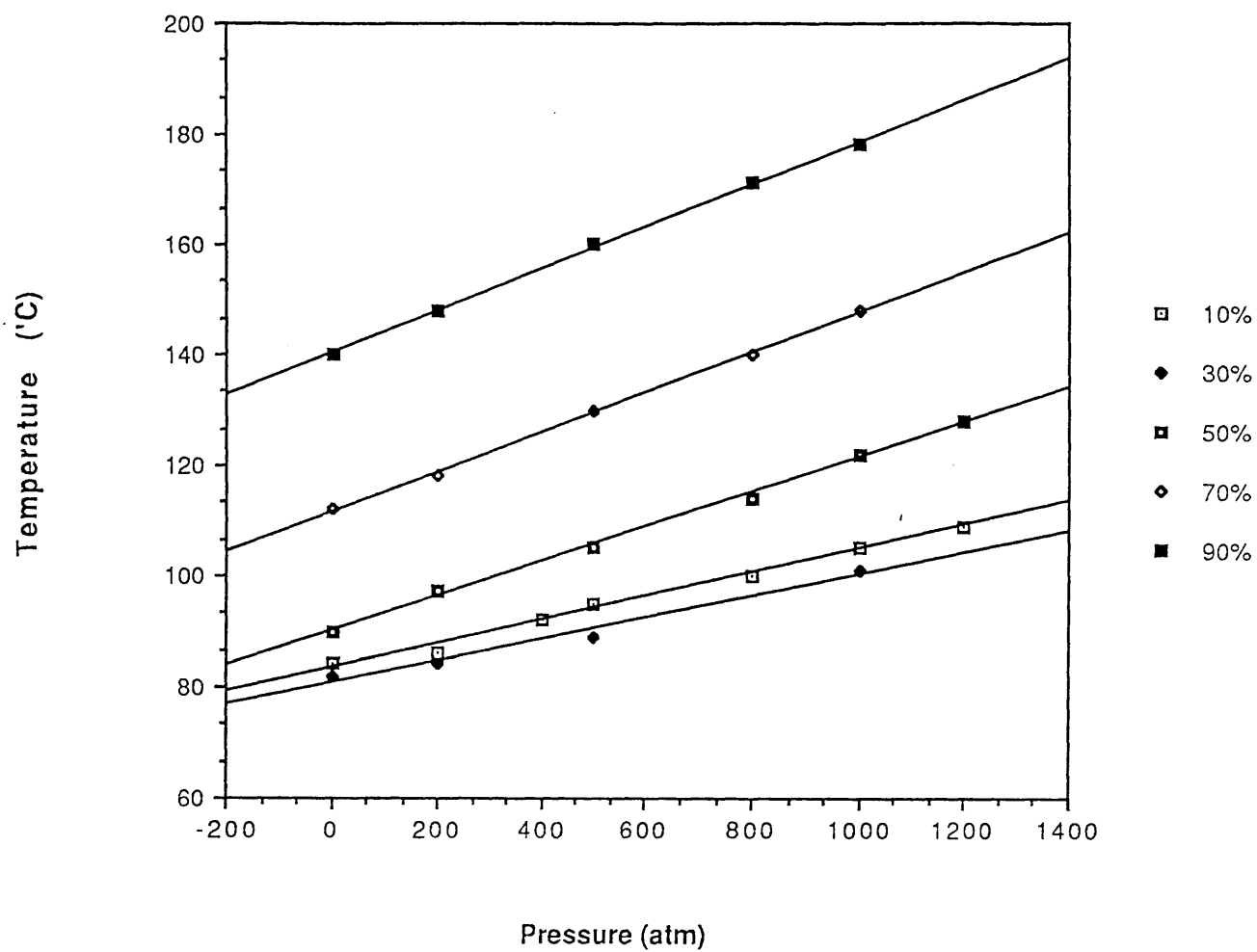


Figure 6.5 A
Pressure dependence of cloud points at various compositions

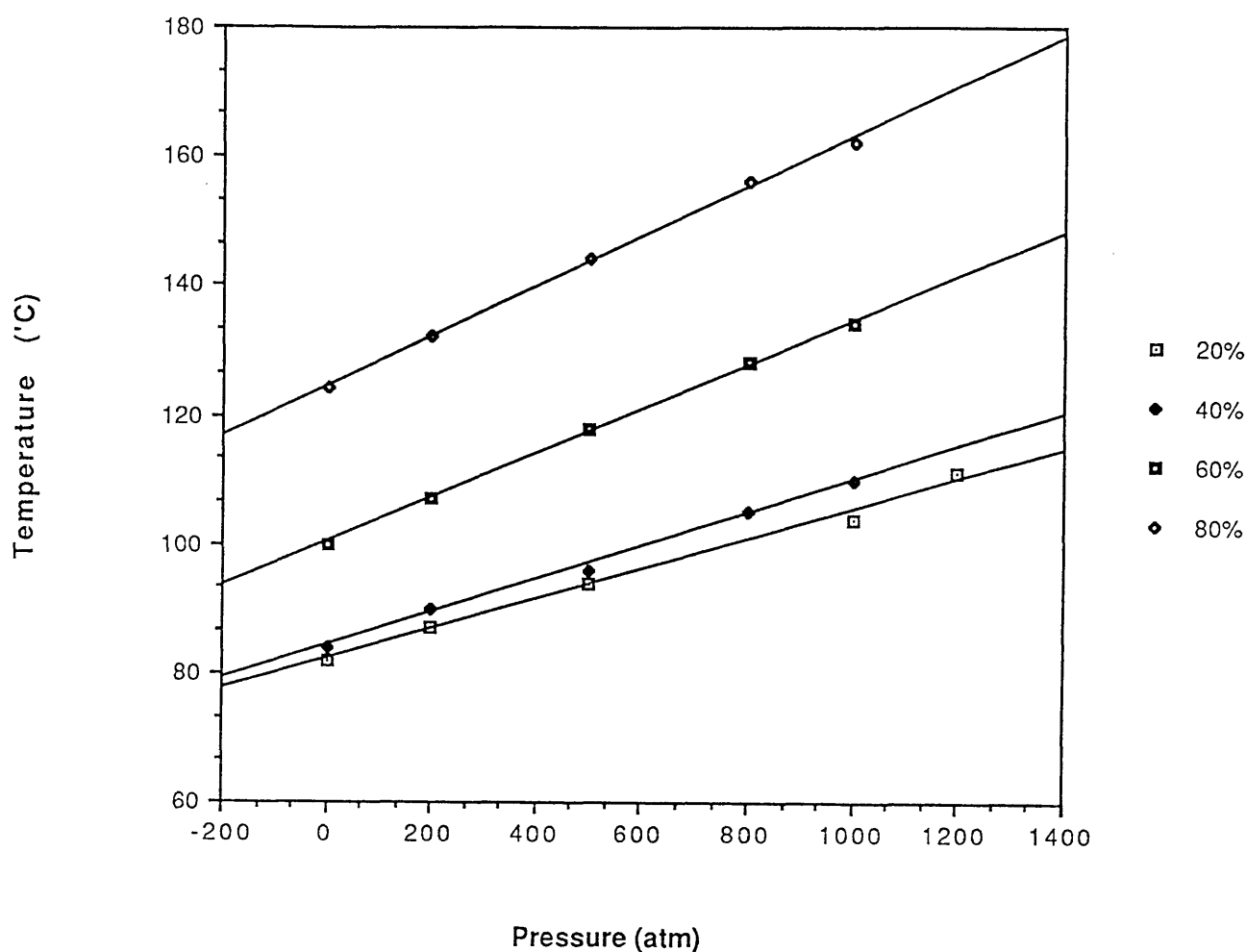


Figure 6.5 B

The effect of pressure on the LCST phase boundary of PS-PVME blends

In their theoretical calculation based on Equation (3.2), Patterson and Robard (1978) obtained a value of $0.13^{\circ}\text{C}/\text{atm}$. Our result is about six times lower than their theoretical estimation. Fig. (6.6) shows that the increase in the pressure dependence of the cloud points is non-linear in composition. The greatest effect of pressure is observed in the mid-composition range.

In their investigation on the effect of pressure on chain dimensions, Gaeckle and Patterson (1972) observed that the effect of pressure is most significant at high temperatures where there is a large difference in the free volume of the components. This observation also supports the experimental

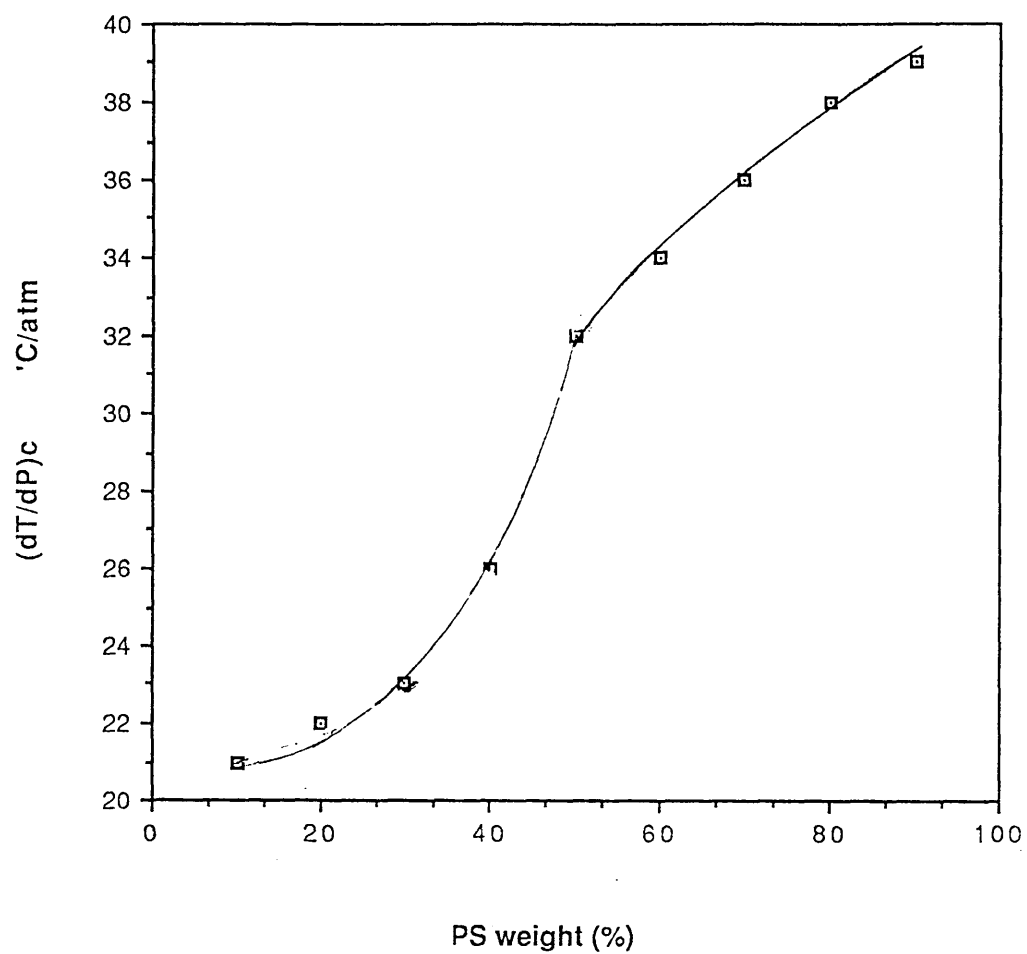


Figure 6.6

Pressure dependence of Cloud point on composition of blend

Table 6.1
Pressure dependence of cloud points on blend composition

Composition (% PS)	$\frac{\partial T_c}{\partial P}$ ($\times 10^3$ Atm)
10	22
20	22
30	23
40	26
50	32
60	34
70	36
80	38
90	39

data presented in Table (6.2) which shows that the pressure dependence of the cloud point increases with a decrease in the molecular weight of PS; our experimental result agrees with their observation because the cloud point increases with the weight fraction of PS and with a decrease in the molecular weight of PS.

It is suggested that the lower rate of increase at higher PS contents (Fig. (6.5)) is due to the difference in the thermal expansion coefficients, α , of the components of this blend. Equation (3.3) suggests that an increase in pressure affects the more expanded component to a greater extent. For this blend PVME is the more expanded component. At 50°C, for example, α for PVME is

$6.911 \times 10^{-4} \text{K}^{-1}$ while α for PS is $5.74 \times 10^{-4} \text{K}^{-1}$; thus at high PS contents, the net effect of pressure gradually diminishes.

Table 6.2
Pressure dependence of molecular weight of PS at
the critical composition

Molecular Weight ($\times 10^{-3}$)	T_c ($^{\circ}\text{C}$)	$\frac{\partial T_c}{\partial P}$ ($\times 10^3$ Atm)
51	98	32
76	93	29
95	88	27
110	85	23
PVME ($\bar{M}_n = 8,000$) blended with PS ($\bar{M}_n = 110,000$)	55	15

Table 6.3
Effect of molecular weight of PSd on the
cloud point of a PSd-PVME blend

Mol. Wt. of PSd ($\times 10^{-3}$)	T_c ($^{\circ}\text{C}$)	$\frac{\partial T_c}{\partial P}$ ($\times 10^3$ Atm)
163	121	46
196	93	38

6.7 Effect of molecular weight of perdeuterated-PS (PSd) on the cloud point of PSd-PVME blends

Only a small quantity of PSd-2 ($\overline{M}_n$ 163,000) was available, hence only one blend composition (30% PSd) could be prepared from this polymer. The cloud point of this composition was determined both at atmospheric and at 500 atm. pressure.

Table (6.3) compares the results obtained using the above-mentioned polymer with a similar blend composition using PSd-1 ($\overline{M}_n$ 196,000).

The result shows that similar to blends of hydrogenous-PS-PVME, an increase in the molecular weight of perdeuterated-PS decreases both the cloud point and its pressure dependence.

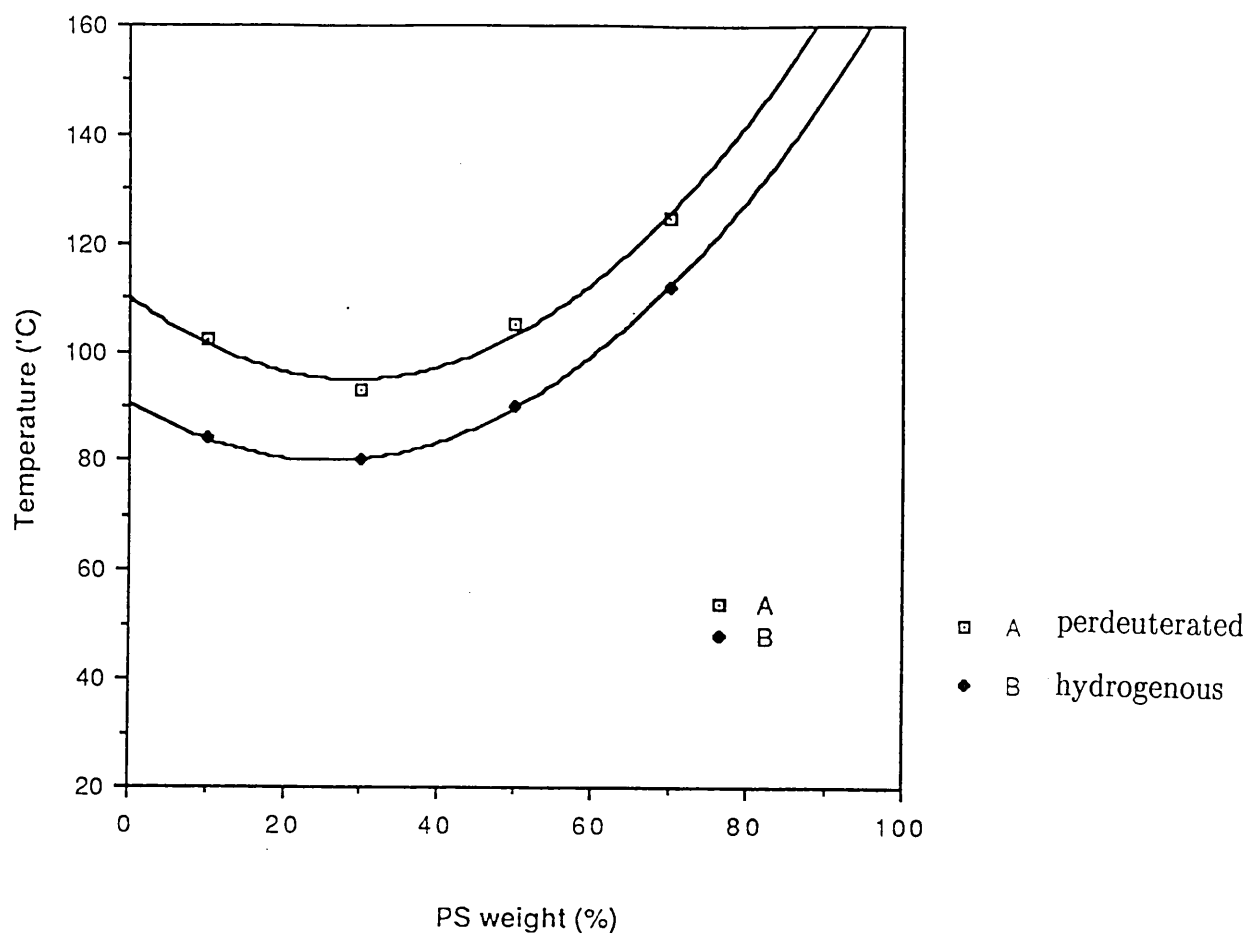


Figure 6.7
Effect of deuteration on LCST Phase Boundary
of PS-PVME blends.

6.8 Effect of deuteration on LCST phase boundary of PS–PVME blends

The cloud point curves for the two blends, PSh–PVME and PSd–PVME, are illustrated in Fig. (6.7). The difference in the behaviour of both blends is apparent. The two polymers are not 'matched' in terms of molecular weight, hence it is not possible to accurately assess the increase in the LCST arising from the substitution of PSd for PSh.

6.9 Effect of pressure on LCST phase boundary of PSd–PVME blends

The pressure dependence of PSd–PVME phase–boundary was investigated, using blends of PSd–1/PVME. Fig. (6.8) shows the miscibility limits of the phase boundary at atmospheric pressure and at the indicated higher pressure.

Similar to its effect on PSh–PVME phase–boundary (discussed in Section 6.5), pressure shifts the phase –boundary of PSd–PVME blend to higher temperatures, thus improving miscibility.

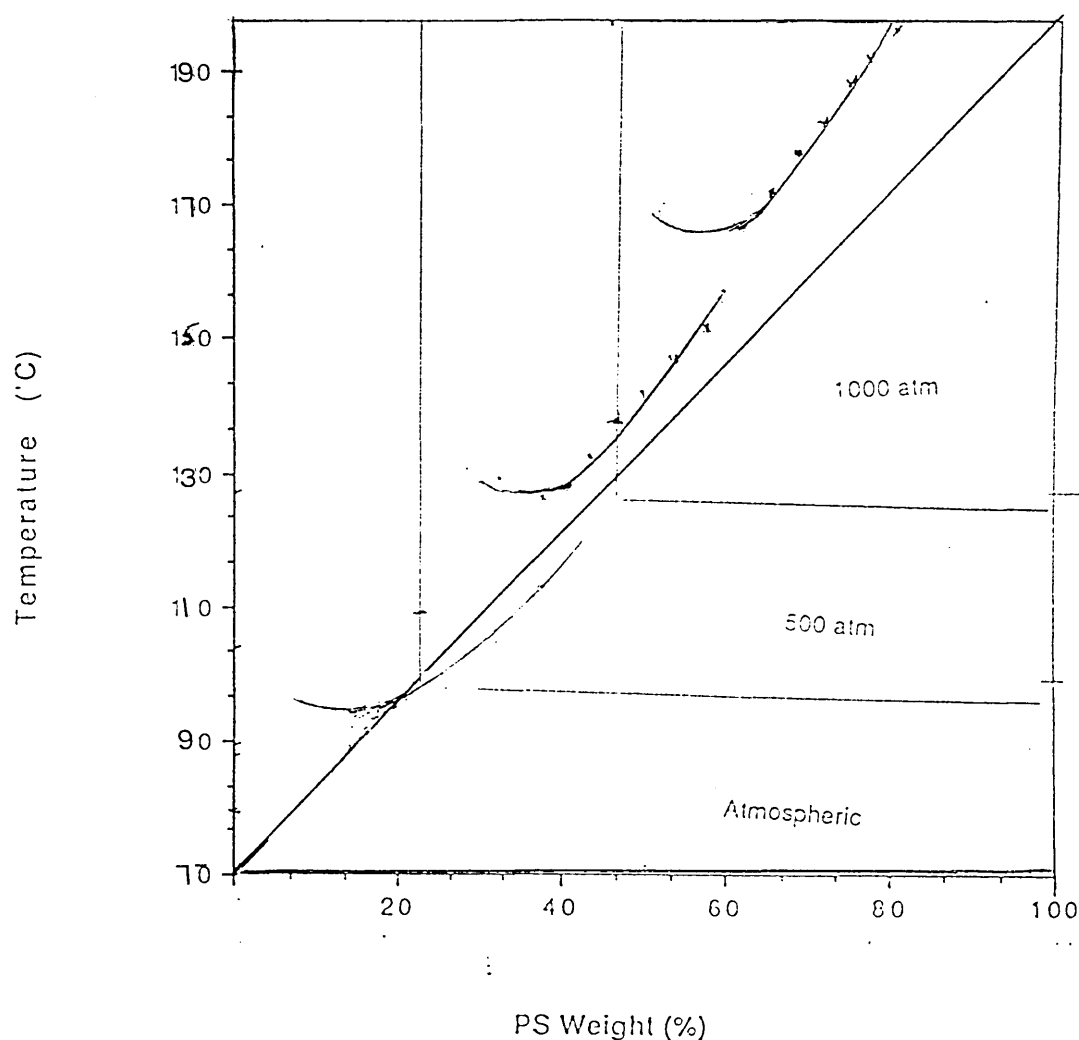


Figure 6.8

Effect of pressure on the LCST phase boundary of PSd–PVME blends

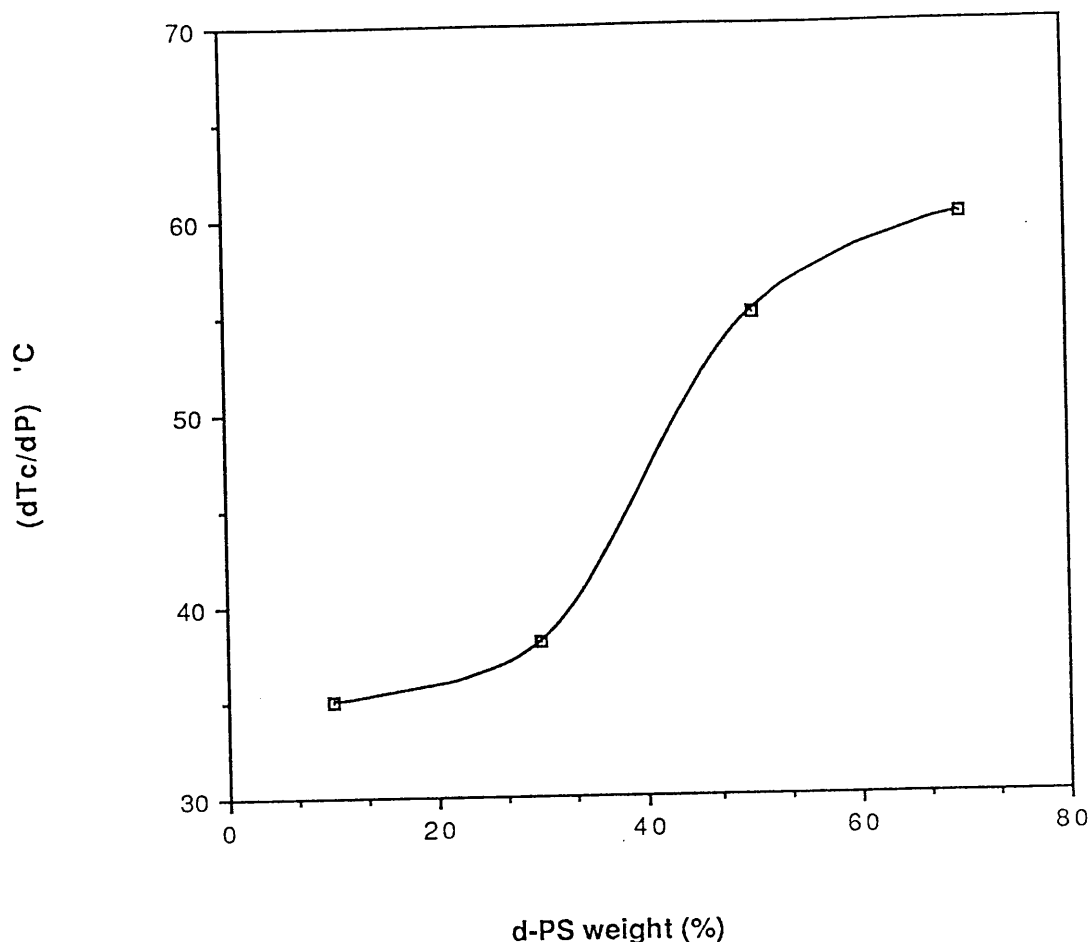


Figure 6.9

Pressure dependence of cloud points on composition of PSd–PVME blends

6.10 Pressure dependence of PSd–PVME phase boundary at different blend composition

The pressure dependence of the cloud points obtained from the results of Fig. (6.8) is shown in Fig. (6.9). Similar to the results discussed in Sections (6.5 and 6.6) for PSh–PVME, the cloud points show a linear pressure dependence which varies with blend composition, for the compositions investigated. This latter observation is demonstrated in Fig. (6.10) and Table (6.4). For the same composition however, the pressure dependence for PSd–PVME blend is higher

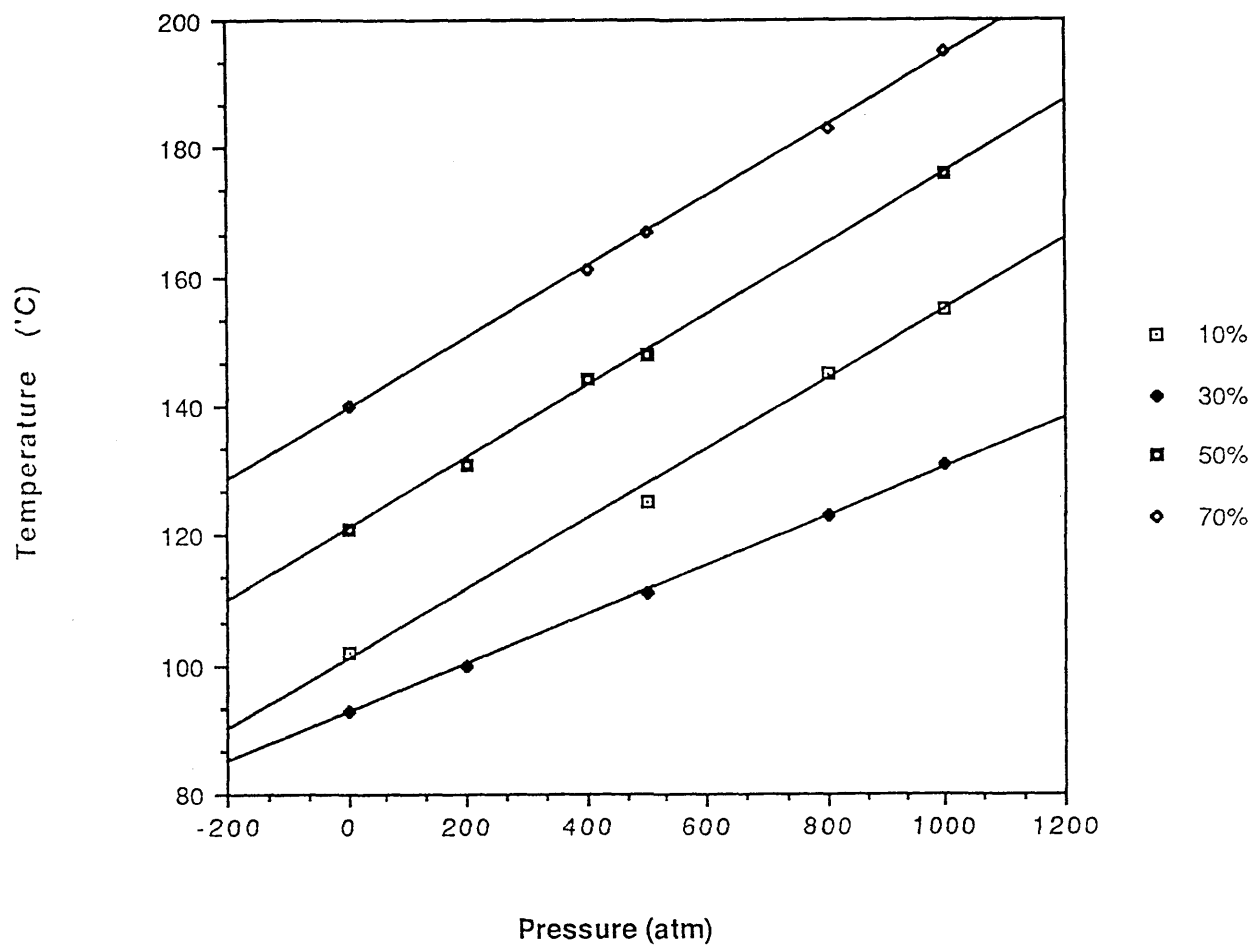


Figure 6.10
Pressure dependence of cloud points of PSd-PVME blends
as a function of composition

Table 6.4
Pressure dependence of cloud points of
PSd-PVME on blend composition

Composition (% PS)	$\frac{\partial T_c}{\partial P}$ ($\times 10^3$ Atm)
10	36
30	38
50	55
70	60

than that for PSh–PVME blend. The pressure dependence at the critical composition for the perdeuterated system is 0.038°C/atm ($\pm 0.002^\circ\text{C/atm}$).

6.11 Heat of Mixing (ΔH_m)

Figs. (5.8) and (5.9) show the electrical calibration of the equipment using a 77 ohm resistor immersed in distilled water and also in a 50/50 w/w%

mixture of the oligomers at the stated temperatures. The F values decrease with an increase in temperature. The area of the exothermal peak obtained for the 30% oligo-PS (critical composition) at 50°C is 26.01 cm².

Using the calibration constant, F , the area A , and $Q = FA$, the heat of mixing, $\Delta H_m = Q$, is -3.44 J/gm. This exothermic heat of mixing indicates the presence of specific interactions between the components of the mixture. Cruz *et al* (1979) and Ziska *et al* (1981), have discussed the role of specific interactions in the miscibility of various polyesters. The heat of mixing is an approximate measure of the free energy of mixing, Flory (1954); Krause (1972) and may be used as an indication of possible miscibility of the system.

The above indication of the miscibility of the present system is supported by the observed clarity of the high molecular weight blends as well as that of the oligomeric mixtures.

Schneier (1973) deduced the following equation for a 2-component high molecular weight polymer blend,

$$\Delta H_m = \{ \bar{x}_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \times [\bar{x}_2 / (1 - \bar{x}_2) M_2 \rho_2 + (1 - \bar{x}_1) M_1 \rho_1]^2 \}^{\frac{1}{2}} \quad (6.3)$$

where $\bar{x}$, ρ and M are the weight fractions of polymer, polymer density and the monomer unit molecular weight, respectively. In the above equation the choice of which polymer is taken as component 1 does not have a significant effect on the shape of the curve of ΔH_m against the blend composition.

