

**Imperial College  
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# **Application of Advanced Vibrational Spectroscopy to Polymers Processed with Supercritical CO<sub>2</sub>**

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*Never venture, never win*



## **DECLARATION OF OWN WORK**

This dissertation is a description of the work carried out in the Department of Chemical Engineering, Imperial College London between March 2003 and February 2006 under the supervision of Dr. Sergei G. Kazarian. Except where acknowledged the material presented is the original work of the author and no part of it has been submitted for a degree at this or any other university.

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## ABSTRACT

Increasing scrutiny over industrial activity has driven the search for environmentally friendly processing alternatives. Supercritical (sc) CO<sub>2</sub> functions as a transient plasticiser in polymer processing applications and offers intrinsic advantages. Exploiting the potential benefits provided by CO<sub>2</sub> requires a detailed understanding of the implications of CO<sub>2</sub> exposure to polymeric material. This thesis describes the use of the confocal Raman microscopy (CRM) and FTIR imaging to characterise polymers processed with scCO<sub>2</sub>.

The processing of semicrystalline polymers is a complex process due to possible CO<sub>2</sub>-induced morphological alterations to the matrix. The development of an experimental approach for studying semicrystalline polymers processed with scCO<sub>2</sub> via CRM, Raman mapping and FTIR imaging is described. A significant gradient in the degree of crystallinity normal to the surface of poly(ethylene terephthalate) (PET) film has been observed non-destructively with CRM and confirmed by a complementary analysis of microtomed film sections via Raman mapping and transmission FTIR imaging. A model system of PET film impregnated with Disperse Red 1 (DR1) from a scCO<sub>2</sub> solution was developed and a one-dimensional Fickian diffusion model was used to evaluate the diffusion coefficient of the dye as a function of pressure and temperature. This approach has been extended to investigate other scCO<sub>2</sub> processed polymer systems including PET fibres, syndiotactic polystyrene impregnated with DR1 and a biocompatible polymer impregnated with a model drug.

The interdiffusion of polyvinylpyrrolidone and poly(ethylene glycol) subjected to scCO<sub>2</sub> was studied using a novel application of *in situ* attenuated total reflection (ATR) FTIR imaging. Visualisation of the dynamic miscible polymer system was achieved and the influence of pressure and molecular weight elucidated, revealing the ability to control the rate of the dynamic process. The feasibility to apply *in situ* ATR FTIR imaging to study CO<sub>2</sub>-induced alterations in PET and CO<sub>2</sub>-induced polymer phase separation is explored.

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## LIST OF PUBLICATIONS

The results presented in this thesis are described in the following publications:

1. O.S. Fleming and S.G. Kazarian (2004). "Confocal Raman microscopy of morphological changes in poly(ethylene terephthalate) film induced by supercritical CO<sub>2</sub>" *Applied Spectroscopy*, 58, 391-394.
2. O.S. Fleming, K.L.A. Chan and S.G. Kazarian (2004). "FTIR imaging and confocal Raman microscopic study of the morphology of poly(ethylene terephthalate) film processed with supercritical CO<sub>2</sub>" *Vibrational Spectroscopy*, 35, 3-7.
3. O.S. Fleming, S.G. Kazarian, E. Bach and E. Schollmeyer (2005). "Confocal Raman study of poly(ethylene terephthalate) fibres dyed in supercritical carbon dioxide: dye diffusion and polymer morphology", *Polymer*, 46 (9), 2943-2949.
4. O.S. Fleming, F. Stepanek and S.G. Kazarian (2005). "Dye diffusion in polymer films subjected to supercritical CO<sub>2</sub>: confocal Raman microscopy and modelling". *Macromolecular Chemistry and Physics*, 206, 1077-1083.
5. O.S. Fleming and S.G. Kazarian (2005). Chapter 10 in "Supercritical Carbon Dioxide: in Polymer Reaction Engineering" Maartje F. Kemmere (Editor), Thierry Meyer (Editor), 205-238.
6. O.S. Fleming, K.L.A. Chan and S.G. Kazarian (2006). "High-pressure CO<sub>2</sub>-enhanced polymer interdiffusion studied with in situ ATR FTIR spectroscopic imaging" *submitted to Polymer*.

The following publication is not directly related to the work presented in this thesis:

7. K.L.A. Chan, O.S. Fleming, S.G. Kazarian, D. Vassou, G.D. Chryssikos and V. Gionis (2004). "Polymorphism and devitrification of nifedipine under controlled humidity: a combined FT-Raman, IR and Raman microscopic investigation" *Journal of Raman Spectroscopy*, 35, 353-359.

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**LIST OF SYMBOLS AND ABBREVIATIONS**

|                 |                                         |
|-----------------|-----------------------------------------|
| $\mu$ :         | Effective mass                          |
| $\varepsilon$ : | Molar extinction coefficient            |
| $\alpha$ :      | Molecular polarisability                |
| $\lambda$ :     | Wavelength                              |
| $\mu'$ :        | Induced dipole moment                   |
| $\theta_c$ :    | Critical angle                          |
| $\tilde{\nu}$ : | Wavenumber ( $\text{cm}^{-1}$ )         |
| $\Delta E$ :    | Energy difference                       |
| A:              | Absorbance                              |
| $\text{\AA}$ :  | Angstrom                                |
| AFM:            | Atomic force microscopy                 |
| atm:            | Atmosphere                              |
| ATR:            | Attenuated total reflection             |
| CCD:            | Charge coupled detector                 |
| CRM:            | Confocal Raman microscopy               |
| $d_p$ :         | Depth of penetration                    |
| DR1:            | Disperse Red 1                          |
| $D^f$ :         | Diffusion coefficient of dye in polymer |
| DSC:            | Differential scanning calorimetry       |
| DY23:           | Disperse Yellow 23                      |
| FPA:            | Focal plane array                       |
| FTIR:           | Fourier Transform Infrared              |
| $h$ :           | Planck constant                         |
| I:              | Transmitted intensity                   |
| $I_0$ :         | Incident intensity                      |
| k:              | Boltzmann's constant                    |
| K:              | Equilibrium partitioning coefficient    |
| $k$ :           | Force constant                          |
| $k'_m$ :        | Reduced mass-transfer coefficient       |
| l:              | Pathlength                              |

|                   |                                                                                |
|-------------------|--------------------------------------------------------------------------------|
| LCST:             | Lower critical solution temperature                                            |
| $M_{\infty}$ :    | Amount of dye absorbed at equilibrium                                          |
| MCT:              | Mercury-cadmium-telluride                                                      |
| $M_t$ :           | Amount of dye absorbed at time $t$                                             |
| $M_w$ :           | Molecular weight                                                               |
| $n$ :             | Refractive index                                                               |
| NA:               | Numerical aperture                                                             |
| NIR:              | Near Infrared                                                                  |
| P(MMA-EHA-EGDMA): | poly(methylmethacrylate-co-ethylhexylacrylate-co-ethyleneglycoldimethacrylate) |
| Pa:               | Pascal                                                                         |
| $P_c$ :           | Critical pressure                                                              |
| PCL:              | Poly( $\epsilon$ -caprolactone)                                                |
| PDMS:             | Poly(dimethylsiloxane)                                                         |
| PEG:              | Poly(ethylene glycol)                                                          |
| PET:              | Poly(ethylene terephthalate)                                                   |
| PLGA:             | Poly( $D,L$ -lactide-co-glycolic acid)                                         |
| PMMA:             | Poly(methylmethacrylate)                                                       |
| PSF:              | Point spread function                                                          |
| PTFE:             | Polytetrafluoroethylene                                                        |
| PVP:              | Polyvinylpyrrolidone                                                           |
| $Q_k$ :           | Normal coordinate of $k^{\text{th}}$ vibration                                 |
| $r$ :             | Distance between two points required to be fully resolved                      |
| sc:               | Supercritical                                                                  |
| sPS:              | Syndiotactic polystyrene                                                       |
| $T_c$ :           | Critical temperature                                                           |
| $T_g$ :           | Glass transition temperature                                                   |
| $T_m$ :           | Melting temperature                                                            |
| UCST:             | Upper critical solution temperature                                            |
| $\nu$ :           | Frequency ( $s^{-1}$ )                                                         |
| $\nu$ :           | Vibrational quantum number                                                     |
| wt%:              | Weight percent                                                                 |

$\chi$ : Flury-Huggins interaction parameter

# **CHAPTER 1**

## **GENERAL INTRODUCTION**

## 1. GENERAL INTRODUCTION

### 1.1. MOTIVATION FOR WORK

High-pressure and supercritical (sc) CO<sub>2</sub> present a viable alternative to the harmful organic solvents currently employed in polymer processing. In addition to conforming to environmental requirements desired in modern industrial practice, intrinsic advantages in polymer processing are offered. Examples include reduction of glass transition and melting temperatures in some polymers, polymer swelling and the facilitation of solute mass transport within polymer matrices. A unique feature of CO<sub>2</sub> is its transient plasticising property, which is responsible for the “solvent-free” processing offered. The processing of polymeric material with scCO<sub>2</sub> may potentially lead to new materials with unique properties, and therefore accurately designing and optimising CO<sub>2</sub> processes require the elucidation of the effect of the CO<sub>2</sub> fluid phase on the final product characteristics. The molecular level insight offered by vibrational spectroscopy provides valuable information to interpret the effect of processing variables and to guide process optimisation.

The performance of polymers processed with high-pressure or scCO<sub>2</sub> is highly dependent on the distribution of specific chemical species throughout the system and the intrinsic morphology of the polymer matrix. The integrity and reproducibility of the chemical and mechanical performance of the product are likely to be dependent on these factors. The dyeing of poly(ethylene terephthalate) from a scCO<sub>2</sub> solution is an example of scCO<sub>2</sub>-assisted impregnation where information regarding the distribution of the guest solute and host matrix represent key pieces of information to correlate with the performance of the finished material. The engineering principles facilitating the impregnation of the textile relevant polymer system are analogous to those used to impregnate a polymer matrix with active drug molecules for pharmaceutical formulations. The performance of such a formulation in terms of the release profile will be highly dependent on the distribution of the impregnated drug in the matrix. The depth profiling sampling capability offered by CRM permits the non-invasive analysis of polymeric materials and thus presents an opportunity to reveal spatially resolved information in these CO<sub>2</sub> processed polymers for quantitative diffusion analysis.



The blending of polymers enables one to combine desirable properties in order to prepare novel materials with the required performance characteristics. The use of high-pressure or scCO<sub>2</sub> facilitates processing at reduced temperature conditions and, in some cases, the formation of blends with potentially unique architectures that are not accessible by conventional methods. The phase behaviour of polymer blends in high-pressure CO<sub>2</sub> environments defines the processing window available for a particular system. The recent development of ATR FTIR imaging realises the study of heterogeneous polymer systems under high-pressure and scCO<sub>2</sub> environments. The chemical specificity inherent to FTIR spectroscopic imaging provides a molecular level assessment of the studied system in addition to spatially resolved information, permitting the study of dynamic polymer systems. The rich information content offered by ATR FTIR imaging provides important details to identify critical parameters as a function of system conditions and to establish quantitative relationships required for the successful adoption of scCO<sub>2</sub> technology.

## 1.2. OBJECTIVES

This thesis explores the use of advanced vibrational spectroscopy to characterise and provide quantitative information on CO<sub>2</sub> processed polymeric material. Specifically, the use of confocal Raman microscopy and FTIR spectroscopic imaging are applied to acquire spatially resolved chemical information to elucidate aspects of the CO<sub>2</sub> processing routes. Important aspects of CO<sub>2</sub> processing are explored: polymer morphology modification, polymer impregnation and polymer interdiffusion. The specific objectives of this research are:

- Development of an experimental approach and establishment of a protocol for studying semicrystalline polymers processed with scCO<sub>2</sub> via CRM, Raman mapping and FTIR imaging. The reliability of CRM with the oil immersion objective is to be validated via Raman mapping of film cross-sections for studies of CO<sub>2</sub>-induced morphological alterations in PET as a function of depth. The effect of CO<sub>2</sub> exposure as a function of time, pressure and temperature are to be studied. Raman spectroscopic measurements are to be confirmed using transmission FTIR imaging.
- The distribution of disperse dyes in PET samples impregnated from a scCO<sub>2</sub> solution is to be studied using CRM. Information on the dye distribution and polymer morphology for polymeric fibres dyed under scCO<sub>2</sub> conditions is to be assessed. A model system of PET film impregnated with Disperse Red 1 (DR1) will be used to generate data for modelling purposes. Process variables will be examined using this approach to determine the dye diffusion mechanism and to calculate the dye diffusion coefficient from the confocal Raman data. The suitability of the established CRM approach to study other CO<sub>2</sub> impregnated polymer systems will be assessed to investigate the distribution of DR1 in syndiotactic polystyrene and the distribution of a model drug in a biocompatible polymer.
- ATR FTIR imaging is to be applied to investigate the mixing of miscible polymer systems in the presence of high-pressure CO<sub>2</sub> *in situ*. The interdiffusion process occurring between polyvinylpyrrolidone and poly(ethylene glycol) is to be studied as a function of time and space. The effect

of polymer molecular weight and CO<sub>2</sub> pressure on the dynamics of polymer interdiffusion will be elucidated.

- The feasibility of applying *in situ* ATR FTIR imaging to study other dynamic polymer systems e.g. CO<sub>2</sub>-induced crystallisation of PET and CO<sub>2</sub>-induced phase separation will be explored.

### 1.3. STRUCTURE OF THESIS

This thesis comprises three main components: a review of relevant literature that provides the required background knowledge for the work presented, the experimental study followed by general conclusions and a description of suggested future work. The reviewed literature covers polymer processing with scCO<sub>2</sub> and vibrational spectroscopy. Chapter 2 serves to introduce and define supercritical fluids and provides a brief overview of successful applications and the current status of supercritical fluid technology. A comprehensive review of some of the key issues associated with polymer processing using scCO<sub>2</sub> is given in Chapter 3. Important concepts such as the phase behaviour in CO<sub>2</sub>/polymer systems, diffusion in polymers (CO<sub>2</sub> and solutes), phase separation and specific applications that utilise these aspects are detailed. Vibrational spectroscopy is introduced in Chapter 4 and the advanced spectroscopic techniques employed throughout this research described. The theory of IR and Raman spectroscopy are provided and specific details relating to the sampling techniques discussed.

Chapter 5 marks the beginning of the experimental section in which the high-pressure apparatus employed in this work is introduced and general experimental protocols described. Studies of CO<sub>2</sub>-induced morphological alterations in PET film using CRM, transmission FTIR imaging and *in situ* ATR FTIR imaging are presented in Chapter 6. Chapters 7 and 8 describe the application of CRM to assess the distribution of disperse dyes in PET impregnated from a scCO<sub>2</sub> solution for industrially dyed fibres and a model PET/Disperse Red 1 system, respectively. The generic approach established is extended to investigate additional semicrystalline polymer systems and a pharmaceutical formulation in Chapter 9. The use of *in situ* ATR FTIR imaging to study polymer interdiffusion in the presence of high-pressure CO<sub>2</sub> is found in Chapter 10. The feasibility to study CO<sub>2</sub>-induced phase separation in a pharmaceutically relevant

polymer system using *in situ* ATR FTIR imaging is described in Chapter 11. Finally, general conclusions and suggestions for future work are detailed in Chapter 12.

## **CHAPTER 2**

# **SUPERCRITICAL FLUIDS AND SUPERCRITICAL CO<sub>2</sub>**

## 2. SUPERCRITICAL FLUIDS AND SUPERCRITICAL CO<sub>2</sub>

### 2.1. SUPERCRITICAL CO<sub>2</sub>

A supercritical fluid (SCF) is any substance whose temperature and pressure are higher than the critical values, and the density is close to or higher than the critical density.<sup>1</sup> In close proximity to the critical point the compressibility of the fluid is extremely high and a gas cannot be liquefied under any pressure once the critical temperature is exceeded. The properties of the SCF are somewhat a combination of a liquid and a gas. These “hybrid” properties retain the solvent power of a liquid combined with the viscosity and mass transfer characteristics of a gas. A particular feature of the fluid is that the density, and consequently the solvent properties, may be “tuned” by adjusting the temperature and pressure of the system. This feature enables the precipitation of a solute to occur for small changes in the system pressure.

To a first approximation the solvent power of the SCF is proportional to the solvent density behaviour in the critical region. The non-ideal behaviour exhibited by a gas when compressed to liquid-like densities is responsible for the enhanced solvent properties. The observed solubility of a solid in the SCF will be dependent on both the solid sublimation pressure and the density of the SCF at a specific condition. Modification of the solvent properties of the SCF may be achieved with the addition of a co-solvent, such as an alcohol, to extend the range of soluble materials. However, the removal of the co-solvent is likely to require an additional separation step which complicates an essentially single step SCF operation.

Supercritical (sc) CO<sub>2</sub> is the most commonly used SCF owing to its ready availability, relatively low cost, environmentally benign nature, chemical inertness under many conditions and moderate critical parameters (72.8 bar and 31.1°C). The pressure–temperature phase diagram for CO<sub>2</sub> is shown in Figure 2.1. It should be noted that CO<sub>2</sub> may be solidified at extremely high pressure conditions.

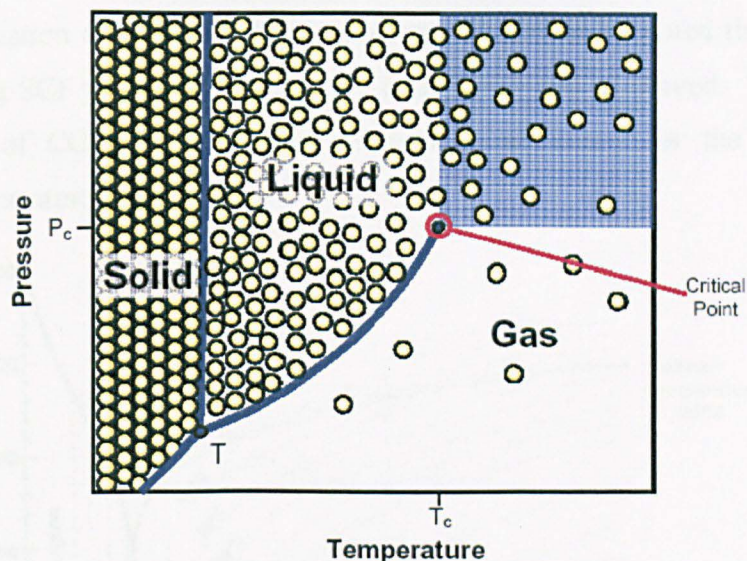


Figure 2.1. Pressure–temperature phase diagram for CO<sub>2</sub>. The blue shaded area corresponds to the supercritical fluid phase,  $P_c$  and  $T_c$  are the critical pressure and temperature respectively, and  $T$  the triple point.

CO<sub>2</sub> is a non-polar, linear triatomic molecule which in the supercritical state exhibits solvent properties typical of hydrocarbon solvents, such as toluene, with the addition of the supercritical properties e.g. low surface tension and viscosity, and ease of solute recovery.<sup>2</sup> The charge separation and electronic structure of CO<sub>2</sub> allows it to act as a weak Lewis acid or Lewis base. The solvent properties of high-pressure and scCO<sub>2</sub> arise due to weak interactions of the solute with the CO<sub>2</sub> molecules, which possesses a significant quadrupole moment. The complex polar attributes responsible for the solvating characteristics exhibited by CO<sub>2</sub> have recently been summarised by Raveendran et al.<sup>3</sup> The phase behaviour of CO<sub>2</sub> is shown in the liquid-vapour phase diagram presented in Figure 2.2. The figure demonstrates the influence of temperature and pressure on the density and hence solvating power of the CO<sub>2</sub> fluid phase. Due to the observed large variation in conditions as a function of temperature and pressure, the value of describing CO<sub>2</sub> in terms of density may be appreciated. Consideration must also be given to the solute sublimation pressure as a function of temperature to rationalise the system behaviour.



CO<sub>2</sub> is recognised as a “green house” gas that is generated in many industrial operations including combustion and fermentation processes. It should be noted that CO<sub>2</sub> is not generated during SCF processes but rather it is captured and employed. The recycling and utilisation of CO<sub>2</sub> for alternative purposes is necessary for the reduction of emissions into the atmosphere.

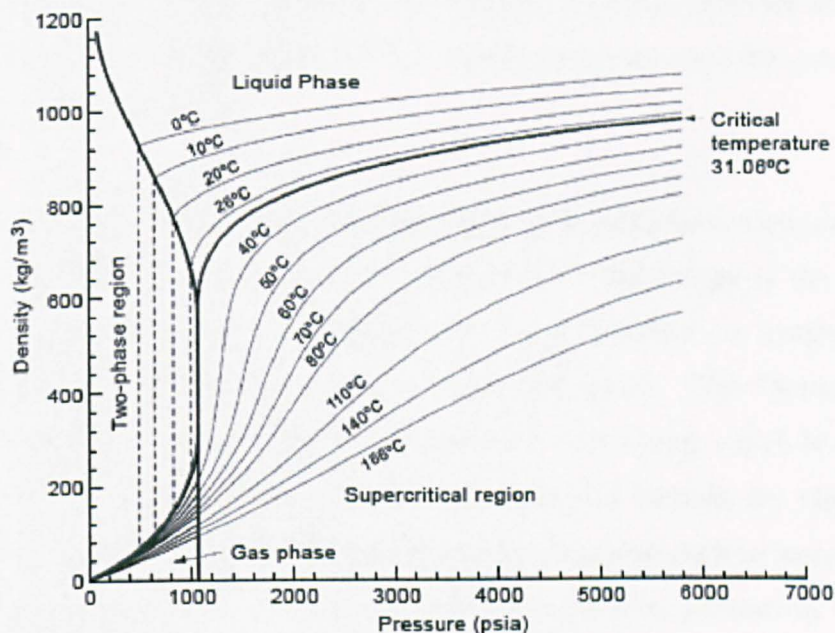


Figure 2.2. Variation of the density of pure carbon dioxide as a function of pressure for various isotherms.<sup>4</sup>

## 2.2. SUPERCRITICAL CO<sub>2</sub> APPLICATIONS

The current environmental climate issues have raised the scrutiny over industrial practice and have consequently increased the awareness towards SCF technology. CO<sub>2</sub> is recognised as a potential environmentally benign replacement for various organic solvents used in industrial activities. Many review and commentary articles have been published since 2000 that provide an overview of areas of successful implementation of SCF technology.<sup>5-7</sup> A common feature is the recognition that the implementation of SCF technology has fallen short of the widely anticipated industrial expectations of the 1980's. The misconception that CO<sub>2</sub> would provide a direct replacement for traditional solvents has been limited, in part, due to the relatively small range of materials which are soluble in CO<sub>2</sub>. Enhancing the CO<sub>2</sub>-philicity of solutes in the SCF phase has now



become more economically viable with the introduction of copolymer surfactants<sup>8</sup> as an alternative to the relatively expensive fluorinated additives.<sup>9</sup> It is widely acknowledged that a detailed understanding of CO<sub>2</sub> as a solvent is still required for the widespread adoption of scCO<sub>2</sub> technology. Nevertheless, scCO<sub>2</sub> has been successfully implemented in numerous industrial applications and emerging technologies where intrinsic advantages and benefits are offered. The following section provides an overview of industrial examples of high-pressure and scCO<sub>2</sub> processes and the current status of emerging scCO<sub>2</sub> applications.

SCF technology has historically been associated with extraction processes in the food industry. Probably the best-known example of SCF technology is the extraction of caffeine from coffee beans<sup>10</sup> although the same practice is employed for the decaffeination of tea and the extraction of hops and spices. This “natural” extraction process demonstrates the concept of “solvent-free” processing which is central to the role in many SCF applications. More recent examples include dry cleaning<sup>11</sup> using liquid CO<sub>2</sub>, nanotechnology applications that exploit the zero-surface tension of scCO<sub>2</sub><sup>12</sup> and the degreasing of mechanical components with complex geometries.<sup>13</sup> The use of scCO<sub>2</sub> in processes where water was traditionally implemented include textile dyeing which has been implemented to various degrees across Europe and the USA,<sup>14</sup> enhanced oil recovery<sup>15</sup> and photolithography.<sup>16</sup> These applications would conventionally require remediation steps, the nullification of which presents significant process simplifications. CO<sub>2</sub> also fulfils the role as an alternative solvent for chemical synthesis and reactions. UK activity in this area has been led by Thomas Swan<sup>17</sup> who in conjunction with Nottingham University have recently commissioned a full-scale hydrogenation plant, while in North America DuPont have invested heavily into fluoropolymer processing with scCO<sub>2</sub>.<sup>18</sup>

The pharmaceutical sector presents an area of significant potential for scCO<sub>2</sub> technology<sup>19</sup> and falls under the umbrella of “niche”, high added-value applications. Significant research efforts have been invested into the practice of particle generation using scCO<sub>2</sub>.<sup>20</sup> The specific processes employed are described by various acronyms that are summarised in Table 1. The techniques utilise the “solvent-free” nature of CO<sub>2</sub> to deliver to increasingly stringent material performance demands in this sector. Many

of the techniques function on the basis of the variable solvent power of CO<sub>2</sub> to prepare particles and encapsulated materials. The underlying function of polymeric materials in these applications requires a thorough understanding of the consequences of CO<sub>2</sub> exposure. The integration of scCO<sub>2</sub> technology presents an attractive alternative to conventional approaches that are hampered by economical and environmental limitations. A comprehensive review of the issues associated with CO<sub>2</sub>-assisted polymer processing is presented in Chapter 3.

Table 1. Abbreviations used to describe various SCF applications

| <i>Acronym</i> | <i>Description</i>                                       |
|----------------|----------------------------------------------------------|
| SAS            | Supercritical antisolvent                                |
| RESS           | Rapid expansion of supercritical solutions               |
| DELOS          | Depressurisation of an expanded organic solution         |
| CAN-BD         | CO <sub>2</sub> -assisted nebulization and bubble drying |
| SFC            | Supercritical fluid chromatography                       |
| SFE            | Supercritical fluid extraction                           |
| SFF            | Supercritical fluid fractionation                        |

The implementation and development of SCF technology faces challenges that are generic to any new approach. It is often stated that environmental benefits alone are not sufficient to drive change but are rather bonus promotional features in examples where inherent benefits are offered. The use of CO<sub>2</sub> offers some intrinsic advantages and benefits in materials processing in addition its environmental benign nature. This makes scCO<sub>2</sub> by far the most widely used SCF and a viable option for modern chemical processes.