Using the above equation, Hourston and Hughes (1978) calculated heats of mixing for a range of compositions of the PS-PVME system. A graphic

illustration of the variation of the heat of mixing with blend composition was also presented by these workers. On the basis of 'Schneier criterion', immiscibility was predicted by them, over most of the composition range. Further, the shape of the curve was dependent on which polymer was chosen as component 1.

6.12 Density Measurements

The result of the density measurements on polystyrene, poly(vinyl methyl ether) and their blends containing from 10.0 to 90.0% by weight of PS is shown in Table (6.5). It is seen that the densities of the blends exceed the values for either PS or PVME.

Table 6.5
Data of Density and Specific Volume for PS-PVME blends
and for the blend components

Wt. % PS	$\bar{\rho}_{\text{exptl.}}$	V_s	V_{blend}	$\Delta V_m \times 10^4$ cm ³ /g
0	1.0430	0.9588		
10	1.0510	0.9515	0.9582	- 67.2
30	1.0525	0.9501	0.9569	- 68.3
50	1.0580	0.9452	0.9556	- 104.0
70	1.0590	0.9443	0.9543	- 100.0
90	1.0610	0.9425	0.9531	- 106.0
100	1.050	0.9524		

Work (1973) and Shur and Randy (1975) observed that the densities and volumes of immiscible polymer blends and phase-separated block copolymers agree with the values calculated from the simple additivity relationships given by Hickman *et al* (1973) and Zakrozewski (1973),

$$\frac{1}{\rho_{\text{blend}}} = \frac{W_A}{\rho_A} + \frac{W_B}{\rho_B} \quad (6.4)$$

$$V_{\text{blend}} = W_A V_A + W_B V_B \quad (6.5)$$

where W_i , ρ_i are the weights and densities of the components of the blend. Kwei *et al* (1974) have defined ΔV_m , the volume change on mixing as:

$$\Delta V_m = V_s - V_{\text{blend}} \quad (6.6)$$

where V_s is the experimental specific volume of the blend and V_{blend} is that calculated according to Equation (6.5).

The negative volume of mixing, ΔV_m , for all the blends, as shown in Table (6.5), suggests that the intermolecular interactions between the components favour better packing between the molecules in the above blends.

Polymer molecules mix with a decrease in their free volumes, Patterson (1982). The 'free volume' effect brings the molecules of the system closer together and hence causes negative contributions in ΔH_m and ΔS_m .

The experimental result is in agreement with the 'free volume theories' of polymer mixtures, as earlier presented in Chapter 2.

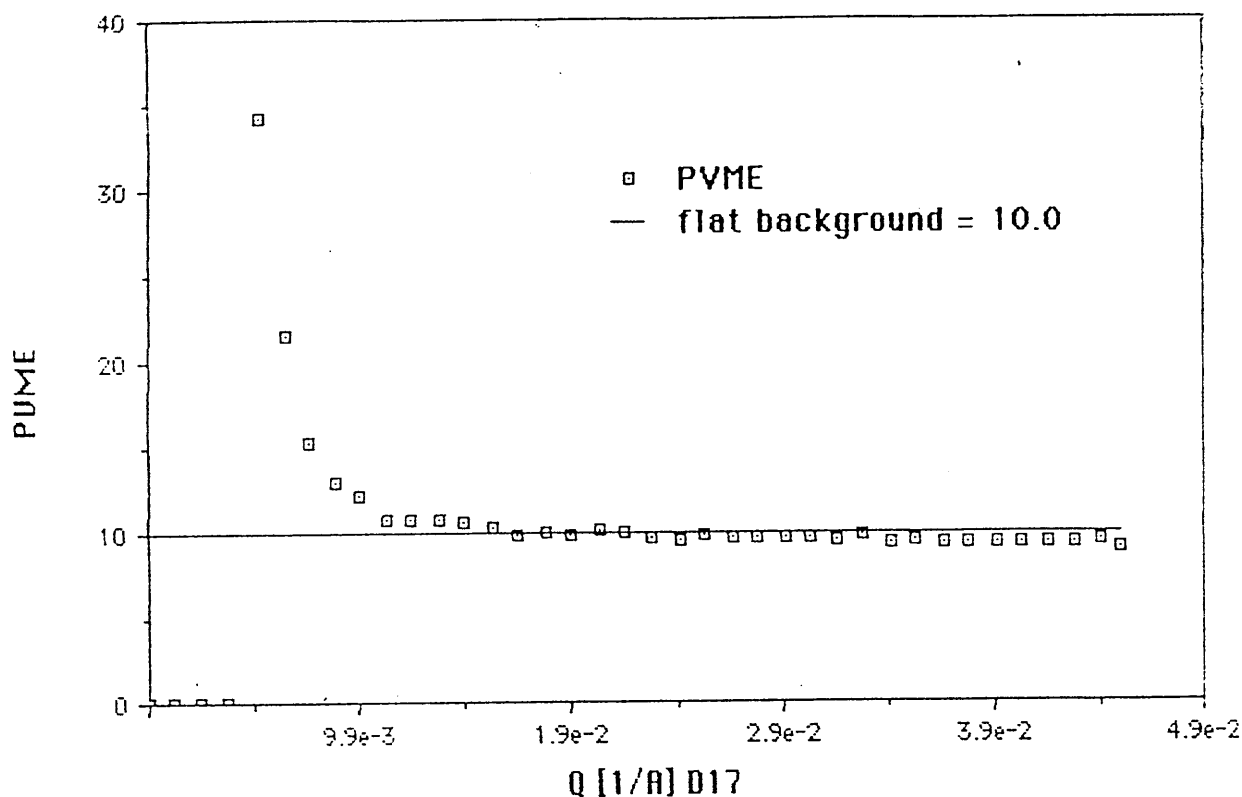


Figure 6.11

The scattered intensity from the background

6.13 Small angle neutron scattering (SANS)

Treatment of Data

The experimental data were normalised by the isotropic incoherent scattering from pure water in order to correct for detector efficiency. This was followed by the subtraction of the appropriate incoherent background, Fig. (6.11), using the 'transmission factor' subtraction, Maconnachie and Richardson (1978).

The scattered intensity at zero angle was obtained from the intercept of a plot of $(I_s)^{-1}$ against q^2 , as shown in Fig. (6.12, A–E). By the use of Equation (5.9) and the relevant parameters listed in Tables (5.4) and (6.6) the interaction parameter was evaluated:

$$2\chi_{12} = [\phi_1 N_1]^{-1} + [\phi_2 N_2]^{-1} - \left[\frac{(d - \beta b)^2 / V_1}{I(0)} \right] \quad (6.7)$$

where d and b are scattering lengths per monomer unit of deuterated and hydrogenous components, respectively,

V_1 is the molar volume of one repeat unit of polymer 1,

β is the relative volume of monomer 1 and monomer 2: (V_1/V_2),

N_1 and N_2 are the degrees of polymerisation,

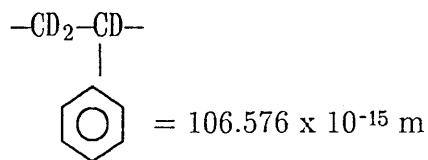
χ_{12} is the interaction parameter,

b is the scattering length of hydrogenous component

$$-\text{CH}_2\text{CHOCH}_3- = -3.314 \times 10^{-15} \text{ m}$$

$$= -3.314 \times 10^{-13} \text{ cm}$$

d is the scattering length of deuterated component



$$= 106.576 \times 10^{-13} \text{ cm}$$

$$V_1 \text{ for d-PS) } = 1.7 \times 10^{-22} \text{ cm}^3$$

$$\text{Molar volume of PSd is } 100.54 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{Molar volume of PVME is } 55.47 \text{ cm}^3 \text{ mol}^{-1}$$

$$\beta = \frac{100.54}{55.47} = 1.813$$

$$N_1 = 3438$$

$$N_2 = 3414$$

$$\text{Transmission factor} = \left[\frac{1 - T_S}{1 - T_{PVME}} \right] \times \text{flat background} \left[\frac{T_{PVME} \cdot t_{PVME}}{T_S \cdot t_S} \right]$$

where

T_S , t_S are the sample transmittance and the sample thickness, respectively,

T_{PVME} and t_{PVME} are the background (PVME) transmittance and the thickness, respectively.

Table 6.6
Scattered intensity from the samples

Run No.	Transmittance	Transmission Factor	ϕ_1 (PSd)	ϕ_2 (PVME)	$I/I(0)$ (cm)	$I(0)$ (cm^{-1})
6597	0.638	0.1822	0.6860	0.2930	0.177	5.64
6594	0.638	0.1822	0.6857	0.2867	0.210	4.76
6632	0.570	0.2420	0.6858	0.2980	0.282	3.54
6593	0.576	0.3007	0.2897	0.6752	0.158	6.32
6607	0.691	0.1827	0.2922	0.6820	0.108	9.25
6608	0.149					
(PVME)						

Results

The results are presented in Table (6.7).

The negative values of the Flory–Huggins interaction parameter, χ_{12} , confirm miscibility of the blend for the compositions examined at the relevant temperatures.

The observed temperature dependence of χ_{12} confirms that an increase in temperature is less favourable for miscibility. Han *et al* (1988) measured the binary interaction parameter of PSd–PVME by SANS, as a function of temperature, component molecular weight and blend composition. Although an obvious molecular weight dependence of χ_{12} was not observed, their results show a similar temperature dependence as in the present investigation.

Table 6.7

Flory-Huggins interaction parameter from SANS measurements

Run Number	Sample Code	Temperature	Weight % PSd	χ_{12}
6607	GD30	Room Temp.	30	-5.84×10^{-2}
6593	D30	50°C	30	-3.97×10^{-2}
6632	D70	Room Temp.	70	-10.5×10^{-2}
6594	D70	71.2°C	70	-7.78×10^{-2}
6597	D70	50°C	70	-6.6×10^{-2}

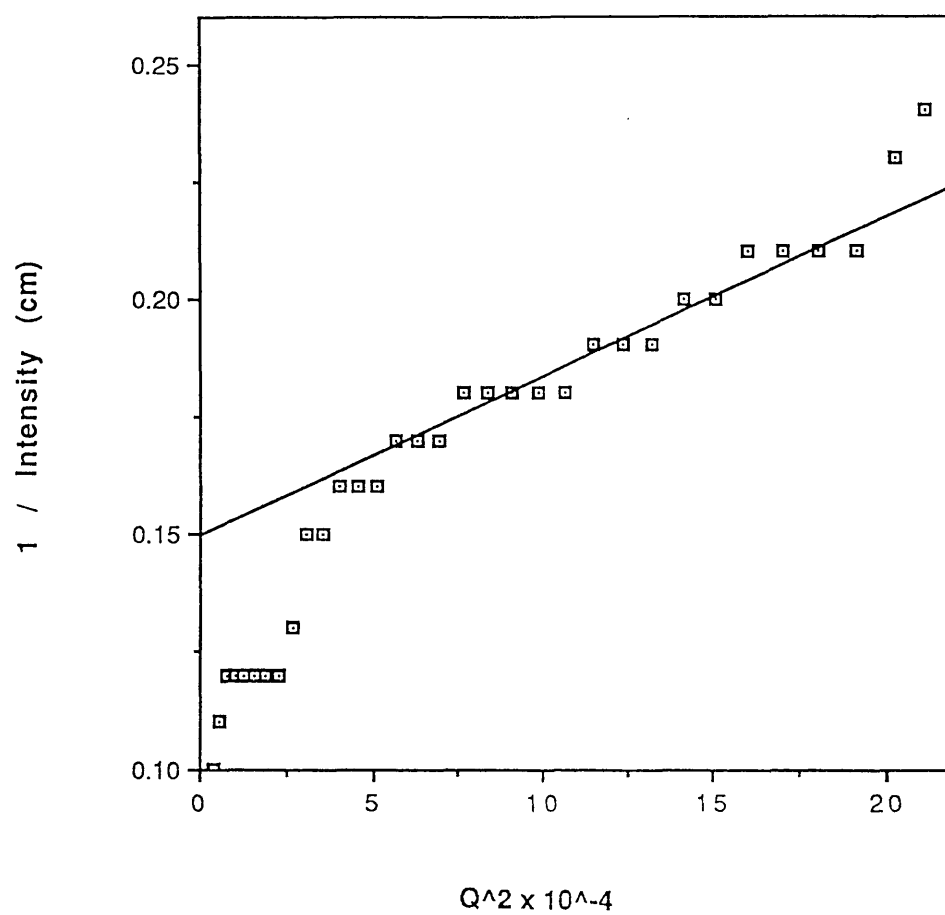


Figure 6.12 A

The scattered intensity at various angles

D6593

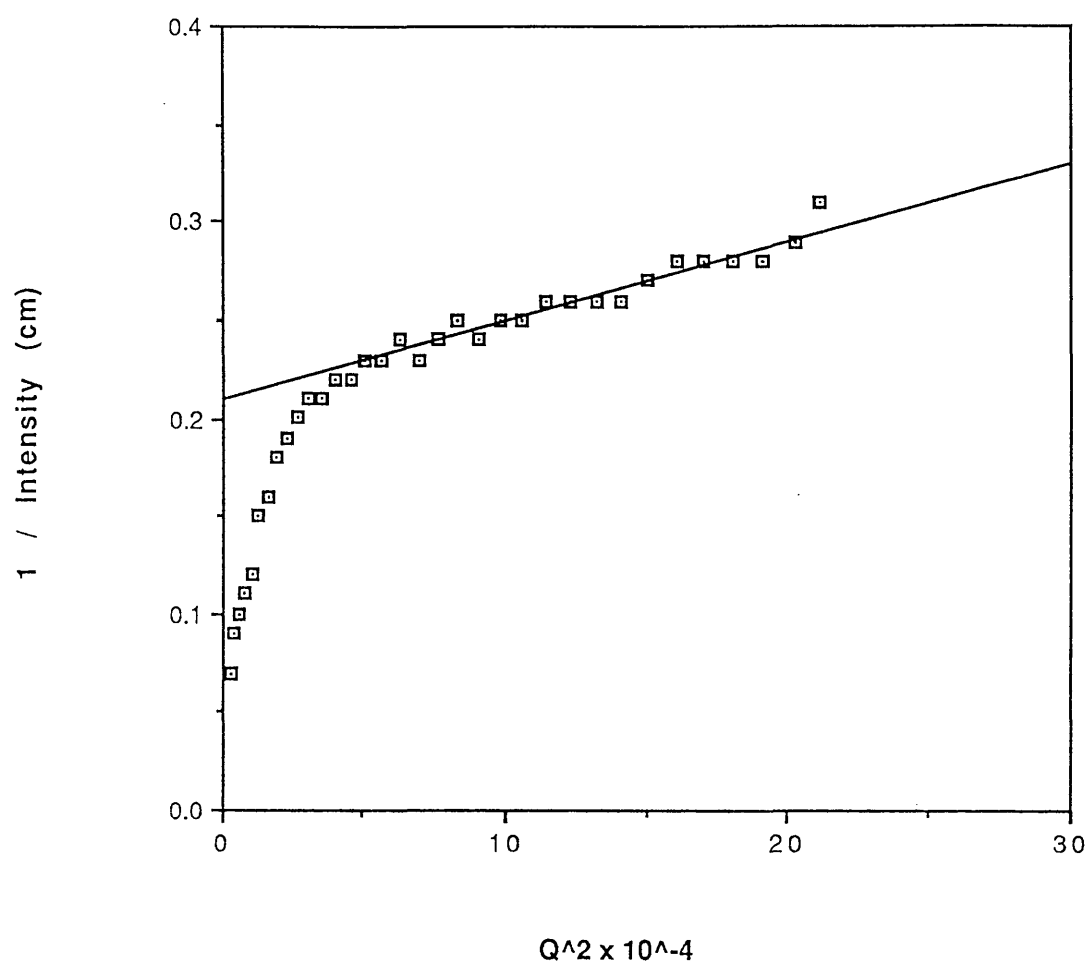


Figure 6.12 B

The scattered intensity at various angles

D6594

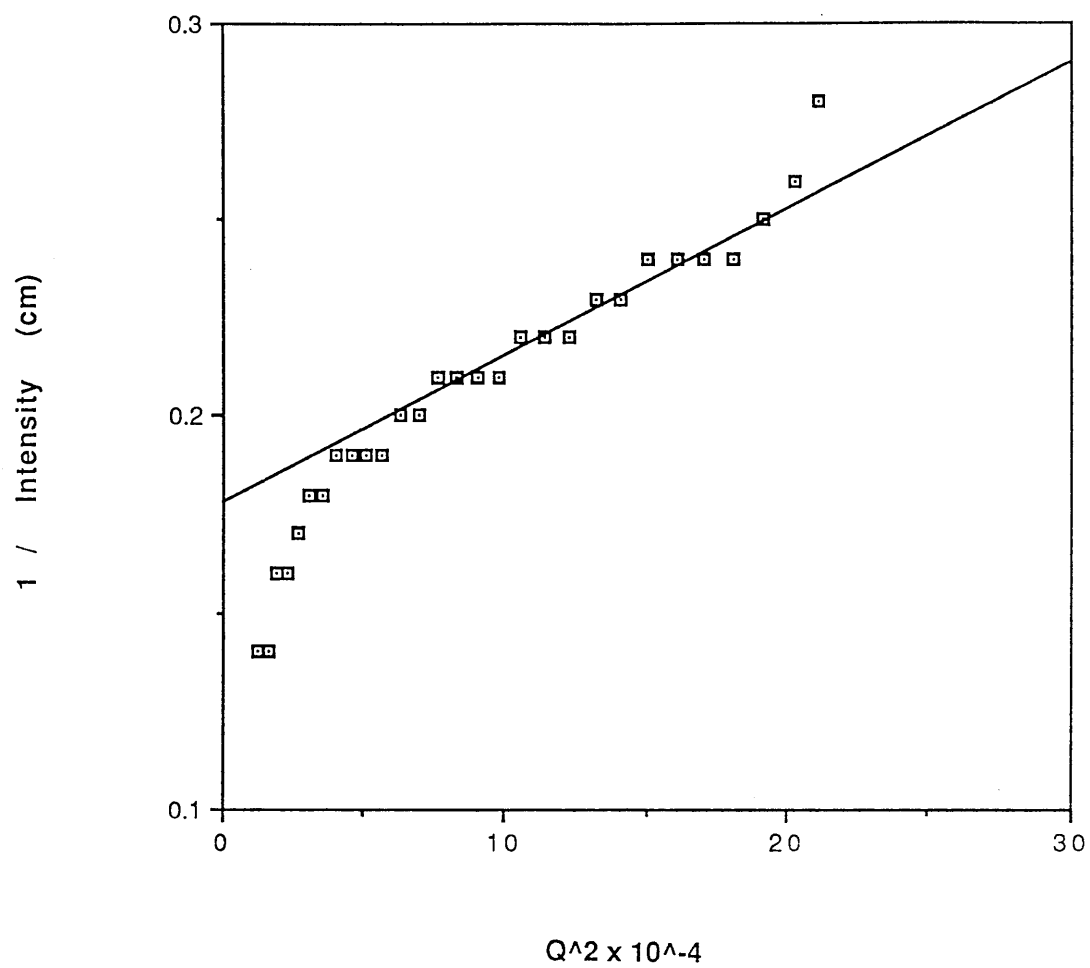


Figure 6.12 C

The scattered intensity at various angles

D6597

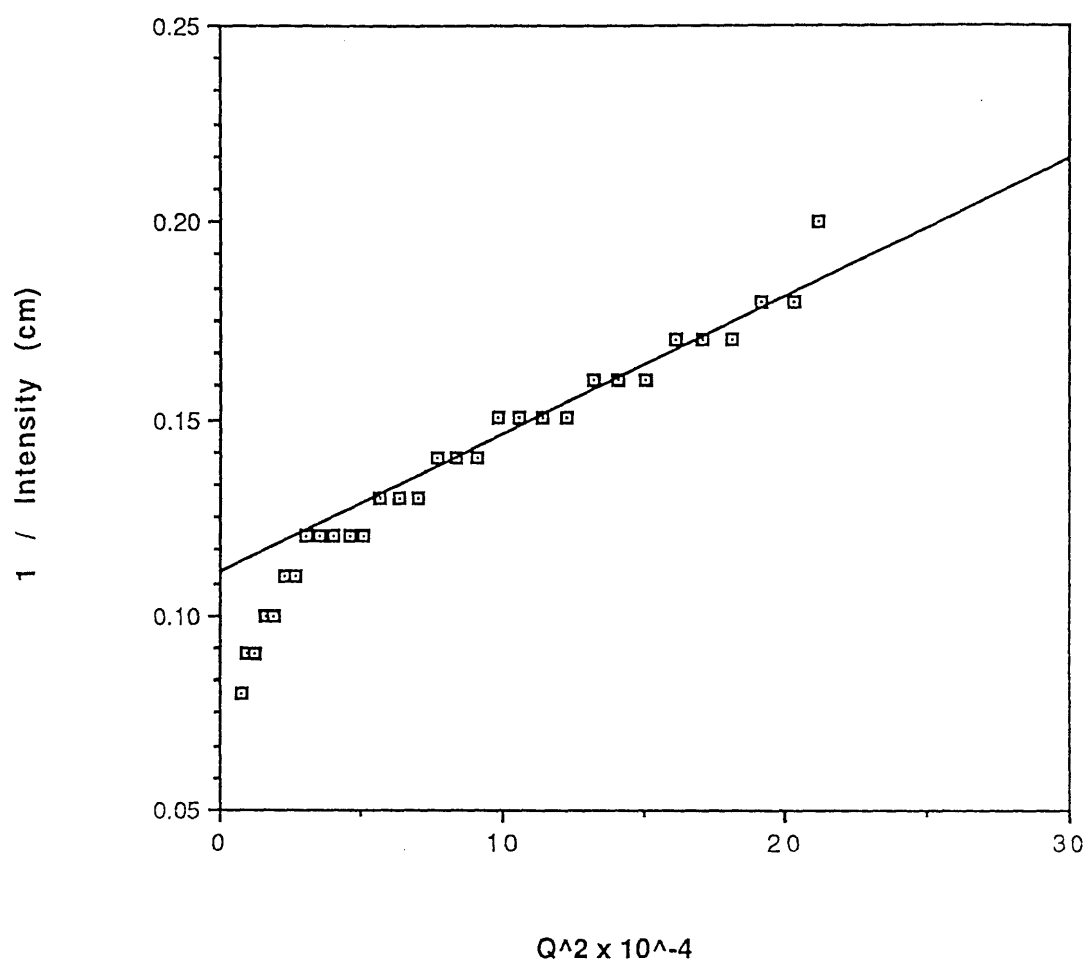


Figure 6.12 D

The scattered intensity at various angles

GD 6607

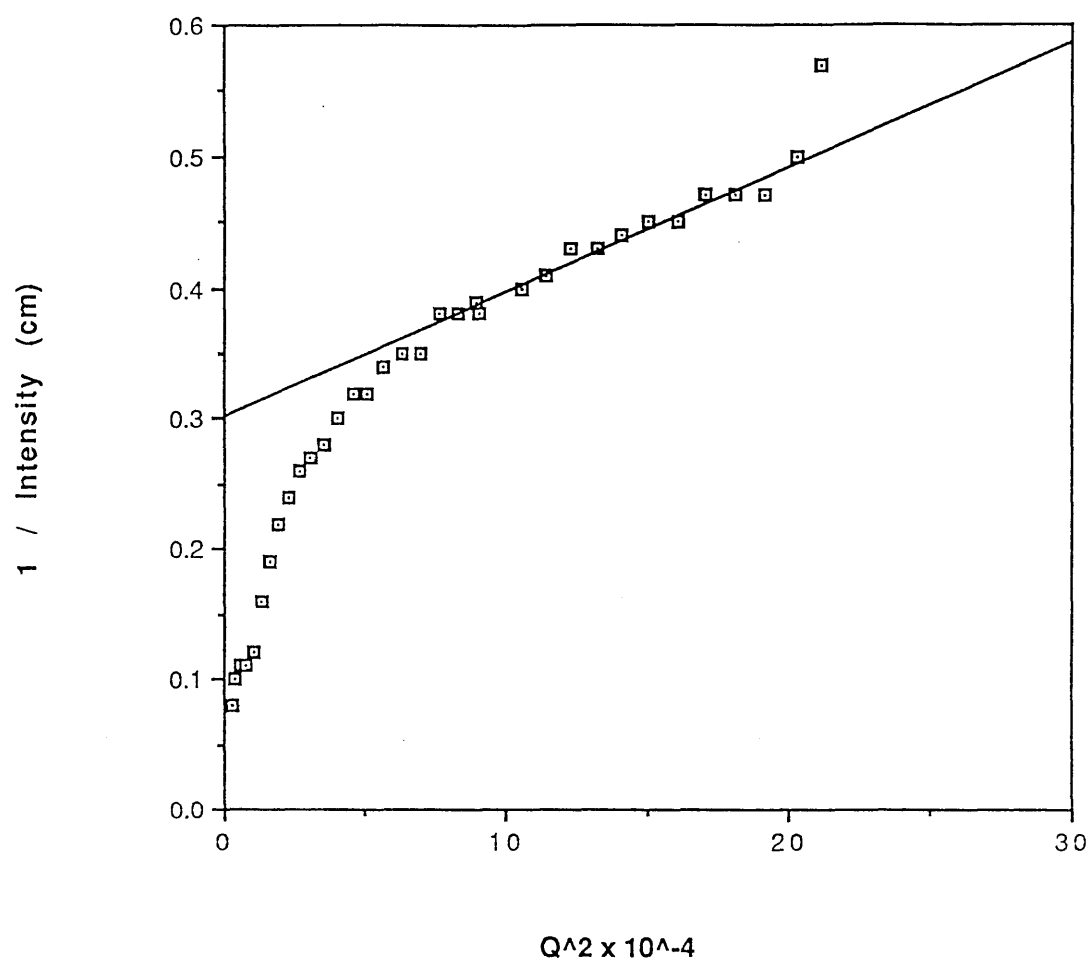


Figure 6.12 E

The scattered intensity at various angles

D6632

6.14 The interaction term, X_{12} from ΔH_m

The interaction term, X_{12} , is evaluated from the measured heat of mixing, using the relationship given by Equation (2.46) which on rearranging becomes

$$X_{12} = \frac{\tilde{v}}{\phi_1 \theta_2} \left\{ \frac{\Delta H_m}{\bar{r} N_V^*} - \phi_1 P_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) - \phi_2 P_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) \right\} \quad (6.8)$$

where:

the equation-of-state parameters for PS, PVME (subscripts 1,2) respectively at 50°C are given in Table (7.1)

$N = N_1 + N_2$ are the molar fractions,

$\bar{r} = \{(\phi_1/r_1 + \phi_2/r_2)\}^{-1}$,

ϕ_1 and ϕ_2 are the volume fractions of the polymers,

r_1 and r_2 are their chain lengths,

$\theta_2 = \phi_2$ (θ_2 is the site fraction of component 2, assumed = ϕ_2) and

$\tilde{v}$ is the reduced volume of the mixture.

Origin and characteristics of the polymers, PS-3 and PVME-E are listed in Table (5.1).

X_{12} is evaluated as -14.8. The negative value of the interaction term predicts miscibility for the two components.

X_{12} is related to the Flory-Huggins interaction parameter, χ_{12} , by:

$$\chi_{12} = P_1^* V_1^* / RT \phi_2^2 \{ 3 \tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + X_{12} \theta_2^2 / P_1^* \tilde{v} \} \quad (6.9)$$

χ_{12} for the above listed polymers at the relevant temperature is evaluated as -51.3×10^{-2} . The negative value of χ_{12} predicts miscibility for the polymers.

The interaction parameter between two polymers is given by:

$$\chi_{12} = \frac{V_r}{RT}(\delta_1 - \delta_2)^2, \text{ Hildebrand and Scott (1962, 1964)} \quad (6.10)$$

where

V_r is the molar volume of the smaller polymer repeat unit and

δ_1, δ_2 are the solubility parameters of the polymers.

Scott (1949) derived the following equation which defines the critical condition for a mixture of two polymers:

$$(\chi_{12})_{cr} = \frac{1}{2} \left[\frac{1}{x_1^{\frac{1}{2}}} + \frac{1}{x_2^{\frac{1}{2}}} \right]^2 \quad (6.11)$$

where

$(\chi_{12})_{cr}$ is the interaction parameter at the critical point,

x_1 and x_2 are the degrees of polymerisation of components 1 and 2 respectively.

Krause (1972) also presented an equation to calculate $(\chi_{12})_{sp}$, the interaction parameter at the spinodal,

$$(\chi_{12})_{sp} = \left[\frac{1}{2x_1(v_1)_{sp}} + \frac{1}{2x_2(v_2)_{sp}} \right] \quad (6.12)$$

$(v_1)_{sp}$ and $(v_2)_{sp}$ are the volume fractions of the polymers at the spinodal.

Hurstun and Hughes (1978) applied these equations to the PS–PVME system and indicated that immiscibility is predicted over most of the

composition range because χ_{12} , the calculated interaction parameter is generally greater than $(\chi_{12})_{cr}$ and $(\chi_{12})_{sp}$.

Table (6.8) shows their calculated values of χ_{12} , $(\chi_{12})_{cr}$, $(v_1)_{cr}$ and $(v_2)_{cr}$.

Table 6.8

Parameter	Value
χ_{12}	0.024
$(\chi_{12})_{cr}$	0.0045
$(v_1)_{cr}\%$	23
$(v_2)_{cr}\%$	77

Table (6.9) compares the value of χ_{12} obtained from SANS with that obtained from heat of mixing experiments. Both values are for a 30% PS blend at 50°C. The measured enthalpy of mixing, ΔH_m , from which the χ_{12} value is obtained is also included. The larger negative value from this latter experiment is more favourable to mixing than χ_{12} from SANS experiment. The difference between the neutron and heat of mixing results arises because the latter is a purely enthalpic measurement whereas the former comes from the free energy of mixing via the concentration gradient of the chemical potential and therefore includes both enthalpic and entropic contributions. In the equation of state theory the interaction term, X_{12} , obtained by fitting the heat of mixing data leads automatically to an entropic contribution because of the inclusion of volume changes. Discrepancies in the value of X_{12} thus obtained led to the inclusion of an extra interaction entropy term, Q_{12} , as earlier discussed in Chapter 2. Q_{12} is an arbitrary adjusting parameter which is used to fit the theoretical data with the experimental result. In the simulation of the spinodal

TABLE 6.9
Values of Flory-Higgins interaction parameter

χ_{12} (from SANS)	ΔH_m $\pm 5\%$	χ_{12} (from heat of mixing)
- 3.97×10^{-2} (± 0.02)	- 3.44 J/g	- 51.3×10^{-2}

curve (Chapter 7) it is found that the calculated X_{12} is too favourable and that an unfavourable Q_{12} is required in order to be consistent with the experimental data.

The data from both measurements confirm that there is an extra (non-combinatorial) entropy of mixing for blends of PS with PVME which is unfavourable for mixing.

6.15 Differential scanning calorimetry (DSC)

Typical DSC results for various miscible PSh–PVME blend compositions at a heating rate of $20^{\circ}\text{C min}^{-1}$ are shown in Fig. (6.13). The optically–clear blends which gave single T_g 's were heated to above their phase–separation temperatures and then 'quenched' in liquid N_2 , to preserve the phase–separated structure.

These cloudy samples were found to give two T_g 's, as shown in Fig. (6.14). This result confirms that miscible PSh–PVME blends phase separate on heating, as previously mentioned in Chapter 3, on 'Methods of Study'. The T_g 's obtained from the above–miscible blends as well as those obtained from miscible PSD–PVME blend compositions are given in Table (6.10).

Table 6.10

Effect of composition on temperature of thermal transition of
PSH/PVME and PSD/PVME blends cast from toluene

The measurements were made at a heating rate of 20°C/min. and a range of 2 mcal/s using Perkin-Elmer Model DSC-2

%PS	T_g $\frac{\text{PSH}}{\text{PVME}}$ $^{\circ}\text{C}$	T_g $\frac{\text{PSD}}{\text{PVME}}$ $^{\circ}\text{C}$	Data from Bank <i>et al</i> on PSH/PVME $T_g^{\circ}\text{C}$
100	106.5	106.5	102
50	-17.5	-17.5	-14
40	-20.2	-20.2	-20.5
10	-23.0	-23.0	-26
0	-27.8	-27.8	-28

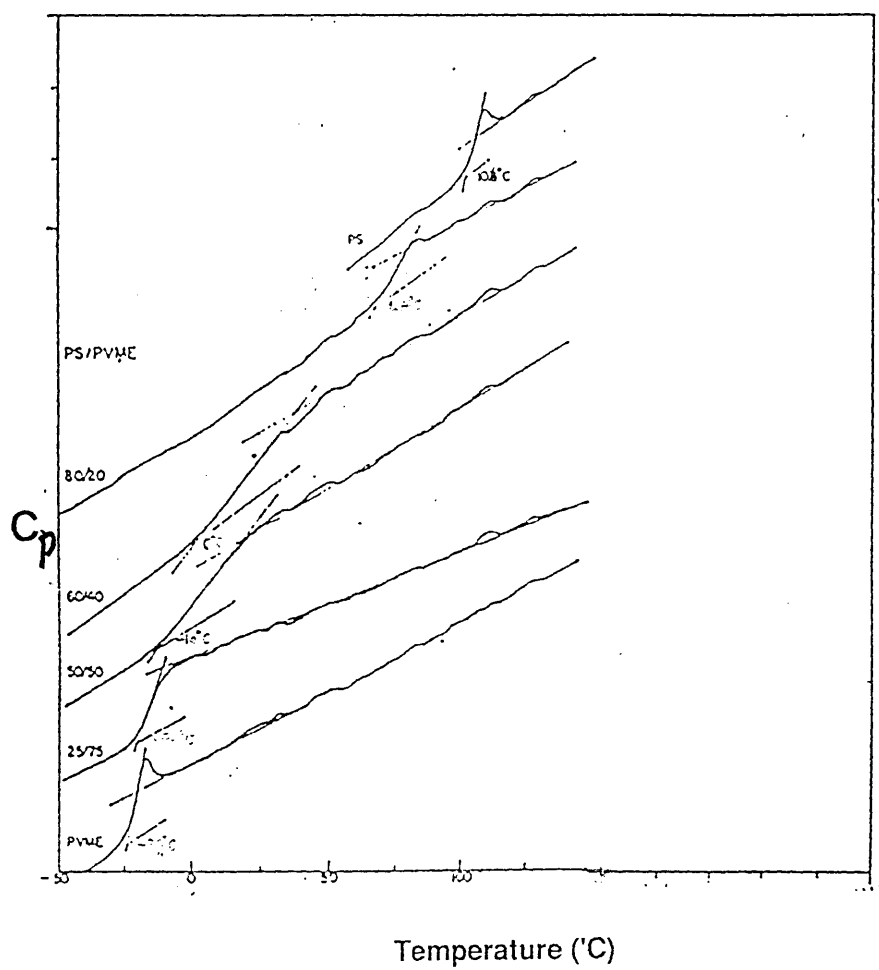


Figure 6.13

Differential scanning calorimeter traces of miscible PS–PVME blends

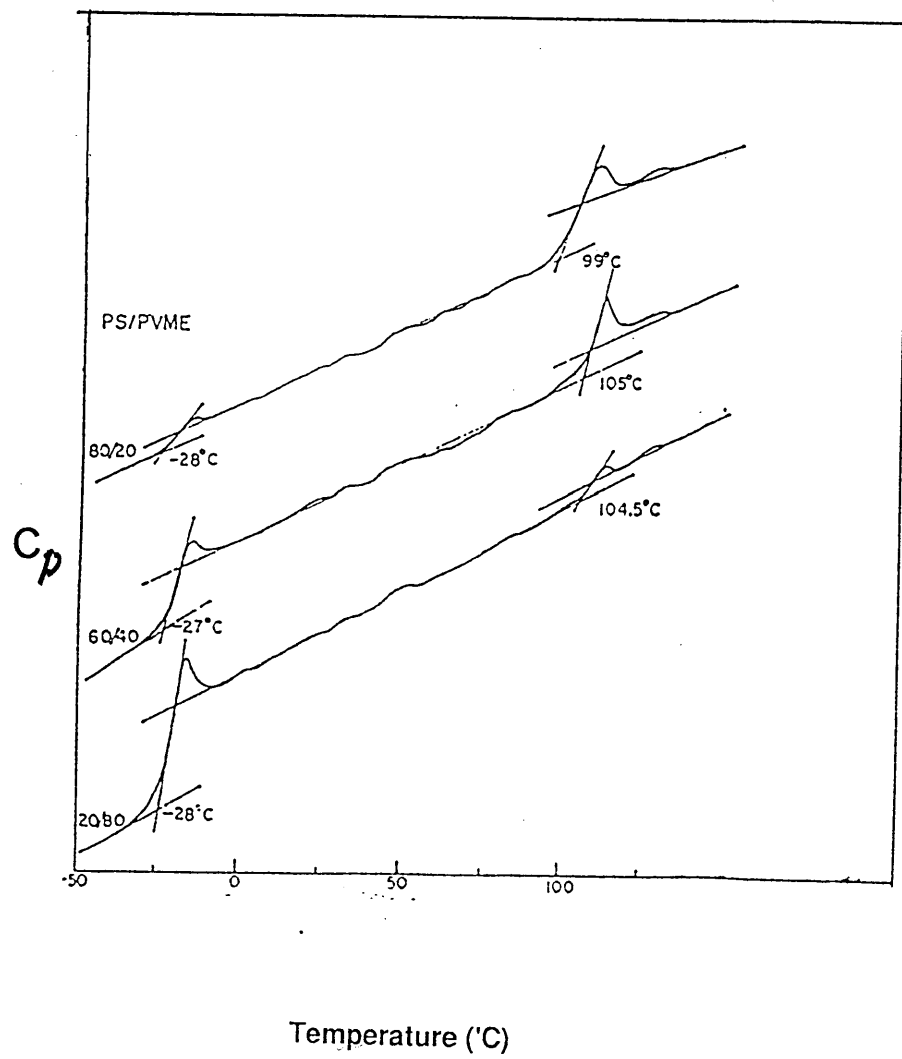


Figure 6.14

Differential scanning calorimeter traces of phase-separated blends

For both blends, a single composition-dependent T_g that was the same for the same composition was obtained. The IR observations made by Lu *et al* (1983) and Garcia (1984) suggest strongly that the interaction between the two polymers involve the ether lone pair electrons of PVME with the benzene ring of PS. The glass transition temperature reflects local interactions and since the T_g is the same for each blend, it implies that the interactions are the same for PSh–PVME and PSd–PVME blends.

The substitution of perdeuterated–PS for hydrogenous–PS in PS–PVME blends raised the LCST of the blend and changed the excess volume. Yang *et al* (1986) suggested that since both blends have the same glass transition temperature for the same composition, this 'deuteration effect' should be qualitatively interpreted as resulting partially from the larger percentage of negative excess volume of mixing for PSd–PVME relative to that of PSh–PVME.

Various empirical expressions have been proposed to relate the T_g of miscible polymer blends to their blend composition. These include the equations of Gordon–Taylor (1952)

$$T = \frac{kC_2T_2 + kC_1T_1}{C_1 + kC_2} \quad (6.13)$$

and Fox (1956),

$$\frac{1}{T} = \frac{C_1}{T_1} + \frac{C_2}{T_2} \quad (6.14)$$

where C_1 and C_2 = the weight fractions of polymer 1 and polymer 2, respectively.

T_1 , T_2 and $T = T_g$ of polymers 1, 2 and the mixture, respectively

k = constant.

Fig. (6.15) shows plots of the transition temperature of blends of PS–PVME as a function of PS concentration –

A is the experimental data;

B, using the Gordon–Taylor T_g rule where $k = 0.5$

C, using the Fox expression.

The experimental curve shows a poor overall fit to the empirical curves. A reasonable fit of the experimental data to the expressions occurs only at high PS contents. Schneider and Brekner (1985) have shown that the composition dependence of glass transition in the miscible PS–PVME blend exhibits deviations from additivity rules because these rules were derived in the supposition of continuity of the thermodynamic excess functions of mixing. It was noted that at the T_g of the blend, the pure components are in a mixed phase – the one (PVME) in the liquid and the other (PS) in the glassy state. They concluded that only the acceptance of an additional adjusting parameter which accounts for possible differences in interactions between the components in the mixed phase, would enable the interpretation of experimental T_g data. This adjusting parameter was quite different for the blends of PVME with oligomeric and high molecular weight PS respectively, due to the mobility of the chain ends in oligomeric PS. The chain–end mobility creates supplementary free volume in the blend thus causing a substantial depression of the T_g .

Jenkel and Heusch (1953) had earlier shown that asymmetric T_g – composition curves can be reproduced by the addition of a quadratic term to the arithmetic additivity rule of Gordon–Taylor type equations. Kwei (1984) observed that both asymmetric and S-shaped curves can be fitted by adding the quadratic term to the Gordon–Taylor equation, to account for specific interactions.

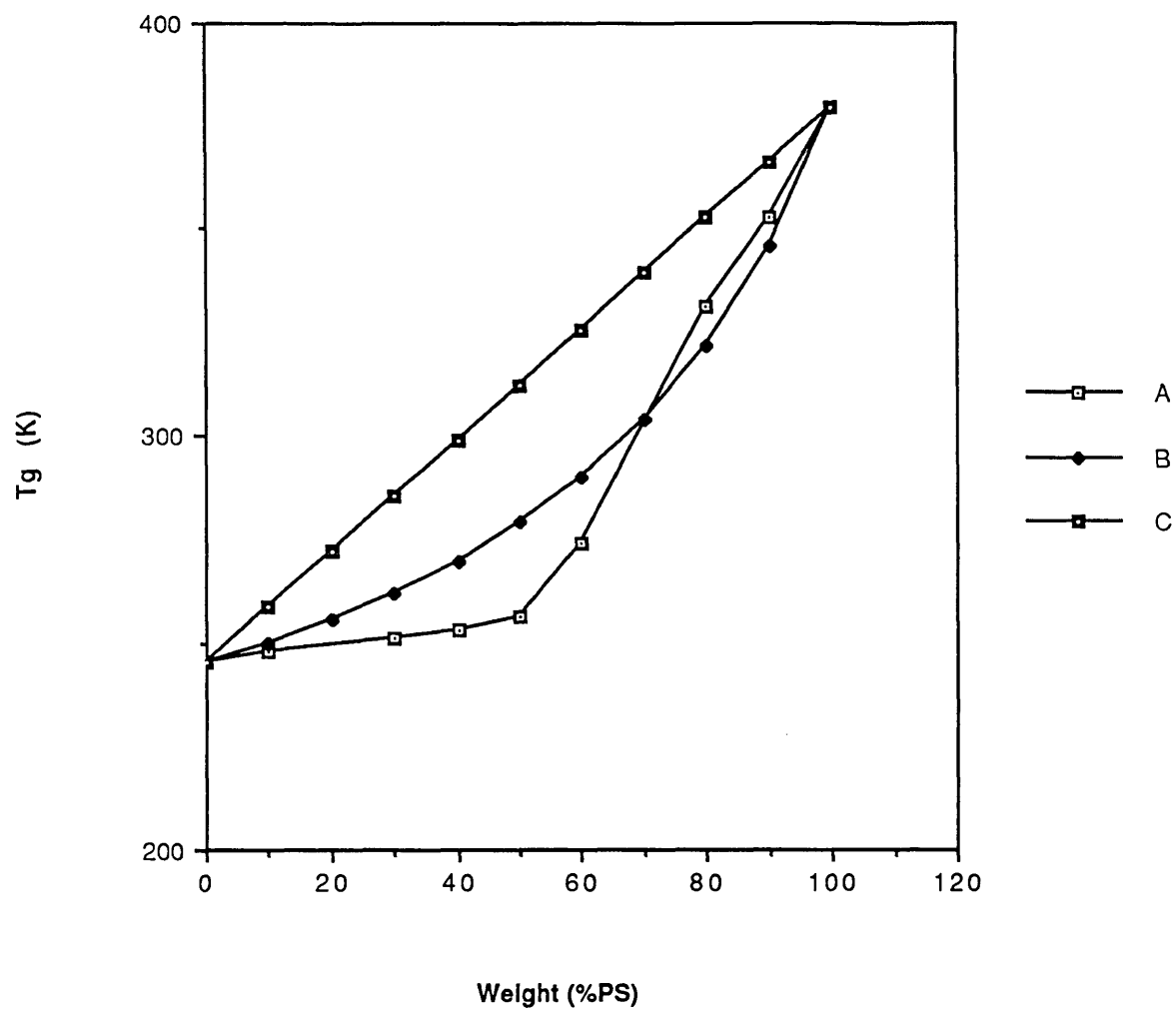


Figure 6.15

The transition temperature of blends of PS–PVME
as a function of PS concentration

- A. The experimental data
- B. Gordon Taylor T_g rule ($k = 3$)
- C. Fox expression

6.16 Dynamic mechanical thermal analysis

Table (6.11) gives the glass transition temperatures for PS/PVME as determined by the DMTA method. Fig. (6.16) shows typical plots of $\tan \delta$ against temperature for various blend compositions. The blends show a single composition-dependent T_g . Compositions containing more than 70 weight percent PVME were too rubbery to be tested by this method.

In general the DSC results were lower than the T_g 's obtained from DMTA.

6.17 Scanning electron microscopy

Scanning electron micrographs of a 30% PS blend are shown in Fig. (6.17 a and b). These show the morphology of the stages indicated as A and B, Fig. (6.18), at the onset of spinodal decomposition and when there is no further change in the transmitted light intensity, respectively. No obvious differences were observed in the morphology of the deuterated and hydrogenous blends of identical composition. It was noted however, that phase separation is generally faster with the deuterated blends since it took a shorter time for the transmitted light intensity to 'level off'.

6.18 Heat treatment under pressure

Fig. (6.19) shows typical profiles of the transmitted light intensity as a function of time, at the indicated pressure. The rate of phase separation is generally faster at atmospheric pressure since the intensity decreases rapidly soon after the onset of phase separation. The intensity however, slowly increases with time to point D as shown by the 'solid' line. The 'broken' line shows the decrease in transmitted light intensity at 1 Kbar pressure. Although the decrease is more gradual the intensity does not increase with time.

Fig. (6.20), a, b, c, and d show the morphology of a 30% PS blend at the stages indicated as A, B, C, and D respectively, Fig. (6.19).

The increase of light intensity beyond point C has been suggested, by Hiramatsu *et al* (1983) to be due to the decrease of the scattering from the phase boundaries. This is because the size of the phase becomes much larger than the wavelength of light and also because the number of the phases decreases due to their interconnection.

Bank *et al* (1971) had earlier reported the effect of domain size on the film clarity for this system. As the two polymers phase separate and the domain size of the dispersed phase enlarges, the cloudy film 'clears' to a bluish appearance. Fig. (6.21) shows the morphology of a 50% PS blend at the stages indicated as A, B, C and D in Fig. (6.19). Figs. (6.20) and (6.21) confirm that the rate of phase separation is generally slower under pressure.

DMTA V1.5 (I.C.)

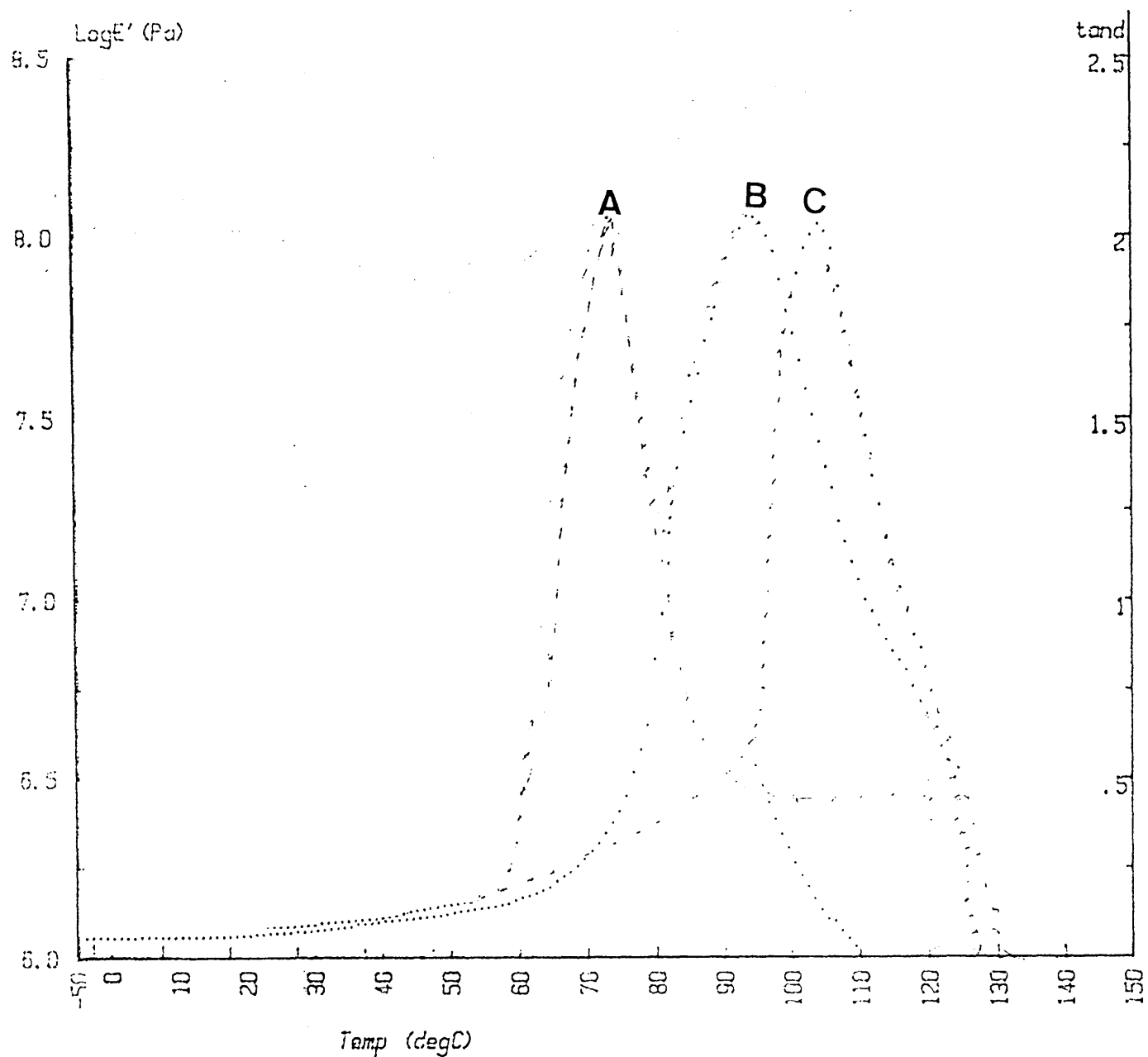


Figure 6.16

Dynamic mechanical relaxation curves of miscible blends
as a function of composition

TABLE 6.11

Effect of composition on thermal transition of PSH/PVME
blends cast from toluene

The measurements were made using a 'Dynamic Mechanical Thermal
Analyser', (Model PL-DMTA, Polymer Laboratories LTD, U.K.) at a constant
oscillating frequency of 1 Hz on x 4 strain.