## **CHAPTER 3**

# **POLYMER PROCESSING WITH SUPERCRITICAL CO<sub>2</sub>**

### **3. POLYMER PROCESSING WITH SUPERCRITICAL CO<sub>2</sub>**

#### **3.1. INTRODUCTION**

Supercritical CO<sub>2</sub> has proven its applicability in the area of polymer processing due to its unique properties as a temporary plasticiser. CO<sub>2</sub> is a gas under normal conditions and is therefore easy to remove which distinguishes it from traditional plasticisers. This transient property is an attractive feature due to the absence of solvent residues in the matrix following processing. The processing of polymeric material is possible at milder conditions and the enhancement of solute diffusion is possible. Control over the concentration of CO<sub>2</sub> sorbed into the matrix provides an important process variable that permits manipulation of the system and hence allows one to alter the characteristics of the material. Knowledge of the implications of CO<sub>2</sub> on the material is required in order to capitalise on the benefits offered by this novel processing route.

This chapter serves to review some of the key issues associated with scCO<sub>2</sub> processing of polymeric materials and provides an overview of the current trends in the field. The phase behaviour of CO<sub>2</sub>/polymer systems is described and CO<sub>2</sub>-induced changes in the chemical and physical properties explained. The experimental techniques employed to quantify these changes are introduced and the applications that exploit these favourable processing capabilities are reviewed. A specific focus on mass transport enhanced impregnation for the preparation of guest-host systems is given.

#### **3.2. PHASE BEHAVIOUR OF CO<sub>2</sub>/POLYMER SYSTEMS AND EFFECT OF CO<sub>2</sub> ON POLYMERS**

##### **3.2.1. SOLUBILITY OF CO<sub>2</sub> IN POLYMERS**

The solubility of high-pressure CO<sub>2</sub> in a polymeric matrix is the fundamental concept that facilitates all forms of processing discussed in this chapter. In contrast to polymer synthesis with CO<sub>2</sub>, polymer processing involves CO<sub>2</sub> as the relatively minor phase dissolved within the polymeric matrix. Typically the equilibrium fraction of CO<sub>2</sub> in common polymers such as poly(methylmethacrylate) (PMMA) reaches ca. 10 % (35°C

and 41 bar), although it has been shown to reach levels of 21 % in high molecular weight poly(dimethylsiloxane) (PDMS) (50°C and 90.9 bar).<sup>21</sup> The solubility of CO<sub>2</sub> in polymers is largely based on its ability to weakly interact with basic sites along the macromolecular chains.

The importance of polar groups in polymers for CO<sub>2</sub> solubility has been recognised for almost two decades,<sup>22</sup> with enhancement in CO<sub>2</sub>-philicity observed for an increase in the number of electron donating groups for a given polymer density.<sup>23,24</sup> The accessibility of the polar group is an important factor,<sup>25</sup> for example CO<sub>2</sub> solubility is greater in PMMA than poly(ethylene terephthalate) glycol modified (PETG) due to the access of CO<sub>2</sub> to the main chain ester group in PETG being more hindered than in the side chain ester functionality of PMMA.<sup>26</sup> The morphology of the polymer matrix also affects CO<sub>2</sub> solubility, thus glassy polymers<sup>26</sup> usually exhibit higher CO<sub>2</sub> solubility compared to semicrystalline polymers.<sup>27</sup>

Many experimental<sup>23,26-32</sup> and theoretical<sup>33-36</sup> methods have been applied to investigate the solubility of CO<sub>2</sub> in polymers. IR spectroscopy stands out as the key technique that provided the first experimental evidence for the interaction between CO<sub>2</sub> and functional groups in polymers (such as carbonyl groups or phenyl rings).<sup>37</sup> *In situ* FTIR spectroscopy was applied to probe the molecular level interaction of CO<sub>2</sub> with a wide range of polymers. Specifically, interactions were assessed by the splitting of the  $\nu_2$  degenerate bending mode of the CO<sub>2</sub> which is indicative of a Lewis acid–base interaction. This was further substantiated by Nelson and Borkman<sup>33</sup> who applied *ab initio* molecular orbital calculations to study the interaction of CO<sub>2</sub> with poly(ethylene terephthalate) (PET). They predicted that the CO<sub>2</sub> molecule is slightly bent when bound to the carbonyl oxygen of PET, indicating a transfer of electron density to CO<sub>2</sub> which acts as a Lewis acid. Furthermore, preferential interaction was found to occur at the carbonyl group over the electron-donating ring system in PET. The interaction of CO<sub>2</sub> with polymers containing fluorinated groups was investigated by Fried and Hu<sup>36</sup> using computational chemistry. Quadrupole-dipole interactions were predicted to make a substantial contribution to the total energy of interaction, estimated to occur at a close (4.3 Å) approach distance.

The dependence of CO<sub>2</sub> solubility with temperature<sup>38</sup> is a feature that is exploited in polymer processing. Temperature control provides an effective way to alter the conditions within the matrix. This is exemplified in the application of CO<sub>2</sub>-induced foaming, which can be initiated by rapid temperature ramping from a supersaturated state. At low temperatures the solubility of CO<sub>2</sub> in the polymer matrix is relatively high and is lowered with increasing temperature which dictates the requirement for careful temperature control during processing. A thorough understanding of CO<sub>2</sub> solubility in polymers is required to facilitate process optimisation. For a concise summary of CO<sub>2</sub> solubility data in polymers and detailed information regarding the measurement techniques, the reader is directed to a recent review article compiled by Tomasko et al.<sup>39</sup>

### 3.2.2. CO<sub>2</sub>-INDUCED PLASTICISATION OF POLYMERS

The plasticisation of polymers involves an increase in the inter-chain distances and an enhanced degree of chain and segmental mobility. Polymer plasticisation is accompanied by changes in mechanical and physical properties and thus the knowledge of this phenomenon is vital for processing applications. Plasticisation facilitates the processes described in this chapter with the important characteristic that following processing there is no residual CO<sub>2</sub> remaining in the matrix. The plasticisation of the polymer matrix occurs at the glass transition temperature ( $T_g$ ) and may be induced thermally or with the use of an organic solvent, which acts to depress the  $T_g$ . The use of an organic solvent has obvious drawbacks due to the presence of residues in the matrix that may affect the final material and limit the applicability (i.e. applications such as food, biotechnology and pharmaceutical technology where the presence of the residual solvent may be harmful).

The presence of dissolved CO<sub>2</sub> molecules in a polymer results in the plasticisation of the amorphous component of the matrix. In this respect, CO<sub>2</sub> mimics the effect of heat but with the important distinction that the  $T_g$  is depressed. The extent of the  $T_g$  depression is dependent on the wt% of CO<sub>2</sub> in the matrix. As previously mentioned, one of the characteristics of plasticisation is the enhancement of segmental motion which has been observed spectroscopically for the ester groups of PMMA<sup>40</sup> and the phenyl rings of polystyrene.<sup>41</sup> The consequential increase in free-volume of the matrix has been studied



by methods such as laser dilatometry,<sup>42</sup> *in situ* FTIR spectroscopy,<sup>40</sup> high-pressure partition chromatography<sup>43</sup> and inverse gas chromatography.<sup>44</sup>

This  $T_g$  depression enables the processing of polymeric systems that were previously not possible by conventional methods. With the use of high-pressure CO<sub>2</sub>, and the consequential reduction of the  $T_g$ , the selection of active components for impregnation is broadened to include components that would have suffered from thermal degradation via traditional melt processing. This ability of high-pressure or supercritical CO<sub>2</sub> to plasticise the matrix is central to all applications described in the following sections.

### 3.2.3. CO<sub>2</sub>-INDUCED CRYSTALLISATION OF POLYMERS

CO<sub>2</sub>-induced plasticisation of the amorphous domains in semicrystalline polymers has significant morphological implications due to the formation of crystallites. CO<sub>2</sub>-induced crystallisation stems from free energy considerations in the CO<sub>2</sub>/polymer system. The CO<sub>2</sub>-induced mobility of the polymer chains permits reconfiguration to occur, both in terms of conformation and 3-D arrangement (intra and inter), into the lowest energy configuration and thus results in the formation of crystallites. Following depressurisation of the system, CO<sub>2</sub> escapes quickly from the matrix and leaves the induced morphological alterations “frozen”, shown schematically in Figure 3.1. In this manner, CO<sub>2</sub> can be viewed as “temporary morphological modification tool” as once the desired morphology has been induced, CO<sub>2</sub> can be completely removed from the polymer.

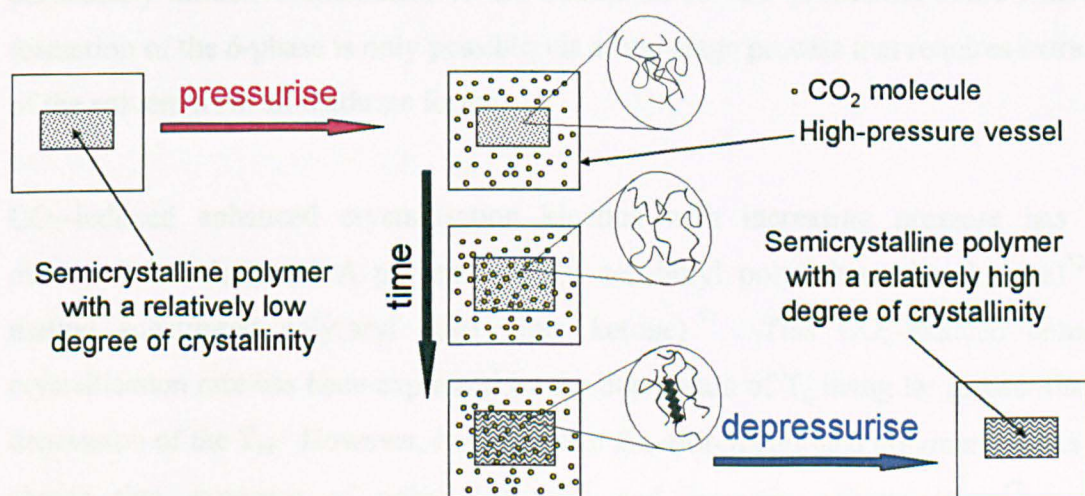


Figure 3.1. Schematic diagram of CO<sub>2</sub>-induced crystallisation.

CO<sub>2</sub>-induced crystallisation of PET has received much attention due to the industrial relevance of this polymer.<sup>45-48</sup> The rate of the crystallisation has been shown to increase with increasing pressure<sup>49</sup> and follow the Avrami equation.<sup>47</sup> As expected, IR and Raman spectroscopy have proved to be highly valuable techniques to study the CO<sub>2</sub>-induced crystallisation of PET,<sup>50</sup> enabling Brantley et al.<sup>38</sup> to study the crystallisation process using *in situ* FTIR spectroscopy. That work established that at 0 °C crystallisation was suppressed even at a CO<sub>2</sub> pressure of 175 bar and thus demonstrated the possibility to process PET without inducing morphological alterations. Other examples of polymer systems crystallised by CO<sub>2</sub> include bisphenol A polycarbonate<sup>51</sup>, *tert*-butyl poly(ether ether ketone),<sup>52</sup> poly(L-lactide)<sup>53</sup> and methyl-substituted poly(aryl ether ether ketone).<sup>54</sup>

The facet of “morphological selectivity” is demonstrated by CO<sub>2</sub> in its ability to induce a specific polymorph of syndiotactic polystyrene (sPS). The morphology of sPS is rather complex in that it may exhibit a gamut of polymorphs:  $\alpha$  and  $\beta$  which possess planer structures, and two helical forms denoted as the  $\gamma$  and  $\delta$  phases. Handa and colleagues<sup>55</sup> investigated the effect of compressed CO<sub>2</sub> on the morphology of sPS by applying high-pressure DSC and X-ray diffraction. They observed a transition from glassy sPS to the  $\alpha$ -phase and the formation of the  $\beta$ -phase via a transition from the  $\gamma$ -phase under compressed CO<sub>2</sub>. Kazarian et al.<sup>56</sup> applied *in situ* FTIR spectroscopy to investigate CO<sub>2</sub>-induced morphology under supercritical conditions which proved to be a route to the formation of the helical, nano-porous  $\delta$ -phase. The use of scCO<sub>2</sub> is a particularly attractive alternative to the traditional solvent processing route where the formation of the  $\delta$ -phase is only possible via a two-stage process that requires extraction of the solvent from all clathrate forms.

CO<sub>2</sub>-induced enhanced crystallisation kinetics with increasing pressure has been observed for bisphenol A polycarbonate,<sup>51</sup> *tert*-butyl poly(ether ether ketone)<sup>52</sup> and methyl substituted poly(aryl ether ether ketone).<sup>54</sup> This CO<sub>2</sub>-induced enhanced crystallisation rate has been explained by the depression of  $T_g$  being far greater than the depression of the  $T_m$ . However, in contrast to the aforementioned polymers, it has been shown that exposure of poly(L-lactide)<sup>53</sup> and isotactic polypropylene<sup>57</sup> to CO<sub>2</sub> suppresses the crystallisation rate. This observation was suggested to be due to the  $T_m$  being depressed to the same extent as the  $T_g$  which prevents the formation of critical



size nuclei. It has recently been demonstrated that the crystallisation process may be manipulated using nano-scale clays<sup>58</sup> and the presence of co-solvents.<sup>59</sup> These process variables present additional control measures in the CO<sub>2</sub>-induced crystallisation process, providing extra control over the extent of CO<sub>2</sub>-induced morphological modification. The selection of operating conditions requires control over the diffusivity of CO<sub>2</sub> combined and the kinetics of crystallisation.

#### 3.2.4. INTERFACIAL TENSION IN CO<sub>2</sub>/POLYMER SYSTEMS

Interfacial tension in CO<sub>2</sub>/polymer systems is an important parameter in applications such as the preparation of composite fibres,<sup>60</sup> nucleation of polymer or void phases, and the growth and coalescence of dispersed phases.<sup>61</sup> CO<sub>2</sub> acts to lower the interfacial tension in polymer systems by “shielding” unfavourable contacts at the interfaces between the system phases. The reduction of interfacial tension in a binary CO<sub>2</sub>/polymer system with increasing CO<sub>2</sub> density has been succinctly described by the “free energy densities of the two fluids becoming more alike”.<sup>61</sup> Interfacial tension is directly related to miscibility and responsible for (as well as viscosity) droplet break-up and coalescence during blending. However, the reduction of domain size in immiscible polymer blends due to exposure to high-pressure CO<sub>2</sub> has generally been interpreted in terms of viscosity reduction of one of the phases as a result of the preferential affinity of CO<sub>2</sub>. Measuring interfacial tension may be performed using equilibrium or transient methods.<sup>62</sup> The pendent drop method is the most commonly applied technique to measure interfacial tension under pressure and involves the measurement of density differences between two fluids and the equilibrium drop profile shape. In the following section, examples of interfacial tension reduction are presented for binary polymer/CO<sub>2</sub> systems and for polymer blends.

Harrison and colleagues<sup>61</sup> measured the interfacial tension between scCO<sub>2</sub> and polyethylene glycol (600 MW) using a tandem variable-volume pendent drop tensiometer, as shown schematically in Figure 3.2. At 45°C the interfacial tension between the PEG-CO<sub>2</sub> rich phase and the scCO<sub>2</sub> phase was reduced from 0.69 mN/m at 100 bar to 0.308 mN/m at 300 bar. In another work the effect of surfactants on polymer/CO<sub>2</sub> interfacial tension was addressed.<sup>63</sup>

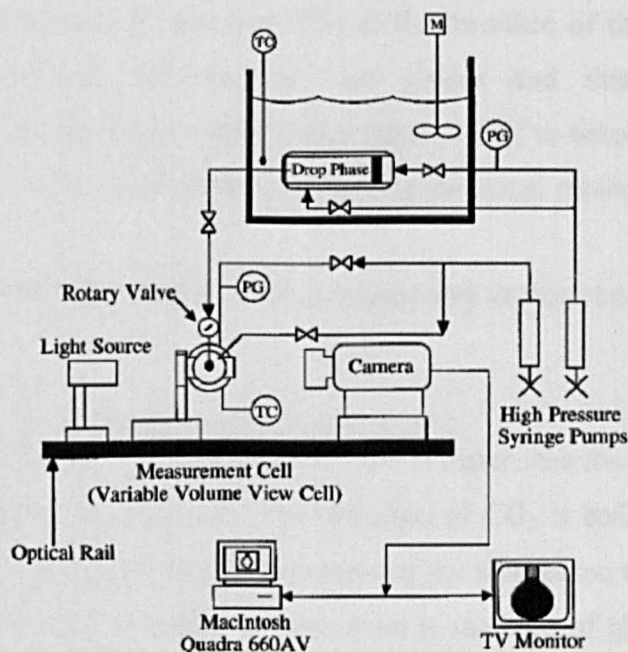


Figure 3.2. Schematic diagram of a tandem variable volume pendent drop tensiometer.<sup>61</sup>

Li et al.<sup>64</sup> applied the pendent drop method to study the interfacial tension of a polystyrene (PS)/CO<sub>2</sub> system. A linear decrease in interfacial tension was observed in the temperature range of 190 to 240°C. Interfacial tension was reduced from 2.4 – 1.2 mN/m up to a pressure of 70 bar, but at higher temperature the rate of reduction was suppressed. These observations were explained by two competing effects: interfacial tension reduction with increasing temperature combined with a reduction in CO<sub>2</sub> solubility with increasing temperature. In the same study the interfacial tension in an immiscible blend of PS and polypropylene (PP) saturated with CO<sub>2</sub> was measured. Experiments were recorded at 220°C and pressures up to 165 bar for two molecular weights of PP. In both cases, the interfacial tension was found to decrease by more than 20 %.

The importance of interfacial tension reduction in polymer blends by CO<sub>2</sub> was addressed by Xue et al.<sup>65</sup> The pendent drop method was utilised to investigate the interfacial tension between PS/low density polyethylene (LDPE) saturated with scCO<sub>2</sub> and compared to the same system in the absence of CO<sub>2</sub>. At 200°C the interfacial tension decreased from 6.62 mN/m at 10 bar to 4.69 mN/m at CO<sub>2</sub> pressure of 92 bar, corresponding to a 30 % absolute reduction. This decreased interfacial tension was

explained by the presence of dissolved CO<sub>2</sub> at the interface of the polymers reducing unfavourable interactions between the two phases and thereby enhancing the miscibility. These examples demonstrate the value of CO<sub>2</sub> to enhance the miscibility in polymer blend systems with the potential to lead to the novel materials.

### 3.2.5. DIFFUSION OF CO<sub>2</sub> IN POLYMERS AND SOLUTES IN POLYMERS SUBJECTED TO CO<sub>2</sub>

Above the  $T_g$  the rate of polymer chain relaxation is faster than the diffusion of CO<sub>2</sub> and hence Fickian diffusion is expected. The diffusion of CO<sub>2</sub> is believed to occur within the amorphous domains of the polymer matrix and for this reason the diffusion in semi-crystalline polymers may be more complex than in the case of glassy polymers. The degree of crystallinity in a semicrystalline matrix therefore dictates the available amorphous fraction for CO<sub>2</sub> molecules, which may influence the diffusion characteristics. Furthermore, CO<sub>2</sub>-induced crystallisation is likely to lead to an increase in tortuosity factor and thus the diffusion pathway length may increase as a function of time. Syndiotactic polystyrene and poly(4-methyl-1-pentene)<sup>66</sup> are semicrystalline polymers which have crystalline phases (helical in the case of sPS) with lower densities than the amorphous phase, and represent exceptions because CO<sub>2</sub> access is not restricted to the amorphous domains. In fact, CO<sub>2</sub> diffuses faster in the helical sPS than in the amorphous polymer.<sup>67</sup>

The techniques available to study the diffusion of CO<sub>2</sub> through polymeric material include the barometric method, gravimetric method<sup>68</sup> and *in situ* FTIR spectroscopy.<sup>38</sup> Visual inspection of the polymer via an optical view cell enables the swelling characteristics to be assessed during the diffusion analysis.<sup>69</sup> It should be noted that diffusion coefficient determinations from these measurements rely on information from the total mass uptake of the polymer and, hence, do not permit region specific determination, since the measurements correspond to the overall changes occurring throughout the total polymer sample. The diffusion coefficients of CO<sub>2</sub> in a range of solid and liquid polymers are summarised in Table 2.

Table 2. Summary of CO<sub>2</sub> diffusion coefficients in a selection of polymers

| <i>Polymer</i>                                  | <i>Temp<br/>(°C)</i> | <i>Pressure<br/>(bar)</i> | <i>Diffusion Coefficient<br/>(m<sup>2</sup>s<sup>-1</sup>)</i> | <i>Ref</i> |
|-------------------------------------------------|----------------------|---------------------------|----------------------------------------------------------------|------------|
| Poly(butylenes succinate)<br>(PBS)              | 120                  | 123.41                    | $1.23 \times 10^{-9}$                                          | 70         |
|                                                 | 180                  | 24.66                     | $2.04 \times 10^{-9}$                                          |            |
|                                                 | 180                  | 83.04                     | $2.68 \times 10^{-9}$                                          |            |
| Poly(butylenes succinate-co-<br>adipate) (PBSA) | 120                  | 122.29                    | $0.95 \times 10^{-9}$                                          | 70         |
|                                                 | 180                  | 23.4                      | $2.06 \times 10^{-9}$                                          |            |
|                                                 | 180                  | 86.16                     | $2.05 \times 10^{-9}$                                          |            |
| Gelatinized starch                              | 70                   | 26                        | $7.5 \times 10^{-10}$                                          | 71         |
|                                                 | 70                   | 92                        | $1.9 \times 10^{-10}$                                          |            |
|                                                 | 70                   | 118                       | $0.9 \times 10^{-10}$                                          |            |
| Polyamide 11                                    | 215                  | 103                       | $2.29 \times 10^{-9}$                                          | 69         |
|                                                 | 215                  | 379                       | $5.29 \times 10^{-9}$                                          |            |
| PVAc                                            | 40                   | 3.29                      | $2.15 \times 10^{-12}$                                         | 72         |
|                                                 | 40                   | 30.39                     | $60.9 \times 10^{-12}$                                         |            |
|                                                 | 40                   | 66.26                     | $554 \times 10^{-12}$                                          |            |
| PS                                              | 100                  | 83.20                     | $1.67 \times 10^{-10}$                                         | 72         |
|                                                 | 150                  | 83.19                     | $5.33 \times 10^{-10}$                                         |            |
|                                                 | 200                  | 84.20                     | $9.90 \times 10^{-10}$                                         |            |
| HDPE                                            | 180                  | 39.65                     | $9.2 \times 10^{-9}$                                           | 73         |
|                                                 | 180                  | 97.43                     | $9.1 \times 10^{-9}$                                           |            |
|                                                 | 180                  | 139.8                     | $16.43 \times 10^{-9}$                                         |            |
| PMMA                                            | 40                   | 105                       | $1.04 \times 10^{-10}$                                         | 30         |
| Poly(chlorotrifluoroethylene)<br>(PCTFE)        | 40                   | 105                       | $7.08 \times 10^{-12}$                                         | 30         |
| Cross-linked PDMS                               | 40                   | 105                       | $7.08 \times 10^{-14}$                                         | 30         |
| LDPE                                            | 150                  | 6.54                      | $4.4 \times 10^{-9}$                                           | 74         |
|                                                 | 150                  | 15.64                     | $3.9 \times 10^{-9}$                                           |            |
|                                                 | 150                  | 29.97                     | $4.6 \times 10^{-9}$                                           |            |
| PET                                             | 28                   | 177.5                     | $8.2 \times 10^{-12}$                                          | 38         |
|                                                 | 28                   | 54.9                      | $5.4 \times 10^{-12}$                                          |            |
|                                                 | 50                   | 174                       | $2.2 \times 10^{-11}$                                          |            |
|                                                 | 50                   | 62                        | $1.8 \times 10^{-11}$                                          |            |

The diffusion of CO<sub>2</sub> in PET has received much attention due to the industrially viable technology of scCO<sub>2</sub> dyeing, as described in detail in section 3.5.1. Schnitzler and Eggers<sup>75</sup> implemented a gravimetric approach to study the mass transport of CO<sub>2</sub> in PET. The diffusion coefficient range was estimated at  $3.5 \times 10^{-10}$  to  $5.3 \times 10^{-9} \text{ m}^2\text{s}^{-1}$  with a temperature increase from 80°C to 120°C at various pressures. The sorption isotherm exhibited an S-bend shape, which is characteristic of a change in mass transport mechanism from dual mode sorption at low pressure to Fickian diffusion at higher pressures, also observed by Tang et al.<sup>76</sup> for CO<sub>2</sub> in polycarbonate. The sorption of CO<sub>2</sub> into PET was measured using *in situ* FTIR spectroscopy by Brantley et al.,<sup>38</sup> who also observed Fickian diffusion.

The plasticisation and swelling effect of CO<sub>2</sub> dissolved in a polymeric matrix can accelerate the diffusion of additives into the matrix. The “molecular lubrication”<sup>40</sup> provided by dissolved CO<sub>2</sub> molecules within the polymer matrix enables the diffusion of solutes to proceed in a less hindered manner to that in the absence of CO<sub>2</sub>. The ease of diffusion of the solute through the matrix is due to the increase in the free-volume as a consequence of the polymer being in a plasticised state, combined with the possibility of CO<sub>2</sub> molecules solvating the solute and thus transporting them through the matrix. It should be noted that the ease of the diffusion is dependent on the extent of “molecular friction” occurring between functionalities of the diffusing solute and the polymer chains.<sup>40</sup> The impregnation mechanism under which the solute may diffuse into the polymer matrix is an important distinction, which may occur via deposition or partitioning. In the case of deposition, the CO<sub>2</sub>-phase-soluble component is “carried” into the matrix and precipitated during depressurisation. Partitioning occurs when the affinity of the solute to the matrix results in a favourable partition coefficient in relation to the matrix and results in successful loading. In both cases the depressurisation results in the “freezing” of the solute distribution.

The CO<sub>2</sub> content in the matrix may be varied up to the equilibrium weight limit at a certain pressure. This enables one to manipulate the polymer free-volume and thus the diffusion characteristics of the solute may be “tuned” through temperature and pressure control. At low concentrations of dissolved CO<sub>2</sub> the polymer inter-chain distances are less than at higher concentrations and thus the diffusion rate is lower. An increase in

the weight fraction of CO<sub>2</sub> in PS at 60°C from 4 % to 11 % enhanced the diffusion of pyrene from  $10^{-10} \text{ m}^2\text{s}^{-1}$  to  $10^{-6} \text{ m}^2\text{s}^{-1}$ , revealed by steady state fluorescent measurements.<sup>77</sup> Similarly, for the case of the diffusion of the relatively large molecule of decacyclene in PS, an increase in CO<sub>2</sub> weight fraction from 7 % to 11 % resulted in the diffusion coefficient increasing from  $6.6 \times 10^{-10} \text{ m}^2\text{s}^{-1}$  to  $1.4 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ .<sup>78</sup> This typical diffusion enhancement has been observed for phenol in poly(bisphenol A carbonate),<sup>79</sup> azo-dye/PMMA<sup>80,81</sup> and azo-dye /PET<sup>82-84</sup> systems. The ability to control the diffusion rate simply by adjusting the operating conditions enables the possibility to tailor the properties, making it possible to prepare novel materials with a high degree of accuracy and customisation. The control over solute diffusivity lends itself to the preparation of a surface-restricted distribution, as seen in examples of grafting and blending which are discussed in a later section.