Wt % PS	T _g (°C)
90	104
80	95
60	67

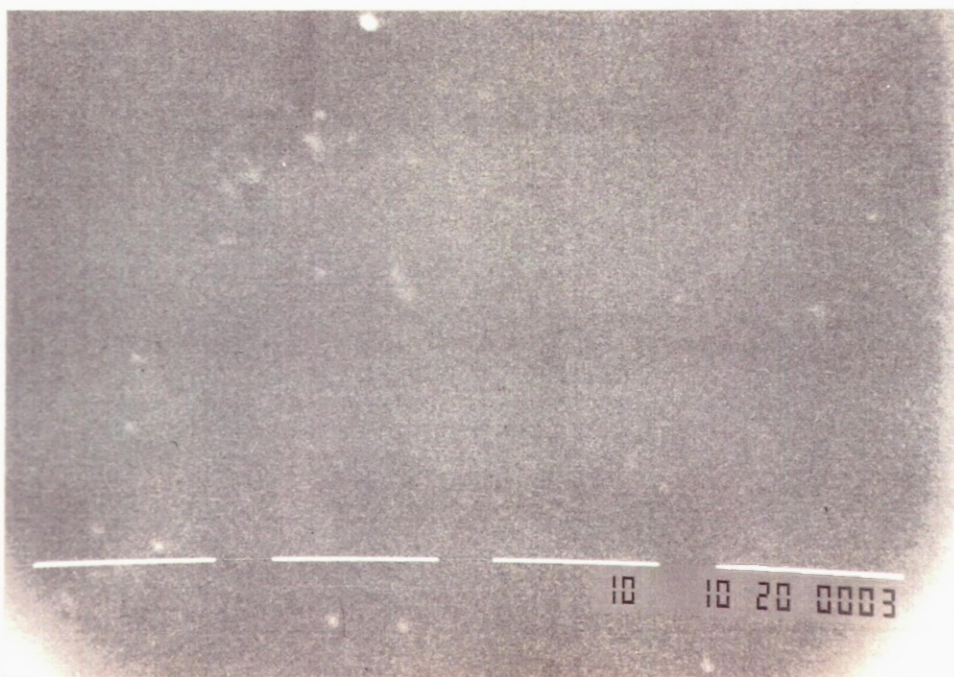


Figure 6.17A

Scanning electron micrographs of a 30% PS blend

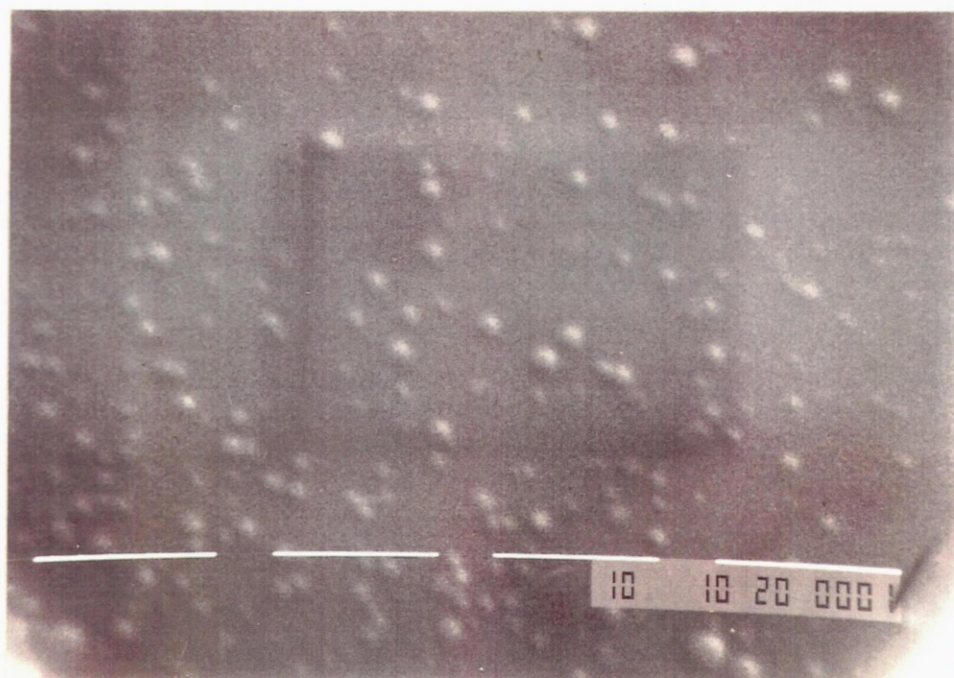


Figure 6.17B

Scanning electron micrographs of a 30% PS blend

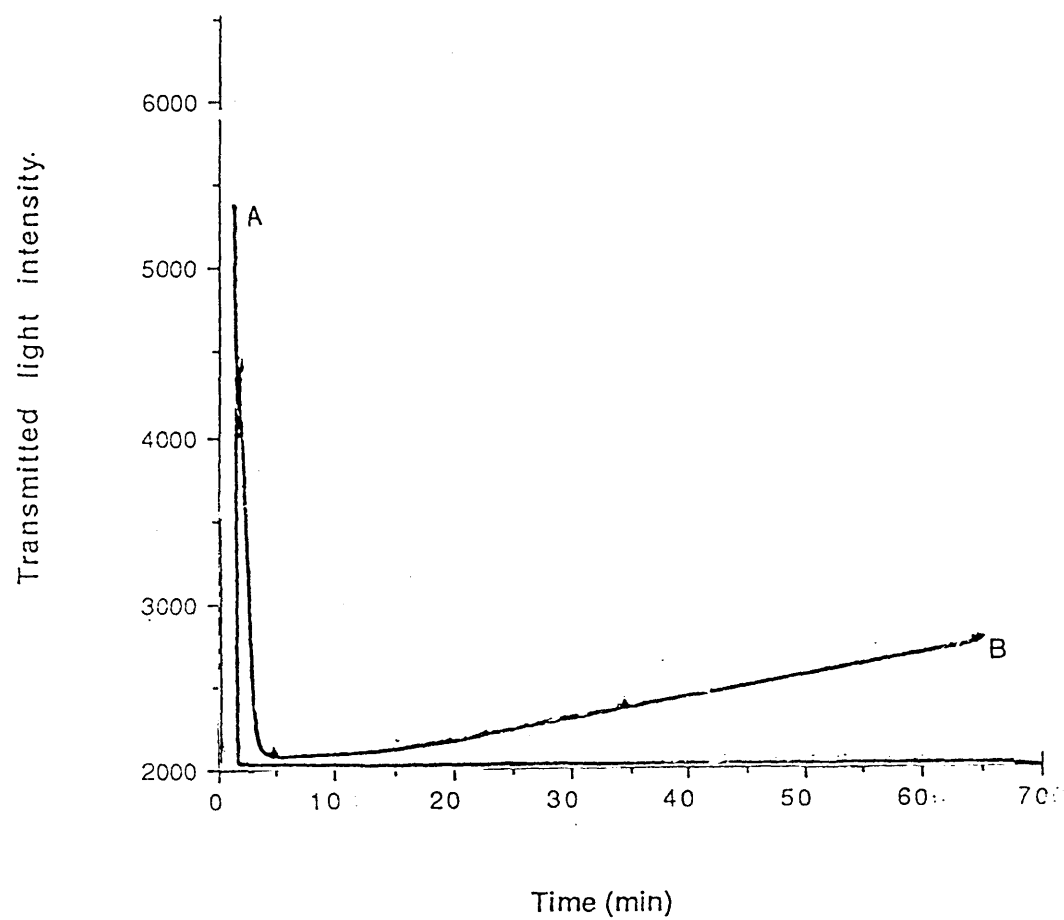


Figure 6.18

Transmitted light intensity as a function of time for a 30% PS blend

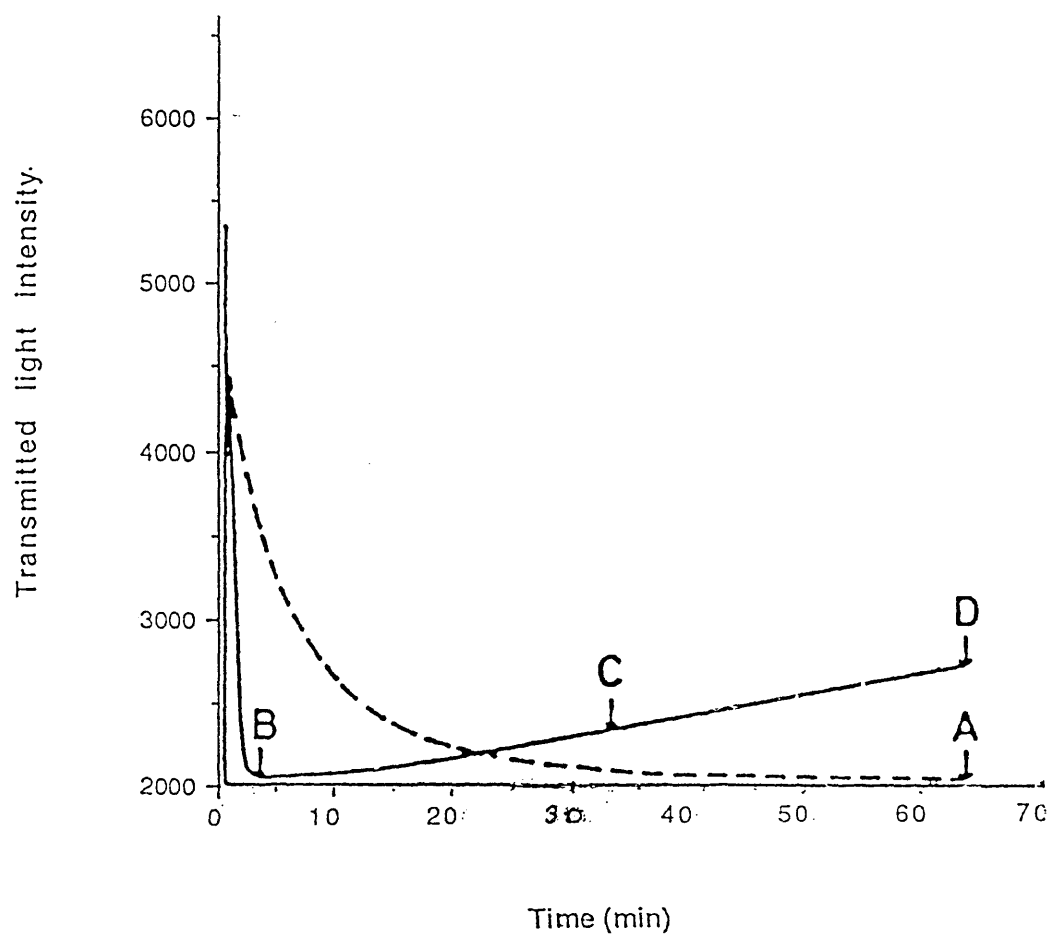


Figure 6.19

Transmitted light intensity as a function of time under pressure

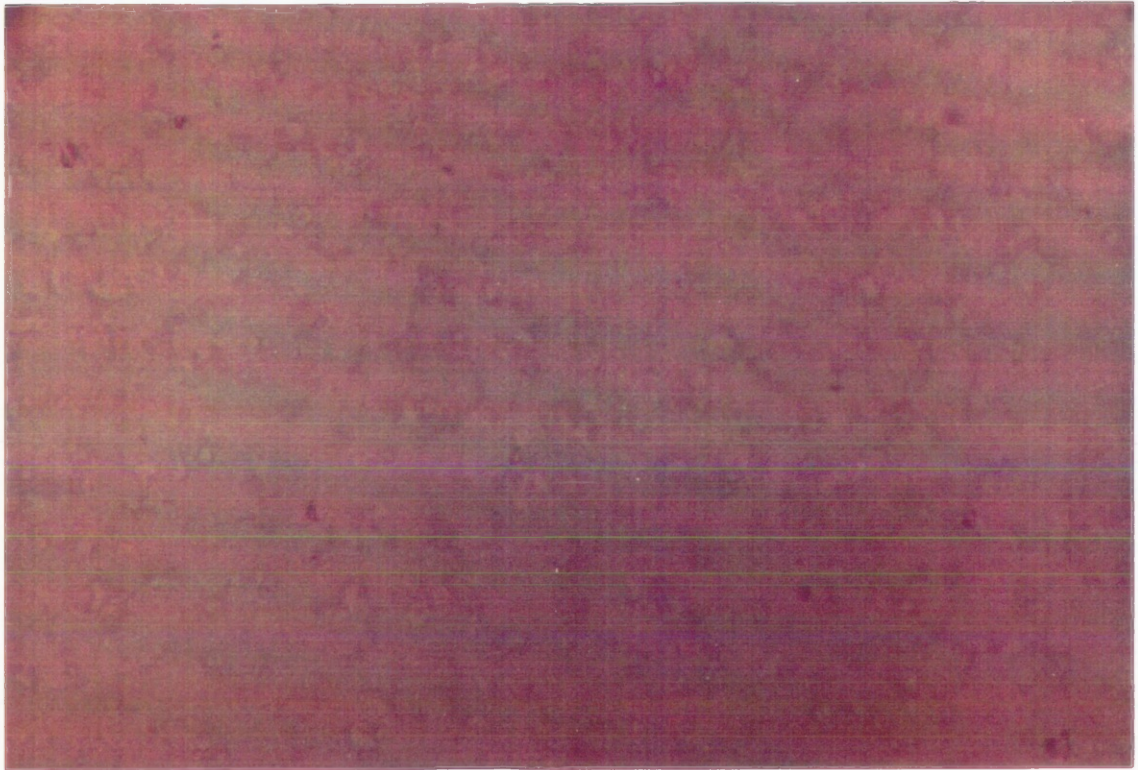


Figure 6.20A

Optical micrographs of a 30% PS blend



Figure 6.20B

Optical micrographs of a 30% PS blend

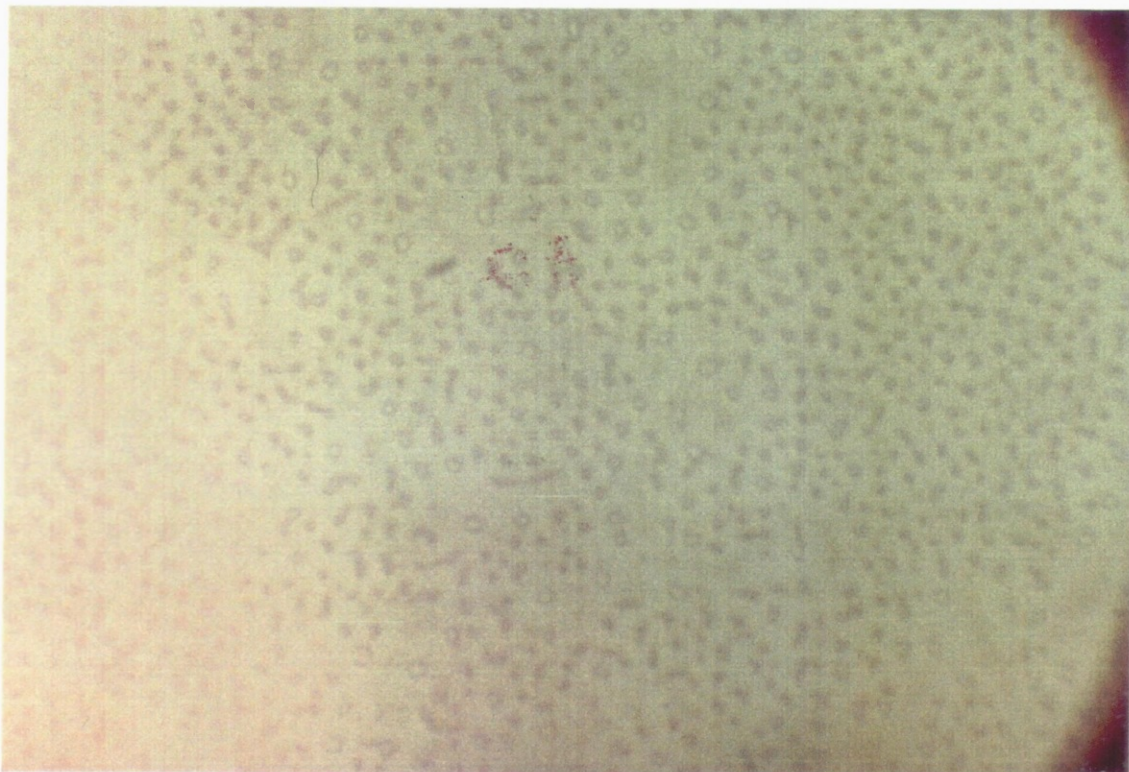


Figure 6.20C

Optical micrographs of a 30% PS blend



Figure 6.20D

Optical micrographs of a 30% PS blend

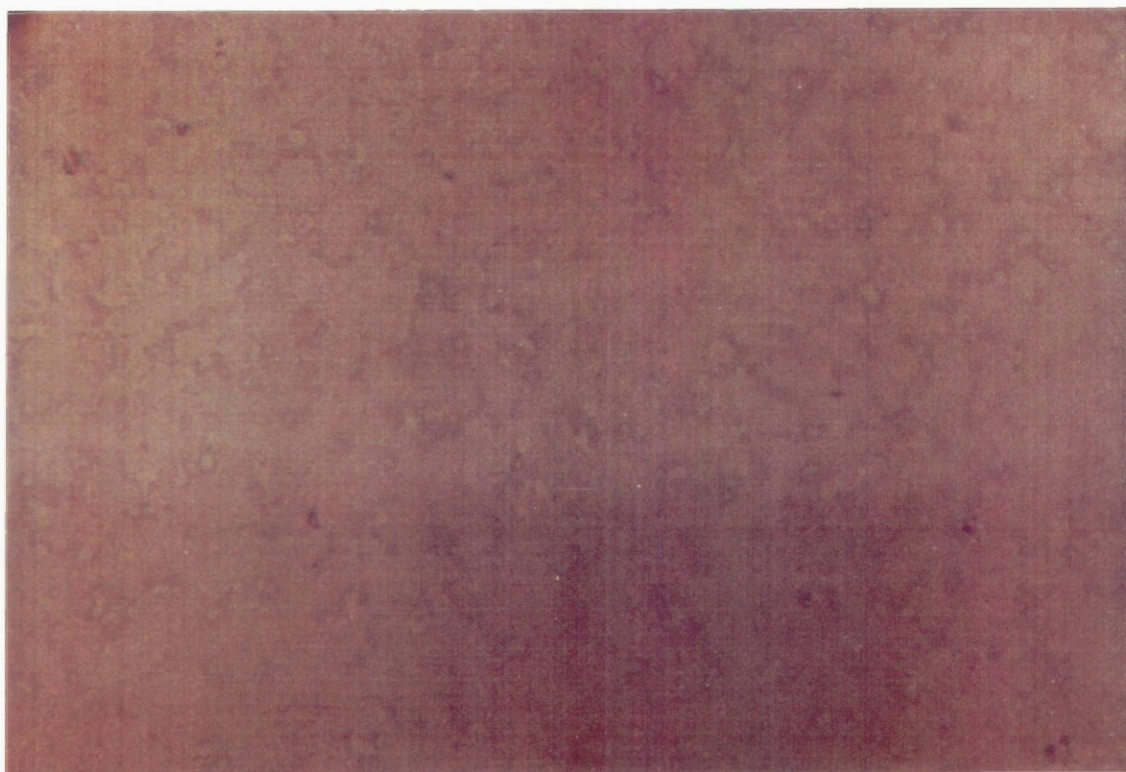


Figure 6.20A

Optical micrographs of a 30% PS blend



Figure 6.20B

Optical micrographs of a 30% PS blend

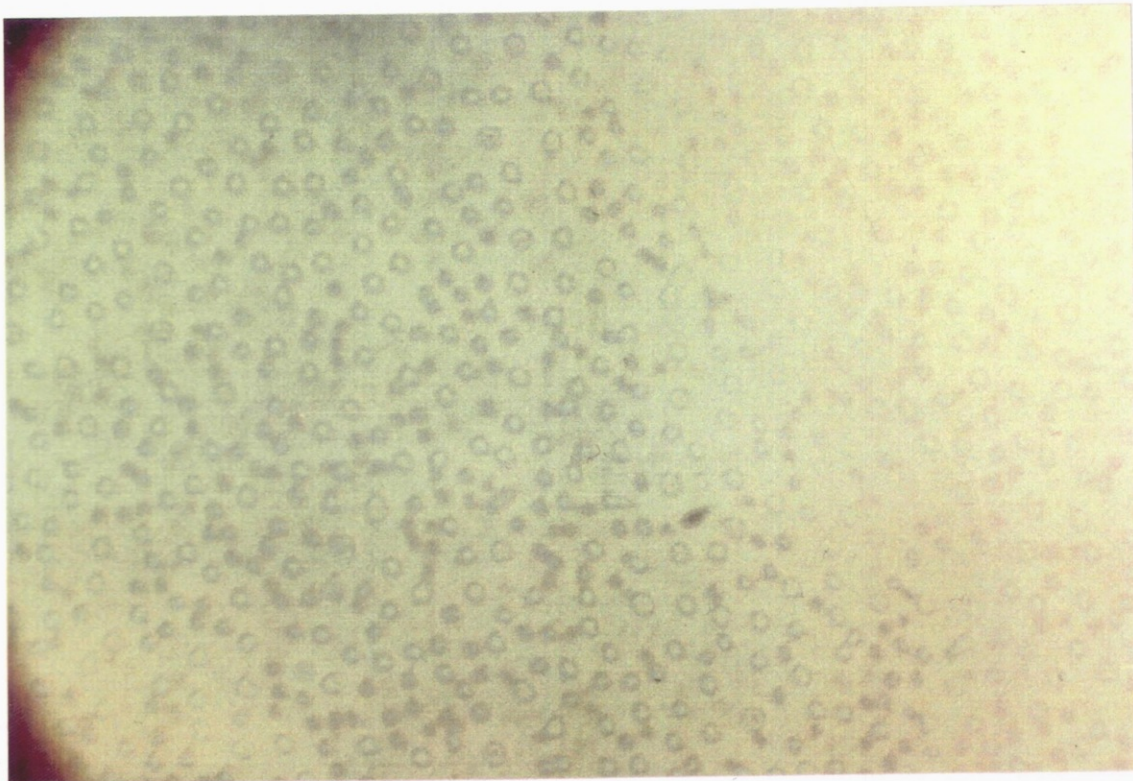


Figure 6.21 C

Optical micrographs of a 50% PS blend

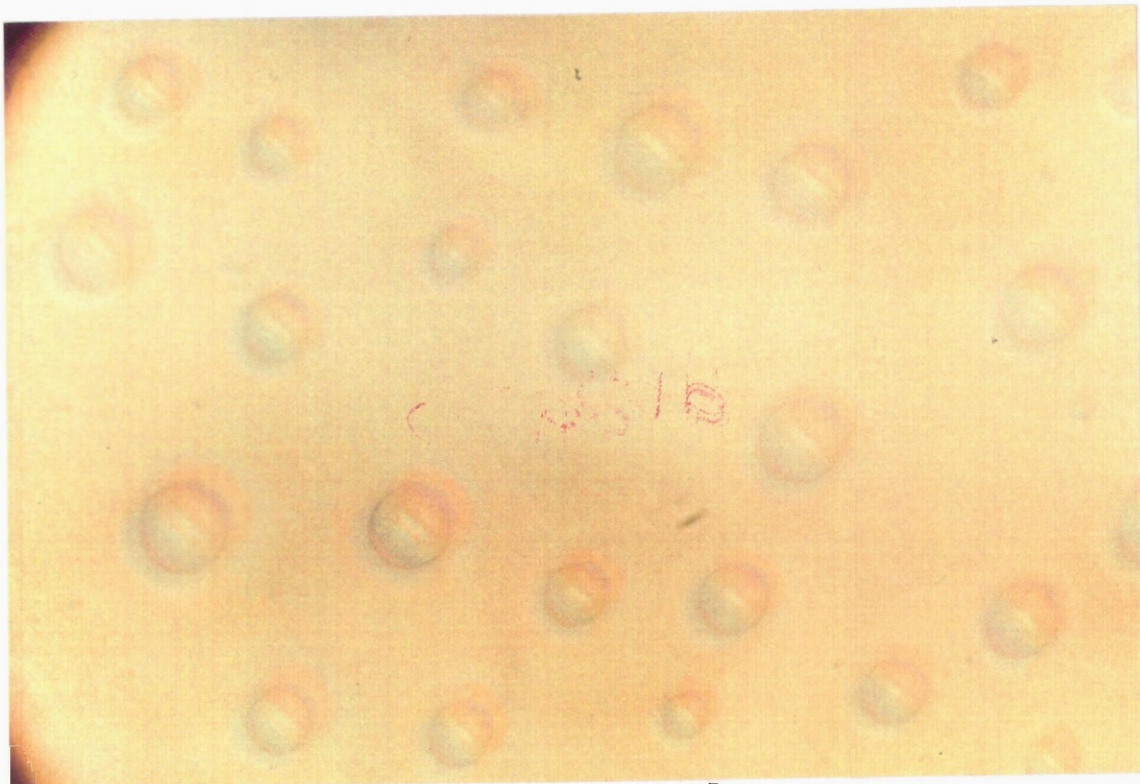


Figure 6.21 D

Optical micrographs of a 50% PS blend

CHAPTER 7

SIMULATION OF PHASE DIAGRAMS

7.1 General

The statistical – thermodynamic theory of solutions developed by Flory and his coworkers (1964, 1965) has been applied to a number of binary mixtures including low molecular weight solutions, Abe and Flory (1965), Flory (1968), Orwoll and Flory (1967); polymer – solvent systems, Eichinger and Flory (1968), Flory *et al* (1968) and polymer – polymer systems, McMaster (1973), Olabisi (1975), ten Brinke *et al* (1981).

In order to use this theory to simulate the phase diagram of a high molecular weight polymer blend, the chemical potential of either component of the blend must be calculated at the spinodal condition. The chemical potential of component 1 in a polymer blend is given by:

$$\begin{aligned} \frac{\Delta\mu_1}{RT} = & \ln\phi_1 + \left[1 - \frac{r_1}{r_2}\right]\phi_2 + P_1^*V_1^*/RT\{3\tilde{T}_1\ln(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_1^{1/3} - 1) \\ & + 1/\tilde{v}_1 - 1/\tilde{v} + \tilde{P}_1(\tilde{v} - \tilde{v}_1)\} + V_1^*X_{12}\theta_2^2/RT\tilde{v} - V_1^*Q_{12}\theta_2^2/R \end{aligned} \quad (7.1)$$

Applying the spinodal condition,

$$\begin{aligned} \left[\frac{\partial}{\partial\phi_1}\right]\left[\frac{\Delta\mu_1}{RT}\right] &= \left[\frac{\partial}{\partial\phi_2}\right]\left[\frac{\Delta\mu_1}{RT}\right] = 0 \\ &= -\frac{1}{\phi_1} + \left[1 - \frac{r_1}{r_2}\right] + \frac{P_1^*V_1^*}{RT_1^*}\left[\frac{-D}{(\tilde{v} - \tilde{v}^{2/3})}\right] + \frac{P_1^*V_1^*D}{RT\tilde{v}^2} + \frac{PV_1^*D}{RT} \end{aligned}$$

$$+ \frac{V_1^* X_{12} 2 \theta_2^2 \theta_1}{RT v \phi_1 \phi_2} - \frac{V_1^* X_{12} D \theta_2^2}{RT v^2} - \frac{V_1^* Q_{12} 2 \theta_2^2 \theta_1}{R \phi_1 \phi_2} \quad (7.2)$$

which for computational convenience can be expressed in the form:

$$0 = \left[-\frac{1}{\phi_1} + \left[1 - \frac{r_1}{r_2} \right] \right] \frac{R}{V_1^*} + \frac{P_1^*}{T_1^*} \left[\frac{-D}{\left(\frac{v}{v^*} - \frac{v}{v^*} \right)^2 / 3} \right] + \frac{D}{T} \left[\frac{P_1^*}{v^2} + P \right] \\ + \frac{2X_{12} \theta_2^2 \theta_1}{T v \phi_1 \phi_2} - \frac{X_{12} D \theta_2^2}{T v^2} - \frac{2Q_{12} \theta_2^2 \theta_1}{\phi_1 \phi_2} \quad (7.3)$$

where D , $\frac{\partial \tilde{v}}{\partial \phi_2}$, $\frac{\partial \bar{P}}{\partial \phi_2}$ and $\frac{\partial \tilde{T}}{\partial \phi_2}$ are as previously defined in Equations (2.52) to (2.55) respectively. To solve this equation, the following state parameters of the pure components must be known:

- the specific volume, v_{sp}
- the thermal expansion coefficient, $\alpha = \frac{1}{V} \left[\frac{\partial V}{\partial T} \right]_P$
- the thermal pressure coefficient, $\gamma = \left[\frac{\partial P}{\partial T} \right]_V$
- the interaction terms, X_{12} , Q_{12}
- the surface per unit of core volume ratio, $s = \frac{s_2}{s_1}$
- the ratio of the component chain length, $\frac{r_2}{r_1}$

7.2 Evaluation of equation of state parameters, v_{sp} , α , γ

For polymers, results of the required accuracy are seldom available. In the case of PS, for example, determination of these quantities is complicated by the fact that the polymer is a glass at ordinary temperature whereas v_{sp} , α and γ for the liquid, as opposed to the glass, are required for evaluation of the parameters specified for the theory. Hence it is necessary to resort to

extrapolation by one or other of two alternative procedures: measurements conducted on liquid PS above its T_g (100°C) may be extrapolated to the temperature range of experimentation on solutions, or the properties of concentrated solutions of PS in a low molecular weight diluent may be extrapolated as a function of concentration. In the latter procedure a sufficient amount of diluent is maintained for depression of the T_g below ordinary temperatures. The former method was used by Hocker *et al* (1971) for the determination of the specific volume and the thermal expansion coefficient of liquid PS at equilibrium. The latter method was used by them for the determination of the thermal pressure coefficient of the liquid polymer. Contrary to previous indications, Spencer (1944), Spencer and Dillon (1949), Krimm *et al* (1951), Fox and Flory (1950, 1954) Holt and Edwards (1965), Hocker (1971), found that $\partial\alpha/\partial T$ changed by approximately 0.2×10^{-6} in the vicinity of 170°C. Below this temperature the experimental values of α for PS were found independent of temperature.

The dependence of γ on composition is very small; throughout the range from 20° – 100°C the error is estimated to be $\pm 2\%$.

At the temperature, T , where the expansion coefficients α and the thermal pressure coefficient γ of the component polymers are known and at atmospheric pressure, ($\bar{P} = 0$), the component parameters can be calculated from

$$\bar{v}_i^{1/3} = 1 + \alpha_i T / (3 + 3\alpha_i T) \quad (7.4)$$

$$P_i^* = \gamma_i T \bar{v}_i^2 \quad (7.5)$$

$$\bar{T}_i = (\bar{v}_i^{1/3} - 1) / \bar{v}_i^{4/3} \quad (7.6)$$

and hence T_i^* , the hard core temperature from

$$T_i^* = T/\tilde{T}_i \quad (7.7)$$

The pressure P^* and temperature T^* of the mixture can be calculated from

$$P^* = P_1^*\phi_1 + P_2^*\phi^2 - \phi_1\theta_2X_{12} \quad (7.8)$$

$$T^* = P^*/(\phi_1P_1^*/T_1^* + \phi_2P_2^*/T_2^*) \quad (7.9)$$

$\tilde{v}$ can then be found iteratively by using the equation of state,

$$\tilde{v}^{1/3} = 1/\{(1 - \tilde{T}\tilde{v})/(\tilde{P}\tilde{v}^2 + 1)\} \quad (7.10)$$

which at atmospheric pressure ($\tilde{P} = 0$) becomes

$$\tilde{v}^{1/3} = 1/(1 - \tilde{T}\tilde{v}) \quad (7.11)$$

Since phase diagrams extend over a range of temperatures, the temperature dependence of these parameters are important. Theoretical $\partial\alpha/\partial T$ and $\partial\gamma/\partial T$ can be obtained from the equation of state theory, Orwoll and Flory (1967):

$$(\partial\alpha/\partial T)_{\tilde{P}=0} = (7 + 4\alpha T)\alpha^2/3 \quad (7.12)$$

$$(\partial\gamma/\partial T)_{\tilde{P}=0} = -\left[\frac{\gamma}{T}\right]\left[1 + \alpha T\right] \quad (7.13)$$

Theoretical values of $\partial\alpha/\partial T$ for PS at 0°C yields $8.3 \times 10^{-7} \text{ deg}^{-2}$ whereas the experimental value is $0.75 \times 10^{-7} \text{ deg}^{-2}$. This disparity of the theory is manifested in changes of the characteristic parameters V^* , T^* and P^* with temperature. For this reason it is more reliable to extrapolate the values obtained from experimental data instead of theoretical calculation using Equation (7.12).

For PS at 0°C, the experimental value ($-8.6 \times 10^{-3} \text{ deg}^{-2}$) for the variation of γ with temperature is in good agreement with the theoretical value ($-7.5 \times 10^{-3} \text{ J cm}^{-3} \text{ deg}^{-2}$) obtained using Equation (7.13).

The equation of state data and characteristic parameters at 50°C for PS, Hocker *et al* (1971) and for PVME, Shiomi *et al* (1985) are presented in Table (7.1). v_{sp} , α and γ are experimental values obtained by these workers and extrapolated to 50°C.

The rest of the parameters in Table (7.1) are evaluated by the use of Equations (7.8) to (7.11). The hard-core volumes v_i^* and v^* of the components and the mixture respectively are assumed equal ($v_1^* = v_2^* = v^*$).

7.3 Determination of X_{12} , Q_{12}

X_{12} is determined from the relationship given by Equation (2.46). In the above equation the value of ΔH_m is that measured for the critical composition (30% PS).

The value of X_{12} thus obtained is -14.8 . The negative value of the interaction parameter predicts miscibility of the two components.

The non-combinatorial entropy parameter, Q_{12} , is used as an adjustable parameter to fit the minimum of the spinodal to the minimum of the experimental cloud point curve.

TABLE 7.1
Equation-of-state parameters for PS and PVME at 50°C

POLYMER	v_{sp} $\text{cm}^3 \text{ g}^{-1}$	$\alpha \times 10^4$ deg^{-1}	γ $\text{J cm}^{-3} \text{ deg}^{-1}$	$\tilde{v}$	T^*	P^*	v^*
PS	0.9471	5.74	1.212	1.1647	7592	532	0.8132
PVME	0.8085	6.911	1.120	1.1939	6741	516	0.6772

7.4 Determination of the segmental surface area and chain length ratios

The ratio of the segmental surface area s_2/s_1 , (s_{21}), is an important parameter in the solution of the spinodal equation because it influences both the magnitude of the interaction energy and the concentration dependence of the interaction parameter. It is related to the site fractions, θ_1 , θ_2 , which govern the number of 1,2 contact in mixtures by:

$$\theta_2 = \phi_2 s_{21} / (\phi_1 + \phi_2 s_{21})$$

Two methods have been reported in the literature for the determination of the surface area of a molecule.

Bondi (1964) devised a group contribution technique whereby the total surface area of a molecule is taken to be the sum of those of the constituent atoms. The surface area of a monomer unit is obtained in a similar manner in the case of polymers. This method can be applied to evaluate the surface area of a large number of molecules.

The second method (Eichinger and Flory (1968)) is based on the information about the geometry of molecules obtained from either crystallographic data or molecular models. In calculating the surface area polymeric molecules are treated as cylinders and small molecules as spheres with the appropriate core volumes. Usually reliable information about molecular geometry is difficult to obtain for polymers.

Neither method of evaluating the surface area provides a satisfactory result for polymers. While the former method overestimates the surface area the latter underestimates it. However, the errors in the surface area of the two polymers could be partially cancelled in the ratio. Arbitrary adjustments of s_2/s_1 have been made by authors to permit agreements between calculated and experimental results, Eichinger and Flory (1968).

In the simulation, the segmental surface area ratio is initially set at 1. The chain length is the ratio of the molecular weight of the polymer to that of the monomeric unit. The chain lengths for PS (r_1) and PVME (r_2) are respectively 1058 and 1707, giving a ratio r_2/r_1 of 1.6.

7.5 Simulated Spinodals

McMaster (1973) applied Flory's equation of state theory to simulate the spinodal curves of hypothetical polymer blends. By varying the values of the equation-of-state parameters for the pure components and the binary parameters of the mixtures, he observed that:

- the theory is capable of predicting both LCST and UCST behaviour individually or simultaneously.
- the shape and position of these phase boundaries depend on the above-stated parameters.

Olabisi (1975) applied McMaster's treatment to a real system of poly(caprolactone) and poly(vinyl chloride). His simulation shows that for a constant negative value of X_{12} , the spinodal curve tends to show a bimodality with an increase in $\frac{S_2}{S_1}$ ratio.

ten Brinke *et al* (1981) attributed the occurrence of the asymmetric phase boundary to the condition:

$$Q_{12} = 0.0, \quad X_{12} < 0, \quad \frac{S_1}{S_2} < 1, \quad \frac{r_1}{r_2} < 1 \text{ and } c_{12} > 0$$

where c is the number of external degrees of freedom per molecule.

In the present work, the spinodal equation has been calculated; although the effect of pressure is considered, those of polydispersity and the c_{12} factor are neglected.

The spinodal curve is first simulated at atmospheric pressure using the parameters earlier defined for this system and the procedure as outlined in Section (7.4). This is shown in Fig. (7.1).

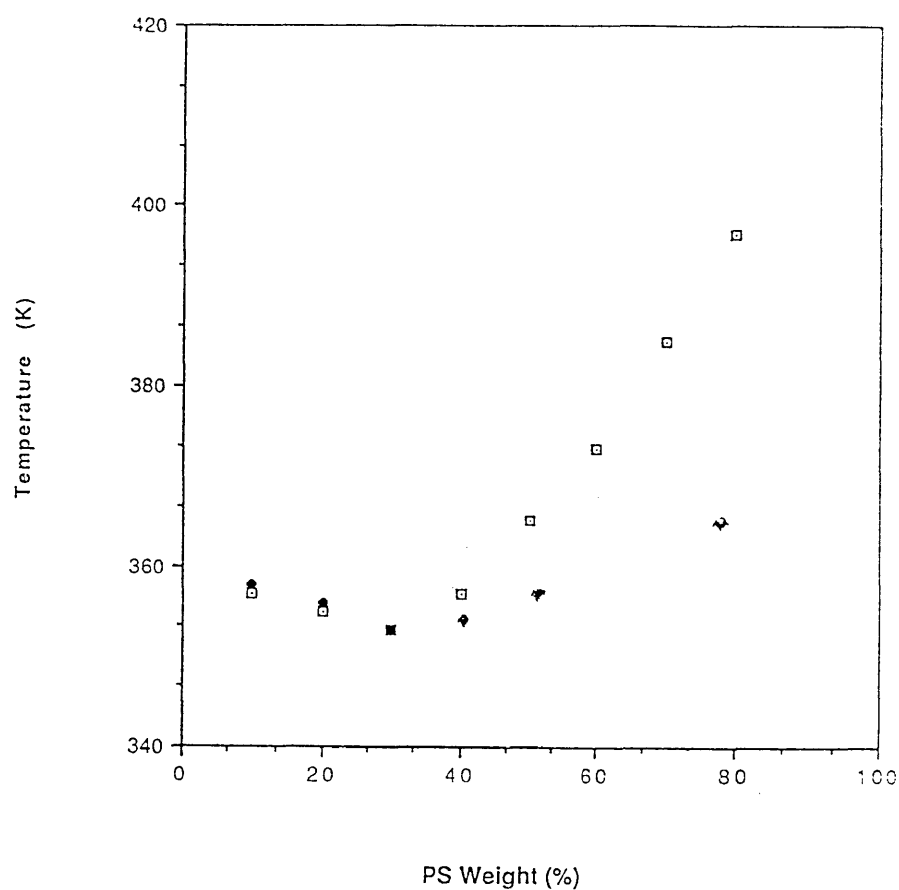


Figure 7.1

Calculated spinodal

□ [1] Experimental

◆ [2] Calculated

$$X_{12} = -14.8; Q_{12} = -0.032$$

Fig. (7.1) shows that the calculated spinodal is a poor fit to the shape of the experimental curve. No allowance was made in the theory for the concentration dependence of X_{12} and Q_{12} but Chai (1982) found that the shape of the calculated spinodal could be greatly improved by the inclusion of an arbitrary concentration dependence of the entropic contribution. The above Figure also shows that with the value of X_{12} obtained from the heat of mixing studies and with the value of Q_{12} necessary to match the spinodal to the

minimum of the cloud point, the calculated spinodal is 'flatter' than the experimental curve. This discrepancy could be caused by the temperature and pressure dependence of X_{12} and Q_{12} , both of which have been neglected in the present treatment. Coleman and Zarian (1979) have shown from FTIR studies that X_{12} is temperature dependent.

A number of curves are further simulated under the various conditions which are shown in the figure caption, in order to estimate the effect on the spinodal curve of the binary parameters of the mixtures.

7.5.1 Effect of the non-combinatorial entropy parameter, Q_{12}

In order to ascertain the effect of Q_{12} , a value of the interactional parameter, X_{12} , is first selected. Q_{12} is then used as an adjustable parameter to fit the minimum of the spinodal to the minimum of the experimental cloud point curve. The full spinodal curve is then calculated. Generally it is found that a favourable (negative) X_{12} has to be balanced by an unfavourable (negative) Q_{12} in order to be consistent with the experimental data, as shown in Fig. (7.2).

The shape of the curve for $Q_{12} = 0.0$ is similar to that of Olabisi (1975) and ten Brinke *et al* (1981) and occurs at a very high temperature range. The negative value of Q_{12} reduces the interaction term which in turn reduces the miscibility gap. This is in agreement with the conclusion reached by McMaster (1973) that a negative Q_{12} decreases the miscibility by reducing the contact energy. The spinodal equation is very sensitive to the value of Q_{12} , as shown in the above figure.

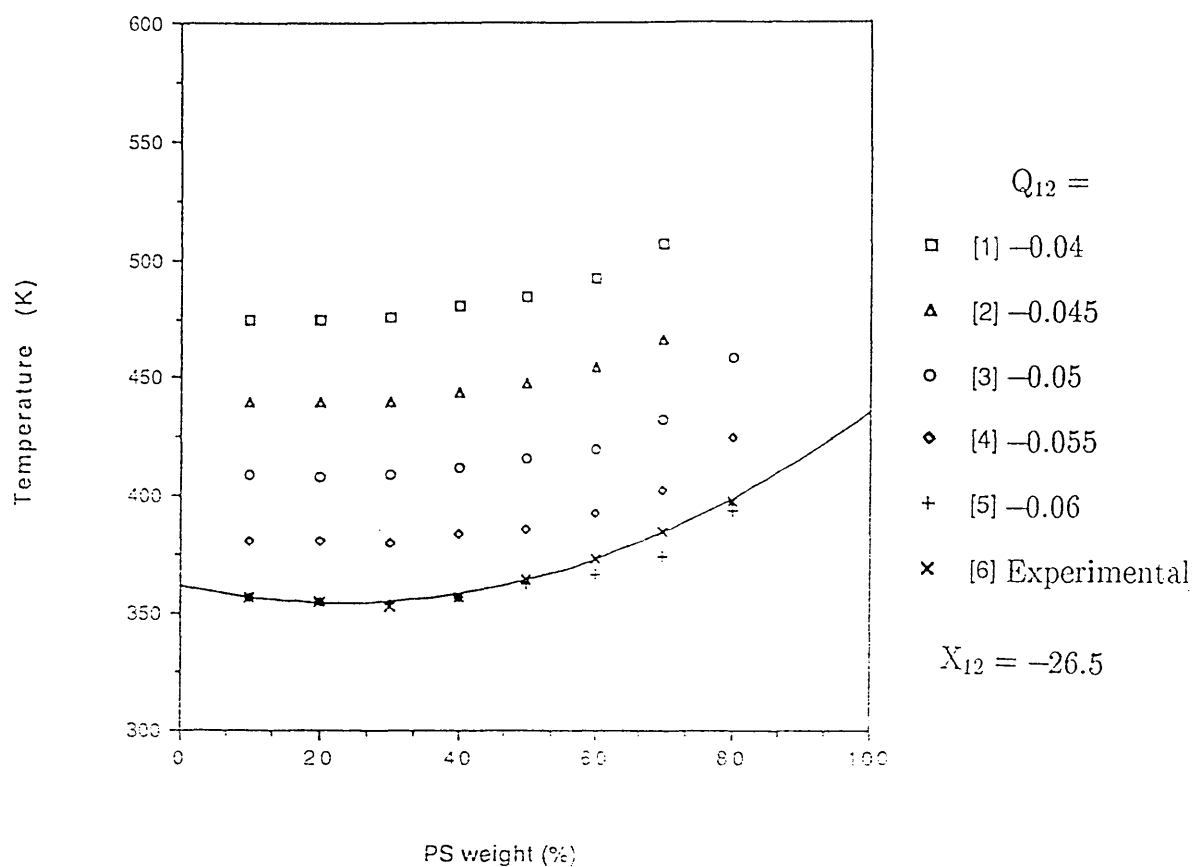


Figure 7.2

Effect of Q_{12}

7.5.2 The Effect of X_{12}

While Q_{12} is kept constant, the interaction energy parameter, X_{12} , is varied as shown by the caption in Fig. (7.3). It is seen that the spinodal curve is very sensitive to the value of X_{12} . As X_{12} is made more negative, the curve is raised and miscibility is improved. A more positive X_{12} is unfavourable to mixing and so the curve is lowered. This behaviour is in agreement with

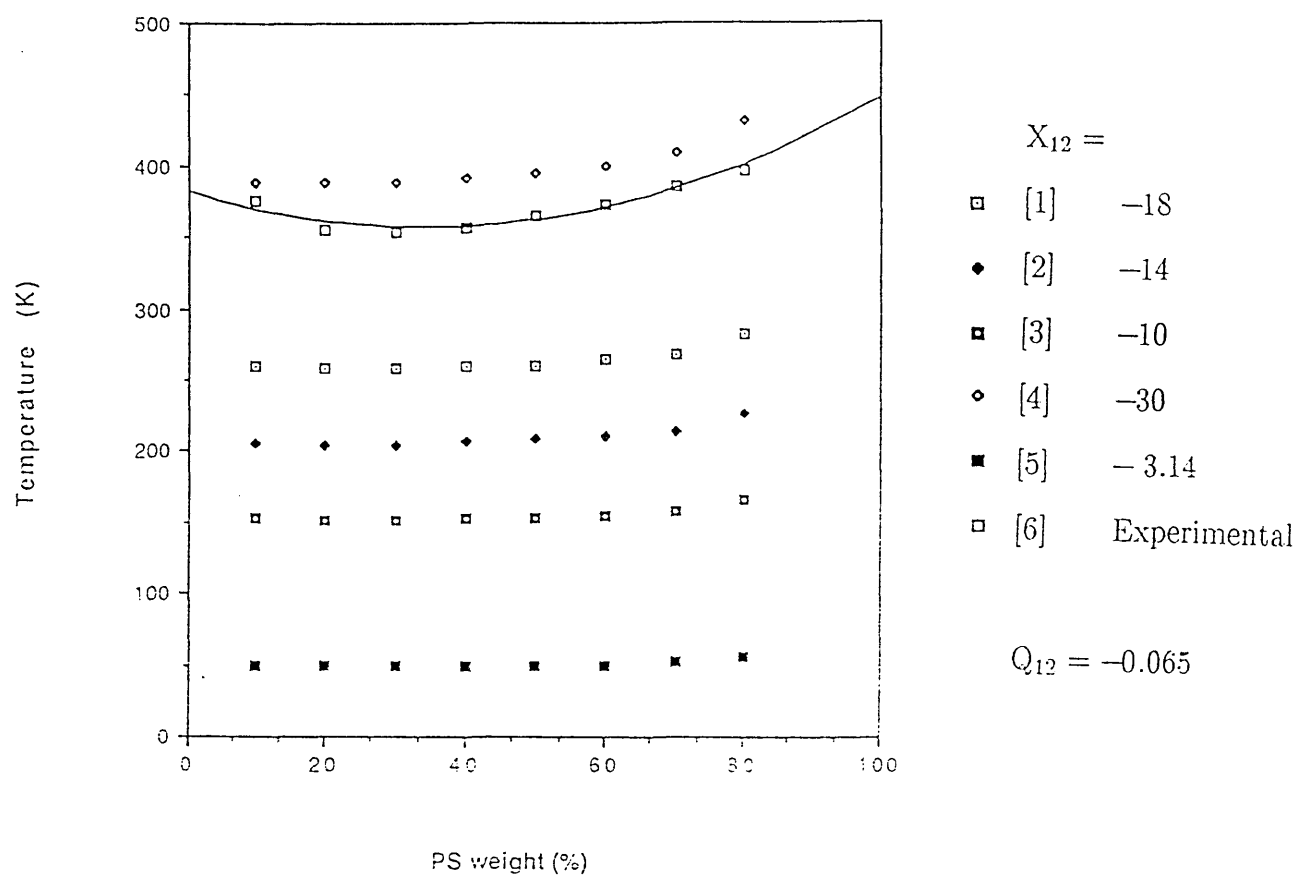


Figure 7.3
Effect of X_{12} on the position of the spinodal curve

McMaster's observation. Fig. (7.4) shows that the larger the negative values of X_{12} the flatter is the spinodal curve. McMaster (1973) also found a similar effect of X_{12} on the spinodal curve.

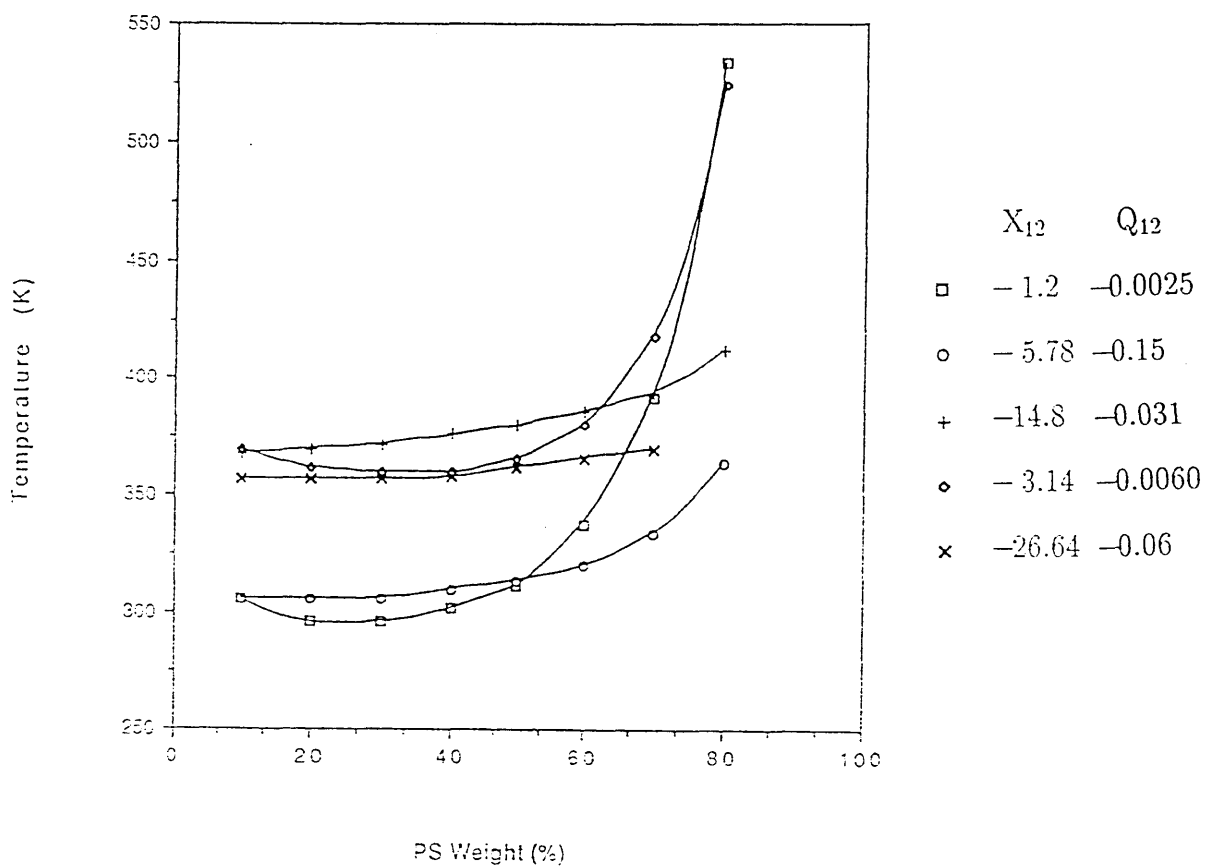
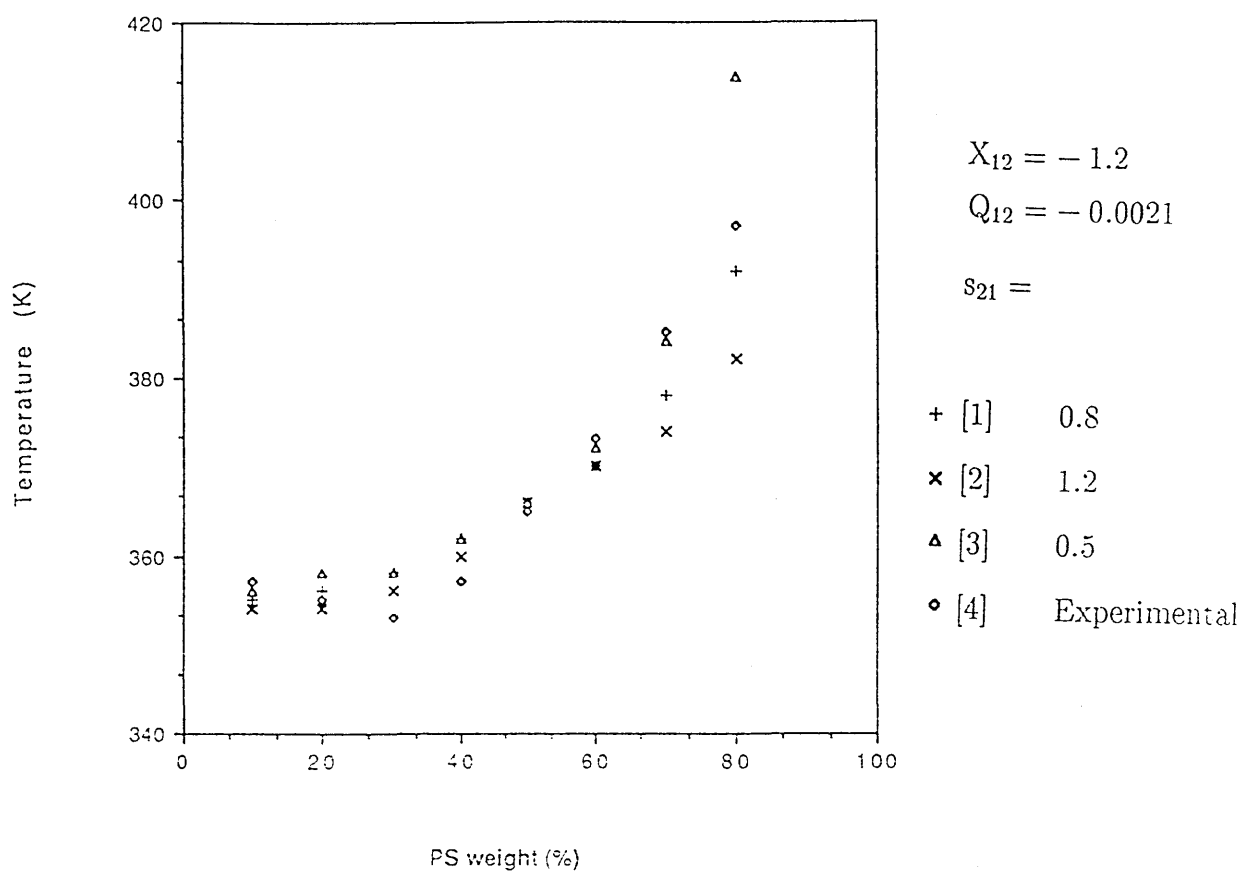


Figure 7.4

Effect of X_{12} on the shape of the spinodal curve

7.5.3 The Effect of $\frac{s_2}{s_1}$ and $\frac{r_2}{r_1}$

Small variations of $\frac{s_2}{s_1}$ and $\frac{r_2}{r_1}$ ratios have no significant effect on the magnitude of the spinodal curves as shown by Figs. (7.5) to (7.6).



7.6 The Effect of Pressure

Flory's equation of state theory abandons a fixed lattice and so it is capable of predicting volume changes on mixing and hence the effects of pressure on the phase diagram.

Fig. (7.7) shows the simulated spinodal at the various indicated pressures. The spinodal temperature (T_{sp}) at the critical composition shows a shift of up to 24°C for elevated pressure up to 1200 atm.

7.6.1 Volume changes on mixing

Table (7.2) gives the values for $\left[\frac{\partial T}{\partial P}\right]_c$ based on the theoretical calculation and on the experimental results. It also gives the value of ΔH_m , the heat of mixing of the oligomers at the critical composition. By the use of these values and Equation (3.1), the fractional volume change on mixing, ΔV_m can be calculated:

$$\Delta V_m = \Delta H_m \left[\frac{\partial T}{\partial P}\right]_c / T \quad (7.18)$$

These values, based on both theoretical and experimental values of $(\partial T / \partial P)_c$, are also presented.

If the value of $\tilde{v}$, the reduced volume of the mixture, is calculated by the method outlined previously in Section 7.2, a value of ΔV_m can also be calculated from the relationship given in Appendix (A.50):

$$\Delta V_m = \tilde{v} / (\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2) - 1 \quad (7.19)$$

The value of ΔV_m thus derived is presented in Table (7.2).

Also shown in the Table are values of ΔV_m for blends of PES/PEO (10 : 90) and EVA 45/CPE3 (50 : 50) for which favourable heats of mixing were measured for their low molecular weight analogues at the same compositions, Walsh and Rostami (1985).

The excess volume of mixing obtained from Equation (7.19) at 50°C is larger in comparison with the value from Equation (7.18), obtained by measuring $(\partial T / \partial P)_c$. The former value is based on the assumption of Eichinger and Flory (1968) that the volume should be less dependent on the entropy than

Table 7.2

Volume changes on mixing for a 30% PS blend by various methods as described in the text

$(\partial T/\partial P)_C$, K atm ⁻¹			$10^4 \Delta V_m$ cm ³ /g at 323 K (50°C)		$10^4 \Delta V_m$ cm ³ /g at 308 K (35°C)	
Theoretical	Experimental	ΔH_m , J gm ⁻¹	Theoretical (Eqn. 7.18)	Experimental (Eqn. 7.18)	Theoretical (Eqn. 7.19)	Experimental from density measurements
0.020	0.023	- 3.44	- 21.3	- 24.5	- 67.5	- 68.3 - 170.0 at 23°C, Kwei et al (1974) - 100.0 at 25°C, Yang et al (1986)
0.022	0.020	- 1.3	- 7.8	- 7.1	- 7.2	EVA45/CPE3 (50 : 50)
0.044	0.046	- 4.0	- 48	- 50	- 48	PES/PEO (10 : 90)

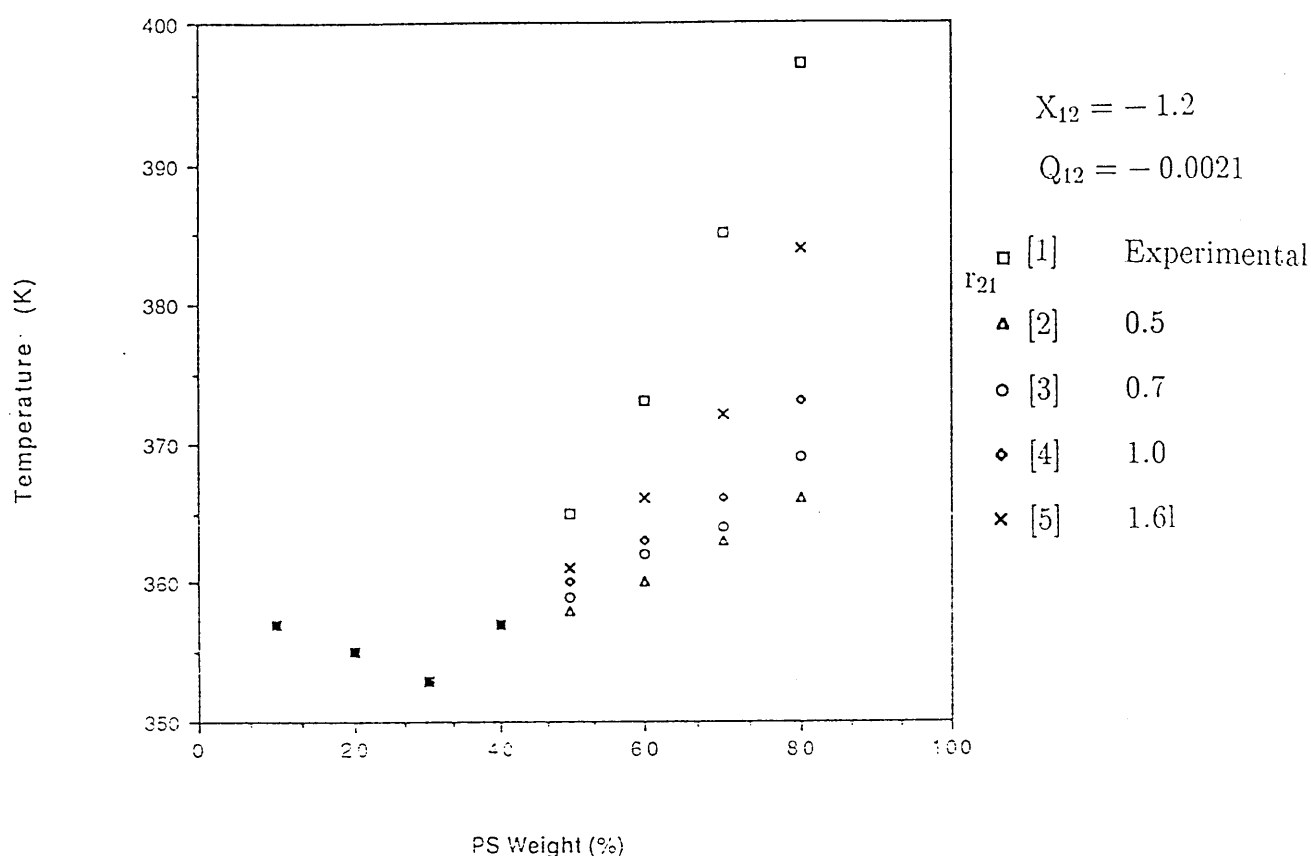


Figure 7.6

Effect of r_{21}

on the energy. After entropy correction by the use of Equation (A.50), Equation (7.19) predicts a lower excess volume change on mixing. Such an entropy correction reduced the value of ΔV_m for a blend of EVA 45–CPE 3 (50 : 50) at 83.5°C from -13.8×10^{-4} to -10×10^{-4} , Rostami (1983).

Finally it should be pointed out that the large favourable heat of mixing for this blend is due to specific interactions between the polymers. Although the equation-of-state theory was not originally designed to cope with such

systems, the theory however describes the general behaviour of this blend fairly satisfactorily.

Table (7.2) also gives the value of ΔV_m for the critical composition, as obtained from density measurements at 35°C, Kwei *et al* (1974); at 25°C, Yang *et al* (1986) and at 35°C (present studies), using Equation (6.6).

These values obtained at lower temperatures are larger than the value at 50°C. This observation is in accord with the theoretical predictions of the free volume theories (Chapter 2) for an LCST behaviour. The mixing process occurs with a negative volume change which results in a negative contribution to ΔH_m and ΔS_m . An increase in temperature reduces the value of this negative volume change.

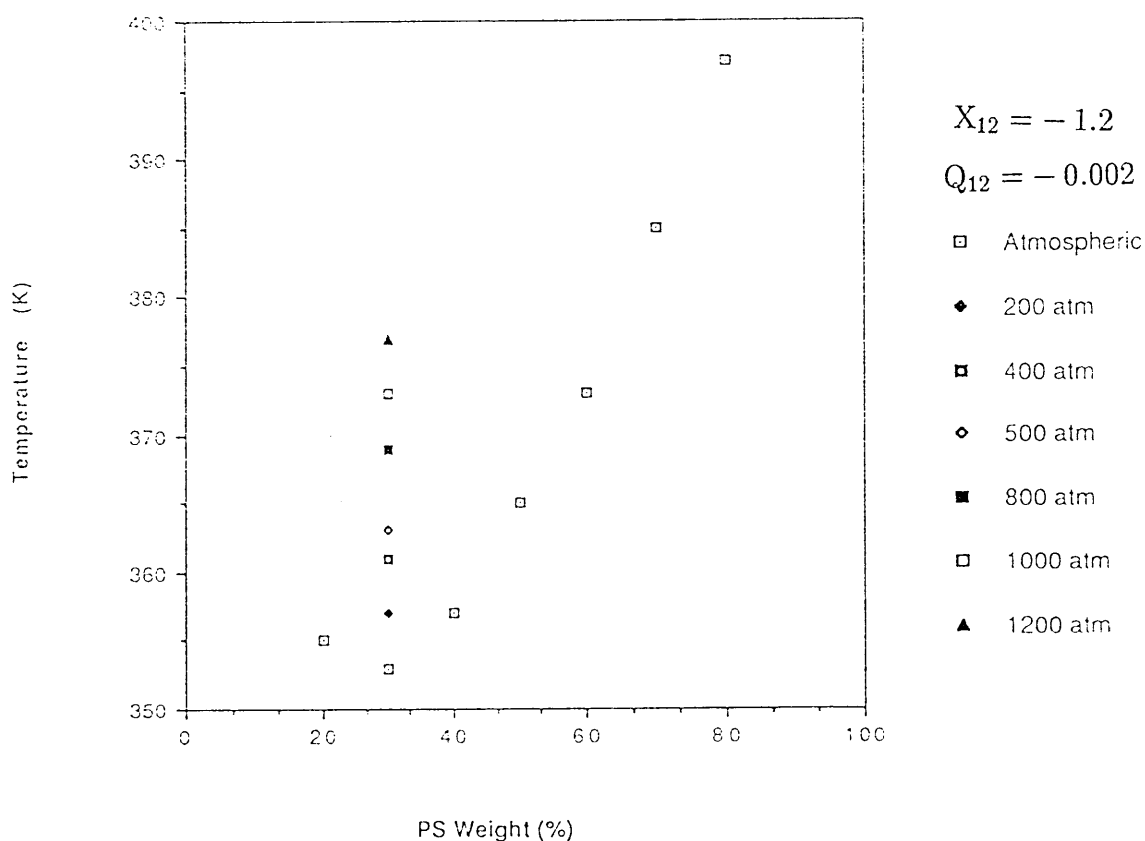


Figure 7.7
Effect of pressure

CONCLUDING REMARKS

This project has involved building and commissioning part of a pressure rig in order to observe the effects of pressure on the miscibility limits of high molecular weight polymer blends. Other analytical measurements have also been undertaken in order to be able to interpret the pressure data using modern thermodynamic theories. For this latter work computer programs have been written for simulation of the miscibility — temperature — pressure — concentration diagrams. A few problems were encountered during the experimental investigation and these are briefly mentioned prior to the conclusions.

8.1 Problems related to the high pressure rig

The high pressure rig described in Chapter 4 operates efficiently within the range of $1 < P_{\text{appl}} < 1500 \text{ atm}$ and $18^\circ < T^\circ\text{C} < 200^\circ\text{C}$ — the limits set by PS–PVME system. The accuracy of the equipment is $\pm 0.5^\circ\text{C}$.

Sample loading for high pressure experiments is both tedious and time-consuming. A modification of the sample loading procedure should make the loading and the removal of sample both easier and faster. In the present investigation, morphological studies on quenched samples were limited because of the difficulty of sample removal.

Experiments on the pressure rig take several hours but only one sample can be studied at a time. Provision for multiple sample loading, for instance by the enlargement of the diameter of the sapphire windows should result in faster

experiments. This latter modification might also make it possible to incorporate a camera-loaded optical microscope so that optical micrographs of the sample could be taken during an experiment. Alternatively, the sample holder could be modified for the loading of smaller samples.

The pressure of the system increases with temperature, therefore for isobaric experiments the pressure is manually adjusted as the temperature rises. Automation of the pressure-release operation would greatly ease the tedium of the manual operation.

8.2 Problems related to sample preparation

PVME absorbs moisture readily and this leads to cloudiness in the blends(films), even at room temperature. This cloudiness may be mistaken for phase separation. Several samples were discarded at the earlier part of the work due to this effect. This can be prevented by thoroughly drying the polymers and all glassware and by ensuring that evaporation of the solvent takes place in a dry environment.

8.3 Conclusions

The effect of pressure on the cloud point curves of blends of hydrogenous PS–PVME and perdeuterated PS–PVME have been investigated.

The polymers were miscible over the molecular weight range studied. A single glass transition temperature obtained for the miscible blend was used as a criterion for miscibility. Both systems showed an LCST behaviour over the molecular weight range reported.

The cloud point curve was lowered with a decrease in the molecular weight of PVME due to an unfavourable contribution by the higher number of PVME chain-ends to the thermodynamic excess functions of mixing.

The effect of increasing the molecular weight of PS was to lower the phase boundary due to an entropic destabilisation of the blend.

A combination of optical and electron microscopy have provided information about the morphological behaviour of the blends as a function of temperature.

Negative interaction parameters between the oligomeric mixtures have been deduced by microcalorimetry.

SANS measurements also gave negative interaction parameters for high molecular weight perdeuterated PS–PVME blends. The contractions of the blends have been quantified by density measurements and by the effect of pressure on the cloud points. Pressure also increased the miscibility gap – a characteristic feature of LCST behaviour with negative interaction terms.

The substitution of perdeuterated PS for hydrogenous PS in PS–PVME blends raised the LCST of the blend and changed the excess volume. The pressure dependence of the cloud point $\left[\frac{\partial T_c}{\partial P}\right]$ at the critical composition was found to be $+ 0.023 \text{ } ^\circ\text{C/atm}$ ($\pm 0.005^\circ\text{C}$) for the hydrogenous system and $+ 0.038^\circ\text{C/atm}$ for the perdeuterated system.

Flory's equation of state theory was used to simulate the thermodynamic behaviour of the blends. It was demonstrated that the theory can predict the excess quantities such as the excess volume change on mixing, the pressure effect on the cloud points and the spinodal phase boundary of the mixture when the segmental surface area ratio of the components, s_2/s_1 , and the entropy correction factor Q_{12} , were used as adjustable parameters. The factor, Q_{12} , was quantified by fitting the minimum of the spinodal to the minimum of the

experimental cloud point curve. The interaction term, X_{12} , obtained by fitting the heat of mixing data in the equation of state theory was more favourable to miscibility than that obtained from SANS. As a result of this discrepancy it was found that a favourable (negative) X_{12} had to be balanced by an unfavourable (negative) Q_{12} in order to be consistent with the experimental data.

No allowance was made in the theory for the concentration dependence of X_{12} and Q_{12} but the calculated spinodal was a poor fit to the shape of the experimental curve, which could have been improved by an inclusion of an arbitrary concentration dependence of this entropic contribution.

It was found that with the value of X_{12} obtained from the heat of mixing studies at 50°C on the oligomeric mixture and with the value of Q_{12} necessary to match the spinodal to the minimum of the cloud point, the resulting spinodal was 'flatter' than the experimental curve.

This discrepancy could be caused by the temperature and pressure dependency of X_{12} and Q_{12} . In the present treatment, both effects have been neglected although it had been shown from FTIR studies that X_{12} is temperature dependent, Coleman and Zarian (1979).

Finally, in order to accurately predict the experimental findings, it would be necessary to include an entropy correction factor within the concept of the partition function.

APPENDIX A

Flory's Equation-of-State Theory

Pure liquids

For a pure liquid, which may be polymeric, Flory obtained the free energy of mixing (ΔG_m) in terms of an appropriate partition function, Z , because

$$\Delta G_m = kT \ln Z \quad \text{A.1}$$

Thus for a pure liquid

$$Z = \Omega e^{-E_0/kT} \quad \text{A.2}$$

where Ω is Tonk's partition function for N non-interacting molecules in a volume V and

E_0 is the mean intermolecular energy of a system per molecule.

For a one-dimensional system of N -hard, non-interacting particles, arranged on a line of length L , Tonks (1936) has shown that

$$\Omega = \{(1 - l^*)_e\}^N \quad \text{A.3}$$

where l^* is the hard-core length of a particle and $l = \frac{L}{N}$

$1 - l^*$ is the free length available to each particle.

In a notation appropriate to three dimensions, Tonk's partition function is extended thus:

$$\Omega = [(\gamma^{1/3}(v^{1/3} - v^{*1/3})_e]^{(3N)} \quad \text{A.4}$$

where $\gamma = \frac{l^{*3}}{V}$ is a purely geometric factor
 $v = \frac{V}{N}$ is the volume per molecule
 V is the total volume
 v^* is the hard-core volume of the molecule.