### 3.2.6. FOAMING

Polymeric foams have a closed shell structure ca. 10 µm in diameter and a cell density between  $10^9 - 10^{15} \text{ cells/cm}^3$ . These foamed materials have superior properties to their unfoamed counterparts in terms of enhanced ratio of flexural modulus to density and impact strength.<sup>85</sup> High-pressure CO<sub>2</sub> offers a particularly attractive alternative to traditional blowing agents due to its environmentally benign nature and relatively low cost. The phase out of ozone-depleting substances associated with the Montreal Protocol acts as a substantial driver towards the acceptance of this novel technology. Polymers that have been foamed using CO<sub>2</sub> include PMMA,<sup>86</sup> poly(vinylidene fluoride) (PVDF),<sup>87</sup> PS,<sup>88</sup> PS nanocomposite foams,<sup>89</sup> PET,<sup>90</sup> poly(ethylene-co-vinyl acetate),<sup>91</sup> styrene-co-acrylonitrile (SAN),<sup>92</sup> conductive polypyrrole/polyurethane foams,<sup>93</sup> conductive elastomeric foams<sup>94</sup> and biodegradable macroporous scaffolds.<sup>95</sup>

In the preparation of polymeric foams the polymer is saturated with CO<sub>2</sub> and hence the matrix is in a supersaturated state. Rapid temperature-ramping or depressurisation results in CO<sub>2</sub> escaping from the material which can cause nucleation, and as the  $T_g$  rises the foamed structure is “frozen”. The processing route to these microcellular materials can be achieved in a continuous<sup>88,89</sup> or discontinuous manner.<sup>96-100</sup> Rodeheaver and Colton<sup>101</sup> developed a model to predict the conditions required for the formation of open-cell microcellular foams in batch processes. Knowledge of the



relationship of the  $T_g$  depression with pressure is vital in this application, as it dictates the conditions required for cell nucleation and growth to occur.<sup>102</sup>

Microcellular foams prepared via the discontinuous method involve a 3-stage process: polymer saturation with CO<sub>2</sub> at a temperature below the  $T_g$  and a transfer stage followed by a rapid heating stage above the  $T_g$ . A characteristic feature of the foams prepared in this manner is the formation of a dense unfoamed skin layer.<sup>90,99</sup> The appearance of the dense skin layer is due to CO<sub>2</sub> desorption from the film surface during the transfer stage. The thickness of this layer may be controlled by the time of the transfer period and the morphology of the polymer.<sup>90</sup> Krause et al.<sup>97</sup> studied the foaming of thin films of polysulfone (PSU), poly(ether sulfone) (PES), and cyclic olefin copolymer (COC) in a discontinuous manner. Control of the cell size distribution was influenced by the saturation pressure, with higher pressures corresponding to a reduction in cell size diameter and an increase in the cell size distribution. Furthermore, foaming was shown to occur within a finite temperature window in which the cell density passes through a maximum. The temperature dependence on the foam architecture is due to two competing processes: nucleation and growth of cells and the CO<sub>2</sub> solubility. The CO<sub>2</sub> content in the polymer may be used to manipulate the foam architecture as shown with polysulfone/polyimide blends.<sup>98</sup> Closed-cell microcellular structures were formed at low concentration and, at high concentrations, an open nano-porous foam was formed, as confirmed by gas permeation measurements.

### 3.3. RHEOLOGY OF POLYMERS UNDER HIGH-PRESSURE CO<sub>2</sub>

The processing of polymeric material is an engineering challenge due to the high viscosity of the material. The molecular weight and degree of entanglement is generally very high in polymeric systems and consequently challenges are faced in terms of heat and mass transport. CO<sub>2</sub> provides a convenient way to reduce the  $T_g$  of the system, which increases the free-volume and consequently reduces the viscosity of the bulk polymer. The following section introduces the methods used to determine the viscosity of polymer systems subjected to CO<sub>2</sub> and describes the extent of viscosity reduction achievable for a selection of systems. The process of polymer extrusion is a direct beneficiary of the viscosity reduction and is described in the following section.

#### 3.3.1. METHODS FOR MEASUREMENTS OF POLYMER VISCOSITY UNDER HIGH-PRESSURE CO<sub>2</sub>

Viscosity measurement methods for polymers under high-pressure CO<sub>2</sub> may be divided into four classes: pressure driven, falling body, rotational devices and vibrating wire. Accurate viscosity measurements require a homogeneous solution to be prepared thus ensuring phase separation does not occur.<sup>39,103</sup> The following section introduces the various instrumental approaches to measure and quantify the extent of viscosity reduction.

Pressure driven devices include capillary viscometers and slit-die viscometers which share a common feature of the generation of a pressure-driven flow. The flow is generated by an upstream piston in the case of a capillary viscometer and by an extruder in the case of a slit-die. In both cases, measurements of pressure drop and flow rate are used to determine the viscosity. Both techniques have the inherent problem of pressure drop which may result in phase separation. For this reason, the techniques are suitable for low pressure measurements which may lead to the polymer equilibrium fraction not being reached. Capillary viscometers have the advantage of a relatively simple flow field and a small amount of sample required for the measurement. The technique yields an average steady shear viscosity in a precise and reproducible manner. However, the technique is limited to the study of relatively high shear rates and has the disadvantage



of a pressure drop across the capillary which affects the capillary flow. The same advantages are associated with the slit-die rheometer which involves the measurement of viscosity at a fixed shear rate. The technique has been widely applied to study CO<sub>2</sub>/polymer systems at high shear rates.<sup>104-108</sup> A significant disadvantage of the technique is the pressure drop across the die which may severely affect the viscosity.

Falling weight viscometers and rolling ball viscometers are both types of falling body devices. The common feature of both of these techniques is for a known body to fall through a fluid under the influence of gravity. The viscosity of the fluid can be determined by the time required for the body to fall a known distance through the fluid. Falling body techniques are suited to low viscosity systems due to the time required for the body to fall through a high viscosity fluid. Falling weight viscometers calculate viscosity with a single measurement. The application of falling weight viscometers has been limited to the study of very low viscosity polymer/CO<sub>2</sub> systems.<sup>109,110</sup> However, the simple design and ease of operation of the device combined with its high pressure capability make the falling weight viscometer advantageous for the study of Newtonian fluids. The falling ball viscometer has been used to measure the viscosity reduction of PDMS in the pressure range of 10-30 bar.<sup>111</sup>

Rotational viscometers are the most widely used devices for rheological determination; continuous measurements are made at a given shear rate or shear stress for extended periods of time. A specific benefit of rotational viscometers is the ability to perform subsequent measurements on the same sample under different conditions. A particular feature of rotational viscometers is the approximately uniformly distributed shear rate throughout the fluid specimen which gives good control of the fluid deformation, not possible with capillary rheometers. A specific issue relating to operation and design of high-pressure devices is the seal required for the spinning shaft and determining the torque. Flichy et al.<sup>112</sup> adapted a concentric cylindrical rheometer for the use of scCO<sub>2</sub>. The accessory is capable of pressure up to 150 bar and temperature to 300°C using a magnetic coupling to transfer the torque from the instrument motor to the measurement system, as shown in Figure 3.3.

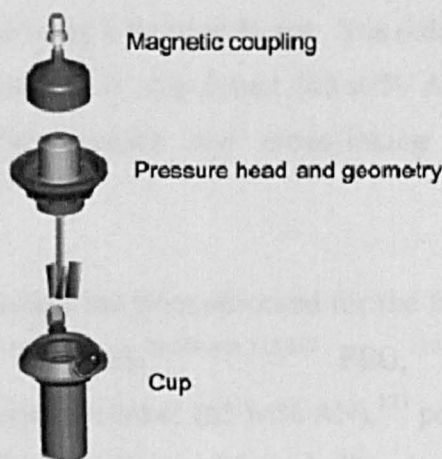


Figure 3.3. High pressure attachment for the rheometer, consisting of a magnetic coupling, pressure head, rotating vane geometry and a cup.<sup>112</sup>

Royer et al.<sup>113</sup> developed a magnetically levitated sphere rheometer (MLSR) based on a falling sphere rheometer and thus measurements are conducted at constant pressure. In essence, magnetic levitation is used to hold the sphere at a fixed point and the cylindrical sample chamber moved vertically with a motor, thus generating shear flow around the sphere. The change in magnetic force required to maintain the sphere in a stationary position is related to the shear stress. Specifically, the effects of pressure and concentration of CO<sub>2</sub> can be decoupled without the need for theoretical modelling.

### 3.3.2. VISCOSITY OF POLYMER MELTS SUBJECTED TO CO<sub>2</sub>

An important implication of the plasticising nature of CO<sub>2</sub> is the associated viscosity reduction of the polymer bulk. An increase in the CO<sub>2</sub> concentration results in a reduction of viscosity due to the associated increase in free-volume of the polymer. The ability to control the viscosity of the polymer with CO<sub>2</sub> concentration is well demonstrated with PS, for which the viscosity can be reduced between 25-80 %, depending on the operating conditions.<sup>107</sup> The  $T_g$  depression enables polymers to be processed at milder temperature conditions compared to conventional melt processing. The processing temperature needs to be optimised due to its consequential reduction in CO<sub>2</sub> solubility and hence viscosity reduction. This provides a route to process high-melt viscosity polymers<sup>114</sup> and enables thermally-sensitive polymers to be manipulated

without thermal degradation being a limiting factor. The reduced operating temperature enable polymers such as acronitrile copolymer (65 wt% AN) to be processed while avoiding unfavourable crystallisation and cross-linking that is associated with traditional melt processing.<sup>115</sup>

CO<sub>2</sub>-assisted viscosity reduction has been observed for the following polymer systems: PMMA,<sup>108</sup> PP,<sup>116</sup> PVDF,<sup>116</sup> PDMS,<sup>21,109,111,113,117</sup> PEG,<sup>118-121</sup> poly(ethylene glycol) nonphenyl ether,<sup>122</sup> acronitrile copolymer (65 wt% AN),<sup>123</sup> polyamide 11,<sup>69</sup> LDPE,<sup>116,124</sup> poly(propylene glycol) and suspensions of fumed silica in poly(propylene glycol),<sup>112</sup> PS,<sup>106,107,125</sup> binary mixtures of PS and toluene<sup>126</sup>, and biomaterials.<sup>127</sup> Viscosity reduction has also been observed for the following blends: PE/PS,<sup>105,110,128</sup> PS/PMMA,<sup>129</sup> PMMA/rubber, and PS/rubber.<sup>130</sup>

### 3.3.3. IMPLICATIONS FOR PROCESSING: EXTRUSION

The extrusion of polymeric material represents an effective way to ensure good heat and mass transfer in high-viscosity material. The introduction of CO<sub>2</sub> into the polymer melt whilst in the extruder housing facilitates operation at reduced conditions for the preparation of polymer blends, microcellular foams, particles and reaction in the case of reactive extrusion.<sup>131</sup> In the continuous method of extrusion, CO<sub>2</sub> is fed into the polymer melt and nucleation initiated (and hence foaming) at the exit die. Pressure and temperature conditions at the exit die are controlled to result in the supersaturation of the polymer. The inter-relationships between the key variables to control cell nucleation and growth in the continuous extrusion foaming process were summarised by Tomasko et al.<sup>39</sup>

Martinache et al. investigated the foaming of polyamide 11 using a slit-die extruder, producing a homogenous foam featuring well-distributed spherical closed shells with an average diameter of ca. 30 µm.<sup>69</sup> Garcia-Leiner and Lesser<sup>114</sup> studied the continuous extrusion of a range of high-melt viscosity polymers using a single screw extruder with a temperature controlled die. Control of the foam morphology (cell density and cell size distribution) of polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer and sPS was possible through the control of the die temperature.

Enhancement of nucleation was found to occur at reduced die temperatures and coalescence of the foamed structure evident at higher temperatures. Polystyrene has been continuously foamed in a two-stage single screw extruder by Han et al.<sup>88</sup> CO<sub>2</sub> concentration was used to restrict the nucleation point within the die and to control the cell morphology (size and density). Han et Al.<sup>89</sup> demonstrated that an introduction of ca. 5 % weight intercalated nanoclay was found to reduce the cell size from 25.3 to 11.1  $\mu\text{m}$  and the density from  $2.7 \times 10^7$  to  $2.8 \times 10^8$  cells/cm<sup>3</sup>, yielding a foam with an enhanced tensile modulus and improved barrier properties.

Siripurapu et al.<sup>87</sup> studied the continuous foaming of highly crystalline PVDF at 175°C with 2 wt% of scCO<sub>2</sub> which resulted in a foam structure with a heterogeneous cell size distribution and a low cell density, attributed to the low solubility of CO<sub>2</sub> in the polymer and therefore little CO<sub>2</sub> available for bubble formation. A further restriction is the semi-crystalline structure of PVDF; as the temperature falls below the  $T_m$ , crystallisation occurs, which expels CO<sub>2</sub> into the amorphous domains and may lead to cracking of the cell walls and therefore form discrete particles. Improvements in the foam characteristics were achieved by blending PVDF with PMMA. The solubility of CO<sub>2</sub> in the blend was increased by 4 % over neat PVDF due to the affinity of CO<sub>2</sub> to PMMA. A significant improvement in the foam morphology was observed for increasing content of PMMA in the blend.

Areerat et al.<sup>124</sup> developed a capillary rheometer equipped with a foam extruder to measure the viscosity of a LDPE/CO<sub>2</sub> system. The design included a near Infrared (NIR) sensor to monitor the CO<sub>2</sub> concentration within the polymer during processing. A schematic diagram of the equipment is shown in Figure 3.4. Viscosity reduction was observed with an increase in CO<sub>2</sub> concentration, with 5 % CO<sub>2</sub> corresponding to a viscosity reduction of 30 % compared to the neat polymer.



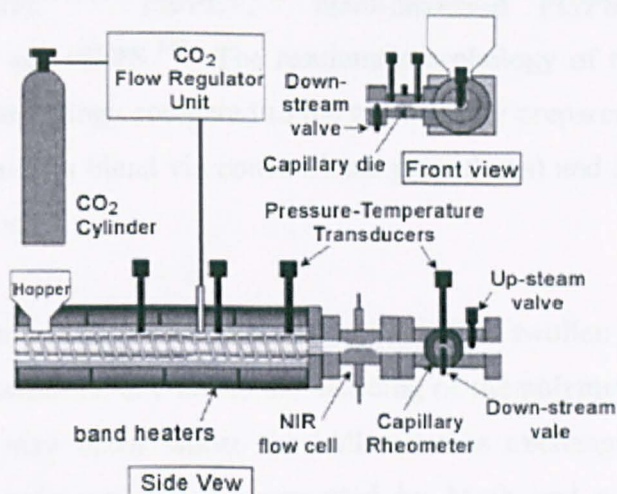


Figure 3.4. Schematic diagram of capillary tube rheometer with a CO<sub>2</sub> injection system, a foaming extruder and a NIR sensor.<sup>124</sup>

### 3.4. POLYMER BLENDS AND CO<sub>2</sub>

#### 3.4.1. CO<sub>2</sub>-ASSISTED BLENDING OF POLYMERS

The role of CO<sub>2</sub> to assist the blending of polymers may be viewed in one of the following manners:

- A transport medium used to impregnate a scCO<sub>2</sub> swollen matrix with an initiator and monomer, thus facilitating *in situ* polymerisation (which may occur in the presence of CO<sub>2</sub> or following venting).
- A viscosity reducing agent to facilitate the blending of high melt viscosity polymers.
- Route to the formation of polymer blends with a unique morphology, as demonstrated by Vega-González et al.<sup>132</sup> who produced fibrous networks of PMMA/ poly( $\epsilon$ -Caprolactone) via a semi-continuous SAS process.

*In situ* polymerisation to prepare immiscible blends was pioneered by Watkins and McCarthy<sup>133</sup> who stimulated other researchers to apply this methodology to prepare novel polymer blends,<sup>134-137</sup> fibre reinforced composite materials<sup>60</sup> and electrically conducting composites.<sup>93,94,138-141</sup> Polymer blends produced in this manner include

PS/poly(vinyl chloride),<sup>142,143</sup> PS/PET,<sup>144</sup> nano-dispersed PP/PS interpenetrating networks,<sup>145</sup> PP/PS<sup>146</sup> and PE/PS.<sup>147</sup> The resultant morphology of the polymer blend may have a unique morphology compared to the traditionally prepared counterpart (if it is feasible to prepare such a blend via conventional procedures) and therefore demands a thorough investigation.

The diffusion of the monomer and initiator within the scCO<sub>2</sub> swollen matrix determines the extent that polymerisation, and hence the blending of the polymers, may occur, i.e. surface modification may occur whilst the bulk remains unchanged. This surface specific blending of polymers was demonstrated by Muth and co-workers,<sup>137</sup> who impregnated and polymerised methacrylic acid within a scCO<sub>2</sub> swollen PVC matrix to a depth of ca. 180 µm. The modification of a polymer surface is obtainable through grafting,<sup>144,147-151</sup> involving the surface modification of the bulk polymer with functional groups.

The ability of CO<sub>2</sub> to induce morphological alterations in polymers requires the morphology of the blends prepared using CO<sub>2</sub> to be examined. Zhang et al.<sup>152</sup> investigated the morphology of a (53/47 w/w) ultra high molecular weight polyethylene (UHMWPE)/PMMA blend. Tapping mode atomic force microscopy (TMAFM) was used to investigate the morphological structure of the resultant blend, revealing the presence of three distinct phases: crystalline UHMWPE, amorphous UHMWPE and domains of amorphous PMMA which were estimated to range in size between 10 – 100 nm. Furthermore, the effect of the CO<sub>2</sub>-assisted polymerisation was found to increase the crystallinity of UHMWPE from 50.4 % in the starting material to 59.2 % following the polymerisation blending. Busby et al.<sup>153</sup> applied a combination of FTIR spectroscopy, DSC, and AFM to characterise nano-structured blends of polymethacrylates in UHMWPE prepared via *in situ* polymerisation. Methacrylates were found to exist in dispersed nano-scale domains which have not been prepared via conventional routes. An increase in methacrylate fraction resulted in the fragmentation of the UHMWPE lamellae into low T<sub>m</sub> crystallites. Shieh et al.<sup>154</sup> probed the CO<sub>2</sub>-induced morphological alterations induced in a PEO/PMMA blend using small angle X-ray scattering (SAXS). The crystal and amorphous layer thickness of PEO was found to increase following exposure to CO<sub>2</sub>, and the extent of the layer thickening was revealed



to be controlled by the fraction of PMMA in the blend. The increase in lamellae thickness was attributed to re-crystallisation of the PEO domains.

The preferential interaction of CO<sub>2</sub> with individual phases of polymer blends is dictated by the affinity of CO<sub>2</sub> to the individual components. Zhou et al.<sup>155</sup> applied AFM and phase contrast microscopy to study the effect of scCO<sub>2</sub> on the surface structure and phase morphology of PMMA/PS (50/50 w/w) thin films. AFM was used to monitor the morphology of the cast film as a function of temperature, pressure and exposure time. Initially PMMA appeared as a dispersed surface phase elevated from a continuous PS matrix. The series of AFM images in Figure 3.5 indicate that the  $T_g$  of PMMA/PS blend at 200 bar is less than 60°C and at a temperature of 70°C the  $T_g$  occurs at a pressure greater than 200 bar, as seen by the initially elevated PMMA phase falling into the PS phase.

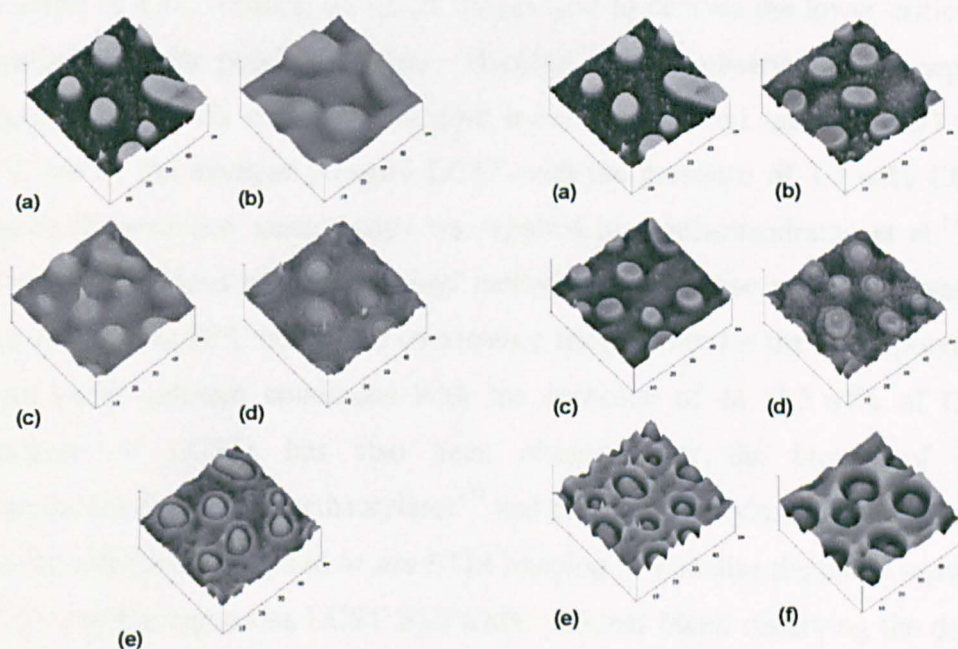


Figure 3.5. Three-dimensional AFM images ( $50 \times 50 \mu\text{m}^2$ ) of PMMA/PS (50/50 w/w) blend thin films. Images on the left were treated for 2 hours in scCO<sub>2</sub> (200 bar) at different temperatures: (a) as cast film, (b) 40 °C, (c) 50 °C, (d) 60 °C, (e) 70 °C. Images on the right were treated for 2 hours in scCO<sub>2</sub> (70 °C) at different pressures: (a) as cast, (b) 50 bar, (c) 100 bar, (d) 200 bar, (e) 300 bar, (f) 400 bar.<sup>155</sup>

### 3.4.2. CO<sub>2</sub>-INDUCED PHASE SEPARATION IN POLYMER BLENDS

Polymer blends may be described in terms of the temperature dependence of the Flory-Huggins interaction parameter ( $\chi$ ). In the case of an upper critical solution temperature (UCST) blend,  $\chi$  decreases with temperature and the blend remains miscible. For phase separation to occur in a UCST blend the temperature must be lower than the critical solution temperature. In a lower critical solution temperature (LCST) blend,  $\chi$  increases with temperature and thus phase separation occurs above the critical solution temperature. The ability of CO<sub>2</sub> to mimic heat means that miscibility is enhanced in the case of UCST blends, but miscibility is depressed for LCST blends. Ramachandrarao et al.<sup>156</sup> explained this phenomenon as being due to a dilation disparity occurring at higher CO<sub>2</sub> concentration as a result of the preferential affinity of CO<sub>2</sub> to one of the components of the blend, inducing free-volume and packing disparity.

The effect of CO<sub>2</sub> sorption on LCST blends acts to depress the lower critical solution temperature of the polymer system. Watkins et al.<sup>157</sup> observed phase separation of homogeneous blends of poly(deuterated styrene)/poly(vinyl methyl ether) more than 115°C below the ambient pressure LCST with the presence of 3.3 wt% CO<sub>2</sub>. High-pressure fluorescence spectroscopy was applied by Ramachandrarao et al.<sup>158</sup> to study various compositions of PS/poly(vinyl methyl ether). Phase separation was found to occur as much as 90°C below the coexistence temperature for the corresponding binary blends under ambient conditions with the presence of ca. 3.5 wt% of CO<sub>2</sub>. The depression of LCSTs has also been observed for the blends of deuterated polystyrene/poly(*n*-butyl methacrylate)<sup>157</sup> and deuterated polybutadiene/polyisoprene.<sup>156</sup> Kazarian and Chan<sup>159</sup> applied *in situ* FTIR imaging to visualise the phase separation of a (50/50 w/w) homogeneous LCST PS/PVME polymer blend observing the domain size of ca. 200  $\mu\text{m}$ .

The presence of CO<sub>2</sub> in UCST polymer blends has shown to enhance blend miscibility. Walker et al.<sup>160</sup> observed a depression of the critical temperature for low-molecular-weight blends of polystyrene/polyisoprene using a combination of visual inspection, small-angle neutron scattering and spectrophotometry. In the presence of 138 bar of CO<sub>2</sub> a reduction of the cloud point was observed compared to the same system in the



absence of scCO<sub>2</sub>. This demonstrates the ability of CO<sub>2</sub> to promote miscibility in UCST blends and consequently an increase in the processing window is available. Walker et al.<sup>161</sup> performed a thermodynamic analysis of the UCST blend of PDMS/PEMS in the presence of high-pressure CO<sub>2</sub>.

### **3.5. SUPERCRITICAL IMPREGNATION OF POLYMERIC MATERIALS**

Polymer impregnation involves the introduction of a guest doping solute into a host polymer matrix. The SCF impregnation of polymeric materials offers a particularly attractive processing route due to the “solvent-free” nature of the technology. Once the system is depressurised, CO<sub>2</sub> quickly escapes from the polymer and the guest solute remains “trapped” in the matrix without the presence of CO<sub>2</sub> in the finished product. Supercritical CO<sub>2</sub> has been successfully used to impregnate various dyes, drugs and metal complexes into polymer hosts.

#### **3.5.1. DYEING OF POLYMERIC MATERIALS**

Traditionally the textile industry dyes hydrophobic polymer fibres using an aqueous medium containing surfactants and dispersing agents to assist the dyeing process. Not only does this method require a clean water source, but also necessitates post processing of the effluent water stream to remove the liquor constituents. CO<sub>2</sub> is able to swell hydrophobic fibres by penetrating into them and thus allow the dye to penetrate the polymer matrix. The use of scCO<sub>2</sub> technology as a replacement for the traditional use of water as the dyeing medium offers substantial environmental advantages, and has been the subject of several recent reviews.<sup>162-165</sup> Structural modifications as a result of the dyeing process have been investigated and showed that the migration of oligomers to the surface of PET fibres and the shrinkage of polyolefin fibres (history dependant) occur.<sup>164</sup> The use of scCO<sub>2</sub> technology as a replacement for the traditional aqueous method for dyeing of polyesters is a viable alternative that has grown in international interest since 1995<sup>14</sup> and operates under the principles demonstrated by Berens.<sup>166</sup> An obvious driver for scCO<sub>2</sub> dyeing is the environmental benefit that has been an underlying feature of all of the applications described in this chapter. Additionally, the

use of CO<sub>2</sub> results in a great gain in the rate of the diffusion of dye through the matrix.<sup>81,82</sup>

Initially it was deemed that high dye solubility in the CO<sub>2</sub> phase was required to enable impregnation to proceed via a deposition mechanism, stimulating investigation of solubility characteristics.<sup>167,168</sup> However, successful dyeing has been demonstrated for dye solubility as low as 10<sup>-6</sup> M as a result of the affinity of the dye to the polymer, thus facilitating impregnation via partitioning.<sup>40,81</sup> This impregnation mechanism is beneficial for the dyeing of polymeric materials since at any one time there is a very low concentration of dye in the CO<sub>2</sub> phase and hence dye loss is minimised. The diffusion mechanism under supercritical conditions has been studied by methods including the film roll technique<sup>82,83</sup> and the gravimetric approach,<sup>75</sup> demonstrating that the diffusivity is dye specific and may be “tuned” with temperature and pressure control. West et al.<sup>81</sup> revealed that the functionalities on the diffusing dye molecules need to be taken into account due to so-called “molecular friction” (intermolecular interactions such as H-bonding) that can occur between the functional groups of the dye and the polymer matrix. This was demonstrated by the diffusion rate of 4,4’-(dimethylamino)nitroazobenzene (DENAB) in PMMA being greater than that of Disperse Red 1 (DR1) due to the hydroxyl groups in DR1 interacting with the carbonyl functionalities of PMMA. Dye diffusion in PMMA has also been monitored by *in situ* UV-vis.<sup>40</sup> The diffusion coefficients for a range of disperse dyes in PET are summarised in Table 3.

Table 3. Summary of dye diffusion data on PET/disperse dye systems.

| Temp<br>(°C) | Pressure<br>(bar) | Geometry                                     | Dye                         | Measurement Technique       | $D$ (m <sup>2</sup> s <sup>-1</sup> )          | Ref |
|--------------|-------------------|----------------------------------------------|-----------------------------|-----------------------------|------------------------------------------------|-----|
| 120          | 300               | cylindrical fibre (1.3 mm Ø)                 | C.I Disperse Red 324        | Gravimetric                 | $1.07 \times 10^{-13}$                         | 74  |
| 120          | 300               | cylindrical fibre (1.3 mm Ø)                 | C.I. Disperse Orange<br>149 | Gravimetric                 | $1.93 \times 10^{-11}$                         | 74  |
| 90           | 220               | cylindrical film roll – (effectively 6 mm Ø) | Disperse Yellow             | Film roll method and UV-VIS | $1.4 \times 10^{-14}$                          | 82  |
| 90           | 220               | cylindrical film roll – (effectively 6 mm Ø) | Disperse Blue               | Film roll method and UV-VIS | $2.3 \times 10^{-14}$                          | 82  |
| 110          | 220               | cylindrical film roll – (effectively 6 mm Ø) | Disperse Yellow             | Film roll method and UV-VIS | $1.2 \times 10^{-13}$                          | 82  |
| 110          | 220               | cylindrical film roll – (effectively 6 mm Ø) | Disperse Blue               | Film roll method and UV-VIS | $1.1 \times 10^{-13}$                          | 82  |
| 110          | 250               | cylindrical film roll – (effectively 6 mm Ø) | Disperse Yellow             | Film roll method and UV-VIS | $1.5 \times 10^{-13}$                          | 82  |
| 110          | 250               | cylindrical film roll – (effectively 6 mm Ø) | Disperse Blue               | Film roll method and UV-VIS | $1.6 \times 10^{-13}$                          | 82  |
| 120          | 250               | cylindrical film roll                        | C.I. Disperse Red 324       | Film roll method and UV-VIS | $7.1 \times 10^{-14}$                          | 81  |
| 100          | 250               | cylindrical film roll                        | C.I. Disperse Red 324       | Film roll method and UV-VIS | $1.2 \times 10^{-14}$                          | 81  |
| 100          | 200               | cylindrical film roll                        | C.I. Disperse Red 324       | Film roll method and UV-VIS | $9.0 \times 10^{-15}$                          | 81  |
| 100          | 150               | cylindrical film roll                        | C.I. Disperse Red 324       | Film roll method and UV-VIS | $2.4 \times 10^{-15}$                          | 81  |
| 100          | 150               | cylindrical film roll                        | C.I. Disperse Red 324       | Film roll method and UV-VIS | $7.1 \times 10^{-14}$<br>10% Ethanol Modifier  | 81  |
| 100          | 170               | cylindrical film roll                        | C.I. Disperse Red 324       | Film roll method and UV-VIS | $5.5 \times 10^{-14}$<br>8.5% Ethanol Modifier | 81  |

### 3.5.2. PREPARATION OF MATERIALS FOR OPTICAL APPLICATION

Materials with non-linear optical (NLO) properties are of particular interest to the telecommunications industry and specific to the technology of photonics.<sup>169</sup> The impregnation of polymeric materials with organic, azobenzene dyes is a possible route to the preparation of these materials. Poling techniques are required to avoid the polar molecules aligning anti-parallel to each other which inhibits centro-symmetric arrangements.<sup>170</sup> A thorough review of the preparation and assessment of polymeric materials with azo-dyes for non linear optics has recently been prepared by Yesodha et al.<sup>171</sup>

The preparation of polymeric materials for NLO applications involves the plasticisation of the polymer matrix followed by the impregnation of the chromophore. A specific benefit to this method is that the rapid release of CO<sub>2</sub> enables the matrix to be “frozen” and hence the dye molecules do not have time for reorientation to occur.<sup>103</sup> A general problem with the polymeric guest-host system is the stability of the system due to polymer chain relaxation which can result in the loss of the necessary alignment. SCF treatment of such materials allows one to process them at lower temperatures due to plasticisation and thus to possibly achieve better orientation of the dyes in polymer matrix.

### 3.6. PREPARATION OF BIOMATERIALS AND PHARMACEUTICAL FORMULATIONS

The “solvent-free” nature of CO<sub>2</sub> makes it an ideal choice for the processing of pharmaceutical materials that require stringent control over product integrity and the absence of harmful solvent residues. Retention of the bioactivity of the active component in the formulation is a prerequisite for the processing route of pharmaceutical formulations. The ability to plasticise and reduce the melting temperature<sup>118,172,173</sup> of polymers enables the processing of thermally labile active components, thereby avoiding the possibility of thermal degradation and enabling the bioactivity to remain following release from the formulation. The reduction of polymer viscosity also facilitates the mixing of the polymer with an active component.<sup>174</sup> The

ability of CO<sub>2</sub> to foam polymers provides a convenient method to prepare scaffolds for the application of tissue engineering, providing an environment able to promote the differentiation and growth of tissue. Particle formation<sup>175</sup> provides a route to prepare formulations with controlled release characteristics via encapsulation. The use of CO<sub>2</sub> also provides a convenient method to deliver coatings to pharmaceutical formulations.<sup>176</sup> A detailed discussion of polymer processing for various pharmaceutical applications has been recently provided.<sup>177</sup>

One of the interesting applications where scCO<sub>2</sub> processing of polymeric materials is beneficial is the method of Particles from Gas Saturated Solution (PGSS). PGSS is a technique able to form polymer/active compound foams, solid particles or droplets.<sup>20</sup> The principle of the technique is for CO<sub>2</sub> to form a gas saturated solution/suspension which may then be foamed or passed through a nozzle to produce solid particles or droplets. The technique is suited to thermally labile components since the process is undertaken at near ambient temperature. Control of particle size has been achieved by the introduction of N<sub>2</sub> back-pressure in the collection chamber, as demonstrated by Hao et al.<sup>178</sup> with poly(DL-lactic acid). The PGSS method has been shown to enhance the dissolution characteristics of nifedipine from PEG 400.<sup>179,180</sup>

The foaming of polymeric materials with scCO<sub>2</sub> is an effective, "clean" processing route to the formation of scaffolds. 3-D scaffolds for tissue engineering applications require an environment that is conducive to cell attachment and cell growth, an interconnected/vascularised architecture to facilitate the transport of the necessary components into and out of the scaffold and the mechanical compatibility for the specific tissue. Successful examples involve the preparation of scaffold materials for the delivery of specific factors such as chondrocytes,<sup>181</sup> provide the required environment to promote osteogenesis<sup>174</sup> and the ability to deliver of range of growth factors.<sup>182</sup> The cellular structure of polymers foamed using CO<sub>2</sub> often results in closed-shell morphology. This is disadvantageous for 3-D scaffolds as it does not fulfil the requirement of interconnectivity and thus the diffusion of the required factors into and out of the scaffold is restricted. This limitation may be overcome with the additional step of particulate leaching.<sup>183</sup>

The formation of solid dispersions may be achieved via the impregnation of an active component from a supercritical solution. The benefit of this approach is that it often results in the active component being molecularly dispersed within the host matrix<sup>25</sup> which is advantageous compared to the reduced bioavailability in the crystallised form that may be formed in the case of traditional methods. Furthermore, that study<sup>25</sup> proved that the impregnation of drugs from a supercritical solution reduces the water uptake into the formulation as a result of the interaction between the polymer and the drug which will help to extend the shelf life of the product. The topic of supercritical fluid impregnation of polymers for drug delivery is discussed in more detail in a recent book.<sup>177</sup>

### 3.7. CONCLUSIONS

The key property of CO<sub>2</sub> that facilitates all of the applications described in this chapter is its function as a transient plasticiser. The body of literature summarised in this chapter demonstrates the suitability of high-pressure and scCO<sub>2</sub> to many diverse applications in polymer processing. The key advantages associated with CO<sub>2</sub> have been described and highlighted compared to conventional means of processing. Despite the costs associated with processing under high pressures, the advantages described offer significant value to the finished product and thus act as drivers for the adoption of this novel processing route. A detailed understanding of the effect of CO<sub>2</sub> on polymeric materials and characterisation of the processed materials is still required to fully exploit the tremendous potential of this processing technology.

## **CHAPTER 4**

# **INTRODUCTION TO VIBRATIONAL SPECTROSCOPY**

## 4. INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

### 4.1. INTRODUCTION

Probing the characteristic vibrations of a specific bond or group of bonds is possible due to the quantised nature of the vibrational energy levels. A molecule can be represented by atoms of certain masses that are connected by compressible bonds and capable of undergoing periodic oscillations at characteristic frequencies,  $\nu$  ( $\text{s}^{-1}$ ). The permitted vibrational energy of a diatomic molecule is defined by Equation 4.1, where  $h$  corresponds to the planck constant and  $v$  refers to the vibrational quantum number ( $v = 0, 1, 2, 3 \dots$ ).

$$E = h\nu(v + \frac{1}{2}) \quad (4.1)$$

It is conventional in spectroscopy to use wavenumber ( $\tilde{\nu}$ ) with units  $\text{cm}^{-1}$  rather than  $\nu$  as defined by Equation 4.2, where  $k$  is the force constant,  $\mu$  is the effective mass and  $m_1$  and  $m_2$  are the masses of the respective atoms in a diatomic molecule.

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (4.2)$$

$$\mu = \left( \frac{m_1 m_2}{m_1 + m_2} \right) \quad (4.3)$$

Infrared and Raman spectroscopy are complementary techniques which differ distinctly in terms of instrumental requirements and the mechanism by which changes in the population of vibrational energy levels are induced and studied, as shown schematically in Figure 4.1. Molecular vibrations that can be observed with IR and Raman spectroscopy are governed by selection rules that define the interaction of the molecular vibrations with the external oscillating electric field (electric component of the electromagnetic radiation). Raman activity is defined by a non-zero change in polarisability during a vibration, whereas IR activity requires a non-zero change in dipole moment with vibration coordinate.



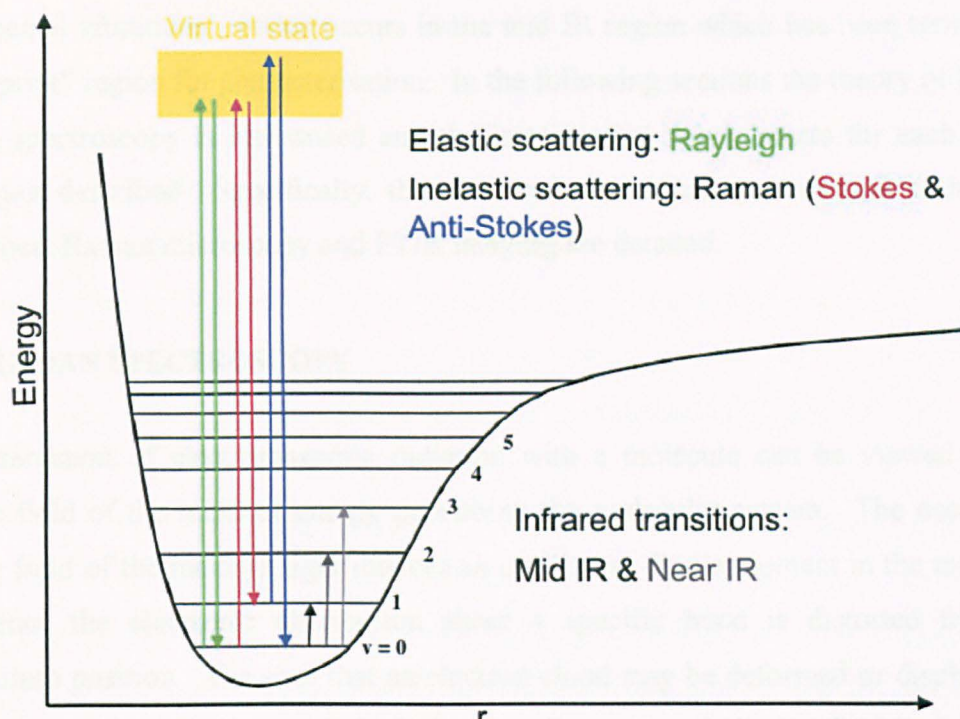


Figure 4.1. Schematic representation of the potential energy of a diatomic molecule showing typical Raman and IR transitions.

The difference in interaction mechanism between Raman and IR active spectroscopic transitions can be appreciated by comparing the Stokes Raman line (red) and the mid IR transition (black) in Figure 4.1. In both situations the result is to excite the molecule from the ground state ( $v = 0$ ) to the first excited state ( $v = 1$ ). However, this occurs directly in the case of IR and via a transitional state (termed “virtual” state) in Raman spectroscopy. The energy required for the IR transition is equal to the difference in energy that occurs between the incident and scattered Raman light. It follows that IR spectroscopy measures the absorption of a specific quantised amount of energy (and hence a particular frequency) while Raman measures the “shift” in energy between the incident and scattered light to give the same difference between the quantised energy levels. In a polyatomic molecule consisting of numerous distinguishable chemical bonds, the number of vibrations is dependent on the structural symmetry and the electronic distribution of the system. In a molecule consisting of  $N$  atoms the number vibrational modes is  $3N - 6$  and for the case of linear molecules  $3N - 5$  vibrational modes are permitted. The resultant spectrum reflects the presence or absence of a specific vibration over a defined range of frequencies. The frequency range of

fundamental vibrational modes occurs in the mid IR region which has been termed the “fingerprint” region for characterisation. In the following sections the theory of Raman and IR spectroscopy is introduced and the instrumental requirements for each of the techniques described. Specifically, the advanced vibrational spectroscopic techniques of confocal Raman microscopy and FTIR imaging are detailed.

## 4.2. RAMAN SPECTROSCOPY

The interaction of electromagnetic radiation with a molecule can be viewed as the electric field of the incident energy perturbing the molecular system. The oscillating electric field of the incident light induces an oscillating dipole moment in the molecule and hence the electronic distribution about a specific bond is distorted from its equilibrium position. The ease that an electron cloud may be deformed or displaced to produce an electric dipole under the influence of an external electric field is described by its polarisability. The induced dipole moment ( $\mu'$ ) resulting from exposure to an external field can be described in terms of the molecular polarisability ( $\alpha$ ) and the electric field strength ( $E$ ) as shown in Equation 4.4.

$$\mu' = \alpha E \quad (4.4)$$

This can be written in the form of three linear equations:

$$\mu'_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \quad (4.5)$$

$$\mu'_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \quad (4.6)$$

$$\mu'_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \quad (4.7)$$

All of the nine components  $\alpha_{ij}$  are components of the polarisability tensor ( $\alpha$ ). The polarisability of a molecule in various directions can be visualised by the polarisability ellipsoid which is a three-dimensional surface proportional to  $1/\sqrt{\alpha_i}$ .

The external field polarises the molecule in a time dependent manner and raises the energy of the system to a so-called “virtual state” thereby inducing a dipole. Relaxation from this virtual state occurs by the emission of a photon. Raleigh scattering describes

the situation of zero energy exchange between the incident radiation and the molecule i.e. elastically scattered light. A discrepancy in energy between the incident and emitted radiation is caused by the Raman effect which produces inelastically scattered photons. The scattered radiation generally exists in pairs that appear in the spectrum at symmetrically distributed positions about the Rayleigh line. Photons that lose energy appear on the lower frequency side of the exciting line, known as Stokes lines, and the high frequency side responses are known as anti-Stokes lines. A diagrammatic representation of Raman and Rayleigh scattering is presented in Figure 4.1.

The relative intensity of the Stokes and anti-Stokes lines reflects the population distribution of the vibrational energy levels as described by the Boltzmann distribution. The population of excited states is less than the ground state at thermal equilibrium, which is reflected in the intensity of the Stokes line being greater than the anti-Stokes. In Raman spectroscopy it is normal practice to study the Stokes response due to its greater intensity. This is of great importance when one considers the low probability of the Raman effect and therefore the need to study the most intense signal generated.

Raman activity dictates a change in polarisability must accompany the change in internuclear distance during a vibration, as described in Equation 4.8.  $Q_k$  is the  $k^{\text{th}}$  normal coordinate associated with vibration of wavenumber  $\nu_k$ . The subscript 0 refers to the derivative taken at the equilibrium configuration. During a Raman active vibration the polarisability changes as a function of normal coordinate and thus the induced dipole is a function of the vibrational frequency  $\nu_k$  and the oscillating incident electric field: the induced dipole moment is modulated by the vibration due to the periodic change in polarisability.

$$\alpha'_k = \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \neq 0 \text{ (Raman activity requirement)} \quad (4.8)$$

The induced dipole oscillates with three distinct frequencies  $\nu_0$  and  $\nu_0 \pm \nu_k$  (Rayleigh, Stokes and anti-Stokes), resulting in the emission of radiation at three distinct frequencies. The derived polarisability tensor is a reflection of the sensitivity of the molecular polarisability to changes of the nuclear configuration along the normal

coordinate of vibration. The intensity of a Raman band in the spectrum is described by Equation 4.9 where the proportionality factor  $k$  accounts for factors including the collection efficiency,  $N$  the number of molecules,  $I_L$  the laser power at the sample, and  $\nu_0$  and  $\nu_L$  are the wavenumber of the laser excitation and the specific vibrational mode respectively.

$$I_{Raman} = kNI_L (\nu_0 - \nu_L)^4 \left( \frac{d\alpha}{dQ} \right)^2 \quad (4.9)$$

The sensitivity of the observed Raman intensity to factors other than solute concentration complicates quantitative analysis with Raman spectroscopy. Quantitative considerations when using Raman spectroscopy have been summarised in a publication by Pelletier.<sup>184</sup>

#### 4.2.1. RAMAN MICROSCOPY

The desire to couple a Raman spectrometer to a microscope is to facilitate the analysis of samples on the micrometer scale. The principal role of the microscope is to focus the laser energy (to a size approaching the diffraction limit) onto a desired location on the sample and then to collect the Raman scatter from the sample. Collection of the scattered light is conventionally performed using the same objective and hence a 180° backscatter configuration is employed. The theoretical spatial resolution achievable is defined by the Rayleigh criteria as shown in Equation 4.10, where  $\lambda$  is the wavelength,  $NA$  is the numerical aperture ( $NA = n \sin\theta$ ) of the objective and  $r$  is the distance between two points required to be just resolved.<sup>185</sup>

$$r = \frac{1.22\lambda}{2NA} \quad (4.10)$$

The use of various objective magnifications enables the resolution of the measurement to be controlled and the local energy, and consequential heating effects, to be regulated. The use of a motorised xyz stage facilitates controlled mapping of a required sample



area which leads to the possibility of generating a map based on the distribution of a specific, spectroscopically distinguishable component. This section serves to describe confocal Raman microscopy and the specific sampling technique of depth profiling/z-sectioning of a sample. The dispersive Raman spectrometer coupled to the microscope used in this thesis is shown in Figure 4.2, the function and necessity of the various instrumental features in a dispersive Raman arrangement are described below.

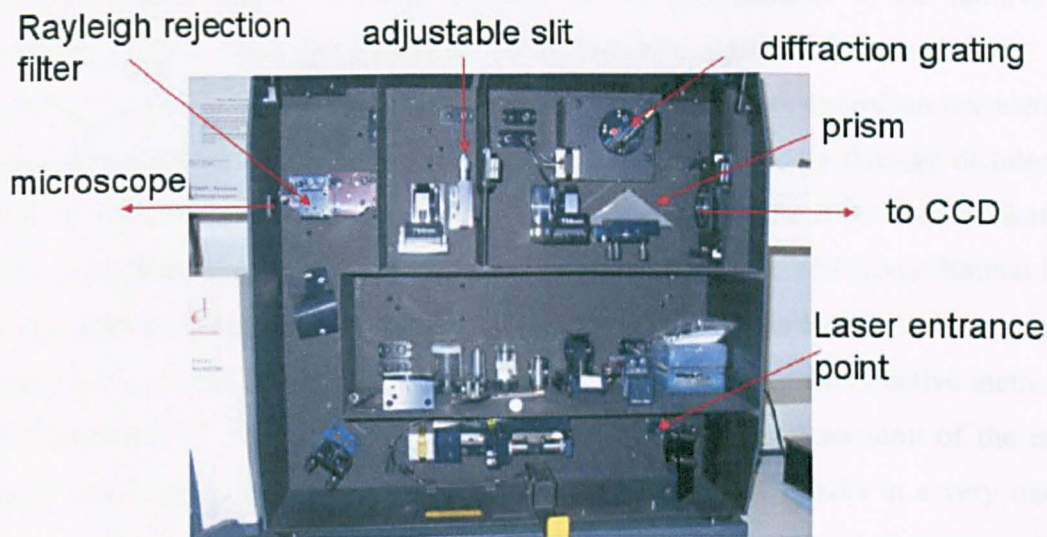


Figure 4.2. Photograph of dispersive Raman spectrometer.

*Source:* A 785 nm solid diode laser was employed to measure all of the data presented in this thesis. The submicron wavelength employed for Raman microscopy is the basis for the inherently high spatial resolution offered by the technique. Employing short excitation wavelength enhances the theoretical spatial resolution, however, fluorescence presents a significant limitation to the observation of the relatively inefficient Raman scatter and appears as a broad background under which the desired Raman information is hidden. One approach to remove the effect of fluorescence caused by an impurity is to irradiate the sample for some time period, whereby the fluorescence is described to be “bleached” out. The success of this approach is limited and sample specific.

Regardless of the origin of the fluorescence, (bulk sample or impurity), it is the excitation wavelength used to probe the sample that is responsible for the observed phenomena. The development of FT Raman has enabled a greater range of samples to be analysed that would otherwise fluoresce. FT Raman utilises laser radiation with a

wavelength greater than 1  $\mu\text{m}$  and hence the “virtual” state that the molecule is excited to is far removed from the electronic excited state.<sup>186</sup> More sophisticated approaches exist to retrieve the desired Raman information *in expense* of the fluorescence signal. The use of time gating has been successfully demonstrated to reject fluorescence by exploiting the distinctive lifetimes of the events. Raman scattering occurs at a timescale less than 1 femtosecond whilst fluorescence has a lifetime of a few picoseconds.<sup>187,188</sup>

*Rayleigh rejection filter:* A key function of the spectrometer is the removal of elastically scattered Rayleigh light from the inelastically scattered Raman photons. The efficiency of the filter to remove only the Rayleigh scatter (laser excitation wavelength) whilst allowing light with any degree of shifted frequency to pass through dictates the ability to access low wavenumber information. In practice, the filter used is likely to have a cut-off approximately 50  $\text{cm}^{-1}$  from the excitation line, and hence Raman light that was shifted within this limit is lost. When low wavenumber Raman spectroscopy is desired, the use of atomic metal vapour filters have proved to be an effective method to accomplish this.<sup>189</sup> The principle is to tune the laser to the absorption of the metal vapour, which has a very narrow absorption frequency. This results in a very narrow filter cut-off and hence gives access to the desired low wavenumber information. Edge filters cut-off all energy below a specific threshold near to the Rayleigh line and thus only the Stokes scatter is available.

*Dispersion element and charge-coupled detector(CCD camera):* The output of the Rayleigh rejection filter is very low intensity Raman signal which is a combination of all the discrete shifted frequencies of the both the Stokes and anti-Stokes lines (when not using an edge type filter). Separation of the frequencies and their subsequent detection is achieved by dispersing the wavelengths into spatially resolved positions which are directed onto and detected by a series of pixels arranged in an array fashion on the charge-coupled detector (CCD).

The diffraction grating is capable of dispersing the Raman light into its constituent frequencies due to the wavelength dependent dispersion characteristics of the grating. The dispersed light is directed onto a CCD, consisting of an array of pixels that convert



incident photons to electric charge which is read-off from the spatially variant pixels. The number of photons converted is proportional to the amount of charge stored on the pixel. In practice it is unlikely that the pixel will detect a discrete wavelength, but rather a range of which determines the spectral resolution of the measurement. When light is collected from the diffraction grating at one position, known as a static scan, the spectral range is limited by the dispersion properties of the grating and ultimately the pixel size on the CCD.

A schematic diagram of the CCD camera function to generate a Raman spectrum is presented in Figure 4.3. The basic arrangement is shown to consist of a rectangular array of pixels with the spectral information dispersed along the columns and the spatial information along the rows. The red circles are representative of photons detected at a particular wavelength, the size of which is a qualitative indicator of number. Control of the active architecture of the CCD enables, in part, confocal operation to be achieved by a process known as “pixel binning” which is described in the following section. Refinement of the active architecture enables one to select the desired spatially dispersed information that is averaged in the resultant Raman spectrum.