Equation (A.4) can be transformed into an appropriate form for chain molecules by dividing a chain into r -segments. v^* becomes the hard-core volume per segment and v is the volume per segment given by

$$v = (V/rN) \quad \text{A.5}$$

For chain molecules of r -segments Equation A.4 becomes

$$\Omega = [(\gamma^{1/3}(v^{1/3} - v^{*1/3})_e]^{3Nr} \quad \text{A.6}$$

Substituting Equation (A.6) into Equation (A.2) gives

$$Z = \Omega_c = [(\gamma^{1/3}(v^{1/3} - v^{*1/3})_e]^{3Nr} e^{-E_0/kT} \quad \text{A.7}$$

where Ω_c is a combinatorial factor which connects the number of ways of mixing Nr segments with each other, as in Flory-Huggins lattice theory. Provided that

only nearest-neighbour interactions are important, the mean intermolecular energy

$$E_0 = (\text{no. of contacts})\eta/v = -(Nrs\eta/2v) \quad \text{A.8}$$

where s is the number of intermolecular contact sites per segment

$-\eta/v$ is the average interaction energy per contact and

N is the number of molecules. The partition function is therefore given by

$$Z = \Omega_c [\gamma^{1/3}(v^{1/3} - v^{*1/3})]^{3Nrc} e^{Nrs\eta/2vkT} \quad \text{A.9}$$

Equation A.8 can be expressed in terms of temperature by introducing the reduced volume, temperature and pressure

$$\tilde{v} = v/v^*, \quad \tilde{T} = T/T^*, \quad \tilde{P} = P/P^* \quad \text{A.10}$$

where the characteristic hard-core parameters, P^* , v^* and T^* satisfy the equation

$$P^*v^* = ckT^* \quad \text{A.11}$$

and

$$\tilde{T} = 2v^*ckt/s\eta \quad \text{A.12}$$

Equation (A.11) gives

$$P^* = s\eta/2v^{*2} \quad \text{A.13}$$

The partition function now becomes

$$\begin{aligned}
 Z &= \Omega_c (\gamma^{Nrc} [(\tilde{v}\tilde{v}^*)^{1/3} - \tilde{v}^{*1/3}])^{3Nrc} e^{(Nrc/\tilde{v}\tilde{T})} \\
 &= \text{constant} \times (\tilde{v}^{1/3} - 1)^{3Nrc} e^{(Nrc/\tilde{v}\tilde{T})}
 \end{aligned} \tag{A.14}$$

the constant being independent of v and T . The pure component equation of state can be derived by differentiating Equation (A.14) with respect to the pressure of the system

$$P = (kT/Nr)(\partial \ln Z / \partial v)_{T,N} \tag{A.15}$$

Substituting Equations (A.10 and A.11) and solving Equation (A.15) gives

$$P = (T/Nrc)(\partial \ln z / \partial v)_{T,N} \tag{A.16}$$

The resulting equation of state is

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - (1/\tilde{v}\tilde{T}) \tag{A.17}$$

At atmospheric pressure $\tilde{P} = 0$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{A.18}$$

This is the effective equation of state for the pure components and it is related to two easily measurable quantities, the coefficient of thermal expansion, α , and thermal pressure, γ , defined by

$$\alpha - (1/v)(\partial v/\partial T)_{P,N} = (\partial \ln v/\partial T)_{P,N} \quad A.19$$

$$\gamma = (\partial P/\partial T)_{V,N} \quad A.20$$

from which it follows:

$$\tilde{v} = (1 + \alpha T)/3(1 + \alpha T)^3 \quad A.21$$

Thus if α is known, Equation (A.21) gives $\tilde{v}$ and Equation (A.18) gives $\tilde{T}$. Differentiation of Equation (A.16) followed by substitution from Equations (A.10) and (A.18) gives

$$P^* = \gamma T \tilde{v}^2 \quad A.22$$

Evaluation of the equation-of-state parameters in this way enables the other parameters such as c and $(s\eta/2v)$, intermolecular energy per segment etc. to be obtained.

Mixtures

The theory can be adapted to binary mixtures by a set of combining rules.

- The core volumes of the pure components are additive; specification of a segment for each component remains arbitrary. Hence, it is convenient to use segments of equal size so that $v_1^* = v_2^* = v^*$. The segment here means monomer repeat unit.
- the intermolecular energy depends on the surface area of contacts between molecules and/or segments.

These assumptions give:

$$N = N_1 N_2 \quad \text{A.23}$$

$$\bar{r} = (\phi_1/r_1 + \phi_2/r_2)^{-1} \quad \text{A.24}$$

$$s = \phi_1 s_1 + \phi_2 s_2 = (r_1 N_1 s_1 + r_2 N_2 s_2)/\bar{r}N \quad \text{A.25}$$

$$\bar{c} = \phi_1/c_1 + \phi_2/c_2 = (r_1 N_1 c_1 + r_2 N_2 c_2)/\bar{r}N \quad \text{A.26}$$

ϕ_1 and ϕ_2 are redefined as segment fractions instead of the volume fractions which are used in the lattice model, thus

$$\phi_2 = 1 - \phi_1 = (r_2 N_2/\bar{r}N) \quad \text{A.27}$$

The molar hard-core volume is given by $V_1^* = r v_1^*$ and $r_2/r_1 = (V_2^*/V_1^*)$ and we may write the segment fraction as

$$\phi_2 = N_2 V_2^*/(N_2 V_2^* + N_1 V_1^*) \quad \text{A.28}$$

or

$$\phi_2 = M_2 v_{sp,2}^*/(M_2 v_{sp,2}^* + M_1 v_{sp,1}^*) \quad \text{A.29}$$

where M_i is the mass of component i and $v_{sp,i}^*$ is the hard-core volume per gm. From these the partition function

$$Z = Z_{\text{comb}} (\gamma v^*)^{\bar{r}Nc} (\bar{v}^{1/3} - 1)^{3\bar{r}Nc} e^{(E_{0m}/kT)} \quad \text{A.30}$$

can be obtained where Z_{comb} is the combinatorial factor for intermixing the two components. Provided that only the nearest neighbour contacts are assumed, the energy E_0 of the mixture takes the form of that for a pure component.

$$E_{0m} = (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})/v \quad \text{A.31}$$

where A_{ij} is the number of nearest neighbour contacts of energy, $-N_{ij}/v$.

Assuming random mixing, it follows from Equation (A.8)

$$A_{12} = s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \quad \text{A.32}$$

$$2A_{11} + A_{12} = s_1 r_1 N_1 \quad \text{A.33}$$

$$2A_{22} + A_{12} = s_2 r_2 N_2 \quad \text{A.34}$$

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \quad \text{A.35}$$

θ_2 and θ_1 are site fractions and defined by

$$\theta_2 = 1 - \theta_1 = s_2 r_2 N_2 / (s_2 r_2 N_2 + s_1 r_1 N_1)$$

$$= (s_2/s_1) \phi_2 / \{ \phi_1 + (s_2/s_1) \phi_2 \}$$

$$= s \phi_2 / (s \phi_2 + \phi_1)$$

$$= s_2 \phi_2 / (s_1 \phi_1 + s_2 \phi_2) \quad \text{A.36}$$

Substitution of these equations into Equation (A.31)

$$E_{0m} = - (S \bar{r} N / 2v) (\theta_1 \eta_{11} + \theta_2 \eta_{22} - \theta_1 \theta_2 \Delta \eta) \quad \text{A.37}$$

By analogy with Equations (A.8) and (A.13), the energy for the pure component mixture can be defined by

$$- E_{0m} / \bar{r} N = P^* v^* / \bar{v} \quad \text{A.38}$$

Comparison of this equation with Equations (A.36) and (A.13) gives the first characteristic parameter for a mixture

$$P^* = P_1^* \phi_1 + P_2^* \phi_2 - \phi_1 \theta_2 X_{12} \quad \text{A.39}$$

$$\text{where} \quad X_{12} = \frac{s_1 \Delta \eta}{2v^*} \quad \text{A.40}$$

and is the interaction term, with dimensions of energy per unit volume and arises from the chemical nature of the components.

Since Equation (A.11) is also applicable to the mixture, it follows that the second parameter T^* is obtained.

$$P^*v^* = \bar{c}kT^* \quad \text{A.41}$$

and
$$T^* = P^*/(\phi_1 P_1^* T_1^{*-1} + \phi_2 P_2^* T_2^{*-1}) \quad \text{A.42}$$

Equations (A.39) and (A.42) show that the reduced parameters, $\tilde{P}$ and $\tilde{T}$, for the mixture are composition dependent. Knowing $\tilde{T}$ for the mixture, Equation (A.18) provides $\tilde{v}$, which is essential in order to specify the binary mixture quantitatively.

The enthalpy change on mixing

The enthalpy change on mixing is equal to the energy change on mixing at low pressure

$$\Delta H_m = E_{01,2} - (E_{01} + E_{02}) \quad \text{A.43}$$

where (1,2) refers to cross terms; (0₁) and (0₂) refer to pure components.

Equation (A.43) could be expressed in terms of a subscripted version of Equation (A.38), thus:

$$\Delta H_m = \bar{r}Nv^*\{\phi_1 P_1^*/\tilde{v}_1 + \phi_2 P_2^*/\tilde{v}_2 - P^*/\tilde{v}\} \quad \text{A.44}$$

Introducing p^* from Equation A.38 gives

$$\Delta H_m = \bar{r}Nv^*\{\phi_1P_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + \phi_2P_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1}) + \phi_1\theta_2X_{12}/\tilde{v}\} \quad \text{A.45}$$

Since $\phi_i\bar{r}N = r_iN_i$ and r_iN_i and $r_iv^* = V_i^*$, Equation (A.44) can be written:

$$\Delta H_m = N_1P_1^*V_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + N_2P_2^*V_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1}) + N_1V_1^*\theta_2X_{12}/\tilde{v} \quad \text{(A.46)}$$

The last term in Equations (A.45) and (A.46) represent the contributions from contact interactions attributable to a difference between 1,2 pairs and the mean of 1,1 and 2,2 contact pairs. The terms preceding it are the equation-of-state terms. Their contribution to the enthalpy change on mixing depends on the reduced volume of the mixture. The conventional expression for the heat of mixing,

$$\Delta H_m = BN_1\phi_2 \quad \text{A.47}$$

where B is assumed to be constant and independent of concentration.

B is determined from the measured heat of mixing of one polymer with a large excess of the other. The parameter B can be obtained in the limit of infinite dilution by a series of expansions of Equation (A.44) in powers of ϕ_2 ,

$$\begin{aligned}
B &= \lim_{\phi_2 \rightarrow 0} (\Delta H_m / N_1 \phi_2) = \lim_{N_2 \rightarrow 0} (\Delta H_m / N_2) (V_1^* / V_2^*) \\
&= (V_1^* / \tilde{v}_1) \{ P_2^* [\tilde{v}_1 / \tilde{v}_2 - 1 - \alpha_1 T (1 - \tilde{T}_2 / \tilde{T}_1)] \\
&\quad + (1 + \alpha_1 T) (s_2 / s_1) X_{12} \}
\end{aligned} \tag{A.48}$$

If $\tilde{T}_1 > \tilde{T}_2$ the equation-of-state contribution within the square bracket is negative, and enthalpy change on mixing, for a large excess of solvent will be negative unless X_{12} is large enough to dominate the terms in the brackets. The negative change on mixing will ensure a negative excess volume change on mixing defined by:

$$\tilde{v}^E = \tilde{v} - \tilde{v}^0, \quad \tilde{v}^0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \tag{A.49}$$

$$\tilde{v}^E / \tilde{v}^0 = \tilde{v} / (\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2) - 1 \tag{A.50}$$

Equation (A.50) is related to the composition through $\tilde{T}$ or T^* .

Measurement of the volume change on mixing, ΔV_m and the unmixed V^0 directly gives

$$\tilde{v}^E / \tilde{v}^0 = \Delta V_m / V^0$$

Differentiating the enthalpy Equation (A.45) with respect to N_i gives the partial molar heat of mixing of component i , which in turn is related to the enthalpy interaction parameter, X_H :

$$\Delta \bar{H}_1 = \bar{H}_1 - H_1^0 = (\partial \Delta H_m / \partial N_1)_{T,P,N_2} \quad A.51$$

$$\begin{aligned} & (\partial H_m / \partial N_1)_{N_2, \tilde{T}, \tilde{v}} + (\partial \Delta H_m / \partial \tilde{v})_{N_2, \tilde{T}, N_1} \\ & (\partial \tilde{v} / \partial N_1)_{N_2, T, V} \end{aligned} \quad A.52$$

The final result is

$$\begin{aligned} \Delta \bar{H}_1 &= P_1^* V_1^* \{ (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + (\alpha T / \tilde{v}) (\tilde{T}_1 - \tilde{T}) / \tilde{T} \} \\ &+ (V_1^* X_{12} / \tilde{v}) (1 + \alpha T) \theta_2^2 = RT X_H \phi_2^2 \end{aligned} \quad A.53$$

Applying a similar procedure, the entropy equation gives TS_1^{-R} , which is similarly related to the entropy interaction parameter, X_s :

$$\begin{aligned} TS_1^{-R} &= -P_1^* V_1^* \{ 3T_1 \ln(\tilde{v}_1^{1/3} - 1) / (\tilde{v}^{1/3} - 1) \\ &- (\alpha T / \tilde{v}) (\tilde{T}_1 - \tilde{T} / \tilde{T}) \} + (V_1^* \theta_2^2 / \tilde{v}) (\alpha T X_{12} + T \tilde{v} Q_{12}) \\ &= -RT X_s \phi_2^2 \end{aligned} \quad A.54$$

where Q_{12} is the entropy correction parameter. The partial molar residual chemical potential of component 1 is therefore:

$$\begin{aligned}
\mu_1^R &= P_1^* V_1^* \{ 3 \bar{T}_1 \ln(\bar{v}_1^{1/3} - 1) / (\bar{v}^{1/3} - 1) \\
&+ (\bar{v}_1^{-1} - \bar{v}^{-1}) \} + (V_1^* \theta_2^2 / \bar{v}) (X_{12} - T \bar{v} Q_{12}) \\
&= RT X_t \phi_2^2
\end{aligned} \tag{A.55}$$

where X_t is the total interaction parameter,

$$\text{i.e. } X_t = X_H + X_s \tag{A.56}$$

The equations (A.53 – A.55) serve as definitions of X_H , X_s and X_t respectively. The values of X_{12} and Q_{12} are supposed to be composition independent, whereas the composition dependence of X_H , X_s and X_t are given by:

$$X_t = X_{t,1} + X_{t,2} \phi_2 + X_{t,3} \phi_2^2 + \dots \tag{A.57}$$

$$X_H = X_{H,1} + X_{H,2} \phi_2 + X_{H,3} \phi_2^2 + \dots \tag{A.58}$$

$$X_s = X_{s,1} + X_{s,2} \phi_2 + X_{s,3} \phi_2^2 + \dots \tag{A.59}$$

The chemical potential of component 1 in the mixture is composed of a combinatorial and residual part. The combinatorial part is given by the Flory–Huggins theory. Therefore:

$$(\mu - \mu_1^0) = (\mu_1 - \mu_1^0)_{\text{comb}} + (\mu_1 - \mu_1^0)^R \quad \text{A.60}$$

$$(\mu - \mu_1^0)_{\text{comb}} = RT\{\ln \phi_1 + (1 - r_1/r_2)\phi_2\} \quad \text{A.61}$$

On this basis, the chemical potential of component 1 in the mixture may be written:

$$\begin{aligned} (\mu - \mu_1^0)/RT &= \ln(1 - \phi_2) + (1 - r_1/r_2)\phi_2 \\ &+ \{(\mu - \mu_1^0)^R/RT\}\phi_2^2 \end{aligned} \quad \text{A.62}$$

By equating the chemical potential from the two theories a relation between X_{12} and χ_{12} (the Flory–Huggins) interaction parameter may be obtained:

$$\begin{aligned} \chi_{12} &= p_1^* v_1^*/RT \phi_2^2 \{3\bar{T}_1 \ln(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1) \\ &+ (\bar{v}_1^{-1} - \bar{v}^{-1}) + X_{12} \theta_2^2/P_1^* \bar{v}\} \end{aligned} \quad \text{A.63}$$

The free energy change on mixing

The free energy of mixing is obtained from the partition function. Equation (A.14), with the appropriate renotation for the pure components and the solution,

$$Z^J = \Omega c^J (\gamma^*)^{N_j} r_j c_j (\bar{v}_j^{1/3} - 1)^{3N_j} r_j c_j e^{N_j r_j c_j / v_j T_j} \quad \text{A.64}$$

where $j = \{1, 2, (1, 2)\}$

Thus

$$\Delta G_m = kT \ln(Z^{(1,2)} / Z^1 Z^2) \quad A.65$$

The actual mathematical manipulation is not difficult but the subsequent substitutions are complicated, therefore the result only is given here, thus:

$$\begin{aligned} \Delta G_m = & kT(n_1 \ln \phi_1 + n_2 \ln \phi_2) + 3\bar{r}Nv^* \\ & \{ \phi_1 P_1^* \bar{T}_1 \ln(\bar{v}_1^{1/3} - 1) / (\bar{v}^{1/3} - 1) + \phi_2 P_2^* \bar{T}_2 \ln(\bar{v}_2^{1/3} - 1) / (\bar{v}^{1/3} - 1) \} \\ & + TNv^* \{ (\phi_1 P_1^* (1/\bar{v}_1 - 1/\bar{v}) + \phi_2 P_2^* (1/\bar{v}_1^{1/3} - 1/\bar{v})) + (\phi_1 \theta_2 X_{12} / \bar{v}) \} \end{aligned} \quad A.66$$

Eichinger and Flory (1968), derived the above equation for the free energy of mixing. The first term is the combinatorial entropy term. The second term reflects the equation-of-state contributions and the third represents the enthalpy which contains interaction contributions (X_{ij}). The reduced volume, $\bar{v}$, of the mixture contains both the equation-of-state and interaction contributions. Varying the value of $\bar{v}$ can cause ΔG_m to change from negative to positive and hence influence the state of miscibility under conditions when the interaction term is small. The equation-of-state theory successfully predicts lower and upper critical solution phase boundaries for polymer mixtures. It can also predict negative heats of mixing, interaction parameters and excess volumes of mixing.

APPENDIX B

Derivation of partition function, Ω

In order to obtain Ω , a one-dimensional system of N impenetrable non-interacting particles on a line of length L is considered. If l^* is the hard-core length of a particle, and $l = L/N$ then $l - l^*$ is the free length available to each particle

$$\Omega = \{(l - l^*)_e\}^N \quad \text{B.1}$$

The above equation has its origin in the modeling of a liquid in a disordered cell of free volume V . e^N is an entropy function of melting and the partition function is defined by

$$\Omega_{\text{liquid}} = (2\pi mkT/h^2)^{3N/2} V^N / N! \quad \text{B.2}$$

For an ordered solid, this partition function becomes

$$\Omega_{\text{crystal}} = (2\pi mkT/h^2)^{3N/2} V^N / N^N \quad \text{B.3}$$

$N!$ appears in Equation (B.2) because the molecules in a liquid are indistinguishable. The entropy change from crystalline to liquid state is:

$$\Delta s_{c-l} = k \ln \frac{\Omega_{\text{liquid}}}{\Omega_{\text{crystal}}} = k \ln \frac{N^N}{N!} \quad \text{B.4}$$

Applying Stirling's theorem

$\ln! = N \ln N - N$, to equation (B.4) gives

$$\Delta s_{c-1} = kN = k \ln e^N \quad \text{B.4}$$

or
$$\Omega_{\text{liquid}} = \Omega_{\text{crystal}} \times e^N \quad \text{B.6}$$

Equation (B.1) follows from the realisation that

$$\Omega_{\text{crystal}} = (1 - l^*)^N \quad \text{B.7}$$

and

$$\Omega_{\text{liquid}} = \{(1 - l^*)_e\}^N = \{\gamma^{1/3}(v^{1/3} - v^{*1/3})_e\}^N \quad \text{B.8}$$

APPENDIX C

Thermal expansion coefficient

$$\alpha = \left[\frac{1}{v} \right] \left[\frac{\partial v}{\partial T} \right]_p$$

Substituting $\tilde{v} = v/v^*$ and $\tilde{T} = T/T^*$ gives

$$\frac{1}{v^*v} \frac{\partial v^* \tilde{v}}{\partial T^* \tilde{T}}$$

$$= \frac{1}{T^*v} \frac{\partial v}{\partial T}$$

$$\alpha T = \frac{\tilde{T}}{v} \frac{\partial v}{\partial \tilde{T}}$$

but

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}}$$

$$\alpha T = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{7/3}} \frac{\partial v}{\partial \tilde{T}}$$

Now

$$\frac{\partial \tilde{T}}{\partial v} = \frac{\tilde{v}^{4/3} \left[\frac{1}{3} \tilde{v}^{-2/3} \right] - \left[\tilde{v}^{1/3} - 1 \right]^{4/3} \tilde{v}^{1/3}}{\tilde{v}^{8/3}}$$

$$= \frac{\frac{1}{3} \tilde{v}^{2/3} - \frac{4}{3} \tilde{v}^{2/3} + \frac{4}{3} \tilde{v}^{1/3}}{\tilde{v}^{8/3}}$$

$$= \frac{\frac{4}{3} \sqrt[3]{v} + \sqrt[3]{v^2}}{\sqrt[3]{v^8}}$$

Therefore

$$\alpha T = \frac{\sqrt[3]{v} - 1}{\sqrt[3]{v}} \frac{\sqrt[3]{v^8}}{\frac{4}{3} \sqrt[3]{v} - \sqrt[3]{v^2}}$$

$$= \frac{\sqrt[3]{v} \left[\sqrt[3]{v} - 1 \right]}{\frac{4}{3} \sqrt[3]{v} - \sqrt[3]{v^2}}$$

$$= \frac{\sqrt[3]{v^2} - \sqrt[3]{v}}{\frac{4}{3} \sqrt[3]{v} - \sqrt[3]{v^2}}$$

Dividing numerator and denominator by $\sqrt[3]{v}$

$$\alpha T = \frac{\sqrt[3]{v} - 1}{\frac{4}{3} - \sqrt[3]{v}}$$

$$\frac{4}{3} \alpha T - \sqrt[3]{v} \alpha T = \sqrt[3]{v^4} - 1$$

$$1 + \frac{4}{3} \alpha T = (1 + \alpha T) \sqrt[3]{v}$$

$$3 + 4 \alpha T = 3(1 + \alpha T) \sqrt[3]{v}$$

$$3 + 3 \alpha T + \alpha T = 3(1 + \alpha T) \sqrt[3]{v}$$

$$\sqrt[3]{v} = \frac{1 + \alpha T}{3(1 + \alpha T)}$$

APPENDIX D

Thermal pressure coefficient

Thermal pressure coefficient, $\gamma = \left[\frac{\partial p}{\partial T} \right]_{\tilde{v}} = \left[\frac{\partial p^* \tilde{p}}{\partial T^* T} \right]_{\tilde{v}} = \frac{p^*}{T^*} \left[\frac{\partial \tilde{p}}{\partial T} \right]_{\tilde{v}}$

This is applied to

$$\frac{\tilde{p} \tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{-1/3}}{(\tilde{v}^{-1/3} - 1)} - \frac{1}{\tilde{v} \tilde{T}}$$

$$\tilde{p} = \frac{\tilde{v}^{-2/3}}{(\tilde{v}^{-1/3} - 1)} \tilde{T} - \frac{1}{\tilde{v}^2}$$

$$\frac{\partial \tilde{p}}{\partial \tilde{T}} = \frac{\tilde{v}^{-2/3}}{(\tilde{v}^{-1/3} - 1)}$$

Therefore

$$\gamma = \frac{p^* \tilde{v}^{-2/3}}{T^* (\tilde{v}^{-1/3} - 1)}$$

$$p^* = \frac{\gamma T^* \left[\tilde{v}^{-1/3} - 1 \right]}{\tilde{v}^{-2/3}}$$

$$= \frac{\gamma T}{\tilde{T}} \frac{\left[\tilde{v}^{-1/3} - 1 \right]}{\tilde{v}^{-2/3}}$$

but

$$\tilde{T} = \frac{\tilde{v}^{-1/3} - 1}{\tilde{v}^{4/3}}$$

Therefore

$$p^* = \frac{\gamma T}{(\tilde{v}^{1/3} - 1) \tilde{v}^{-2/3}} \tilde{v}^{4/3} \tilde{v}^{1/3} - 1$$

$$= \gamma T \tilde{v}^2$$

APPENDIX E

Partial molar heat of mixing for binary mixtures

To obtain the partial molar heat of mixing, $\Delta \bar{H}_1$, Equation (2.43) is differentiated with respect to N_1 :

$$\frac{\partial \Delta H_m}{\partial N_1} = p_1^* V_1^* (\bar{v}_1^{-1} - \bar{v}^{-1}) + \frac{p_1^* V_1^* N_1}{\bar{v}^2} \frac{\partial \bar{v}}{\partial N_1}$$

$$\frac{p_2^* V_2^* N_2}{\bar{v}^2} \frac{\partial \bar{v}}{\partial N_1} + \frac{V_1^* \theta_2 X_{12}}{\bar{v}}$$

$$+ \frac{V_1^* N_1 X_{12}}{\bar{v}} \frac{\partial \theta_2}{\partial N_1} - \frac{V_1^* N_1 X_{12}}{\bar{v}} \frac{\partial \bar{v}}{\partial N_1}$$

Terms must now be collected and the value of the differential coefficients considered.

First $\frac{\partial \theta_2}{\partial N_1}$:

Since

$$s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1$$

$$\theta_2 = \frac{s_2 r_2 N_2 \theta_1}{s_1 r_1} \frac{1}{N_1}$$

$$\frac{\partial \theta_2}{\partial N_1} = - \frac{s_2 r_2 N_2 \theta_1}{s_1 r_1 N_1} \frac{1}{N_1}$$

$$= - \frac{\theta_1 Q_2}{N_1}$$

To evaluate $\frac{\partial \bar{v}}{\partial N_1}$, three relationships are needed:

$$\frac{\partial \bar{v}}{\partial N_1} = \frac{\partial \bar{v}}{\partial T^*} \frac{\partial T^*}{\partial \phi_2} \frac{\partial \phi_2}{\partial N_1}$$

1. Evaluation of $\frac{\partial \bar{v}}{\partial T^*}$

$$\frac{T^*}{T} = \frac{\bar{v}^{-4/3}}{(\bar{v}^{-1/3} - 1)}$$

Therefore

$$\begin{aligned} \frac{T}{T^*} \frac{\partial T^*}{\partial \bar{v}} &= \frac{(\bar{v}^{-1/3} - 1) \left[\frac{4}{3} \bar{v}^{-1/3} \right] - \bar{v}^{-4/3} \left[\frac{1}{3} \bar{v}^{-2/3} \right]}{(\bar{v}^{-1/3} - 1)^2} \\ &= \frac{\frac{4}{3} \bar{v}^{-1/3} - \frac{1}{3} \bar{v}^{-1/3} - \bar{v}^{-2/3}}{3(\bar{v}^{-1/3} - 1)^2} \\ &= \frac{\bar{v}^{-1/3} (3\bar{v}^{-1/3} - 4)}{3(\bar{v}^{-1/3} - 1)^2} \end{aligned}$$

On substituting, $(\bar{v}^{-1/3} - 1)^2 = \frac{T^2}{T^{*2}} \bar{v}^{8/3}$

Therefore $\frac{T}{T^*} \frac{\partial T^*}{\partial \bar{v}} = - \frac{\bar{v}^{-1/3} (4 - 3\bar{v}^{-1/3}) T^{*2}}{3 T^2 \bar{v}^{8/3}}$

$$\frac{\partial T^*}{\partial \bar{v}} = - \frac{T^*}{T} \frac{(4 - 3\bar{v}^{-1/3})}{3\bar{v}^{7/3}}$$

Therefore $\frac{\partial \bar{v}}{\partial T^*} = - \frac{T}{T^*} \frac{3\bar{v}^{7/3}}{(4 - 3\bar{v}^{-1/3})}$

2. Evaluation of $\frac{\partial T^*}{\partial \phi_2}$

$$T^* = (\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) / \left[\frac{\phi_1 p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*} \right]$$

where the numerator of this expression is p^* and $\phi_2 = 1 - \phi_1$.

$$\begin{aligned} T^* &= \left\{ (1 - \phi_2) p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12} \right\} / \left\{ \frac{(1 - \phi_2) \phi_1^*}{T_1^*} \right. \\ &\quad \left. = \frac{\phi_2 p_2^*}{T_2^*} \right\} \end{aligned}$$

$$\frac{\partial T^*}{\partial \phi_2} = \frac{\left[-\frac{(1 - \phi_2) p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*} \right] \left[-p_1^* + p_2^* - \lambda \right] - p^* \left[\frac{p_2^*}{T_2^*} + \frac{p_1^*}{T_1^*} \right]}{\left\{ \frac{(1 - \phi_2) p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*} \right\}^2}$$

Since
$$\frac{p^*}{T^*} = \frac{(1 - \phi_2) p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*}$$

Therefore

$$\frac{\partial T^*}{\partial \phi_2} = \frac{\left[\frac{p^*}{T^*} \right] \left[p_2^* + p_1^* - \lambda \right] - \left[\frac{p^*}{T^*} \right] \left[\frac{p_2^*}{T_2^*} + \frac{p_1^*}{T_1^*} \right]}{\left[\frac{p^*}{T^*} \right]^2}$$

$$= \frac{T^*}{p^*} \left[p_2^* - p_1^* - \lambda \right] - \frac{T^*}{p^*} \left[p_2^* \frac{T^*}{T_2^*} - p_1^* \frac{T^*}{T_1^*} \right]$$

$$= \frac{T^*}{p^*} \left[p_2^* - \left[1 - \frac{T^*}{T_2^*} \right] - p_1^* \left[1 - \frac{T^*}{T_1^*} \right] \right] - \frac{T^* \lambda}{p^*}$$

$$- \lambda \equiv - \phi_1 Q_2 X_{12}$$

$$- \frac{\partial \lambda}{\partial \phi_2} - X_{12} \left\{ \phi_1 \frac{\partial \theta_2}{\partial \phi_2} + \theta_2 \frac{\partial \phi_1}{\partial \phi_2} \right\}$$

Therefore

$$\frac{\partial T^*}{\partial \phi_2} = \frac{T^*}{p^*} \left[p_2^* - \left[1 - \frac{T^*}{T_2^*} \right] - p_1^* \left[1 - \frac{T^*}{T_1^*} \right] - (\phi_1 - \theta_2) X_{12} \frac{\theta_2}{\phi_2} \right]$$

3. To evaluate $\frac{\partial \phi_2}{\partial N_1}$

$$1 - \phi_2 = r_1 N_1 / r_1 N = r_1 N_1 / (r_1 N_1 + r_2 N_2)$$

$$\begin{aligned} -\frac{\partial \phi_2}{\partial N_1} &= \frac{(r_1 N_1 + r_2 N_2) r_1 - r_1 N_1 r_1}{(r_1 N_1 + r_2 N_2)^2} = \frac{r_1 r_2 N_2}{(r_1 N_1 + r_2 N_2)} \\ &= \frac{r_1 N_1 r_2 N_2}{N_1 (r_1 N_1 + r_2 N_2)} = \frac{\phi_1 \phi_2}{N_1} \end{aligned}$$

Using the results of section 1, 2 and 3

$$\begin{aligned} \frac{\partial \bar{v}}{\partial N_1} &= \left[-\frac{T^*}{T} \frac{3\bar{v}^{7/3}}{(4 - 3\bar{v}^{1/3})} \right] \frac{T^*}{p^*} \left[p_2^* - \left[1 - \frac{T^*}{T_2^*} \right] - p_1^* \left[1 - \frac{T^*}{T_1^*} \right] \right. \\ &\quad \left. - (\phi_1 - \phi_2) X_{12} \frac{\theta_2}{\phi_2} \right] \times \left[-\frac{\phi_1 \phi_2}{N_1} \right] \end{aligned}$$

We now require

$$\frac{\bar{r} N p^{*v*}}{\bar{v}^2} \frac{\partial \bar{v}}{\partial N_1}$$

$$\begin{aligned} &= \frac{\bar{r} N p^{*v*}}{\bar{v}^2} \frac{T}{p^*} \frac{\phi_1 \phi_2}{N_1} \left[\frac{3\bar{v}^{7/3}}{(4 - 3\bar{v}^{1/3})} \right] \left[p_2^* - \left[1 - \frac{T^*}{T_2^*} \right] - p_1^* \left[1 - \frac{T^*}{T_1^*} \right] \right. \\ &\quad \left. - (\phi_1 - \phi_2) X_{12} \frac{\theta_2}{\phi_2} \right] \times \left[-\frac{\phi_1 \phi_2}{N_1} \right] \end{aligned}$$

$$\frac{\bar{r} N \phi_1}{N_1} = r_1$$

Thus only $\frac{r_1 v^* \tilde{T}}{v^2} \phi_2$ is left. This can be written

$$\frac{V_1^*}{v^2} \tilde{T} \phi_2 = \frac{V_1^*}{v^2} \frac{(v^{1/3} - 1)}{v^{4/3}} \phi_2$$

On combination with the terms in square brackets involving v ,

$$\begin{aligned} \frac{V_1^*}{v^2} \frac{(v^{1/3} - 1)}{v^{4/3}} \phi_2 \frac{3v^{7/3}}{(4 - 3v^{1/3})} &= \frac{V_1^*}{v^2} \phi_2 \frac{v^{1/3} - 1}{4 - 3v^{1/3}} \\ &= \frac{V_1^*}{3v} \alpha T \phi_2 \end{aligned}$$

Since

$$\theta_2 = \frac{s_2 \phi_2}{s_1 + (s_2 - s_1) \phi_2}$$

$$\begin{aligned} \frac{\partial \theta_2}{\partial \phi_2} &= \frac{(s_1 + (s_2 - s_1) \phi_2) s_2 - s_2 \phi_2 (s_2 - s_1)}{(s_1 + (s_2 - s_1) \phi_2)^2} \\ &= \frac{\theta_2^2 [s_1 s_2 + s_2 (s_2 - s_1) \phi_2 - s_2 (s_2 - s_1) \phi_2]}{(s_2 \phi_2)^2} \\ &= \frac{s_1 s_2 \theta_2^2}{(s_2 \phi_2)^2} = \left[\frac{s_1}{s_2} \right] \frac{\theta_2^2}{\phi_2^2} \end{aligned}$$

Therefore

$$-\frac{\partial \lambda}{\partial \phi_2} = X_{12} \left\{ \phi_1 \left[\frac{s_1}{s_2} \right] \frac{\theta_2^2}{\phi_2^2} - \theta_2 \right\}$$

But $s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1$

$$\frac{s_1}{s} = \frac{\theta_1}{\theta_2} \frac{\phi_2}{\phi_1}$$

$$\begin{aligned}
\text{i.e.} \quad -\frac{\partial \lambda}{\partial \phi_2} &= X_{12} \left\{ \phi_1 \frac{\theta_1}{\theta_2} \frac{\phi_2}{\phi_1} \frac{\theta_2^2}{\phi_2^2} - \theta_2 \right\} \\
&= X_{12} \frac{\theta_2}{\phi_2} (\phi_1 - \theta_2)
\end{aligned}$$

The final expression follows from Appendix C

$$\begin{aligned}
&= \frac{V_1^*}{3v} \alpha T \phi_2 \left[p_2^* \left[1 - \frac{T^*}{T_2^*} \right] - p_1^* \left[1 - \frac{T^*}{T_1^*} \right] - (\phi_1 - \theta_2) X_{12} \frac{\theta_2}{\phi_2} \right] \\
&= \frac{V_1^* \alpha T}{3v} \left[p_2^* \phi_2 - \frac{p_2^* \phi_2 T^*}{T_2^*} - p_1^* \left[1 - \phi_1 \right] \right. \\
&\quad \left. + \frac{p_1^* (1 - \phi_1) T^*}{T_1^*} - \phi_1 X_{12} \theta_2 + X_{12} \theta_2^2 \right] \\
&= \frac{V_1^* \alpha T}{3v} \left[p_2^* - T^* \left[\frac{p_2^* \phi_2}{T_2^*} + \frac{p_2^* \phi_2}{T_2^*} \right] - p_1^* \left[1 - \frac{T^*}{T_2^*} \right] + X_{12} \theta_2^2 \right]
\end{aligned}$$

Since the second term in the brace is p^* , the definition of $\bar{T}$ can be used to obtain

$$\frac{V_1^* \alpha T}{3v} \left[-p_1^* \left[1 - \frac{T^*}{T_2^*} \right] + X_{12} \theta_2^2 \right]$$

It is now necessary to assemble terms to obtain the final equation for the enthalpy of mixing:

$$\begin{aligned}
\frac{\partial \Delta H_m}{\partial N_1} &= \bar{H}_1 - H_1^0 \\
&= p_1^* V_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + V_1^* X_{12} \theta_2^2 + \frac{V_1^* \alpha T}{3 v} \left[-p_1^* \left(1 - \frac{T^*}{T_2^*} \right) + X_{12} \theta_2^2 \right] \\
&= p_1^* V_1^* \left[(\tilde{v}_1^{-1} - \tilde{v}^{-1}) - \frac{\alpha T}{3 v} \left[\frac{\tilde{T}}{T_2^*} - \frac{\tilde{T}_1}{T_1^*} \right] \right] + \frac{V_1^* X_{12}}{v} (1 + \alpha T/3) \theta_2^2
\end{aligned}$$

This is the Eichinger and Flory Equation.