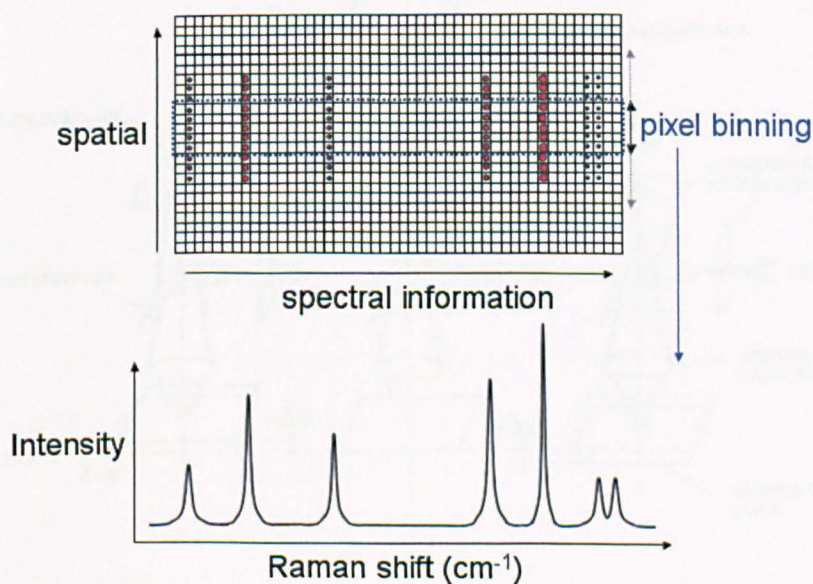


Figure 4.3. Schematic diagram of CCD camera.

## 4.2.2. CONFOCAL OPERATION

The sampling capability of depth profiling/z-sectioning enables the non-destructive measurement of Raman spectra at spatially resolved, sub-surface locations in a sample. The confocal arrangement employed functions on the following principles<sup>190</sup> as shown schematically in Figure 4.4.

- (i) An exact optical conjugation onto the sample of the pinhole apertures (which are employed for both illumination and detection of the specimen) results in combined spatial filtering effects. They produce a narrower point spread function (PSF) than can be obtained with a conventional microscope.
- (ii) The stray background light due to out-of-focus regions of the specimen is strongly attenuated by spatial filtering, so that the main contribution to the signal comes selectively from a thin layer of sample close to the exact focal plane.

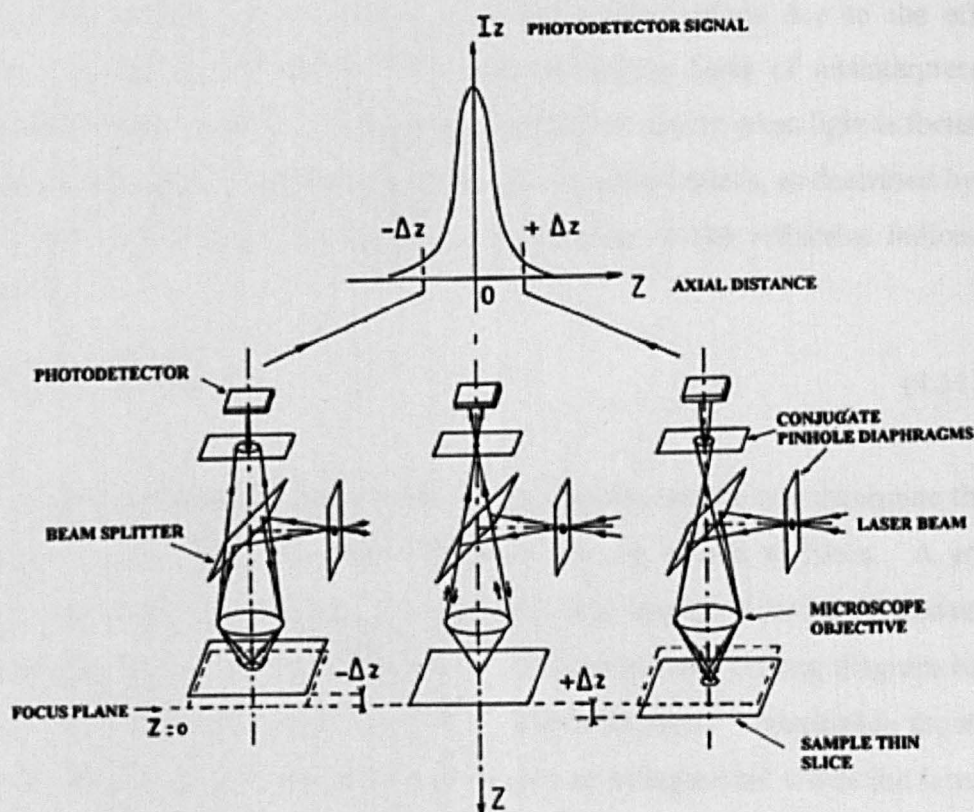


Figure 4.4. Schematic diagram of depth discrimination offered by confocal microscopy.<sup>191</sup>



The confocal aperture, a pinhole in this case, provides depth discrimination by restricting the Raman scatter originating from above and below the focal plane at  $z = 0$  from reaching the detector. Instrument manufacturers who implement the pinhole configuration claim that their setup offers “true” confocal performance. An alternative approach utilises a slit that restricts light entering the spectrometer in combination with pixel binning on the CCD camera, as demonstrated by Williams et al.<sup>192</sup> This so called “pseudo” confocal arrangement forms a “synthetic” confocal aperture by passing the Raman scatter through a series of filtering slits, the first being physical and the second electronic, effectively forming a square. This approach is incorporated in the Renishaw system that has been used throughout this research. The spectral resolution in this arrangement is determined by the first slit, that forms part of the aperture, and therefore the spectral resolution is not an independent variable from the confocality achieved.

The potential of this non-destructive sampling technique to depth profile polymer films has been appreciated by over a decade.<sup>193-196</sup> Pioneering work by Everall exposed major flaws in the analysis performed in these initial publications due to the effects of refraction not being considered.<sup>197,198</sup> The underlying basis of misinterpretation of depth profile data stems from the refraction effect that occurs when light is focussed through an interface of materials with distinct refractive indices, as described by Snell’s law shown in Equation 4.11 where  $n_1$  and  $n_2$  refer to the refractive indices of the materials.

$$n_1 \cdot \sin(\theta_1) = n_2 \cdot \sin(\theta_2) \quad (4.11)$$

It follows that the angle at which a light ray enters the sample will determine the extent of refraction and hence the depth at which that ray comes to focus. A schematic diagram showing the refraction of light rays that emerge from an objective at two different locations is shown in Figure 4.5. This simple ray tracing diagram highlights the key observations made by Everall<sup>197,198</sup> and Michielsen<sup>199</sup> concerning the effects of refraction on the height of the focal volume for an arrangement where the laser light is focussed through air ( $n = 1$ ) into a polymer sample ( $n = 1.5$ ). The illumination is spread over a range of depths along the  $z$ -direction, termed depth of focus, and hence enlarges the illuminating volume.

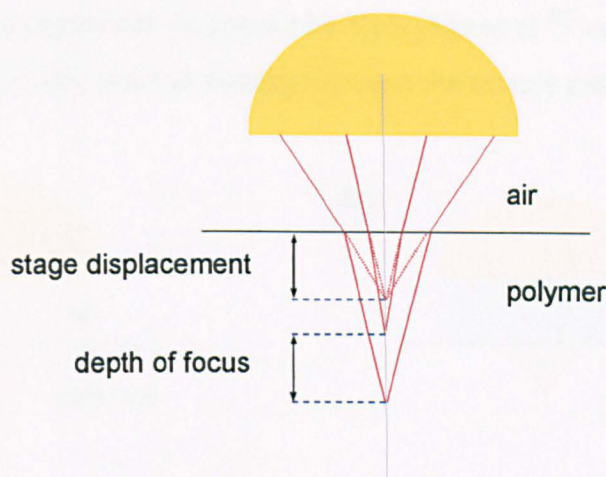


Figure 4.5. Schematic representation of light refraction occurring at air/polymer interface.

Two recent publications by Everall summarise the features of CRM depth profiling of polymeric materials and applications where these effects have been overcome and accurate data generated.<sup>200,201</sup> Despite the continuing efforts to account for and model the consequences of implementing the dry, metallurgical objective for depth profiling,<sup>202-205</sup> the benefits of CRM can be realised with the use of an immersion oil objective coupled with an immersion oil of similar refractive index as the material being studied.<sup>197</sup> The approach acts to remove/minimise the refractive index discontinuity along the optical path and hence the laser can be focussed to a spot size that approaches the diffraction limit at a predictable depth in the sample. If the refractive indices are precisely matched, the sampling may be performed with a PSF that does not alter and hence the depth resolution is constant as a function of depth. When studying polymeric materials this essentially requires the immersion objective to have a refractive index of ca. 1.5. This is a simplification to a real sample due to the variation in refractive index between polymer samples and more subtle difference that result from possible inclusions and morphological variations in a sample.

Examples of oil immersion sampling applications include polymer laminates,<sup>197,206</sup> porous turbid coating,<sup>207</sup> particles,<sup>208</sup> concentration gradient in polymer films<sup>209</sup> and complex biomaterials.<sup>210</sup> Two basic experimental arrangements have been described in the literature, shown schematically in Figure 4.6. The most commonly applied arrangement is the use of one immersion oil in contact with the objective and the sample



(b). The alternative approach introduced by Vyörykka et al.<sup>207</sup> combines two immersion fluid layers to overcome spectral overlap between the sample and the fluid (c).

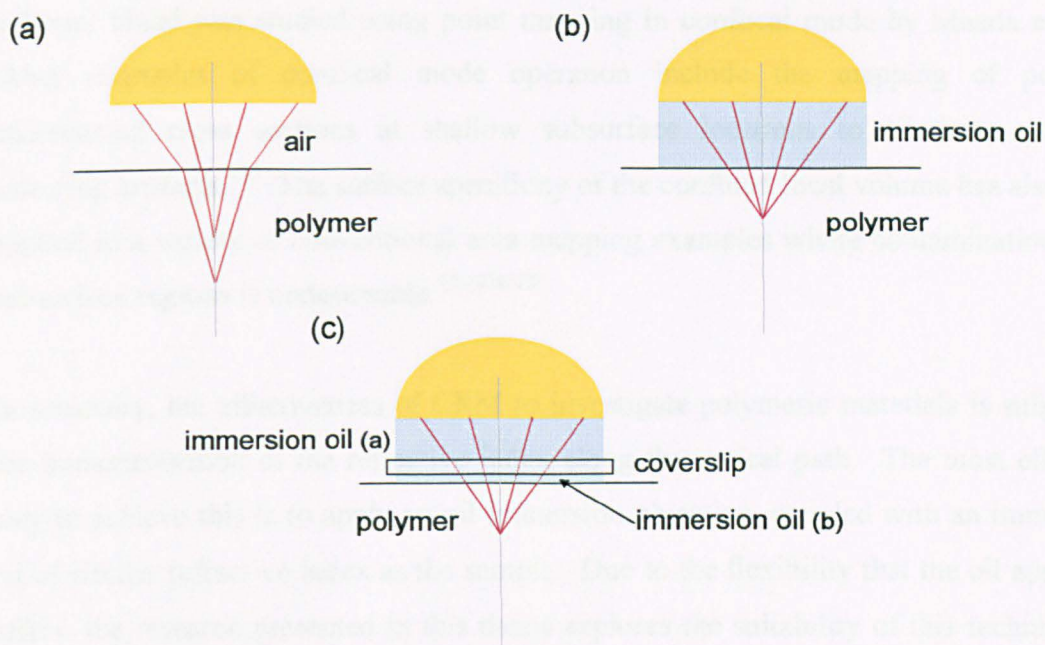


Figure 4.6. Schematic diagram showing various sampling arrangements with the oil immersion approach. Measurements using the traditional “dry” objective (a), oil immersion approach with a single layer (b) and the multi layer (c).

It should be noted that an example of raw data (measured using a traditional dry objective) manipulation by means of thickness scale expansion to the measured thickness of the sample has been described.<sup>211,212</sup> More sophisticated examples of non-destructive Raman depth profiling applications have recently been introduced. These approaches utilise time<sup>213</sup> and spatially<sup>214</sup> resolved measurements to probe the depth characteristics of the sample. However, these require extremely sophisticated experimental apparatus and do not represent available technology for routine measurements.

The application of CRM depth profile analysis to study *in situ* processes is limited to a few publications, presumably due the experimental complications. Schmitt et al.<sup>215</sup> applied confocal Raman resonance spectroscopy to study diffusion of a pharmaceutically relevant species through a PDMS membrane. Raman spectra were acquired at a fixed depth to monitor the drug concentration as a function of time.

Refraction almost certainly played a role in the setup employed; the dynamic nature of the system may lead to distortions to the sampling volume as solvent and drug molecules enter the sampling volume. The *in situ* study of phase separation in a LCST polymer blend was studied using point mapping in confocal mode by Maeda et al.<sup>216</sup> Other examples of confocal mode operation include the mapping of polymer microtomed cross sections at shallow subsurface locations to eliminate possible smearing artifacts.<sup>217</sup> The surface specificity of the confined focal volume has also been applied to a variety of conventional area mapping examples where contamination from subsurface regions is undesirable.<sup>216,218-220</sup>

In summary, the effectiveness of CRM to investigate polymeric materials is subject to the homogenisation of the refractive index along the optical path. The most effective way to achieve this is to apply an oil immersion objective, coupled with an immersion oil of similar refractive index as the sample. Due to the flexibility that the oil approach offers, the research presented in this thesis explores the suitability of this technique to analyse polymers processed with supercritical CO<sub>2</sub>.

### 4.3. IR SPECTROSCOPY

The oscillating electric field component of IR radiation is capable of interacting with matter. Absorption of a specific frequency of IR radiation occurs when it exactly matches the frequency of a molecular vibrational mode that undergoes a change in dipole moment ( $\mu$ ) during the normal coordinate of vibration ( $Q_k$ ) as shown in Equation 4.12.

$$\left( \frac{\partial \mu}{\partial Q_k} \right)_0 \neq 0 \text{ (IR activity requirement)} \quad (4.12)$$

The utilisation of IR spectroscopy for industrial and research applications has historically outstripped Raman spectroscopy. In part this is due to the relatively recent development of Raman spectrometers for routine analysis without the need of highly trained personnel. A prominent feature of IR spectroscopy is the quantitative nature of

the technique which is highly desirable when performing analysis. An IR spectrum corresponds to the ratio of the transmitted intensity ( $I$ ) to the incident intensity ( $I_0$ ), yielding the transmittance ( $T$ ).

$$T = I/I_0 \quad (4.13)$$

The Beer-Lambert Law defines the relationship between the incident and transmitted intensity, pathlength ( $l$ ), concentration ( $c$ ) and molar extinction coefficient ( $\epsilon$ ).

$$\log_{10}(I_0/I) = \epsilon cl \quad (4.14)$$

$$-\log_{10}(T) = \epsilon cl \quad (4.15)$$

It is conventional in spectroscopy to refer to absorbance ( $A$ ):

$$A = -\log_{10}(T) = \epsilon cl \quad (4.16)$$

Quantitative measurements require the pathlength to be known which is an inherent feature of the specific sampling technique employed and the properties of the sample. Both transmission and attenuated total reflection (ATR) IR spectroscopy are described in detail in the following sections and the issues of quantitative analysis discussed.

#### **4.3.1. FOURIER TRANSFORM INFRARED SPECTROSCOPY**

The instrumentation of a modern IR spectrometer differs from the dispersive arrangement described for CRM. In a dispersive system, individual frequencies are dispersed onto the detector whereby the intensity of light at a discrete spatial location (pixel) is read in a consecutive manner. Key disadvantages to this approach are that the spectral information is not recorded simultaneously and a slit is required to improve the spectral resolution of the system, thereby reducing the intensity reaching the detector. An alternative approach to measure the frequency components of incident radiation is the use of an interferometer. The Michelson interferometer is shown schematically in Figure 4.7. The principle of interferometry is to measure the interference pattern of the



constituent frequencies of the radiation. The broadband energy emitted from the IR source can be represented as a collection of cosine waves with unique frequencies. As the IR radiation passes through the beam splitter, half of the energy is transmitted to the stationary mirror and the other half to the moving mirror. The recombination of the beams results in interference, which is a function of the moving mirror position that acts to control the path difference between the two beams. The detector measures the total IR intensity at each mirror position to produce an interferogram. The maximum intensity of the inteferogram is a feature known as the centreburst, which occurs when the pathlength is equal.

The implementation of Fourier transform rather than dispersive instrumentation for IR measurements offers the following advantages:<sup>221</sup>

1. Simultaneous measurement of the entire frequency range.
2. Reduction in scanning time to produce a spectrum of the same sensitivity and resolution as the corresponding dispersive measurement (Multiplex or Fellgett advantage).
3. Enhanced throughput (Jacquinot advantage).
4. Connes advantage.
5. Resolving power

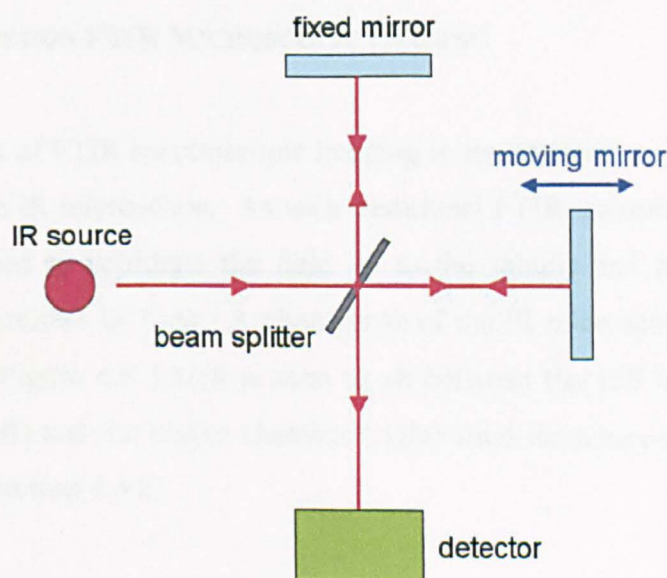


Figure 4.7. Schematic diagram of Michelson interferometer.

The detector shown in Figure 4.7 enables the signal at each mirror position to be recorded to produce an interferogram which is then Fourier Transformed to produce the IR spectrum. The IR spectrum represents a volumetric average of the sample where IR absorption occurred. When information regarding the distribution of heterogeneous material is desired, this approach is unsuitable due to the absence of spatial resolution. The use of microscopy with a single-element detector is then needed to collect IR spectra from various locations on the sample to build a map. An alternative approach is the use of a Focal Plane Array (FPA) detector coupled to the FTIR spectrometer. The FPA used in this study comprises of an array of 4096 individual mercury-cadmium-telluride (MCT) detector elements – also known as pixels. At each pixel, corresponding to a specific location on the sample surface, a complete IR spectrum is recorded in an identical manner to conventional FTIR spectroscopy i.e. an interferogram is recorded at each pixel which is then Fourier transformed to yield a unique FTIR spectrum. The distribution of a component of interest can be visualised in the form of an image, generated on the distribution of the integrated absorbance of the IR band corresponding to that component in the measured area. FTIR imaging has proved to be an excellent tool to study polymer systems.<sup>222-224</sup> The inherently rich chemical specificity offered by conventional IR spectroscopy is enhanced significantly with the imaging sampling capability. The application of FTIR imaging is proving to be a powerful experimental tool to study dynamic polymer systems.<sup>225-230</sup>

#### 4.3.2. TRANSMISSION FTIR MICROSCOPIC IMAGING

The applications of FTIR spectroscopic imaging in transmission mode presented in this thesis utilises an IR microscope. As with traditional FTIR transmission microscopy, a collimator is used to collimate the light on to the sample and an objective used to capture the transmitted IR light. A photograph of the IR microscope used in this work is presented in Figure 4.8 which is seen to sit between the IFS 66/S step scan FTIR spectrometer (left) and the macro chamber (right) used for macro-ATR measurements, as described in section 4.3.3.





Figure 4.8. Photograph of FTIR microscope (IRscopeII).

The importance of sample thickness in quantitative IR measurements was introduced in the Beer-Lambert law. The absorbance is proportional to the sample thickness and thus requires the appropriate selection on a sample specific basis. The field of view imaged when using the 15 x objective with the system used in this thesis is  $266 \times 266 \mu\text{m}^2$  and the spatial resolution, determined from the Rayleigh criterion is ca.  $20 \mu\text{m}$ . A schematic arrangement of transmission FTIR imaging is presented in Figure 4.9.

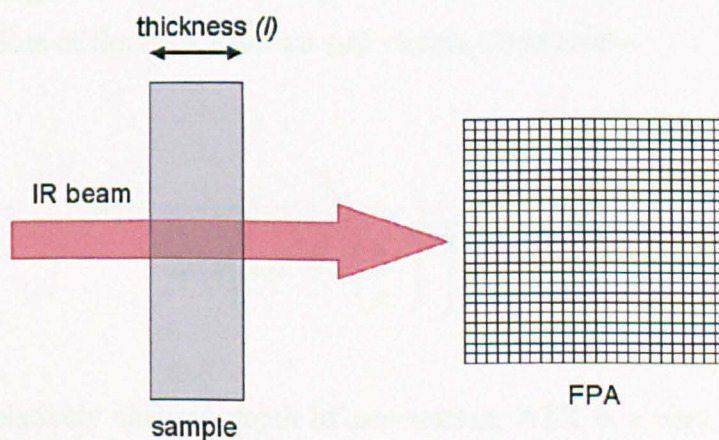


Figure 4.9. Schematic diagram of transmission FTIR imaging using the FPA detector.

The nature of transmission measurements results in the spectrum at a particular position representing the average spectrum through the thickness of the material at that position. This characteristic dictates the necessity to consider the domain size of heterogeneous phases in the sample section. For an accurate representation of the distribution, the thickness should not exceed the smallest domain size to ensure that accurate images are measured. The preparation of samples that conform to these requirements may pose technical challenges and possibly the need for experienced personnel. Nonetheless, the use of transmission FTIR imaging to investigate dynamic polymer systems has been successfully applied to numerous examples.<sup>225,231,232</sup>

#### 4.3.3. ATTENUATED TOTAL REFLECTION FTIR IMAGING

The principle of attenuated total reflection (ATR) FTIR spectroscopy is described in detail in the publication by Harrick.<sup>233</sup> ATR FTIR spectroscopy is an extremely versatile sampling technique for surface characterisation. Total internal reflection describes the behaviour of light that strikes an interface between two media of different refractive indices at an angle beyond the critical angle. Under these conditions all of the light energy is reflected back to the incident medium and an 'evanescent field' develops at the interface with an energy that decreases exponentially into the medium with the lower refractive index. The depth of penetration ( $d_p$ ), defined in Equation 4.17, is on the order of a few micrometers and is dependent on the refractive indices of the ATR medium and the sample, the incident angle of light, and the wavelength of the light.  $\theta$  is the incident angle,  $\lambda$  is the wavelength of the incident light, and  $n_1$  and  $n_2$  are the refractive indices of the ATR medium and sample respectively.

$$d_p = \frac{\lambda}{2n_1 \pi \left( \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right)^{0.5}} \quad (4.17)$$

Due to the relatively shallow depth of penetration, ATR is a very versatile technique that allows the sampling of most liquid and solid samples. A specific feature of ATR FTIR spectroscopy is the ability to investigate aqueous samples which normally pose a significant problem due to the strong absorption of IR radiation by water. The issue of

contact between the sample and the ATR crystal is an inherent experimental challenge. Reproducible and uniform contact is desired to enable a fair comparison between samples. In practice, ATR measurement mode is achieved by placing the sample onto a high refractive index ATR crystal and to allow the IR light to contact the crystal at an angle above the critical angle, resulting in total internal reflection and thus the sample is probed with the evanescent wave of IR radiation. The specific ATR crystal employed for a particular system will be dependent on the desired transmission properties, mechanical stability, chemical inertness, temperature and pressure resistance and refractive index. Common ATR crystals employed include Zinc Selenide, Germanium, Silicon, Zinc Sulphide, Thallium Bromide and Diamond. Diamond offers excellent robustness and is particularly suited to investigations in high-pressure and supercritical environments and thus is the focus of this section.

Various commercial accessories are available for routine ATR measurements of which employ various sampling arrangements (e.g. single and multiple reflection) and ATR crystals. The ATR FTIR data presented in this thesis were measured using the “Golden Gate” accessory (Specac Ltd.), which has a diamond ATR crystal. This accessory has been adapted to enable *in situ* measurements under supercritical conditions and has proved highly suitable to study polymer systems with a conventional, single element detector. This accessory has been used to study systems such as polymer swelling<sup>234</sup> and the decomposition of PET subjected to superheated water.<sup>235</sup> A schematic diagram of the Golden Gate<sup>TM</sup> accessory is presented in Figure 4.10 and shows the path of the IR radiation entering from the left and directed by mirrors ( $M_{1-4}$ ) to focus onto and collect from the sample via lenses  $L_1$  and  $L_2$ .

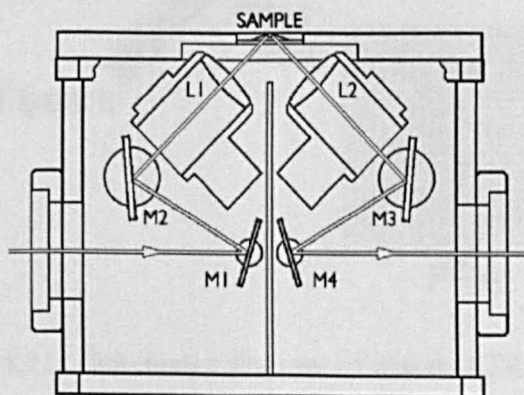


Figure 4.10. Schematic diagram of Golden Gate<sup>TM</sup> accessory.



Pioneering work by Chan and Kazarian demonstrated the ability to perform ATR FTIR imaging using the Golden Gate<sup>TM</sup> diamond ATR accessory, which was not designed for imaging purposes.<sup>236</sup> The principle of this ATR imaging approach is shown schematically in Figure 4.11. This novel application of ATR imaging offers tremendous potential to the numerous examples of *in situ* measurements that have been demonstrated using conventional ATR FTIR spectroscopy. A plethora of publications from Kazarian's group have demonstrated the applicability of this novel imaging technique to areas such as drug release,<sup>237</sup> drug crystallisation,<sup>230</sup> forensic applications,<sup>238</sup> high-throughput technology<sup>239</sup> and polymer systems exposed to high-pressure CO<sub>2</sub> environments.<sup>159</sup>

The imaging capability of the diamond Golden Gate<sup>TM</sup> accessory was rigorously assessed by Chan and Kazarian.<sup>236</sup> The spatial resolution of the technique is ca. 15  $\mu\text{m}$  and the image size is 820 x 1140  $\mu\text{m}^2$  in the optical arrangement used in this study. The significant improvement in spatial resolution compared to that available in air achieved with the single reflection diamond accessory is due to relatively high refractive index of Diamond (2.4) and the magnification effect caused by the focusing lenses. In addition to the robust nature of the accessory, its suitability to investigate polymer processing with high-pressure and scCO<sub>2</sub> stems from its inherent sensitivity to many of the CO<sub>2</sub>-induced phenomena.<sup>25,37,56</sup>

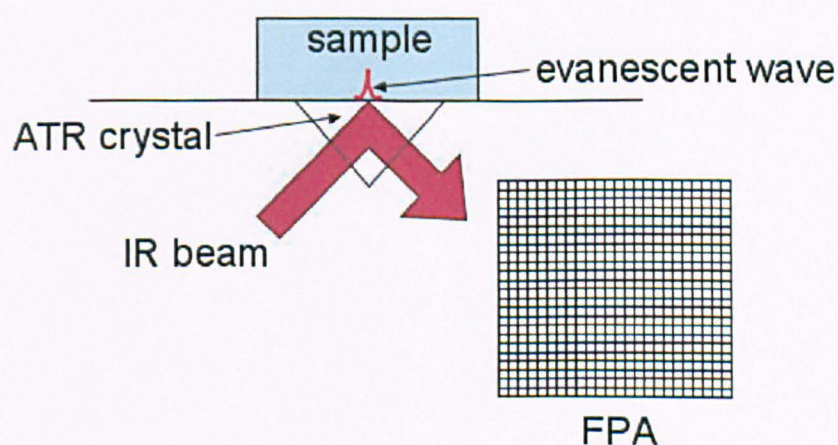


Figure 4.11. Schematic diagram of macro ATR imaging.

The application of ATR FTIR imaging using the Golden Gate<sup>TM</sup> with a diamond ATR crystal to study dynamic polymer systems in the presence of high-pressure and scCO<sub>2</sub> is explored in this thesis. Specifically, the effect of high-pressure CO<sub>2</sub> on the interdiffusion in a miscible polymer system is investigated. The feasibility to study CO<sub>2</sub>-induced crystallisation in semicrystalline polymers and the study of CO<sub>2</sub>-induced phase separation is explored.

## **CHAPTER 5**

# **HIGH-PRESSURE EXPERIMENTAL APPARATUS AND PROCEDURES**

## 5.1. HIGH-PRESSURE EXPERIMENTAL APPARATUS AND PROCEDURES

### 5.1. INTRODUCTION

High-pressure experimentation requires specialist apparatus capable of withstanding the extreme conditions explored. It is conventional to operate with miniature apparatus of small volumes to reduce the risk in the event of apparatus failure. Standard equipment that is commercially available includes valves, connectors, tubing, reducers, etc. The experimental equipment used for this research utilises a combination of standard fittings with in-house, custom built components. The following section describes the various high-pressure systems employed and details regarding their operation and general experimental practice.

### 5.2. HIGH-PRESSURE EQUIPMENT

*Impregnation high-pressure rig:* The preparation of all impregnated film samples was performed using the high-pressure rig shown schematically in Figure 5.1. A typical impregnation experiment required the polymer sample together with an excess amount of solute to be sealed into the pressure vessel. Temperature control was achieved with the use of a water bath at the required condition (40°C - 80°C). The following pressurisation procedure was followed for all experiments conducted:

1. Valve 1 and 3 closed with valve 2 open.
2. The pressure generator was manually controlled to fill the feed line (tubing connecting the pressure generator with valve 1) with CO<sub>2</sub> (ca. 20-30 bar).
3. Valve 1 slowly opened to begin pressurisation of the high-pressure vessel.
4. Steps 1 – 3 were repeated until the desired pressure had equilibrated.
5. Time taken as experiment zero-point.

The pressurisation procedure was performed in this manner to ensure that a rapid release of CO<sub>2</sub> in the pressure vessel did not occur which may disrupt the solute and result in contamination in the pressure generator. A photograph of the high-pressure vessel and a schematic vertical section are presented in Figure 5.2.



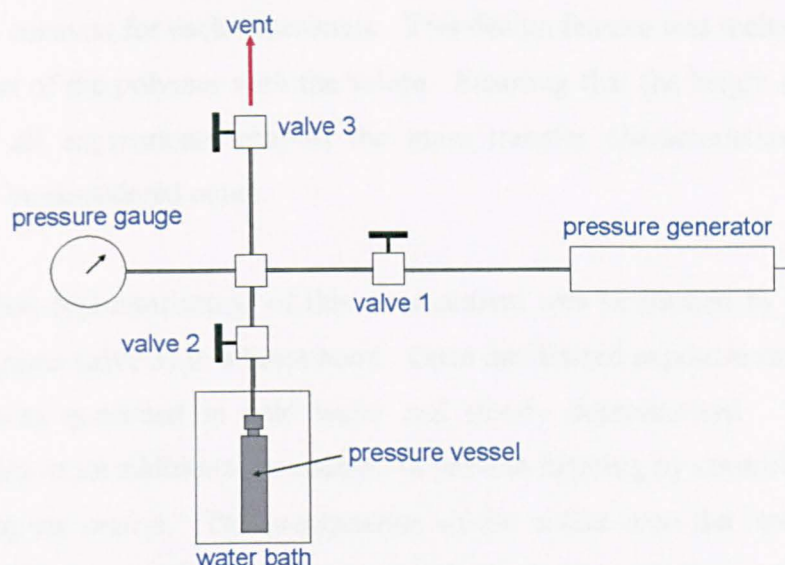


Figure 5.1. Schematic diagram of basic high-pressure rig arrangement used for impregnation experiments.

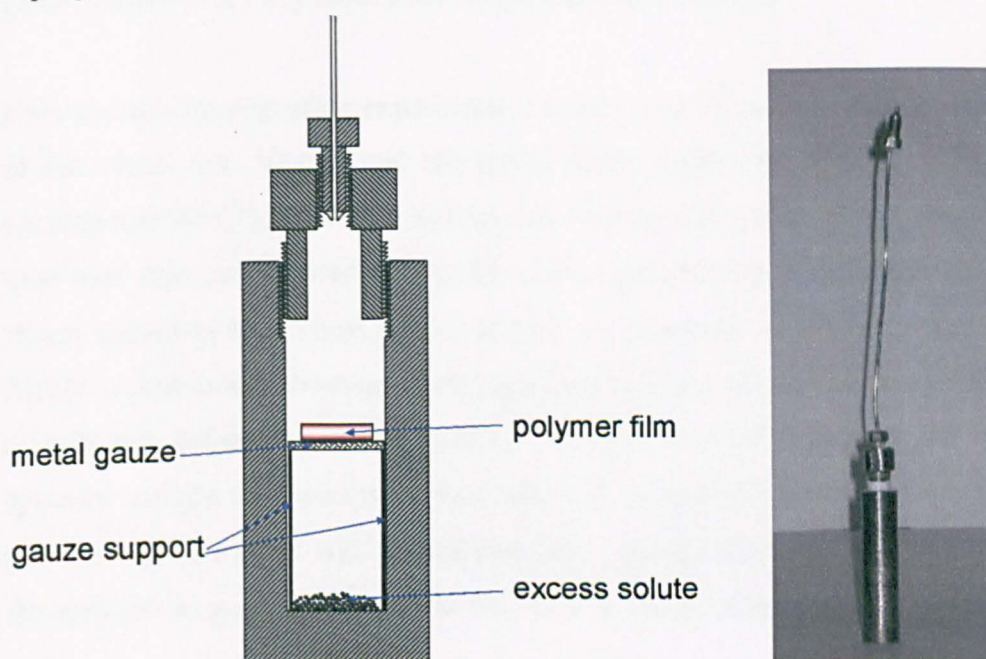


Figure 5.2. Vertical section of the high-pressure vessel showing the internal arrangement used for impregnation experiments (left) and the corresponding photograph of the high-pressure vessel complete with tubing (right).

The arrangement adopted for the impregnation experiments was selected to ensure that the polymer film was physically separated from the solute at the bottom of the cell. The gauze support served to locate the metal gauze upon which the sample rested. The support ensured that the height of the metal gauze, and hence the bottom of the polymer

sample, was constant for each experiment. This design feature was included to limit the direct contact of the polymer with the solute. Ensuring that the height of the film was constant in all experiments enables the mass transfer characteristics at a specific condition to be considered equal.

The controlled depressurisation of this arrangement was performed by slowly venting the system (open valve 3) in a fume hood. Once the desired exposure time had expired, the vessel was quenched in cold water and slowly depressurised. The quenching procedure acts as an additional precaution to prevent foaming by controlling the release of CO<sub>2</sub> from the matrix. The precipitation of the solute onto the internal walls and vessel components, including the film surface is likely to occur during depressurisation. Care was taken not to contact the film with the vessel walls during removal and was gently wiped with a dry cloth prior to spectroscopic analysis.

Prior to each impregnation experiment, an excess of solute was placed into the bottom of the vessel (ca. 10 mg) and the metal gauze washed in ethanol. These measures ensured that the CO<sub>2</sub> solution was kept saturated with the solute throughout the exposure time and that precipitated solute from the previous depressurisation was removed. When changing the impregnation system i.e. polymer and solute, contamination is highly undesirable. Thorough cleaning of the pressure rig was performed using a range of solvents, depending on the solute. Potential contaminants between impregnation systems include the previous solute and any extracted impurities from the previous polymer e.g. monomer and solvent residues. Once the pressure rig had been cleaned, the system was purged with CO<sub>2</sub> to remove any traces of solvent from the pressure rig.

*In situ spectroscopic cells:* The ATR FTIR cell used in the imaging applications utilised a cell designed for conventional measurements on the diamond Golden Gate™ accessory. Temperature regulation of the ATR cell was maintained using the heated Golden Gate™ accessory. Modifications to the standard cell for specific applications are described in the relevant experimental sections. The pressurisation procedure was the same as that described for the impregnation pressure rig but the depressurisation stage was not adhered due to the *in situ* nature of the measurements. The *in situ* high-pressure rig used for ATR FTIR measurements is presented schematically together with a photograph of the arrangement in Figure 5.3.

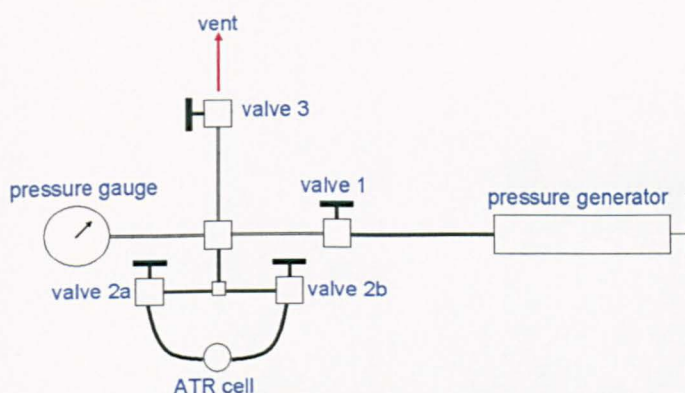


Figure 5.3. ATR FTIR *in situ* high-pressure rig assembly shown schematically (left) and a photograph showing the high-pressure cell in position on the Golden Gate<sup>TM</sup> accessory (right).

The system pressure was monitored during the course of the exposure using a digital pressure transducer (shown in the photograph in Figure 5.3), enabling possible leaks to be identified. Sealing of the various cells was achieved using Teflon (polytetrafluoroethylene) spacers. The use of Teflon tape was also used to ensure good seals were formed on threaded components (as seen in the high-pressure vessel photograph in Figure 5.2).

## **CHAPTER 6**

# **CO<sub>2</sub>-INDUCED MORPHOLOGICAL ALTERATIONS IN POLY(ETHYLENE TEREPHTHALATE)**

## 6.1. CONFOCAL RAMAN MICROSCOPY OF MORPHOLOGICAL CHANGES IN POLY(ETHYLENE TEREPHTHALATE) FILM INDUCED BY SUPERCRITICAL CO<sub>2</sub>

### 6.1.1. INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline polymer with significant industrial applications, ranging from textile fibre to bottle manufacturing. The morphology of PET varies from that found in amorphous domains to that of the 3-D ordered, crystalline domains. Raman and IR spectroscopy have been extensively used to probe the morphology of PET<sup>240-244</sup> due to the conformational sensitivity of the techniques.<sup>245</sup> PET may exist in three possible morphological species: amorphous, ordered amorphous and the true crystalline configuration.<sup>246</sup> PET crystallisation is a complex process<sup>247</sup> involving conformational changes in the amorphous domains, ultimately leading to the all *trans* crystalline structure. In the amorphous phase PET exhibits *gauche* glycol conformers with disordered terephthalate groups. Ordered amorphous has *trans* glycol segments with disordered terephthalate groups whereas the crystalline form exhibits an all *trans* structure with the carbonyl groups coplanar with the benzene ring. The most important changes in the Raman spectrum following crystallisation are the narrowing of the carbonyl band<sup>248</sup> at 1725 cm<sup>-1</sup> (corresponding to the reduction of possible carbonyl group environments with respect to the benzene ring) and the growth of the bands at 1096 cm<sup>-1</sup> (combination of stretching vibrations of the ester, glycol and ring units of the *trans* configuration of the PET chain) and 1000 cm<sup>-1</sup> (*trans* glycol moiety). The chemical structure of the repeat unit of PET is shown in Figure 6.1.

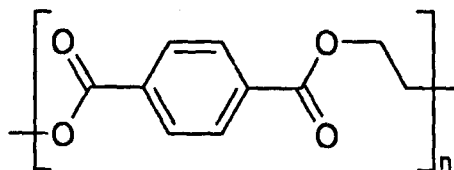


Figure 6.1. Chemical structure of poly(ethylene terephthalate)



The opportunity exists to use scCO<sub>2</sub> to alter the morphology of PET. The sorption of CO<sub>2</sub> molecules into the amorphous domains of PET result in the plasticisation of the polymer matrix as a result of the reduction of the  $T_g$ .<sup>103</sup> CO<sub>2</sub>-induced crystallinity in PET is similar to that of thermal crystallisation,<sup>50</sup> although the size and orientation of the crystallites formed (as shown by wide-angle X-ray diffraction scattering and electron scanning microscopy) are different from those achieved with thermal processing as a consequence of micro-void formation.<sup>45</sup> Furthermore, the solvent nature of scCO<sub>2</sub> and thus its ability to swell the polymer matrix can easily be “tuned” by controlling the pressure, providing an important variable for process manipulation.

FT-Raman spectroscopy was applied by Kazarian et al.<sup>50</sup> to study PET processed with scCO<sub>2</sub>, observing noticeable spectral changes involving an increase in intensity of the bands at 1096 and 997 cm<sup>-1</sup> and a decrease in the intensity of the band at 885 cm<sup>-1</sup>. The band width of the carbonyl band following 5 days of scCO<sub>2</sub> exposure narrowed from 27 cm<sup>-1</sup> in the amorphous state to 23 cm<sup>-1</sup>. Although scCO<sub>2</sub> is able to induce the all *trans* crystalline configuration, the polymer chains are “protected” from chain-chain interactions by dissolved CO<sub>2</sub> molecules. It is possible that the packing of the crystalline domains will be different to those found in thermally crystallised samples which were formed in the presence of chain-chain interactions. *In situ* FTIR spectroscopy was applied to investigate CO<sub>2</sub>-induced changes in PET morphology through the whole thickness of the film.<sup>38</sup> However, scCO<sub>2</sub> processing of PET film offers an opportunity to induce a gradient in the degree of crystallinity as a function of depth along the line normal to the surface of the film. Information regarding the presence of a possible morphological gradient through the film is not available and needs elucidation. In this section confocal Raman microscopy is used as a tool to obtain depth profile information of morphological changes induced by scCO<sub>2</sub> within PET films.

### 6.1.2. EXPERIMENTAL

Largely amorphous PET films of thickness 230 µm were donated by ICI. A custom built high-pressure vessel, described in Chapter 5, containing the amorphous film, was loaded with CO<sub>2</sub> using an ISCO Model 500D syringe pump. The vessel was pressurised to the required level for the allocated exposure time and kept at a constant temperature



using a water bath ( $\pm 0.1^\circ\text{C}$ ). Once the required exposure time had expired, the vessel was slowly depressurised and samples were removed for Raman analysis.

A dispersive Raman Renishaw 1000 confocal system was employed to measure all of the Raman spectra in this study. A 785 nm diode laser with maximum output power of 300 mW was used in conjunction with a 100x objective (oil and dry). The detector used in this study was a two-dimensional Peltier cooled charge-coupled device (CCD) camera. Unless otherwise stated this arrangement was used for all Raman measurements presented in this thesis. Sample analysis involved the following methods:

- i. Dry (metallurgical) confocal Raman: Depth profile was generated through the collection of Raman spectra at 1  $\mu\text{m}$  incremental positions in the z-direction normal to the surface of the polymer film.
- ii. Oil immersion confocal Raman: Same as the dry set-up but with immersion oil of refractive index 1.515, (purchased from Cargille Laboratories Inc, Cedar Grove, NJ, USA) in contact with the sample and objective.
- iii. Raman point mapping: PET films were microtomed and conventional point mapping was performed along the line normal to the surface of the film cross-section.

Confocal performance was achieved by closing the slit in the spectrometer and limiting the pixel binning of the CCD. In these experiments a slit width of 15  $\mu\text{m}$  was selected in combination with a CCD area of 4 x 576 pixels. The depth profiling and point mapping processes were automated and controlled by the computer with an xyz stage. The nominal spectral resolution of this confocal system is 1  $\text{cm}^{-1}$ /pixel with a slit width of 15  $\mu\text{m}$  and has a depth resolution (as measured by z-sectioning a silicon wafer in air) of  $\sim 4 \mu\text{m}$ . However, this resolution will be degraded on focusing below the surface of a transparent sample using a dry (metallurgical) objective.

### 6.1.3. RESULTS AND DISCUSSION

This initial study evaluates the effect of scCO<sub>2</sub> exposure on the induced morphological changes in PET film as a function of depth normal to the surface. To evaluate these changes the combination band at 1096 cm<sup>-1</sup> and the carbonyl band were selected. Raman spectra corresponding to largely amorphous PET film before and after exposure to scCO<sub>2</sub> are presented in Figure 6.2. The film was exposed for 15 minutes at 100 bar and 40°C and thus CO<sub>2</sub> is in the supercritical state.<sup>1</sup>

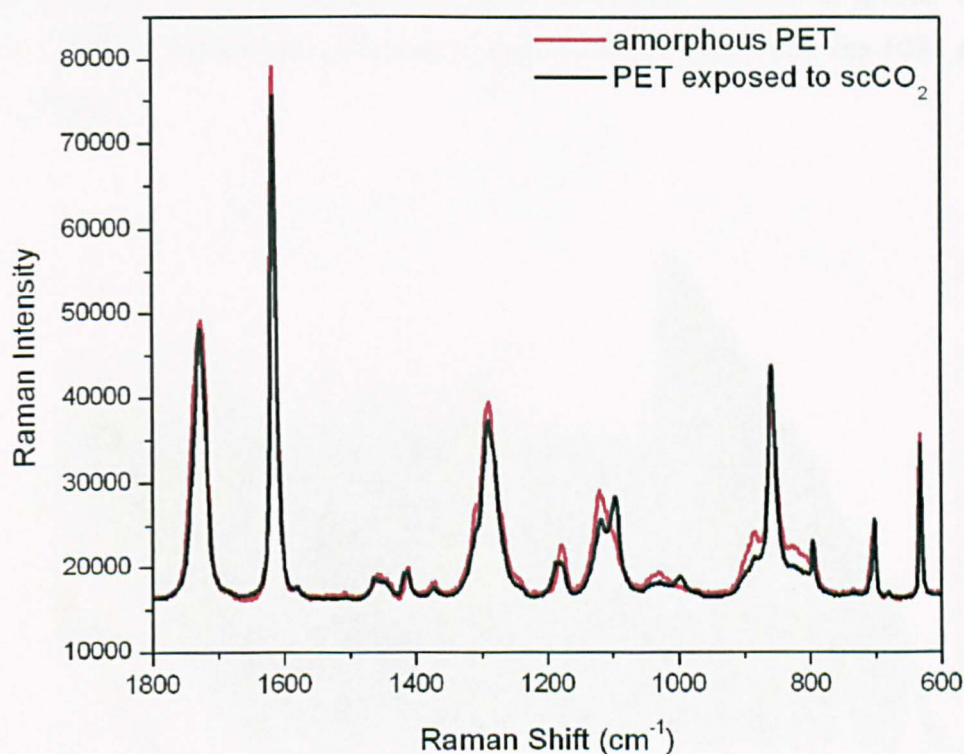


Figure 6.2. Raman spectra of PET film surface before (red) and after (black) scCO<sub>2</sub> exposure.

To investigate the morphology of PET at subsurface locations in the sample, a depth profile was performed. Raman spectra as a function of depth collected during a depth profile measurement of PET film following 15 minutes exposure to scCO<sub>2</sub> are presented in Figure 6.3. The 100x oil immersion objective was used to collect Raman spectra at 1  $\mu$ m increments normal to the film surface with a laser power of 100 % and an acquisition time of 60 seconds per spectrum. Examination of Figure 6.3 reveals the

presence of two bands (1041 and 818 cm<sup>-1</sup>) that disappear as the Raman intensity increases to the maximum value; these bands are attributed to the immersion oil. A more prominent feature of the depth profile is the decay of the 1096 cm<sup>-1</sup> shoulder with depth, shown more clearly in the expanded 1096 cm<sup>-1</sup> region presented in Figure 6.4.

The presence of the 1096 cm<sup>-1</sup> band at the surface of the film is indicative of PET with a relatively high degree of CO<sub>2</sub>-induced morphological alteration. The observed spectroscopic features (1096 and 997 cm<sup>-1</sup>) demonstrate the conformational mobility provided by the presence of plasticising CO<sub>2</sub> molecules. In the 30 µm of PET closest to the surface, the glycol unit is in the *trans* configuration whereas at greater depths the unit exists predominantly in the *gauche* conformation, supporting the 1096 cm<sup>-1</sup> band observation.

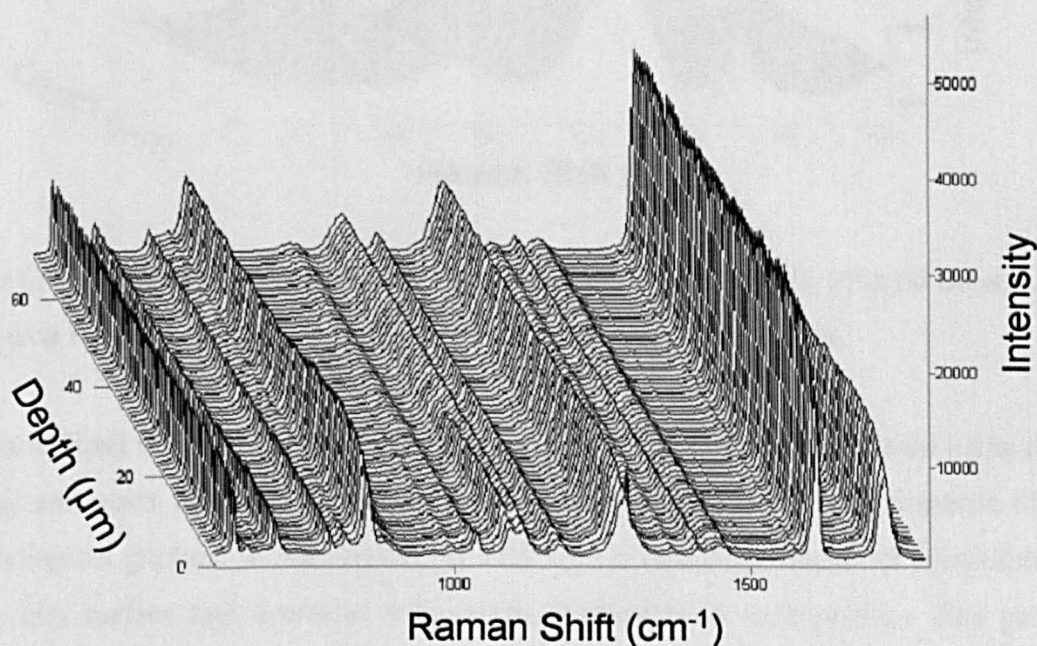


Figure 6.3. Raman spectra as a function of depth measured using the oil immersion approach corresponding to PET film exposed to scCO<sub>2</sub> for 15 minutes at 40°C and 100 bar.

To evaluate changes in the polymer morphology it is necessary to normalise the intensity of the morphology sensitive band with respect to a band that is morphology insensitive. Raman band normalisation is required in order to correct spectra for changes in focus, alignment, laser intensity and signal attenuation etc.<sup>249</sup> The band at



795 cm<sup>-1</sup> was selected for normalisation as it is known to be insensitive to conformation or crystallinity.<sup>217,250</sup> The 1096 cm<sup>-1</sup> band was integrated between the wavenumber range 1109-1089 cm<sup>-1</sup> and the 795 cm<sup>-1</sup> band between 782-805 cm<sup>-1</sup>. Peak area measurements were performed using the original baseline. The area under the peak was integrated with respect to a baseline that connects the data points corresponding to the wavenumber limits of the integral ranges mentioned above. The change in the integrated intensity of the 1096 cm<sup>-1</sup> band as a function of depth was assessed in the ratio:  $I_{1096}/I_{795}$ .

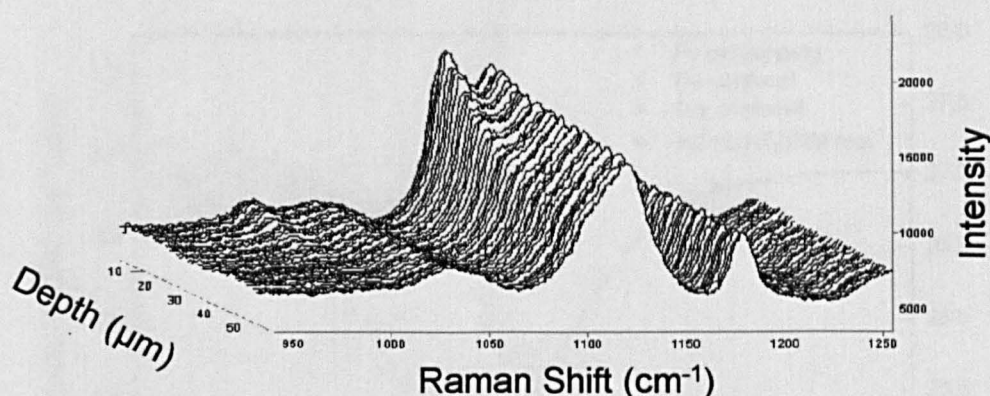


Figure 6.4. Expanded region of the band at 1096 cm<sup>-1</sup> acquired with 100x oil objective. The z-axis has been flipped i.e. surface of film at the back of the figure.