APPENDIX F

Free energy change on mixing

$-E_{0m}/kT$ in Equation (A.30) will be substituted by:

$$-E_{0m}c/P^*v^*\tilde{T} = \tilde{r}Nc/\tilde{v}\tilde{T} \quad \text{F.1}$$

The Helmholtz free energy of a mixture is given by:

$$F_M = -kT \ln Z \quad \text{F.2}$$

$$\text{or} \quad \Delta F_M = F_M - (F_1 + F_2) \quad \text{F.3}$$

where F_1 and F_2 are the free energies of the pure components. Thus Equation (A.30) for condition F.3 gives

$$\begin{aligned} \Delta F_M = kT \ln \frac{Z_{\text{comb}}}{Z_{\text{comb},1}Z_{\text{comb},2}} (\gamma v^*)^{\tilde{r}Nc} - \bar{r}_1 N_1 c_1 - \bar{r}_2 N_2 c_2 \\ + kT \ln \frac{(\tilde{v}_1^{1/3} - 1)^{3r_1 N_1 c_1} (\tilde{v}_1^{1/3} - 1)^{3r_2 N_2 c_2}}{(\tilde{v}^{1/3} - 1)^{3\tilde{r}Nc}} \\ + kT(r_1 N_1 c_1 / \tilde{v}_1 \tilde{T}_1 - kT(r_2 N_2 c_2 / \tilde{v}_2 \tilde{T}_2 - kT(rNc / \tilde{v} \tilde{T})) \quad \text{F.4} \end{aligned}$$

By using $T = \tilde{T}_1 T_1^*$, $P_i^* v_i^* = c_i k T_i^*$ and $\tilde{r} N \phi_i = r_i N_i$, the third term of Equation (F.4) can easily be converted to:

$$\bar{r}Nv^*\{\phi_1P_1^*/\bar{v}_1 + \phi_2P_2^*/\bar{v}_2 - P^*/\bar{v}\} = \Delta H_m \quad A.44$$

while using $\bar{r}Nc = \bar{r}_1N_1c_1 + \bar{r}_2N_2c_2$ in the second term yields:

$$3kTr_1N_1c_1\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1) +$$

$$3kTr_2N_2c_2\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1) \quad F.5$$

or

$$3P_1^*V_1^*N_1\bar{T}_1\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1)$$

$$+ 3P_2^*V_2^*N_2\bar{T}_2\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1) \quad F.6$$

or

$$3rNv^*\{P_1^*\phi_1\bar{T}_1\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1)$$

$$+ P_2^*\phi_2\bar{T}_2\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1)\} \quad F.7$$

Equations (F.6) or (F.7) and (A.44) are equal to Q^R given by Equation (A.).

The first term of Equation (F.4) represents the combinatorial part $(-T\Delta S_{comb})$

and will be replaced from the lattice theory. Hence:

$$\Delta F_M = \bar{r}NkT\{(\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2\}$$

$$+ 3\bar{r}Nv^*\{\phi_1P_1^*\bar{T}_1\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1)$$

$$+ \phi_2P_2^*\bar{T}_2\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}_1^{1/3} - 1) + \phi_2P_2^*/\bar{v}_2 - P^*/\bar{v}\}$$

F.8

The chemical potential of component one in the mixture relative to the pure component is defined by:

$$\begin{aligned}\mu_1 - \mu_1^0 &= -RT\{\partial \ln(Z/Z_1)/\partial N_1\}_{T,V,N_2} \\ &= (\partial \Delta F_M / \partial N_1)_{T,V,N_2} + (\partial \Delta F_M / \partial \bar{v})_{T,N_1N_2} (\partial \Delta F_M / \partial \bar{v})_{T,V,N_2}\end{aligned}\tag{F.9}$$

$$\begin{aligned}&= \bar{R}T\{\ln \phi_1 + (1 - r_1/r_2)\phi_1 + (V_1^*X_{12}/\bar{v})\theta_2^2 \\ &\quad + P_1^*v_1^*\{3\bar{T}_1\ln(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1) \\ &\quad + (\bar{v}_1^{-1} - \bar{v}^{-1}) + P_1(\bar{v} - \bar{v})\}\end{aligned}\tag{F.10}$$

where $\bar{P}_1\bar{v}$ is the contribution of the second term in Equation (F.9), to the chemical potential, $(\partial \bar{v} / \partial N_1)_{T,V,N_2}$

$$= V\delta(\bar{r}\bar{v}^*N)^{-1}/\delta N_1 = -(\phi_1\bar{v}/N_1)$$

Since this contribution is very small at ordinary pressures, it may be neglected but it should be included at higher pressures.

APPENDIX G

Partial molar residual entropy of mixing for binary mixtures.

Differentiating Equation (A.) at constant N_2 gives:

$$\begin{aligned}
 T(\delta S/\delta N_1)_{T,P,N_2} &= -P_1^*V_1^*\{\bar{e}\bar{T}_1\ln(\bar{v}_1^{1/3}-1)/(\bar{v}^{1/3}-1) \\
 &+ \{(P_1^*V_1^*N_1\bar{T}_1 + P_2^*V_2^*N_2\bar{T}_2)/(\bar{v}^{2/3}(\bar{v}^{1/3}-1))\}/(\delta\bar{v}/\delta N_1) \\
 &= T(\bar{S} - \bar{S}^0)
 \end{aligned}
 \tag{G.1}$$

where

$$\begin{aligned}
 P_1^*V_1^*N_1\bar{T}_1 + P_2^*V_2^*N_2\bar{T}_2 &= r_1N_1c_1k + r_2N_2c_2k \\
 &= \bar{r}Nck = rNP^*v^*\bar{T}
 \end{aligned}
 \tag{G.2}$$

$\delta\bar{v}/\delta N_1$ is given by Equation (E.11). Application of Equation (E.13) procedure will give the relation (A.) for TS_1^R .

PROGRAM 'SPIN' FOR CALCULATING THE SPINODALS

PROGRAM SPIN

COMMON /A/VRS(2),LPROB,PHS(2),ALPHA(2),GAMMA(2),TRS(2),THS(2)

COMMON /B/X12,Q12,F1,F2,P,TH,PH,TR,PR,THETA1,THETA2,LASTEP

COMMON /C/V1R,V2R,T1H,T2H,P1H,P2H,T1R,T2R,RV,SF12,S21,V13,R12

COMMON /D/ FIN,TIN,VM,ISTEP,T,S,B5

COMMON/E/D1,D2,D3,D4,D5,D,S1,S2,S3,S4,S5,S6,DPDF2,DTDF2

DIMENSION PSF(20),PST(20),PSP(20),PVM(20),PS(20)

C PROGRAM TO CACULATE SPINODAL CURVE AT ATMOSPHERIC PRESSURE

WRITE(*,445)

445 FORMAT(2X,/, 'PRESSURE IS AT ATMOSPHERIC *****')

C=====TEST RUN AT ATM AND THE SEARCH FOR Q12=ONLY IF ITEST=0*****

ITEST=1

WRITE(*,555)ITEST

555 FORMAT(/, 'ITEST =',I3, /)

C=====

C=====THIS CONDITION SOLVES ONLY FOR THE STATE PARAMETERS AT THE
C TEMPERATUE AT WHICH DELTA H WAS DETERMINED

C=====

C A VALUE OF ZERO MEANS X12 HAS ALREADY BEEN DETERMINED

IVOL=0

C=====

C LIMITS OF ITERATION IN CASES WERE CONVERGENCE PROBLEMS OCCUR
C DUE TO THE FACT THE ONE IS MOVING IN THE WRONG DIRECTION FOR APPROACH

C TO ZERO S

LASTEP=10000

LPROB=LASTEP-5

C***** SYSTEM PARAMETERS *****

P=0.10126

ALPHA(1)=6.911E-4

ALPHA(2)=5.740E-4

GAMMA(1)=1.12

GAMMA(2)=1.212

V1H=80041.5

C V1H=1350.

R=8.314

RV=R/V1H

S21=1.0

R12=1.6

TS=323.

C*****

C EVALUATING COMPONENT PARAMETERS

DO 100 L=1,2

VRS(L)=1.+(ALPHA(L)*TS/(3.+3.*ALPHA(L)*TS))

PHS(L)=GAMMA(L)*TS*VRS(L)**6

TRS(L)=(VRS(L)-1.)/VRS(L)**4

100 THS(L)=TS/TRS(L)

T1H=THS(1)

T2H=THS(2)

P1H=PHS(1)

P2H=PHS(2)

V1R=VRS(1)**3

V2R=VRS(2)**3

T1R=TRS(1)

```

      T2R=TRS(2)
      WRITE(6,182)
182  FORMAT(/,10X,'T1S      T2S      P1S      P2S      T1R
      1 T2R      V1R      V2R ')
      WRITE(6,192) T1H,T2H,P1H,P2H,T1R,T2R,V1R,V2R
192  FORMAT(2X,4F12.2,2X,4F7.4)

```

```

C=====
=====

```

```

C THIS IS T4 ALLOW FOR VARIATION OF PRESSURE

```

```

      DO 7000 JJ=1,2
C   X12=53.+0.5*FLOAT(JJ-1)
      IF(JJ.EQ.1)X12=-8.74
      IF(JJ.EQ.2)X12=-3.12
      DO 4000 IP=1,1
      P=0.10126
      IF(IP.EQ.2)P=200.*P
      IF(IP.EQ.3)P=400.*P
      IF(IP.EQ.4)P=500.*P
      IF(IP.EQ.5)P=800.*P
      IF(IP.EQ.6)P=1000.*P
      IF(IP.EQ.7)P=1200.*P

```

```

C TEMP AT WHICH STATE PARAMETERS ARE DETERMINED OR CLOUD PT TEMP

```

```

      TIN=353.
      IF(IVOL.NE.0) TIN=TS
      T=TIN

```

```

C START OF ITERATION IN TERMS OF VOL FRACTION RANGE TO BE COVERED

```

```

      ISTEP=0
      FIN=0.3
      F2=FIN

```

```

105  CONTINUE
      F1=1.-F2

```

THETA2=F2*S21/(F1+F2*S21)

THETA1=1.-THETA2

SF12=THETA1/F2

C Q12 IS EVALUATED ONLY ONCE

IF(ISTEP.NE.0) GO TO 200

IF(IP.NE.1) GO TO 200

CALL MIX

WRITE(6,120)

IF(IVOL.NE.0) GO TO 660

CALL INTPAR

C Q12=12.00626

WRITE(6,115)F2,T,TH,TR,P,PH,PR,VM,THETA2,X12,Q12

115 FORMAT(/,2X,13F10.4)

IF(ISTEP.EQ.0) GO TO 203

120 FORMAT(/,7X,F2 T TH TR P

1 PH PR VR THETA2 X12 Q12')

200 CONTINUE

IF(F2.GE.0.25)CALL TEMP1

IF(F2.LT.0.25)CALL TEMP2

GO TO 600

203 WRITE(6,205)

205 FORMAT(/,7X,'DPDF DTDF D1 D2 D3 D4

1 D5 D S1 S2 S3 S4 S5

2 S6 S')

IF(ISTEP.EQ.0) GO TO 600

C IF(IVOL.EQ.0) GO TO 600

C EVALUATION OF X12 FROM HEAT OF MIXING DATA

660 CONTINUE

DO 677 JK=1,10

DHM=-3.44 +5.*FLOAT(JK-1)

RN=1.0

VS=0.8132

A=1./V1R

B=1./V2R

```

C=1./VM
C1=F1*P1H*(A-C)
C2=F2*P2H*(B-C)
C3=DHM/RN*VS
C4=F1*THETA2
C5= C1+C2
X12=(C3-C5)*VM/C4
677  WRITE(6,670)DHM,X12,VM
670  FORMAT(/,5X,'DHM =',F10.4,3X,'X12 =',F10.4,'VM =',F10.6)
      IF(IVOL.NE.0)GO TO 5000
600  WRITE(6,300) DPDF2,DTDF2,D1,D2,D3,D4,D5,D,S1,S2,S3,S4,S5,S6,S
300  FORMAT(/,7X,15F8.3)

      ISTEP=ISTEP+1
      PSF(ISTEP)=F2
      PST(ISTEP)=T
      PSP(ISTEP)=P
      PVM(ISTEP)=VM
      PS(ISTEP)=S
C  DECISION NOT TO SOLVE FOR / OR SOLVE FOR PART OR WHOLE OF SPINODAL
C      CURVE

      IF(ITEST.EQ.0) GO TO 1000

C  TO CONTROL NO OF POINTS TO BE SOLVED FOR IN SPINODAL CURVE

C  IF(ISTEP.GT.4 )GO TO 1000

700  F2=F2+0.05
      IF(F2.EQ.FIN) GO TO 1000
      IF(F2.GT.0.96) GO TO 800
      GO TO 105
800  F2=0.05
      GO TO 105
1000 CONTINUE
      WRITE(6,2000)

```

```

2000 FORMAT(/,9X,' FRAC    TEMP    PRESS    VOL    X12
      1 Q12  ERROR    ')
      IF(IVOL.EQ.0) GO TO 5500
5000 GO TO 7000
5500 CONTINUE
      DO 6000 IS=1,ISTEP
6000 WRITE(6,6500)PSF(IS),PST(IS),PSP(IS),PVM(IS),X12,Q12,PS(IS)
6500 FORMAT(5X,7F10.5)
4000 CONTINUE
      ISTEP=0
7000 CONTINUE
      STOP
      END

```

SUBROUTINE SPIN1

```

COMMON /A/VRS(2),LPROB,PHS(2),ALPHA(2),GAMMA(2),TRS(2),THS(2)
COMMON /B/X12,Q12,F1,F2,P,TH,PH,TR,PR,THETA1,THETA2,LASTEP
COMMON /C/V1R,V2R,T1H,T2H,P1H,P2H,T1R,T2R,RV,SF12,S21,V13,R12
COMMON /D/ FIN,TIN,VM,ISTEP,T,S,B5
COMMON/E/D1,D2,D3,D4,D5,D,S1,S2,S3,S4,S5,S6,DPDF2,DTDF2

```

C PRELIMINARIES CALCULATION OF THE QUANTITY D

C NOTE THAT VOLUMES CALCULATED ARE RAISED TO THE POWER $1/3$ $V13$

```

DPDF2=P*(P1H-P2H-X12*THETA2*(1.-SF12))/PH**2
DTDF2=(DPDF2*TR/PR)+(P2H*T2R-P1H*T1R)/PH
D1=(PR/TR)+(1./TR*V13**6)
D2=2./V13**9
D3=3.*V13-2.
D4=3.*V13**5*(V13-1.)**2
D5=D3/D4
D=(DPDF2-DTDF2*D1)/(D2-D5*TR)

```

C SPINODAL EQUATION

C IN THIS EQUATION THE QUANTITY S IS THE LHS OF EQN EXPECTED ZERO

```

S1=(-1./F1+(1.-R12))*RV
S2=(-D*P1H/T1H)*(V13**3-V13**2)

```

```

S3=((P1H/V13**6)+P)*D/T
S4=2.*X12*THETA2**2*THETA1/(T*V13**3*F1*F2)
S5=-X12*D*THETA2**2/(T*V13**6)
S6=(-2.*Q12*THETA2**2*THETA1)/(F1*F2)
S=S1+S2+S3+S4+S5+S6
C   WRITE(6,155) DPDF2,DTDF2,D,S2,S3,S5,S6,S,X12,Q12,PR,TH,TR
C155  FORMAT(2X,13F10.4)
      RETURN
      END

SUBROUTINE MIX
COMMON /A/VRS(2),LPROB,PHS(2),ALPHA(2),GAMMA(2),TRS(2),THS(2)
COMMON /B/X12,Q12,F1,F2,P,TH,PH,TR,PR,THETA1,THETA2,LASTEP
COMMON /C/V1R,V2R,T1H,T2H,P1H,P2H,T1R,T2R,RV,SF12,S21,V13,R12
COMMON /D/ FIN,TIN,VM,ISTEP,T,S,B5
C THIS ROUTINE EVALUATES THE NEW REDUCED TEMPERATURE AND VOLUME
C FOR THE MIXTURE EACH TIME THERE IS A CHANGE OF OPERATING TEMP

PH=P1H*F1+P2H*F2-F1*THETA2*X12
B1=F1*P1H/T1H
B2=F2*P2H/T2H
TH=PH/(B1+B2)
PR=P/PH

TR=T/TH
ADD=0.001
CP=1./3.
VM=1.0
C   IF(F2.GT.0.6)VM=1.4
      IC=0
150  B4=VM
      VM=B4 +ADD
      IF(IP.NE.1) GO TO 151
      A=(1./(1.-TR*VM))**3
      GO TO 154
151  AP=VM*TR/(PR*VM**2+1.)

```

```

      A=(1./(1.-AP))**3
154  B5=ABS(A-VM)
C    IF(IC.LT.5) GO TO 155
C    IF(IC.GT.LPROB) GO TO 155
C    GO TO 156
C 155  WRITE(6,190) B5,T,VM
156  IC=IC+1
      IF(IC.EQ.LASTEP) GO TO 157
      GO TO 159
157  WRITE(6,158)IC
158  FORMAT(20X,'LASTEP NOT ENOUGH FOR V-CAL SEE OUTPUT',I6)
      GO TO 180
159  IF(B5.LT.0.0005)GO TO 180
      GO TO 150
C 170  WRITE(6,190) B5,T,VM
180  V13=VM**CP
      IF(ISTEP.NE.80)GO TO 185
      WRITE(6,190) B5,T,VM
185  CONTINUE
190  FORMAT(/,2X,'DIFF = ',F9.4,' TEMP = ',F9.4,' REDUCED VOLUME OF
1 MIXTURE =',F9.4,/)
      RETURN
      END

```

```

SUBROUTINE INTPAR
COMMON /A/VRS(2),LPROB,PHS(2),ALPHA(2),GAMMA(2),TRS(2),THS(2)
COMMON /B/X12,Q12,F1,F2,P,TH,PH,TR,PR,THETA1,THETA2,LASTEP
COMMON /C/V1R,V2R,T1H,T2H,P1H,P2H,T1R,T2R,RV,SF12,S21,V13,R12
COMMON /D/ FIN,TIN,VM,ISTEP,T,S,B5
C THIS ROUTINE IS TO EVALUATE THE INTERACTION PARAMETER Q12 AT START
C OF THE CALCULATIONS: IT IS CALCULATED ONLY ONCE AT EACH PRESSURE

```

```

      ADD=0.005
      ADD1=0.0025
      Q12=-0.05
      IC=0

```

```

        CALL SPIN1
        IF(S.EQ.0.) GO TO 400
250  IF(S.GT.0.) GO TO 330
280  Q12=Q12-ADD
        LOOP=1
        CALL SPIN1
        Q121=Q12-ADD1
        IC=IC+1
        IF(IC.EQ.LASTEP)GO TO 450
        IF(S.GT.0.) GO TO 390
        IF(S.EQ.0.) GO TO 400
        IF(IC.GT.LPROB) GO TO 281
        GO TO 291
281  WRITE(6,600) IC,F2,Q121,S
291  CONTINUE
        GO TO 280
330  Z=Q12
340  Q12=Q12+ADD
        LOOP=2
        CALL SPIN1
        Z1=Q12+ADD1
        IC=IC+1
        IF(IC.EQ.LASTEP) GO TO 450
        IF(IC.GT.LPROB)GO TO 370
        GO TO 371
370  WRITE(6,600) IC,F2,Z1,S
371  CONTINUE
        IF(S.GT.0.) GO TO 340
        IF(S.EQ.0.) GO TO 400
        WRITE(6,500) LOOP,F2,Z1
        GO TO 400
C    WRITE(6,500) LOOP,F2,Q121
390  Q12=Q121
        GO TO 400
450  WRITE(6,460)
460  FORMAT(/,20X,'LASTEP NOT ENOUGH FOR Q12 CALCULATIONS')

```

```

400 CONTINUE
C 400 WRITE(6,500) LOOP,F2,Q12
500 FORMAT(/,'LOOP=',I3,2X,'AT FRACTION F2='.F5.2,'FINAL Q12=',F9.6)
600 FORMAT(/,I3,10X,3F12.6)
      RETURN
      END

SUBROUTINE TEMPI
COMMON /A/VRS(2),LPROB,PHS(2),ALPHA(2),GAMMA(2),TRS(2),THS(2)
COMMON /B/X12,Q12,F1,F2,P,TH,PH,TR,PR,THETA1,THETA2,LASTEP
COMMON /C/V1R,V2R,T1H,T2H,P1H,P2H,T1R,T2R,RV,SF12,S21,V13,R12
COMMON /D/ FIN,TIN,VM,ISTEP,T,S,B5
C THIS ROUTINE SEARCHES FOR THE TEMPERATURE AT A GIVEN MIXTURE FRACTION
C+++++++ACTIVATE C1-C9 WHEN NOT SURE ABOUT T AS FUNCTION OF S

      IN=0
      IPP=0
100   T=TIN
C     ADD=0.
      TMIN=290.
      TMAX=1000.
C     DO 210 IK=1,25
C     T=T+ADD
      CALL MIX
      CALL SPIN1
C     IF(S.LT.0.)ADD=-1.
C     IF(S.GT.0.)ADD=1.
C     WRITE(6,205)T,S
C 205 FORMAT(/,10X,2F10.5)
C 210 CONTINUE
C     GO TO 1000
      IF(S.EQ.0.)GO TO 400
C ++++++=====CHECK SIGN EITHER LT/GT AND CONS. WITH OTHERS
250 IF(S.LT.0.)GO TO 330
280 T=T+2.
      IF(T.GT.TMAX.OR.T.LT.TMIN ) GO TO 400

```

```

CALL MIX
CALL SPIN1
T11=T-1.
C+++++=====CHECK THIS SIGN ==SAME AS 1=====
  IF(S.LT.0.) GO TO 390
  IF(S.EQ.0.) GO TO 400
  IN=IN+1
  LOPP=1
C   IF(IN.LT.10.AND.F2.LT.FIN)WRITE(6,500)LOPP,IN,T,S
  IF(IN.GT.LASTEP) WRITE(6,500)LOPP,IN,T,S
  IF(IN.GT.LASTEP) GO TO 400
  GO TO 280
330 Z=T
340 T=T-2.
  IF(T.GT.TMAX.OR.T.LT.TMIN ) GO TO 400
  CALL MIX
  CALL SPIN1
  Z1=T-1.
  IPP=IPP+1
  LOPP=2
C   IF(IPP.LT.10.AND.F2.LT.FIN) WRITE(6,500)LOOP,IPP,T,S
  IF(IPP.GT.LASTEP)WRITE(6,500) LOPP,IPP,T,S
  IF(IPP.GT.LASTEP) GO TO 400
C+++++L++++CHECK THIS SIGN SAME 1 AND 2=====
  IF(S.LT.0.) GO TO 340
  IF(S.EQ.0.) GO TO 400
  T=Z1
  GO TO 400
390 T=T11
400 CONTINUE
500 FORMAT(2X,'LOOP=',I3,5X,I3,2X,2F12.6)
C1000 CONTINUE
  RETURN
  END

```

```

SUBROUTINE TEMP2
COMMON /A/VRS(2),LPROB,PHS(2),ALPHA(2),GAMMA(2),TRS(2),THS(2)
COMMON /B/X12,Q12,F1,F2,P,TH,PH,TR,PR,THETA1,THETA2,LASTEP
COMMON /C/V1R,V2R,T1H,T2H,P1H,P2H,T1R,T2R,RV,SF12,S21,V13,R12
COMMON /D/ FIN,TIN,VM,ISTEP,T,S,B5
C THIS ROUTINE SEARCHES FOR THE TEMPERATURE AT A GIVEN MIXTURE FRACTION
C+++++++ACTIVATE C1-C9 WHEN NOT SURE ABOUT T AS FUNCTION OF S

      IN=0
      IPP=0
100   T=TIN
C     ADD=0.
      TMIN=290.
      TMAX=1000.
C     DO 210 IK=1,25
C     T=T+ADD
      CALL MIX
      CALL SPIN1
C     IF(S.LT.0.)ADD=-1.
C     IF(S.GT.0.)ADD=1.
C     WRITE(6.205)T,S
C 205  FORMAT(/,10X,2F10.5)
C 210  CONTINUE
C     GO TO 1000
      IF(S.EQ.0.)GO TO 400
C ++++++=====CHECK SIGN EITHER LT/GT AND CONS. WITH OTHERS
250  IF(S.GT.0.)GO TO 330
280  T=T+1.
      IF(T.GT.TMAX.OR.T.LT.TMIN ) GO TO 400
      CALL MIX
      CALL SPIN1
      T11=T-0.5
C+++++++=====CHECK THIS SIGN ==SAME AS 1=====
      IF(S.GT.0.) GO TO 390
      IF(S.EQ.0.) GO TO 400
      IN=IN+1

```

```

      LOPP=1
C      IF(IN.LT.10.AND.F2.LT.FIN)WRITE(6,500)LOPP,IN,T,S
      IF(IN.GT.LASTEP) WRITE(6,500)LOPP,IN,T,S
      IF(IN.GT.LASTEP) GO TO 400
      GO TO 280
330  Z=T
340  T=T-1.
      IF(T.GT.TMAX.OR.T.LT.TMIN ) GO TO 400
      CALL MIX
      CALL SPIN1
      Z1=T-0.5
      IPP=IPP+1
      LOPP=2
C      IF(IPP.LT.10.AND.F2.LT.FIN) WRITE(6,500)LOOP,IPP,T,S
      IF(IPP.GT.LASTEP)WRITE(6,500) LOPP,IPP,T,S
      IF(IPP.GT.LASTEP) GO TO 400
C++++++L+++++CHECK THIS SIGN SAME 1 AND 2=====
      IF(S.GT.0.) GO TO 340
      IF(S.EQ.0.) GO TO 400
      T=Z1
      GO TO 400
390  T=T!1
400  CONTINUE
500  FORMAT(2X,'LOOP='13.5X,13.2X,2F12.6)
C1000 CONTINUE
      RETURN
      END

```

```

LI.
  10 MODE 0
  20 VDU 24,0;240;1279;1023;
  30 VDU 28,0,31,79,26
  40 VDU 29,0;245;
  50 DIM AP% 500
  60 FOR Z=0 TO 3 STEP 3
  70 P%=AP%
  80 [
  90 OPTZ
100.start
110 LDA#0
120 TAX
130 LDA&FCC0
140 NOP
150.busy
160 LDA&FCC1
170 AND#&40
180 BEQ busy
190.hold
200 LDA&FCC2
210 AND#&EF
220 STA&FCC2
230.strobe
240 LDA&FCC1
250 BMI read
260 JMP strobe
270 .read
280 LDA&FCC0
290 AND#&0F
300 STA&S0,X
310 INX
320 TXA
330 EOR#&5
340 BNE strobe
350 LDA#&10
360 ORA&FCC2
370 STA&FCC2
380 RTS
390 ]
400 NEXT Z
410 CLS
420 PROC initialise
430 PRINT " "
440 INPUT "PROPORTIONAL FACTOR?" K
450 INPUT "INTEGRAL TIME?" TINT
460 INPUT "DIFFERENTIAL TIME?" TDIF
470 INPUT "    " "DATE" "D$"
480 INPUT "    " "SYSTEM" "P$"
490 INPUT "SAMPLE COMPOSITION %" "S$"
500 INPUT "FILE NAME" "R$"