The normalised intensity of the 1096 cm<sup>-1</sup> band as a function of depth obtained using the dry, oil and point mapping approaches are overlaid in Figure 6.5. The presence of a morphological gradient in semicrystalline PET with a maximum degree of crystallinity at the film surface that decreases with depth is revealed in each profile. The point mapping and oil immersion confocal data correlate closely and reveal the same gradient, extending over approximately 30 μm from the film surface. However, the dry confocal data does not describe the same trend, but underestimates the thickness of region of varying morphology. The close correlation of the oil confocal data with the line mapping data verifies the reliability of the oil confocal approach to evaluate the CO<sub>2</sub>-induced morphological gradients in PET film.

As previously mentioned, the 1096 cm<sup>-1</sup> band is a combination of stretching vibrations of the ester, glycol and ring units in the *trans* configuration that increases in intensity

with crystallinity. However, the observation of this band does not distinguish between extended chains found in the amorphous domains and those found in the form of an extended crystalline lattice.<sup>251</sup> This differentiation can be made through the analysis of the carbonyl band which does not narrow in amorphous domains of PET. The carbonyl band has been evaluated in terms of narrowing relative to the amorphous film (27 cm<sup>-1</sup>). At the surface of the film the band narrows to ca. 24 cm<sup>-1</sup> and returns to 27 cm<sup>-1</sup> at 30 μm, supporting the 1096 cm<sup>-1</sup> gradient observation. This correlation provides evidence for using the 1096 cm<sup>-1</sup> band to assess CO<sub>2</sub>-induced crystallinity in PET.

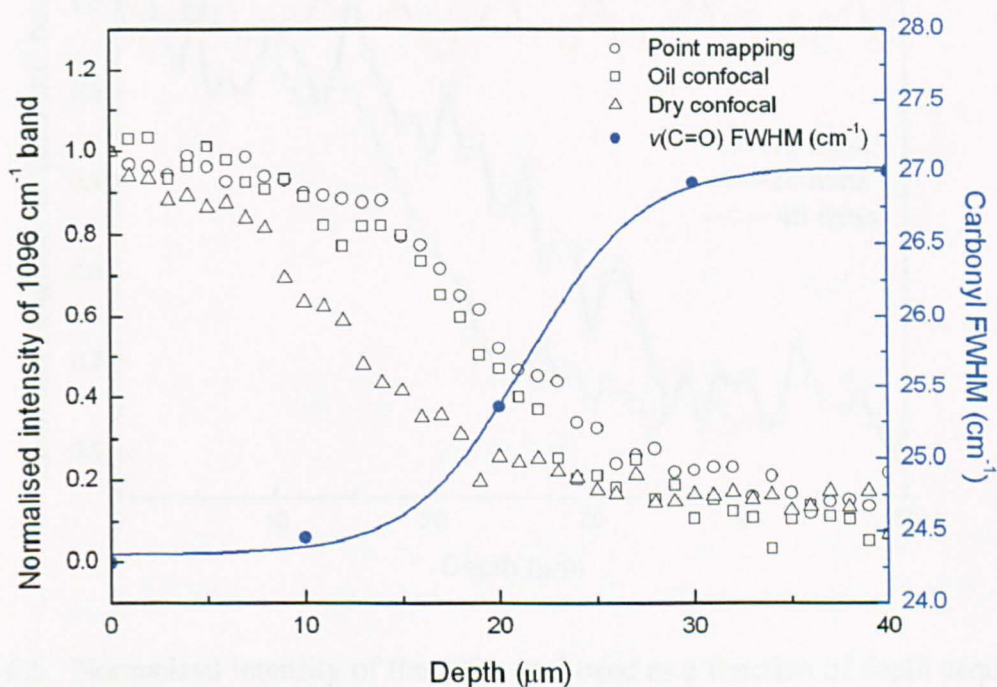


Figure 6.5. Normalised intensity of the 1096 cm<sup>-1</sup> band as a function of depth normal to the surface of PET film exposed to scCO<sub>2</sub> for 15 minutes at 100 bar and 40°C. The same sample was evaluated using the oil confocal approach (100x oil immersion objective), dry confocal and line mapping (100x dry objective). The v(C=O) FWHM data presented corresponds to the line mapping study.

The effect of exposure time is shown in Figure 6.6 where the normalised 1096 cm<sup>-1</sup> band as a function of depth for PET film samples exposed at 100 bar and 40°C for 15, 25 and 45 minutes are presented. Increasing the PET film exposure time results in the “levelling off” of the measured CO<sub>2</sub>-induced morphological gradient, with the presence of PET with a relatively high degree of crystallinity apparent at greater depths in the



sample. The CO<sub>2</sub>-induced morphological changes are the result of two time-dependent processes: diffusion of CO<sub>2</sub> through the polymer film and the kinetics of polymer chain rearrangement. Both of these processes depend on the temperature and pressure of the system. It is therefore important to investigate the role of temperature and pressure on the crystallisation behaviour of PET, which is reflected in the CO<sub>2</sub>-induced morphological gradient.

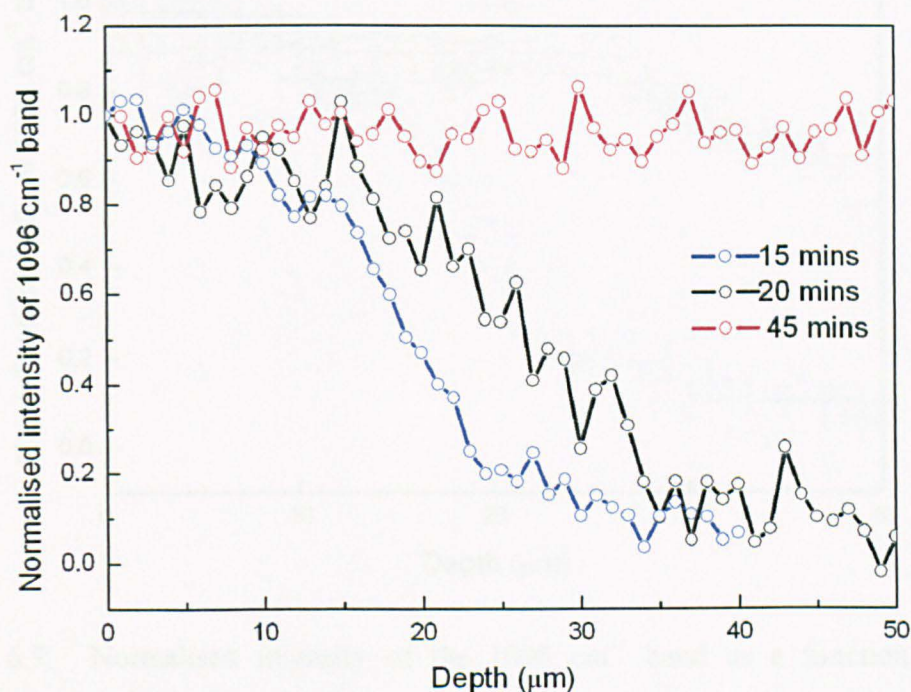


Figure 6.6. Normalised intensity of the 1096 cm<sup>-1</sup> band as a function of depth acquired with 100x oil immersion objective corresponding to PET film sample exposed for 15, 25 and 45 minutes at 100 bar and 40°C.

The effect of pressure is demonstrated in Figure 6.7, showing the changes in the normalised intensity of the band at 1096 cm<sup>-1</sup> for PET films exposed at 100 and 150 bar of CO<sub>2</sub> at 40°C for 15 minutes. The difference in reaction conditions of the two systems is observable in the normalised 1096 cm<sup>-1</sup> gradient, which exemplifies the effect of CO<sub>2</sub> pressure. Increasing the pressure of the system to 150 bar results in the presence of the all *trans* conformation deeper in the film and at a greater concentration compared to the sample exposed to 100 bar, indicating that CO<sub>2</sub> diffusion and chain reorganisation kinetics are apparently altered with pressure change. In essence the pressure increase results in a deeper penetration of CO<sub>2</sub>, combined with a reduction in the time scale of



chain reorganisation. At higher pressures CO<sub>2</sub> is more soluble<sup>38</sup> and hence able to diffuse further into the PET film, observed in the gradient of the normalised intensity of the band at 1096 cm<sup>-1</sup>.

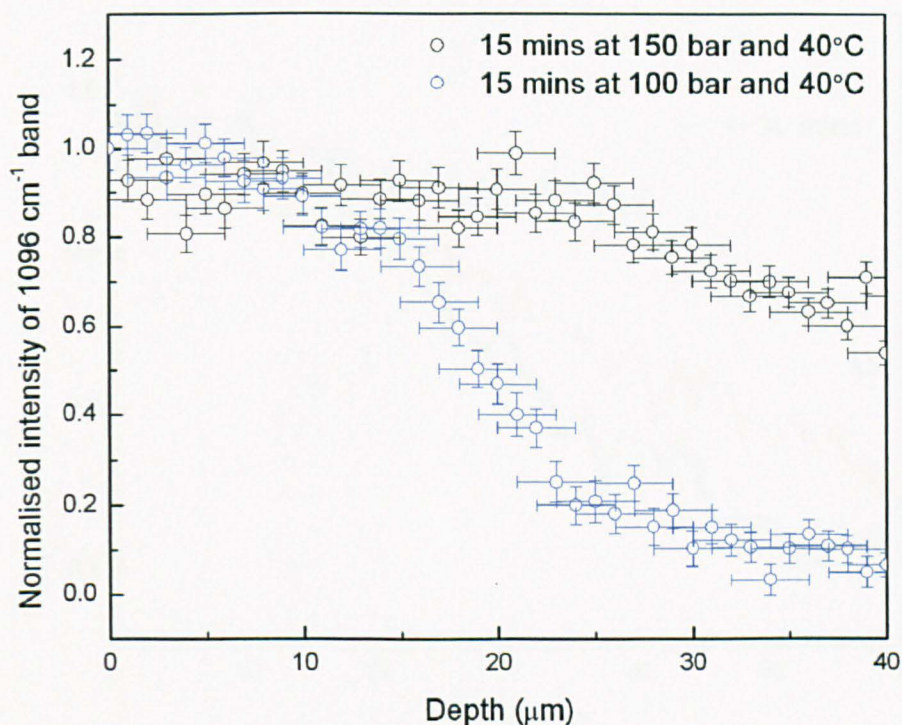


Figure 6.7. Normalised intensity of the 1096 cm<sup>-1</sup> band as a function of depth corresponding to PET film samples exposed for 15 minutes at 100 (blue) and 150 bar (black) at 40°C.

The error bars included in Figure 6.7 correspond to the depth resolution associated with the use of the oil immersion objective (ca. 3 μm in the z direction) and the standard error of the mean calculated for 3 independent measurements. The error bars shown in the plot are typical of all profiles measured in this manner but they have generally been omitted to aid the interpretation of the data.

The influence of temperature on the crystallisation behaviour of PET film is presented in Figure 6.8, showing the normalised intensity of the band at 1096 cm<sup>-1</sup> as a function of depth for samples exposed at 100 bar and 50°C. The presence of PET with a relatively high degree of crystallinity is observed at greater depths compared to films exposed at 100 bar and 40°C (Figure 6.6). The influence of temperature on the crystallisation



behaviour enhances the kinetics of chain reorganisation and hence increases the crystallisation rate. Interpretation of these results also requires consideration the influence of temperature on CO<sub>2</sub> in polymeric material as discussed in Chapter 3.

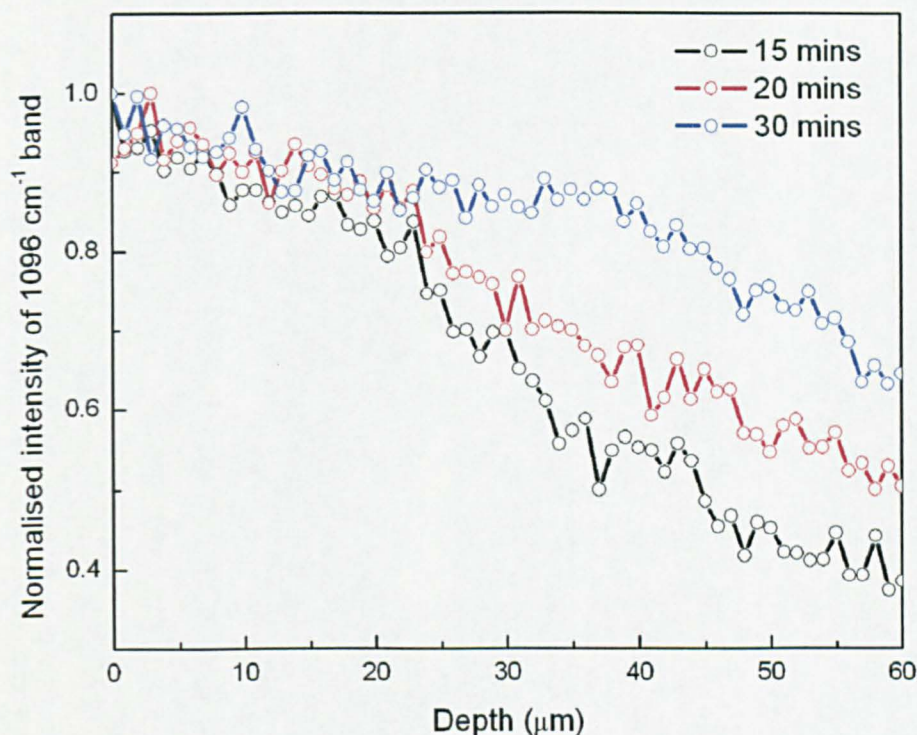


Figure 6.8. Normalised intensity of 1096 cm<sup>-1</sup> band as a function of depth acquired with 100x oil immersion objective corresponding to PET film sample exposed for 15, 20 and 30 minutes at 100 bar and 50°C.

The presented profiles demonstrate the influence of processing conditions on the CO<sub>2</sub>-induced morphological behaviour. For comparative purposes the CO<sub>2</sub>-induced morphological profiles for films exposed at the investigated conditions are presented in Figure 6.9. These effects require the correct combination of processing conditions in order to achieve the desired morphological character of the PET film and material performance.

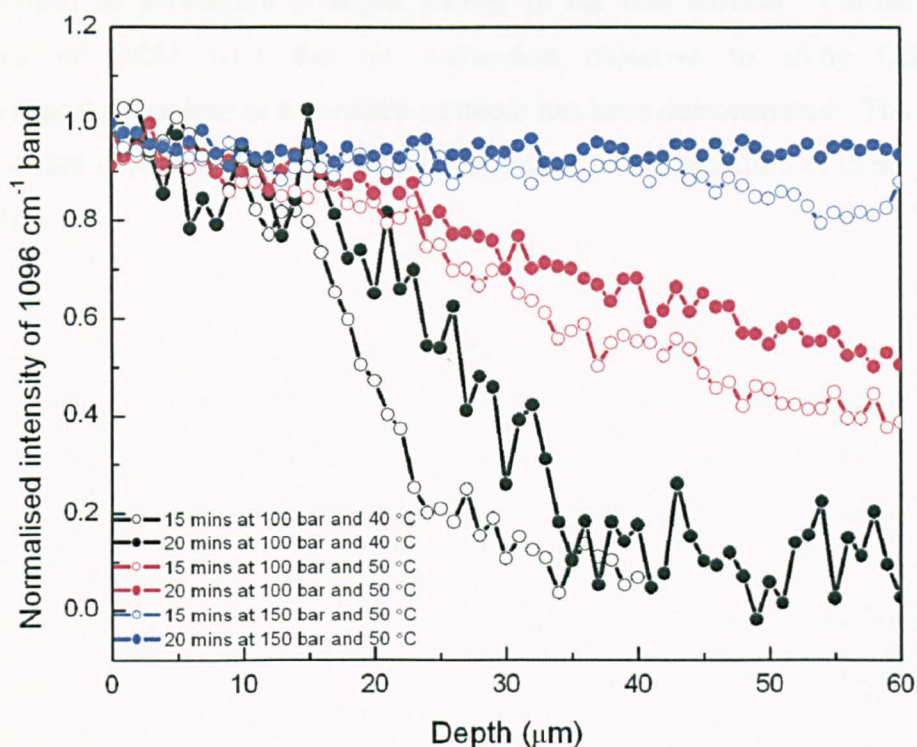


Figure 6.9. Normalised intensity of the  $1096\text{ cm}^{-1}$  band as a function of depth acquired with 100x oil immersion objective corresponding to PET film sample exposed for 15 (open circles) and 20 (closed circles) minutes at 100 bar and  $40^\circ\text{C}$  (black), 100 bar and  $50^\circ\text{C}$  (red), and 150 bar and  $50^\circ\text{C}$  (blue).

#### 6.1.4. CONCLUSIONS

It has been shown that CO<sub>2</sub>-induced morphological changes in PET do not occur uniformly through the film thickness when exposed for a limited time period. The presence of a morphological gradient has been demonstrated and studied as a function of depth normal to the film surface. The effects of exposure time, pressure and temperature have been investigated, exemplifying the possibility to tailor the distribution of CO<sub>2</sub>-induced morphological alterations in PET. This processing route provides the opportunity to control the extent of the modification of the surface layer of PET (morphological reorganisation as a function of depth), combined with the ability to “freeze” the induced morphology. These results provide an insight into the potential of scCO<sub>2</sub> to produce new materials potentially with new mechanical properties. This

technology, in combination with CRM enables the distribution of crystalline material to be controlled as a function of depth normal to the film surface. Furthermore, the reliability of CRM with the oil immersion objective to study CO<sub>2</sub>-induced morphological alterations as a function of depth has been demonstrated. The use of the oil immersion objective enables the non-destructive characterisation of these polymeric materials.



## 6.2. TRANSMISSION FTIR IMAGING ANALYSIS OF POLY(ETHYLENE TEREPHTHALATE) FILM PROCESSED WITH SC<sub>2</sub>CO<sub>2</sub>

### 6.2.1. INTRODUCTION

In the previous chapter the use of CRM was applied to investigate the extent of CO<sub>2</sub>-induced morphological alterations as a function of depth in PET film. Although the sampling capability of CRM does enable an area or volume to be sectioned, thereby forming a slice or volumetric cut, this is a time consuming process. The use of imaging has the advantage of a relatively large field of view that enables the distribution of a component of interest to be visualised rapidly. Transmission FTIR imaging of thin sections enables the CO<sub>2</sub>-induced gradient of modified morphology to be studied, albeit in a destructive manner. This study uses a combined approach of transmission FTIR imaging and Raman microscopy to study the induced morphological gradient in PET film processed with scCO<sub>2</sub>.

Crystallinity sensitive indicators for PET have been identified for both complementary techniques of Raman and IR spectroscopy.<sup>50</sup> The growth of the band corresponding to the CH<sub>2</sub> wagging mode of the *trans* conformer of the glycol moiety at 1340 cm<sup>-1</sup> is indicative of induced crystallinity in IR spectroscopy. In both the IR and Raman spectra of PET, the narrowing of the carbonyl band is indicative of the formation of the planer-crystalline structure.<sup>248</sup> FTIR imaging has previously been used to study the heterogeneous distribution of crystalline domains in PET,<sup>224</sup> but this is the first time that FTIR imaging has been applied to PET processed with scCO<sub>2</sub>. The principles and sampling capability of the arrangement used in this study are detailed in section 4.3.2.

### 6.2.2. EXPERIMENTAL

The sample preparation detailed in section 6.1.2 was used to expose the PET samples used in this study in accordance with the protocols introduced in section 5.2. Thin sections of 5 µm thickness were prepared by cryogenically sectioning the samples with a diamond knife at -80°C. Fourier transform infrared images were measured with a Bruker Optic imaging spectrometer (Hyperion). The system comprises of an IFS 66/S

step scan FTIR spectrometer, infrared microscope (IR-scope II) and a 64 x 64 focal plane array (FPA) detector. Spectra were recorded with a spectral resolution of 8 cm<sup>-1</sup> and an image acquisition time of approximately 5 minutes. The microtomed film samples were placed onto a clean CaF<sub>2</sub> window for transmission FTIR measurements. Background measurements were recorded using the same window in a position free from sample.

### 6.2.2. RESULTS AND DISCUSSION

The visualisation of a specific component using FTIR imaging requires the selection of a suitable band corresponding to the chemical species of interest. ATR FTIR spectra of PET film before and after exposure to scCO<sub>2</sub> are presented in Figure 6.10. The presence of the characteristic band of the *trans* glycol conformer at 1340 cm<sup>-1</sup> is apparent in the sample exposed to CO<sub>2</sub> which has been selected to visualise the distribution of PET with a relatively high degree of crystallinity.

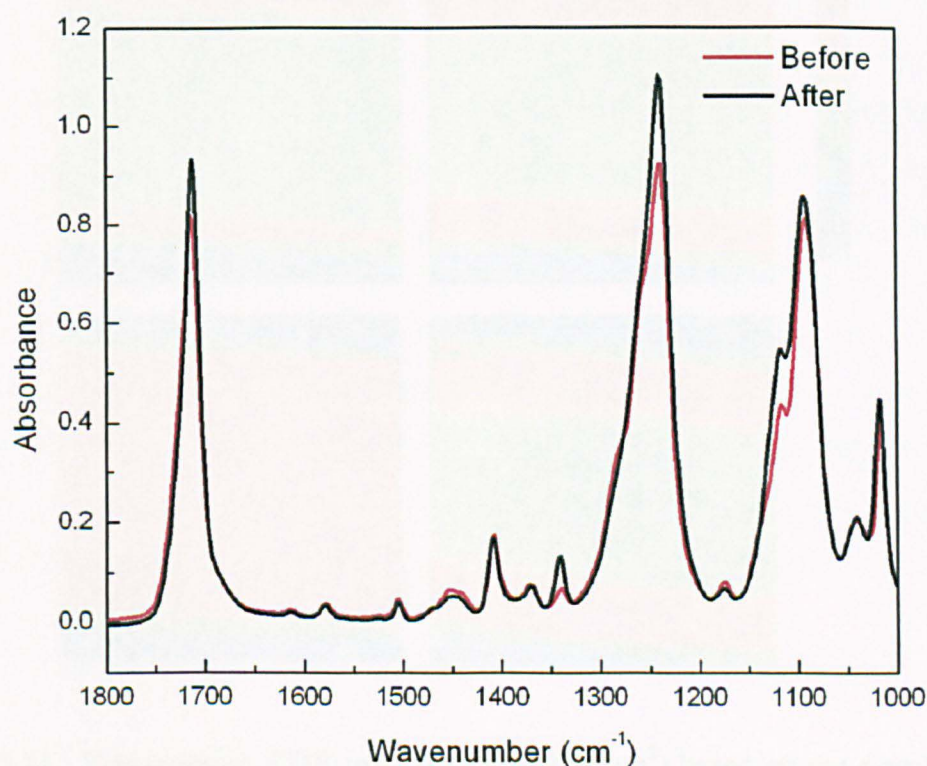


Figure 6.10. ATR FTIR spectra measured at the surface of PET film before (red) and after (black) exposure to scCO<sub>2</sub> at 100 bar and 40°C for 30 minutes.



Transmission FTIR images ( $266 \times 266 \mu\text{m}^2$ ) of PET film sections exposed for 15, 20, 30 minutes and 3 hours at 100 and 40°C are presented in Figure 6.11. The images are based on the distribution of the integrated absorbance of the band at  $1340 \text{ cm}^{-1}$  with a selected baseline (a straight line between the absorbance at  $1353\text{-}1327 \text{ cm}^{-1}$ ), corresponding to the CH<sub>2</sub> wagging mode of the *trans* glycol conformer. The pink/red regions of the images represent PET with a relatively high concentration of glycol units in the *trans* conformation and the green areas correspond to largely amorphous, unmodified PET. The amount of CO<sub>2</sub>-modified material (thickness of red/pink area at the top and bottom of the images) increases with exposure time, consistent with the CRM analysis in the previous section. The film sample exposed for 3 hours displays uniform CO<sub>2</sub>-induced morphology. It should be noted that this sample does not reflect the time required for uniform morphology at these processing conditions, but rather demonstrates that the level of crystallinity induced at short exposure time does not change.

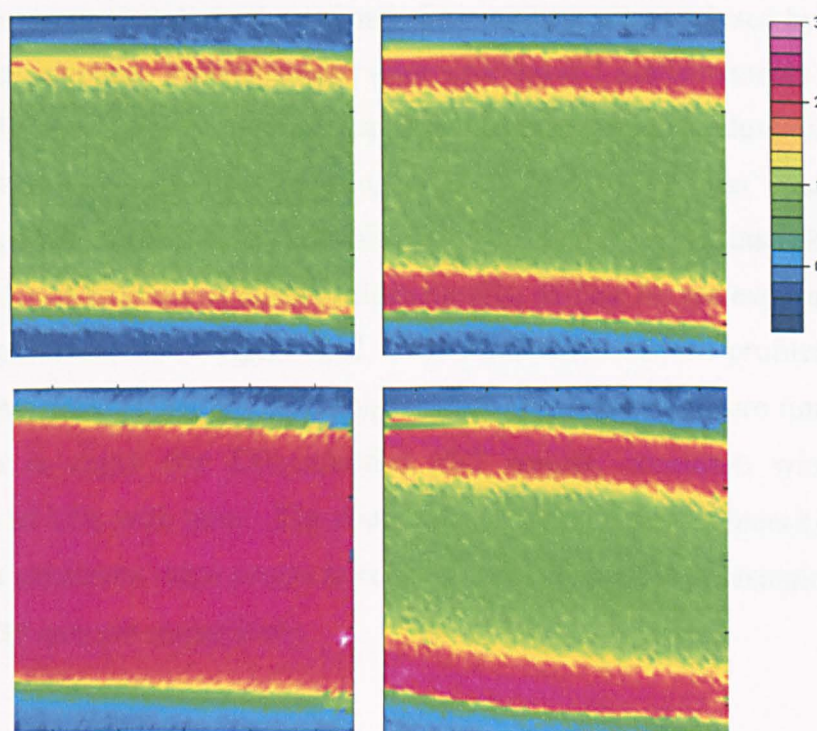


Figure 6.11. Transmission FTIR images ( $266 \times 266 \mu\text{m}^2$ ) based on the distribution of the integrated absorbance of the  $1340 \text{ cm}^{-1}$  band. The images correspond to PET films exposed scCO<sub>2</sub> at 100 bar and 40°C for (clockwise from top left): 15 mins, 20 mins, 30 mins and 3 hours.