```

```

500 INPUT "FILE NAME" "R$
510 INPUT "SAMPLE TIME?" DT
520 INPUT "TEMPERATURE GRADIENT? DEGREES C/MINUTE" TEMPGRAD
530 INPUT "FINAL TEMPERATURE? DEGREES C" FTEMP
540 IF FTEMP>200 GOTO 530
550 SUM=0::LERR=0:PINT=0:R=0:X=0:DRTEMP=0:DRSETPP=0:ALFA=0:BETA=0
560 TIME=0
570 t1=TIME
580 STEMP=FNread(0):STEMP=FNread(0):STEMP=STEMP DIV 10
590 SETP=STEMP+TIME*TEMPGRAD/6000
600 IF SETP<FTEMP GOTO 630
605 datfile=OPENOUT "DATFILE"
610 PROCfinish
620 END
630 PROCpid
640 PROctiming
650 GOTO 590
660 END
665 CLOSE`datfile
670DEF PROCinitialise
680DRA=&FCC0
690CRA=&FCC1
700DRB=&FCC2
710CRB=&FCC3
720?CRA=0
730?DRA=0
740?CRA=&4
750?CRB=0
760?DRB=&FF
770?CRB=&4
780 CLG:GCOL 0,3
790 MOVE 0,0:DRAW 0,1024:MOVE 0,0:DRAW 1279,0
800ENDPROC
810DEF FNread(channel)
820 ?DRB=?DRB AND &9F
830 ?DRB=?DRB OR &10
840dummy=channel*20
850?DRB=?DRB OR dummy
860 CALLstart
870data=0
880FOR digit=0 TO &4
890 data=data+?(&84-digit)*10^digit
900NEXT digit
910=data
920 DEF PROCpid
930 TEMP=FNread(0)
940 TEMP=FNread(0)
950 TEMP=TEMP/10
960 PERR=SETP-TEMP
970 SUM=R+(PERR*X*DT)

```

```

970 SUM=R+(PERR*K*DT)
980 Q=(SUM)/DIV(TINT)
990 R=(SUM)/MOD(TINT)
1000 PINT=PINT+Q
1010 PROP=K*PERR
1020 DERR=PERR-LERR
1030 LERR=PERR
1040 DIF=(K*TDIF*DERR)/DIV(DT)
1050 CONV=PROP+PINT+DIF
1060 CONV=INT CONV
1070 IF CONV<=0 CONV=0
1080 IF CONV>=15 CONV=15
1090 DUM=?DRB
1100 DUM=DUM AND &F0
1110 DUM=DUM+CONV
1120 ?DRB=DUM
1130 ALFA=ALFA+1
1140 BETA=ALFA MOD (15)
1150 IF BETA <> 0 GOTO 1270
1160 DRTEMP=TEMP*5:DRSETP=SETP*5
1170 MOVE X,DRTEMPP:DRAW X,DRTEMP
1180 DRTEMPP=DRTEMP
1190 MOVE X,DRSETPP:DRAW X,DRSETP
1200 DRSETPP=DRSETP
1210 X=X+1
1220 LIGHT=FNread(1):LIGHT=FNread(1)
1230 PRESS=FNread(2):PRESS=FNread(2)
1240 CLS
1250 @%=&20109
1255 VDU2
1260 PRINT"TIME"TIME/100,"TEMPERATURE"TEMP,"PRESSURE"PRESS,"LIGHT"LIGHT
1265 VDU3
1270 ENDPROC
1280 DEF PROctiming
1290 t2=TIME
1300 t3=t2-t1
1310 IF t3<DT*100 GOTO 1290
1320 t1=t2
1330 ENDPROC
1340 DEF PROCfinish
1350 ?DRB=?DRB AND &F0
1360 PRINT" HEATER TURNED OFF"
1370 ENDPROC

```

PROGRAM 'TURB' FOR RUNNING THE TURBIDIMETER

OLD

LI.

```
10 MODE0:%DRIVE1
20 index=0
30 channel=0
40 digit=0
50 INPUT'''DATE "D$
55 INPUT"SYSTEM"P$
60 INPUT"SAMPLE COMPOSITION"S$
70 INPUT"HEATING/COOLING RATE"R$
80 INPUT"WHAT IS THE SAMPLING PERIOD IN SECONDS "seconds
90 samnum=0
100 INPUT'"HOW MANY READINGS WOULD YOU LIKE TO TAKE"/samnum :CLS
110 PRINT'"DATE "D$ :PRINT"SYSTEM "P$:PRINT"SAMPLE COMPOSITION
    "S$ :PRINT"HEATING/COOLING RATE. "R$
111 PRINT"SAMPLING PERIOD IN SECONDS"seconds :PRINT"NUMBER OF
    READINGS"samnum,'''
120 VDUS
130 PRINT "WOULD YOU LIKE TO START ? (Y:N) "
140 INPUT res$
150 IF res$<>"Y" GOTO130
160 CLOSE#0
170 datfile= OPENOUT ("DATFILE")
180 DELAY=0
190 MEMO=&4000
200 DDRA=&FCC0
210 CRA=&FCC1
220 DDRB=&FCC2
230 CRB=&FCC3
240 ?CRA=0
250 ?DDRA=0
260 ?CRA=&4
270 ?CRB=0
280 ?DDRB=&FF
290 ?CRB=&4
300 ?DDRB=?DDRB AND &EF
```

```

300?DDRB=?DDRB AND &EF
310 delay=DELAY%100
320TIME=0
330 time=TIME
340IF time<delay GOTO 330
350 FOR channel=&0 TO &7 STEP 1
360?DDRB=(?DDRB AND &F8)OR(channel AND&07)
370 TIME=0
380 t=TIME
390 IF t<20 GOTO 380
400 ?DDRB=?DDRB OR &8
410 TIME=0
420 t=TIME
430 IF t<20 GOTO 420
440 ?DDRB=?DDRB AND &F7
450 ready=?DDRA
460IF (ready AND &80)=&80 GOTO 450
470FOR digit=&3 TO 0 STEP -1
480?DDRB=?DDRB AND &1F
490?DDRB=?DDRB OR (digit%&20)
500?MEMO=?DDRA AND &0F
510MEMO=MEMO+1
520NEXT digit
530NEXT channel
540?DDRB=?DDRB OR &10
550 index=index+1
560 FOR count=(MEMO-&20) TO (MEMO-&4) STEP 4
570 L=L+1
580 KL=? (count)*1000+?(count+1)*100+?(count+2)*10+?(count+3)
590 IF L>=5 THEN LOT=LOT+KL
600 IF L<5 PRINTKL;
610 IF L<5 PRINT&datfile,KL
620 NEXT count
630 PRINT&datfile,LOT/4 :PRINTLOT/4
640samper=seconds
650 TIME=0
660 t=TIME
670IFt<samper GOTO 660
680 samnum=samnum-1
690 L=0 : LOT=0
700 IF samnum>0 GOTO 300
710 CLOSE&datfile
720 PRINT " "
730 PRINT "SAMPLING FINISHED"
740 %DRIVE0
745 VDU3

```

REFERENCES

A

1. Abe, A. and Flory, P.J. (1965)
J. Am. Chem. Soc., 87:9, 1838
2. Abe, A. and Flory, P.J. (1966)
J. Am. Chem. Soc., 88:13, 2887
3. Allen, G., Gee, G. and Nicholson, J.P. (1960)
Polymer, 1, 56
4. Allen, G., Gee, G. and Nicholson, J.P. (1961)
Polymer, 2, 8
5. Allen, G. and Yip, C.W (1976)
Unpublished Results
6. Aharoni, S.M. (1978)
Macromolecules, 11, 277
7. Akiyama, S. (1972)
Bull. Chem. Soc. Japan, 45, 1381

B

1. Bank, M., Leffingwell, J. and Thies, C. (1969)
Polym. Prepr., 10, 622
2. Bank, M., Leffingwell, J. and Thies, C. (1971)
Macromolecules, 4, 43
3. Bank, M., Leffingwell, J. and Thies, C. (1972)
J. Polym. Sci., A-2 10, 1097

4. Ballard, D.G.H., Rayner, M.G. and Schelten, J. (1976)
Polymer, 17, 640
5. Barlow, J.W., Lai, C.H. and Paul, D.R. (1988)
To be published
6. Bellemans, A. and Naar–Collin, C. (1955)
J. Polym. Sci., 121
7. Beng, G.C and Fox, T.G. (1968)
Adv. Pol. Sci., 5, 261.
8. Billmeyer Jnr., F.W. (1971)
'Textbook of Polymer Science'
2nd Ed., Publishers Wiley & Sons Inc. N.Y.
9. Bohn, L. (1975)
'Polymer Handbook' Bandrup, J. and Immergut, E.H.
2nd Ed., 111–211, Wiley Interscience, N.Y.
10. Bondi, A. (1964)
J. Phys. Chem., 68, 441.
11. Boyer, R.F. and Spencer, R.S. (1944)
J. Appl. Phys., 15, 402.
12. Buchner, E.H. (1906)
Z. Ph. Ch., 54, 665.

C

1. Cahn, J.W. (1965)
J. Chem. Phys., 42, 93.
2. Chai, Z. and Sun, R. (1983)
Polymer, 24, 263.

3. Chai, Z. and Walsh, D.J. (1983)
Eur. Polym. J., 19, 519.
4. Chalal, S.R., Kao, W.P. and Patterson, D. (1973)
Far. Trans., 1, 1834.
5. Cheng, G.L. and Walsh, D.J. (1985)
Polymer, 25, 499.
6. Chien, Y.Y., Pearce, E.M. and Kwei, T.K. (1988)
Macromolecules, 21, 1616.
7. Chiou, J.S., Barlow, J.W. and Paul, D.R. (1987)
J. Polym. Sci., Polym. Phys. Ed., 25, 1459.
8. Chong, C.L. (1981)
PhD Thesis, Imperial College. London.
9. Christner, G.L. and Thomas, E.L. (1977)
J. Appl. Phys., 48, 4063.
10. Claesson, S., McAtee, Jnr., J. L. and Saabz, A. (1983)
J. Polym. Sci., Polym. Phys. Ed., 21, 1873–1881.
11. Coleman, M.M. and Zarian, J. (1979)
J. Polym. Sci., Polym. Phys. Ed., 17, 837.
12. Coleman, M.M., Zarian, J., Varnell, D.P. and Painter, P.C. (1977)
J. Polym. Sci., Polym. Phys. Letts., Ed. 15, 745.
13. Collins, E.A., Bares, J. and Billmeyer, Jr., F.W. (1973) in
'Experiments in Polym. Sci.', Wiley.
14. Cooper, D.R. and Booth, C. (1977)
Polymer, 18, 164.
15. Couchman, P.R. and Karasz, F.E. (1977)
J. Polym. Sci., Polym. Phys. Ed., 15, 1037.

16. Cowie, J.M.G. (1973) in
'Polymers: Chemistry and Physics of Modern Materials'
Published: Intertext Book Co. Ltd., Aylesbury, Bucks.
17. Cowie, J.M.G., Maconnachie, A. and Ranson, R.J. (1971)
Macromolecules, 4(1), 57.
18. Cowie, J.M.G. and Saeki, S. (1981)
Polym. Bull., 6, 75–80.
19. Cruz, C.A., Barlow, J.W. and Paul, D.R. (1979)
Macromolecules, 12, 726.

D

1. Davis, D.D. and Kwei, T.K. (1980)
J. Polym. Sci., Polym. Phys. Ed., 18, 2337.
2. de Gennes, P.G. (1980)
J. Chem. Phys., 72, 4756.
3. Doube, C.P. and Walsh, D.J. (1979)
Polymer, 20, 115.
4. Dowbry, A. and Boyer–Kawenoki, F. (1947)
J. Polym. Sci., 2, 90.

E

1. Eichinger, B.E. and Flory, P.J. (1968)
Trans Faraday Soc., 64, 2035–2053, 2061–2065.
2. Eyring, H. (1936)
J. Chem. Phys., 4, 283.

3. Eyring, H. and Hirschfelder, J. (1937)
J. Phys. Chem., 41, 249.

F

1. Fernandez, A.C., Barlow, J.W. and Paul, D.R. (1986)
Polymer, 27, 1788.
2. Flory, P.J. (1941)
J. Chem. Phys., 9, 660.
3. Flory, P.J. (1942)
J. Chem. Phys., 10, 51.
4. Flory, P.J. (1953)
'Principles of Polymer Chemistry'
Cornell University Press, Ithaca, N.Y.
5. Flory, P.J. (1965)
J. Am. Chem. Soc., 87:89, 1833.
6. Flory, P.J., Ellenson, J.L. and Eichinger, B.E. (1968)
Macromolecules, 1, 279.
7. Flory, P.J. Orwoll, R.A. and Vrij, A. (1964)
J. Am. Chem. Soc., 86, 3507, 3515.
8. Fox, Jnr., T.G. (1956)
Bull. Am. Phys. Soc., 1, 123.
9. Fox, Jnr., T.G. and Flory, P.J. (1950)
J. Appl. Phys., 21, 581.
10. Fox, Jnr., T.G. and Flory, P.J. (1954)
J. Appl. Phys., 14, 315.

11. Fox, T.G. and Flory, P.J. (1954A)
J. Polym. Sci., 14, 314
12. Fowler, M.E., Barlow, J.W. and Paul, D.R. (1987)
Polymer, 28, 1177.
13. Friday, A., Cooper, D.R. and Booth, C. (1977)
Polymer, 18, 171.
14. Fried, J.R. (1983)
'Developments in Polymer Characterisation'
Ed. Dawkins, J.V., Appl. Sci., (London), 4, 39.

G

1. Garcia, D. (1984)
J. Polym. Sci., Polym. Phys. Ed., 22, 107.
2. Garcia, D. (1984)
J. Polym. Sci., Polym. Phys. Ed., 22, 1773.
3. Gaekle, D. and Patterson, D. (1972)
Macromolecules, 2, 136.
4. Geerissen, H., Schmidt, J.R. and Wolf, B.A. (1982)
J. Appl. Polym. Sci., 27, 1277.
5. Gelles, R., Gelles, F. and Curtis, W. (1983)
Macromolecules, 16, 1448–1456.
6. Gilchrist, A., Early, J.E. and Cole, R.H. (1957)
J. Chem. Phys., 26, 196.

1. Hadziioannou, G., Stein, R.S. (1984)
Macromolecules, 17, 567.
2. Halary, J.L., Ubrich, J.M., Monnerie, L., Yang, H, and Stein, R.S.
(1985)
Polymer, 26, (Comm.), 73.
3. Halary, J.L., Ubrich, J.M., Munzi, J.M., Monnerie, L. and Stein, R.S.
(1984)
Polymer, 25, 856.
4. Han. Charles, C., Bauer, Barry, J., Clark, J.C., Yoshio Muroga, Yushu
Matsushita, Mamoru Okada, Qui Tran–cong, and Taihun Chang and
Sanchez, Isaac C.
Polymer, 29, 2002.
5. Harris, J.E., Paul, D.R and Barlow, J.W.
Adv. Chem. Ser., 206, 43.
6. Hashimoto, T., Kumaki, J. and Kawai, H. (1983)
Macromolecules, 16, 641.
7. Hickmann, J.J. and Ikeda, R.M. (1973)
J. Polym. Sci., Polym. Phys. Ed., 11, 1713.
8. Higgins, J.S. (1985) in
'Polymer Blends and Mixtures', Ed. D.J. Walsh, J.S. Higgins and A.
Maconnachie, NATO ASI Series No. 89.
9. Higgins, J.S. and Maconnachie, A. (1985) in
'Methods in Experimental Physics: Neutron Scattering', Ed. K. Scold
and D.L Price, Academic Press, N.Y.

10. Hildebrand, J.H and Scott, R.L. (1964)
'The Solubility of Non-electrolytes', Dover Publications, N.Y.
11. Hildebrand, J.H., Praunsnitz, J.M. and Scott, R.L. (1970)
'Regular and Related Solutions', Van Nostrand Reinhold Co.
12. Hildebrand, J.H. and Scott, R.L. (1962) Ch. 6, 'Regular Solutions',
Prentice-Hall, Englewood Cliffs, N.J.
13. Hildebrand, J.H. and Wood, S.E. (1933)
J. Chem. Phys., 1, 817.
14. Hiramatsu, N., Hashida, S., Muneshisa, J. and Hirakawa, S. (1983)
Fukuoka Univ. Sci. Reports, 13(1), 39-44.
15. Hirshchfelder, J.O., Stevenson, D.P. and Eyring, H. (1937)
J. Chem. Phys., 5, 896.
16. Höcker, H., Blake, G.J. and Flory, P.J. (1970)
Trans. Far. Soc., 67, 2251.
17. Höcker, H., and Flory, P.J. (1968)
Trans. Far. Soc., 64, 1188.
18. Holt, T., Edwards, D. (1965)
J. Appl. Chem., 15, 223.
19. Hourston, D.J. and Hughes. I.D. (1978)
Polymer, 19, 1181.
20. Hsu, C.C. and Prausnitz, J.M. (1974)
Macromolecules, 7, 320.
21. Hugelin, C. and Dondos, A. (1969)
Makrom. Chem., 126, 206.
22. Huggins, M.L. (1941)
J. Chem. Phys., 9, 660.

23. Huggins, M.L. (1942)
Ann. N.Y. Acad. Sci., 43, 1.

I

1. Igonin, L.A., Ovchinnikov, Y.V. and Kargin, V.A. (1959)
Doklady Akad. Nauk, S.S.S.R., 128, 127.

J

1. Jelenic, J., Kirste, R.G. Oberthur, R.C. Schmitt–Stretch, S. and
Schmitt, B.J. (1984)
Makromol. Chem. 185, 129.

K

1. Ke, B. (1964)
'Newer Methods of Polymer Characterisation', Wiley, N.Y.
2. Koberstein, J., Russel, J.P. and Stein, R.S. (1979)
J. Polym. Sci., Phy. Ed., 17, 1719.
3. Konningsveld, R. and Kleintjens, L.A. (1971)
Macromolecules, 4, 637.
4. Konningsveld, R. and Kleintjens, L.A. (1977)
Br. Polym. J., 9, 212.
5. Konningsveld, R., Kleintjens, L.A. and Onclin, M.H. (1980)
J. Macrom. Sci. Phys., B18(3), 363.

6. Konningsveld, R., Kleintjens, L.A. and Schaffelers, H.M. (1977)
Pure Appl. Chem., 39, 1.
7. Krause, S.J. (1972)
Macrom. Sci. (C), 7, 251.
8. Krause, S. in
'Polymer Blends', D. Paul and S. Newman Edn. Acad., N.Y., (1978).
9. Krimm, S. and Tobolsky, A.V. (1951)
J. Polym. Sci., 6, 667.
10. Kwei, T.K., Nishi, T. and Roberts. R.F. (1974)
Macromolecules, 7, 667.
11. Kwei, T. K., Pearce, E.M. and Min. B.Y. (1985)
Macromolecules, 18, 2326.

L

1. Lai, C.H.,
"Predicting Polymer–Polymer Miscibility with a Group Contribution Method", PhD Dissertation, The University of Texas at Austin (1988).
2. Lai, C.H., Paul, D.R. and Barlow. J.W. (1988)
Macromolecules, 21, 2492.
3. Lai, C.H., Paul, D.R. and Barlow, J.W. (in press)
"Group Contribution Methods for Predicting Polymer–Polymer Miscibility from Heats of Mixing of Liquids II. Polyester Containing Binary Blends".
Macromolecules.
4. Larbi, B.C.F., Leloup, S. Halary, J.L. and Monnerie, L. (1986)
Polymer Communications, 27,23.

5. Liddell, A.H., Swinton, F.L. (1970)
Disc. Far. Soc., 49, 115.
6. Lu, F.J., Benedetti, E. and Hsu, S.L. (1983)
Macromolecules, 16, 1525.

M

1. MacKnight, W.J., Karasz, F.E. and Fried, J.R. (1978)
Ch. 5 of 'Polymer Blends', Paul and Newman, ed. Acad. Press, N.Y.,
London.
2. Maconnachie, A. and Kambour, R.P. and Bopp, R.C. (1984)
Polymer, 25, 357.
3. Maconnachie, A. and Richards, R.W. (1978)
Polymer, 19, 739.
4. Malcolm, G.N. and Rowlinson, J.S. (1957)
Trans. Faraday Soc., 53, 921.
5. Manche, E.P. and Carrol, B. (1972) in
'Physical Methods in Macromolecular Chemistry', Vol. 2, Ch. 4, Dekker,
N.Y.
6. Manson, J.A. and Arquette, G.J. (1960)
Die Macromol. Chem., 37, 187.
7. Matsuo, M., Nozaki, C. Jyo, T. (1969)
Polym. Engr. Sci., 9, 197.
8. McDonald, C.J. and Claesson, S. (1973)
Chemica Scripta, 4, 155–162.
9. McDonald, C.J. and Claesson, S. (1976)
Chemica Scripta, 9, 36.

10. McKinney, J.E. and Belcher, H.V. (1961)
presented at Am. Phys. Soc. Meeting, Monterey, California.
11. McMaster, L.P. (1973)
Macromolecules, 6, 760.
12. McMaster, L.P. (1974)
Polym. Prepr. Chem. Soc., Dev. Polym. Chem.
13. McMaster, L.P. (1975)
Adv. Chem. Series, 142, 43.
14. Meyer, M., Sande, J.V. and Uhlman, D.R. (1978)
J. Polym. Sci., Phys. Ed., 6, 2005.
15. Min, K.E. and Paul, D.R. (1987)
Macromolecules, 20, 2828.
16. Min, K.E. and Paul, D.R. (1988)
J. Polym. Sci., Part B, Polym. Phys., 26, 2257–2266.
17. Morawetz, H. (1983)
Polym. Engn. and Sci., 23:12, 689.
18. Murrayama, T. (1986)
Encyclopaedia of Polymer Science and Technology, 5, 299, Wiley and Sons, N.Y.
19. Murray, C.T., Gilmer, J.W. and Stein, R.S. (1985)
Macromolecules, 18, 996–1002.

N

1. Natansohn, A. (1985)
J. Phys. Sci., Polym. Lett. Ed., 305–308.

2. Neilson, L.E. (1978)
'Predicting the Properties of Mixtures: Mixture Rules in Science and Engineering', Marcel Dekker, N.Y.
3. Nishi, T. (1980)
J. Macrom. Sci., Phys., B17, 517.

4. Nishi, T. (1977)
Rep. Prog. Polym. Phys., Japan, 20, 225.
5. Nishi, T. and Kwei, T.K. (1975)
6. Nishi, T. and Wang, T.T. and Kwei, T.K. (1975)
Macromolecules, 8, 227.
7. Nolle, A.W. and Billines, J.J. (1959)
J. Chem. Phys., 30, 84.

O

1. Olabisi, O. (1975)
Macromolecules, 18, 316.
2. Olabisi, O., Robeson, L.M. Shaw, M.T. (1979)
'Polymer-Polymer Miscibility', Acad. Press, N.Y.
3. O'Reilly, J.M. (1962)
J. Polym. Sci., 57, 429-444.
4. Orwoll, R.A. and Flory, P.J. (1967)
J. Am. Chem. Soc., 89, 6814-6822.

P

1. Paul, D.R. and Barlow, J.W. (1982) in
'Polymer compatibility and incompatibility: Principles and practice', K. Solc, Ed. Harwood Acad. Press (N.Y.), MM1 Press Symp. Series, Vol. 2, p 1.
2. Paul, D.R. Barlow, J.W., Bernstein, R.E. and Wahrmond, D.C. (1978)
Polym. Eng. Sci., 18, 1225.

3. Paul, D.R., Newman, S. (1978)
'Polymer Blends', Vol. I & II, Acad. Press, N.Y.
4. Patterson, D. (1968)
J. Polym. Sci., Part C, 16, 3379.
5. Patterson, D. and Delmas, G. (1970)
Disc. Faraday Soc., No. 49, 98.
6. Patterson, D. and Robard, A. (1978)
Macromolecules, 11, 690.
7. Porter, R.S. and Johnson, J.F. (1968)
Rheol. Acta, 7, 332.
8. Prigogine, I. (1957) Ch. 17,
'The Molecular Theory of Solutions', North-Holland Pub., Amsterdam.
9. Prigogine, I. Bellmans, A. and Naar-Collin, C. (1957)
J. Chem. Phys., 26, 751.
10. Prigogine, I., Trappenier, N. and Nathot, V. (1953)
J. Chem. Phys., 21, 559-560.
11. Prigogine, I., Trappenier, N. and Nathot, V. (1953)
Disc. Faraday Soc., 15, 93.

R

1. Rabek, J.F. (1980)
'Experimental Methods in Polymer Chemistry', Wiley.
2. Read, B.E., Dean, G.D., Duncan, J.C.
'Physical Methods of Chemistry', Ed. Rossiter, B.W., Hamilton, J.F.
and Baetzold, R.C., Wiley, Interscience, N.Y., 7 Ch. 1, (to be
published).

3. Reich, R. and Cohen, Y. (1981)
J. Polym. Sci., Phys. Ed., 19, 1255.
4. Rice, O.K. (1944)
J. Chem. Phys., 12, 1.
5. Richards, R.W. (1980) in
'Polymer Characterisation I', Ed. J.V. Dawkins, Appl. Sci., Publishers.
6. Richardson, M.J. (1978) in
'Developments in Polymer Characterisation', Ed. J.V. Dawkins, Appl.
Sci., London, 1, 205.
7. Robard, A., Patterson, D. and Delmas, G. (1977)
Macromolecules, 10, 706.
8. Roe, R.J., Zin, W.C. (1980)
Macromolecules, 13, 1221.
9. Roots, J. and Nyström, B. (1982)
Macromolecules, 15, 553–556.
10. Rosen, S.L. (1967)
Polym. Eng. Sci., 7, 2, 115.
11. Rostami, S. (1983)
PhD Thesis, Imperial College, London.
12. Rostami, S. and Walsh, D.J. (1985)
Macromolecules, 18, 1228.
13. Russell, T.P., Stein, R.S. (1982)
J. Polym. Sci., Polym. Phys. Ed., 20, 1593.

1. Saeki, S., Cowie, J.M.G., McEwan, I.J. (1982)
Polymer, 24, 60.
2. Saeki, S., Kumahara, N. Nakata, M. and Kaneko, M. (1975)
Polymer, 16, 445.
3. Saeki, S., Kumahara, N. and Kaneko, M. (1976)
Macromolecules, 9, 101.
4. Sanchez, I.C. and Lacombe, R.H. (1976)
J. Phys. Chem., 80, 2352–2368.
5. Scatchard, G. (1931)
Chem. Rev., 8, 321.
6. Scatchard, G. (1937)
Trans, Faraday Soc., 33. 160.
7. Schmitt, B.J., Kirste, R.G., Jelenic, J. (1980)
Macromol. Chem., 181, 1655,
8. Schneier, B. (1973)
J. Appl. Polym. Sci., 17, 3175.
9. Schulz, G.V. and Lechner, M. (1970)
J. Polym. Sci., A–2, 8, 1885.
10. Shur, Y.J., Randy, B. (1975)
J. Appl. Polym. Sci., 19, 1337, 2143.
11. Schwahn, D., Martenson, K. and Yee—Madeira, H. (1987)
Phys. Rev. Lett., 58, 1544.
12. Scott, R.L. (1949)
Chem. Phys., 17, 279.

13. Shiomi, T. Kohno, K., Yoneda, K., Tomita, T., Miya, M. and Imai, K.
(1985)
Macromolecules, 18, 414.
14. Simha, R. and Somcynsky, M. (1969)
Macromolecules, 2, 342.
15. Siow, K.S., Delmas, G. and Patterson, D. (1972)
Macromolecules, 5, 29.
16. Smolders, C.A. van Aartsen, J.J. and Steenbergen, A. (1971)
Kolloid Z. Polym., 243, 14.
17. Spencer, R.S. and Dillon, R.E. (1949)
J. Colloid Sci., 4, 241.
18. Sperling, L.H. (1984)
Polym. Engineering and Sci., 24, 1.
19. Stein, R.S. (1978)
Ch. 9 of 'Polymer Blends', Ed. Paul and Newman.
20. Strazielle, C. and Benoit, H. (1975)
Macromolecules, 8, 203.
21. Strobl, G.R. Bendler, J.T., Kambour, R.P. and Shultz, A.R. (1986)
Macromolecules, 19, 2683–2689.
22. Suess, M., Kressler, J. and Kammer, H.W. (1987)
Polymer, 28, 957.

T

1. Tabb, D.L. and Koenig, J.L (1975)
Macromolecules, 8, 929.

2. Tagayanaki, M. (1963)
'Viscoelastic properties of crystalline polymers', Memorandum of Faculty of Engineering, Kyushu University, 23, 1.
3. Tager, A.A., Scholokhovich, T.I. and Bessonov, Ju.S. (1975)
Eup. Polym. J., 11, 321.
4. Timmermans, J. (1936)
'Les solutions concentrées', Paris.
5. Tompa, H. (1956)
'Polymer Solutions', Butterworth Scientific Publications, London, 118, 170.
6. Tonks, L. (1936)
Phys. Rev., 50, 955.
7. Toshiaki, O., Takashi, I. and Kammer, H.W. (1985)
Macromolecules, 18, 2092–2094.
8. Tripathi, J.B.P. (1979)
PhD Thesis, Imperial College, London.
9. Turi, E.A. (1981)
'Thermal Characterization of Polymeric Materials', Acad. Press, N.Y.

U

1. Ubrich, J.M., Larbi, B.—C.F., Halary, J.L., Monnerie, L., Bauer, B. and Han, C.C. (in press)
Macromolecules.

V

1. Van Aartsen, J.J. (1970)
Eur. Polym. J., 6, 919.
2. van der Lee, (1900)
Z. Ph. Ch., 33, 622.
3. van Oene, H in Ch. 7 of
'Polymer Blends', D.R. Paul and S. Newman.

W

1. Walsh, D.J. and Cheng, G.L. (1982)
Polymer, 23,1965.
2. Walsh, D.J., Higgins, J.S., Doube, C.P. and McKeown, J.G. (1981)
Polymer, 22, 168.
3. Walsh, D.J. and McKeown, J.G. (1980)
Polymer, 21, 1330.
4. Walsh, D.J. and Rostami, S. (1985)
Polymer, 26, 418.
5. Warner, M., Higgins, J.S. and Carter, A.J. (1983)
Macromolecules, 16, 1931.
6. Weeks, N.E., Karasz, F.E. and MacKnight, W. J. (1977)
J. Appl. Phys., 48, 4068.
7. Wetton, R.E. (1986)
'Developments in Polymer Characterisation', Ed. Dawkins, J.V.,
Elsevier, (London), 5, 179.
8. Wignall, G.D., Child, H.R., Li-Aravena, F. (1980)
Polymer, 21, 131.

9. Wolf, B.A. and Geerissen, H. (1981)
Colloid Polym. Sci., 259, 1214.
10. Wolf, B.A. and Jend, R. (1979)
Macromolecules, 12, 732.
11. Wolf, B.A. and Schmidt, J.R. (1979)
Makrom. Chem., 180, 517.
12. Woo, E.M., Barlow, J.W. and Paul, D.R. (1985)
Polymer, 25, 763.
13. Wood, L.A. (1958)
J. Polym. Sci., 28, 319.
14. Work, J.L. (1973)
Polym. Engineering Sci., 13, 46.

Y

1. Yang, H., Hadziiodannou, G. and Stein, R.S. (1983)
J. Polym. Sci., Polym. Phys., Edn. 21,159.
2. Yang, H., Shibayama, M., Stein, R., Shimizu, N. and Hashimoto, T.
(1986)
Macromolecules, 19, 1667.
3. Yee, A.F. (1977)
Polym. Eng. Sci., 17, 213.

Z

1. Zachaius, S.L., ten Brinke, G., MacKnight, W.J. and Karasz, F.E. (1983)
Macromolecules, 16, 381.
2. Zakrzewski, G.A. (1973)
Polymer, 14, 347.
3. Ziska, J.J., Barlow, J.W. and Paul, D.R. (1981)
Polymer, 22, 918.