The relatively large field of view enables the uniformity of CO<sub>2</sub>-induced morphological alterations to be visualised at both film surfaces. For the images where a gradient is present (15, 20 and 30 mins) the distribution is seen to be symmetrical with respect to both surfaces, indicative that the high-pressure vessel does not preclude the access of CO<sub>2</sub> to either of the surfaces. It is expected that the surface of the sample should exhibit the highest crystallinity. However, there is a thin green region at the surface of all samples (top and bottom extremities of the film surfaces shown in Figure 6.11). This is due to the effect of diffraction of the IR light near the surfaces resulting in the apparent reduction of all absorption bands of PET, including the crystalline band. This effect and the issue of spatial resolution in FTIR imaging has been discussed in more detail elsewhere.<sup>236</sup> Visual inspection of the images enables one to estimate the thickness of the surface layer of CO<sub>2</sub>-modified PET. The thickness of the modified region corresponds to ca. 30, 40 and 50  $\mu\text{m}$  for samples exposed for 15, 20 and 30 minutes respectively.

As a complementary analysis, the polymer film sections were analysed by conventional Raman point mapping. Raman spectra were recorded at 1  $\mu\text{m}$  increments along the line normal to the surface of the film surface. The normalisation procedure was identical to that described in the previous section, with the band at 795  $\text{cm}^{-1}$  used due to its insensitivity to conformation or crystallinity.<sup>217,250</sup> The normalised intensity of the band at 1096  $\text{cm}^{-1}$  as a function of distance from the film surface for the exposure time range investigated are shown in Figure 6.12. The normalised Raman profiles confirm the general trend observed in the FTIR images, with increasing exposure time resulting in an increase in depth that CO<sub>2</sub>-modified PET resides, consistent with the greater penetration of CO<sub>2</sub> with time. The distance that the normalised intensity drops to ca. 10 % of the maximum value occurs at ca. 30, 40 and 50  $\mu\text{m}$  for the samples exposed for 15, 20 and 30 minutes respectively.



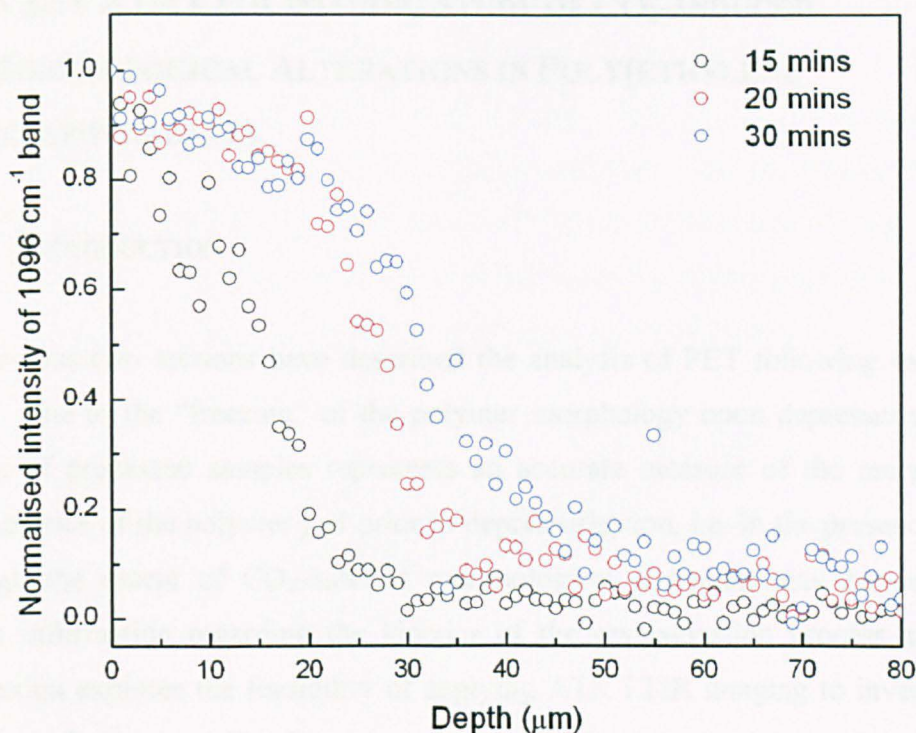


Figure 6.12. Normalised intensity of the band at 1096 cm<sup>-1</sup> measured using Raman mapping along the line normal to the surface of microtomed PET film sections.

### 6.2.3. CONCLUSIONS

The CO<sub>2</sub>-induced morphological gradient in PET film has been investigated using a combined approach of Raman microscopy and FTIR imaging. Confirmation of the induced morphology in PET has been achieved (in a destructive manner) through the measurement of the same film cross-sections in transmission FTIR imaging and by conventional Raman point mapping. Using the combination of the complementary techniques of IR and Raman spectroscopy, confident characterisation of the CO<sub>2</sub>-induced morphological gradient was possible.

### 6.3. *IN SITU* ATR FTIR IMAGING STUDY OF CO<sub>2</sub>-INDUCED MORPHOLOGICAL ALTERATIONS IN POLY(ETHYLENE TEREPHTHALATE)

#### 6.3.1. INTRODUCTION

The previous two sections have described the analysis of PET following exposure to scCO<sub>2</sub>. Due to the “freezing” of the polymer morphology upon depressurisation, the analysis of processed samples represents an accurate measure of the morphological characteristics of the polymer just prior to depressurisation, i.e. in the presence of CO<sub>2</sub>. Although the extent of CO<sub>2</sub>-induced morphological alteration may be determined, specific information regarding the kinetics of the crystallisation process are absent. This section explores the feasibility of applying ATR FTIR imaging to investigate the dynamics of the crystallisation process *in situ* via the simultaneous study of the distribution of CO<sub>2</sub> and CO<sub>2</sub>-modified material as a function of time and space.

The success of ATR FTIR imaging to study polymers under high-pressure CO<sub>2</sub> was demonstrated by Chan and Kazarian.<sup>159</sup> The combination of a miniature high-pressure cell with a Golden Gate<sup>TM</sup> diamond accessory permits ATR measurements under high-pressure and supercritical environments. Developing the imaging approach to investigate uniaxial diffusion under high-pressure environments requires modifications to the high-pressure cell to enable the polymer film to be sandwiched against the diamond.

#### 6.3.2. EXPERIMENTAL

*High-pressure apparatus:* A schematic diagram of the miniature cell used in this study is shown in Figure 6.13. The absence of fragile windows and the small volume of the cell result in an inherently safe design. The cell was sealed with a polytetrafluoroethylene (PTFE) washer against the diamond support plate and is held in position using the gate of the accessory. The contact bar was hand made for this application from stainless steel. The temperature in the high-pressure cell can be adjusted using the temperature control unit and was maintained at 40°C for all



experiments so that it was above the critical temperature of CO<sub>2</sub>. Once thermal equilibrium was reached, the cell was slowly loaded with CO<sub>2</sub> (99% purity provided by BOC) using an ISCO model 500D syringe pump. Cell pressurisation was typically completed within 1 minute and the system pressure was monitored during the pressurisation stage and throughout the course of the experiment using a digital pressure transducer. Once the required pressure was obtained, the image acquisition procedure was initiated which served as time zero for the dynamic experiments.

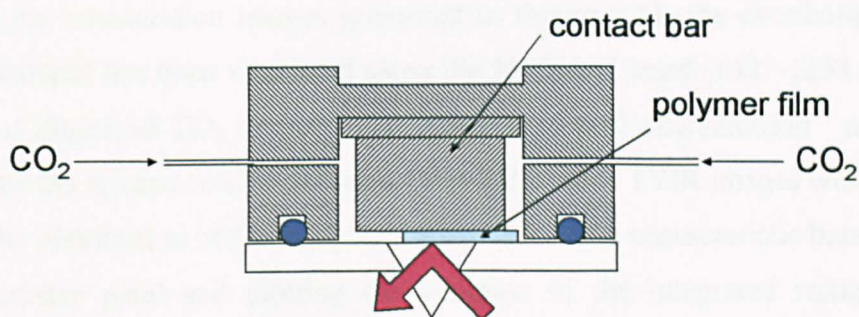


Figure 6.13. Schematic diagram of miniature high-pressure cell assembly. The PET film, shown in blue, is sandwiched onto the diamond ATR crystal by the contact bar.

*ATR FTIR imaging:* Fourier transform infrared images were collected using a 64 x 64 focal plane array (FPA) detector through the diamond ATR accessory in a macro chamber with a step scan spectrometer. Spectra were recorded using 5 coadditions with a spectral resolution of 8 cm<sup>-1</sup> which took ca. 3 minutes to acquire an image.

### 6.3.3. RESULTS AND DISCUSSION

A piece of largely amorphous PET film of approximate dimensions 3 mm x 2 mm x 0.25 mm was placed onto the crystal so that it formed a straight edge extended over the diamond surface. The film size was selected so that once sandwiched, the area was such that the CO<sub>2</sub> concentration measured across the image was not contributed to by the diffusion occurring perpendicularly to the surface of the imaged area, and hence uniaxial diffusion conditions were studied. Once in position the film was pressed under the contact bar and kept in position using the top of the high-pressure cell. The load required on the film must be sufficient to form adequate contact between the film and the diamond, thus preventing leakage of CO<sub>2</sub> into the polymer-diamond interface. The



anvil of the Golden Gate<sup>TM</sup> accessory was used to secure the high-pressure cell in position and enabled a measurable amount of force to be applied directly onto the film. To study the spatial distribution of the components of interest in this system, FTIR spectra of the chemical species have to be compared and vibrational bands selected in regions of the spectra that are absent from contributions from the other components. The basis of IR characterisation of PET using the 1340 cm<sup>-1</sup> band of the *trans* glycol conformer was described in section 6.2. ATR FTIR spectra of largely amorphous PET film before and after exposure to scCO<sub>2</sub> are presented in Figure 6.10. In an identical manner to the transmission images presented in Figure 6.11, the distribution of CO<sub>2</sub>-modified material has been visualised using the 1340 cm<sup>-1</sup> band (1327-1353 cm<sup>-1</sup>). The spectrum of dissolved CO<sub>2</sub> in polymeric material is well characterised<sup>37</sup> and may be identified by the  $\nu_3$  band of CO<sub>2</sub> between 2300-2350 cm<sup>-1</sup>. FTIR images were generated based on the distribution of the integrated absorbance of a characteristic band measured at each detector pixel and plotting the variation of the integrated values over the measured area.

ATR FTIR images of largely amorphous PET film exposed to 75 bar of CO<sub>2</sub> at 40°C representing the distribution of amorphous PET, CO<sub>2</sub>-modified PET and CO<sub>2</sub> are presented in Figure 6.14. The images correspond to an area of ca. 820 x 1140  $\mu\text{m}^2$  and are accompanied with a scale bar which associates the colour used in the images with integrated absorbance values. Once the cell had been pressurised, the image acquisition process was initiated. As time increases the presence of CO<sub>2</sub> can be seen to advance into the bulk PET, travelling from the left to the right side of the image. Inspection of the right hand side of the images corresponding to PET (top), reveal the presence of two spots of relatively low absorbance. The nature of the evanescent wave penetrating the sample provides an effective measure of the amount of material probed by the field and thus an indication of the contact/force applied to the sample. The low absorbance regions of the sample represent poor contact between the film and the diamond in those regions. The small size of the areas of poor contact suggests that they are attributed to defects on the film surface rather than non-uniformities in the applied force. Due to the positions of the regions of poor contact, they are essentially insignificant for the purpose of this preliminary analysis but they would pose a problem if they were located in the proximity of the “free” edge.

The presence of dissolved CO<sub>2</sub> molecules in the PET matrix consequently results in an increase in free-volume. In conventional ATR measurements of CO<sub>2</sub> sorption into polymer films, swelling can be observed from the reduction in absorbance of the polymer due to less material being probed by the IR field. A comparison of the images corresponding to PET and CO<sub>2</sub> show a small reduction in PET absorbance in the areas of CO<sub>2</sub> presence. Swelling in the x-direction is apparent in the images and should not be as restricted as the z-direction. Swelling will also occur in the y-direction but, due to limited field of view, it is not possible to observe this. As CO<sub>2</sub> diffuses into the bulk polymer morphological alterations are induced and the amount of crystalline material is seen to increase at regions of relatively high CO<sub>2</sub> concentration. This *in situ* observation provides additional confirmation for the presence and dynamics of a CO<sub>2</sub>-induced morphological gradient in PET.

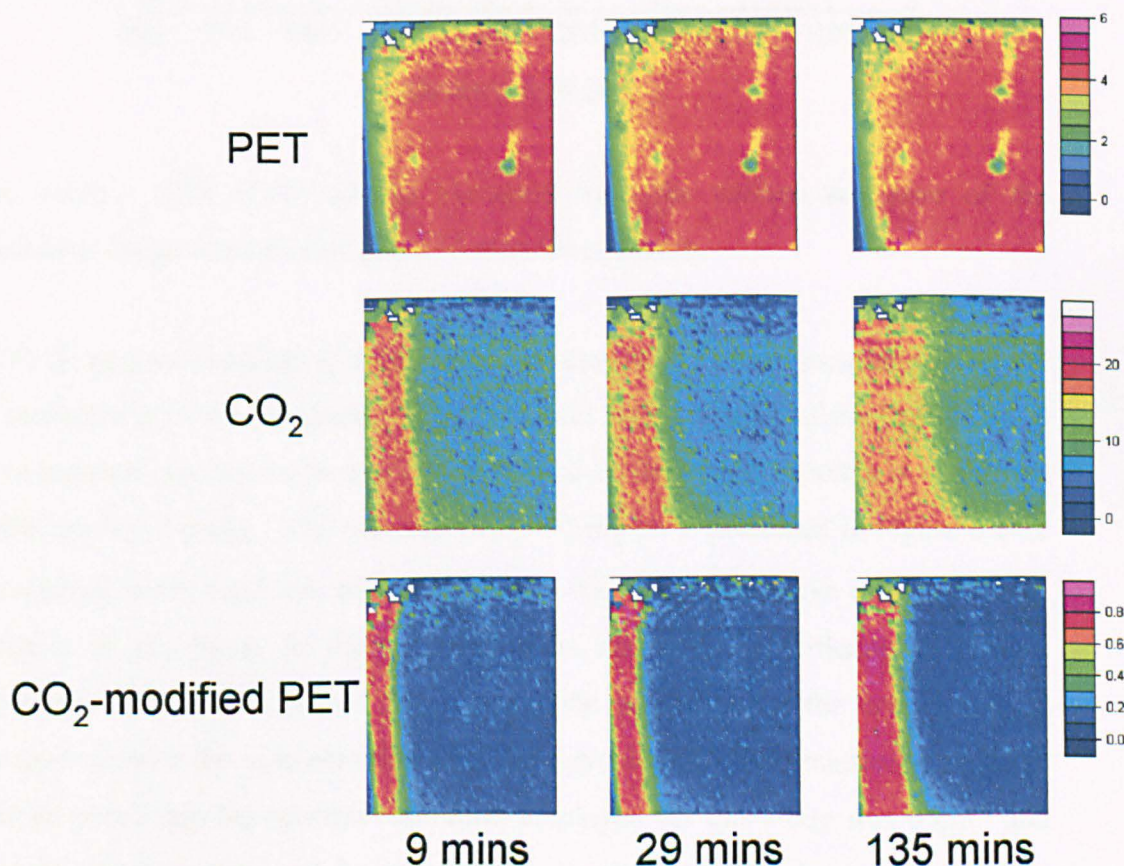


Figure 6.14. ATR FTIR images of largely amorphous PET exposed to CO<sub>2</sub> at 75 bar and 40°C. Images were generated using the carbonyl band of PET (top), antisymmetric stretching mode of CO<sub>2</sub> (middle), and the PET crystalline band at 1340 cm<sup>-1</sup> (bottom).



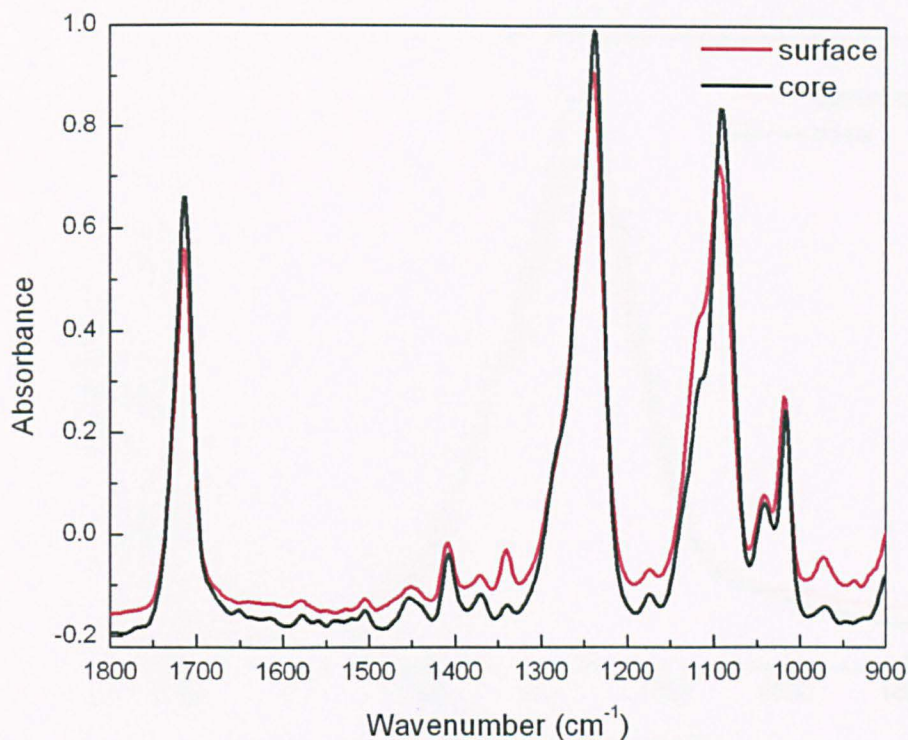


Figure 6.14a. ATR FTIR spectra extracted from the surface and core of the transmission image corresponding to 135 minutes exposure.

ATR FTIR spectra extracted from the edge and core of the image measured after 135 mins in Figure 6.13 are presented in Figure 6.14a. The presence of the band at 1340 cm<sup>-1</sup> is apparent and the reduction in absorbance in the surface spectra is consistent with the matrix swelling. The expanded  $\nu(\text{C}=\text{O})$  region is presented in Figure 6.14b. As previously mentioned, the narrowing of the  $\nu(\text{C}=\text{O})$  is indicative of crystallinity. Inspection of the bands in Figure 6.14b does not reveal significant differences between the extracted regions. This observation suggests that the crystallinity is unchanged despite the concentration of *trans* glycol unit being relatively high. It should be noted that the spectral resolution employed for this study was 8 cm<sup>-1</sup> and thus small changes may not be resolvable. Furthermore, the interaction of CO<sub>2</sub> molecules with the carbonyl oxygen is likely to result in a shift to the band. Nonetheless, the use of the 1340 cm<sup>-1</sup> band in 6.2 was shown to be indicative of crystallinity in CO<sub>2</sub> processed PET.

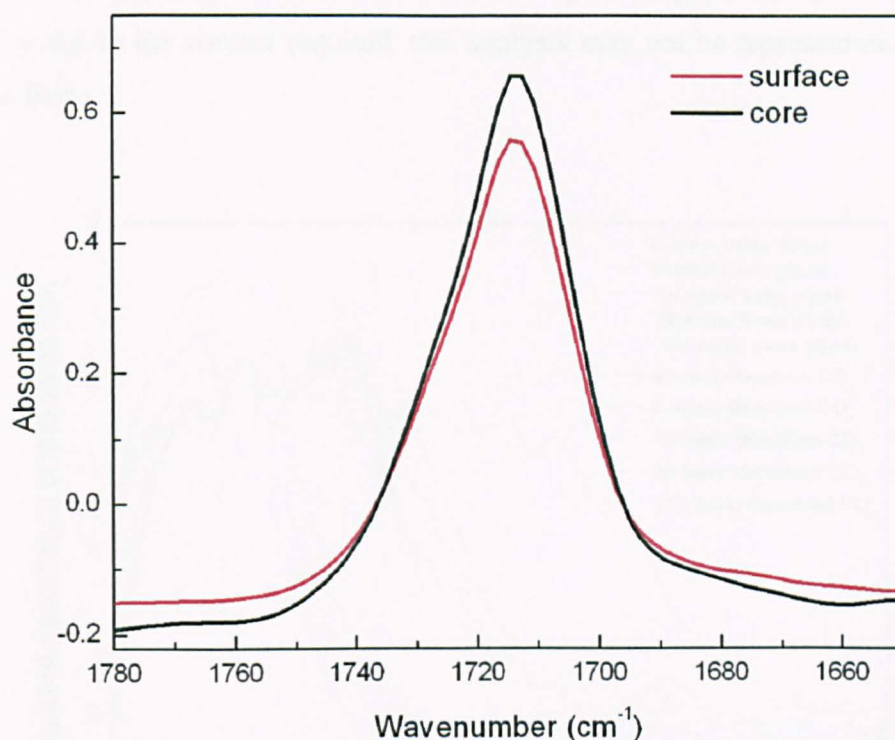


Figure 6.15b. Expanded  $\nu(\text{C}=\text{O})$  region of the extracted spectra of the surface and core polymer.

To evaluate the CO<sub>2</sub> diffusion mechanism, the evolution of the CO<sub>2</sub> absorbance profile as a function of time is required. The arrangement of the PET film on the diamond ATR crystal permits the concentration profile of a specific component of the system to be studied along the line that intersects the interface perpendicularly. The concentration profile of a specific component corresponds to the integrated absorbance values for a row of pixels that span this line. This process was applied to 5 consecutive lines and an average value for each pixel position along the line calculated to improve signal to noise. The concentration-distance profiles extracted from the imaging data, corresponding to CO<sub>2</sub> and CO<sub>2</sub>-modified PET are presented in Figure 6.16.

Inspection of Figure 6.16 reveals that the formation of crystalline PET occurs at some time after the equilibrium fraction (max absorbance) of CO<sub>2</sub> at a specific location within the matrix has been reached. Therefore, under these experimental conditions, the characteristic time for CO<sub>2</sub> diffusion is small compared to the kinetics of CO<sub>2</sub>-induced



crystallisation. It is important to stress that due to the film being sandwiched between two rigid and impermeable surfaces, i.e. swelling is only permitted in the x and y directions due to the contact required, this analysis may not be representative of a free-standing film.

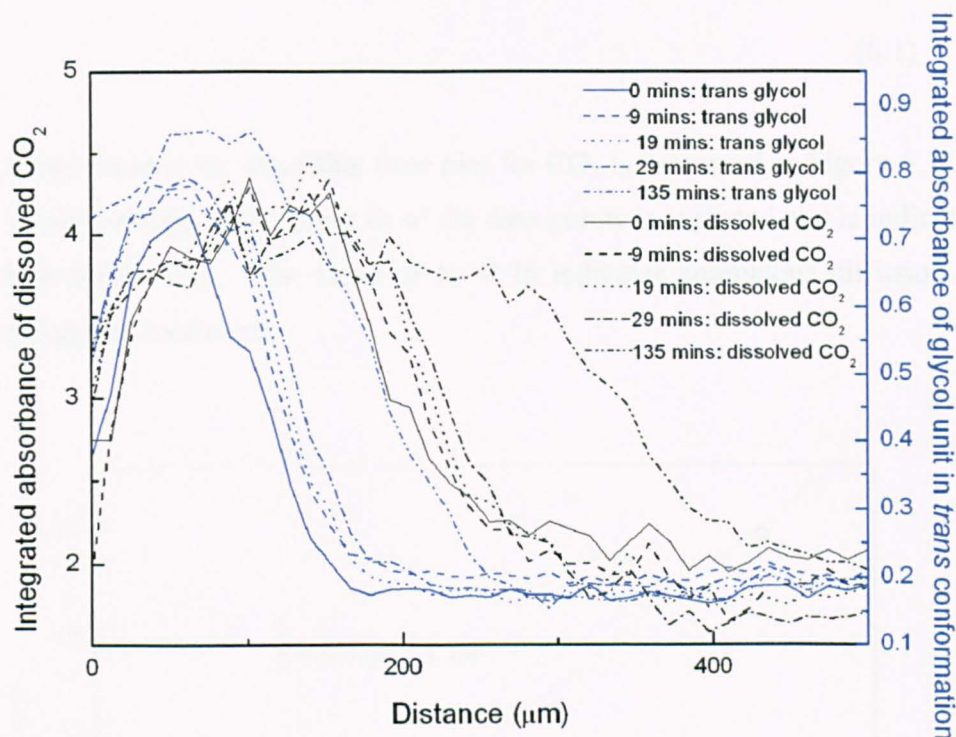


Figure 6.16. Extracted concentration-distance profiles for CO<sub>2</sub> (black) and crystalline PET (blue). Each profile represents an average signal from 5 consecutive lines that intersect the interface perpendicularly.

One may assess the diffusion mechanism of CO<sub>2</sub> using the power law defined in Equation 6.1, which requires the position of the CO<sub>2</sub> diffusion front ( $d$ ) to be determined as a function of time ( $t$ ). Equation 6.1 describes the time dependence of the diffusion distance where  $A$  is the proportionality factor and  $\alpha$  is the diffusion time exponent. Elucidation of the diffusion mechanism is possible through evaluation of the gradient of a plot of logarithm distance vs. logarithm time. A gradient of 0.5 describes Fickian/case I diffusion whereas a value of 1 corresponds to case II diffusion. Anomalous diffusion occurs when the gradient of the regression line of the measured points has an alternative value. The distance refers to the diffusing front of CO<sub>2</sub> which has been defined as the distance where the concentration of CO<sub>2</sub> falls to ca. 75 % of the maximum value.



The concentration profiles of PET (not included) demonstrate swelling, seen by the edge of the film advancing toward the left hand side of the image with time. The distance that the value of PET absorbance dropped to ca. 75 % of the max value served as the reference point to determine the distance that CO<sub>2</sub> had diffused after various times.

$$d = At^\alpha \quad (6.1)$$

The logarithm distance vs. logarithm time plot for CO<sub>2</sub> is presented in Figure 6.17. The equation corresponding to the linear fit of the data points is included and is indicative of the diffusion mechanism. The value of ca. 0.76 indicates anomalous diffusion under these experimental conditions.

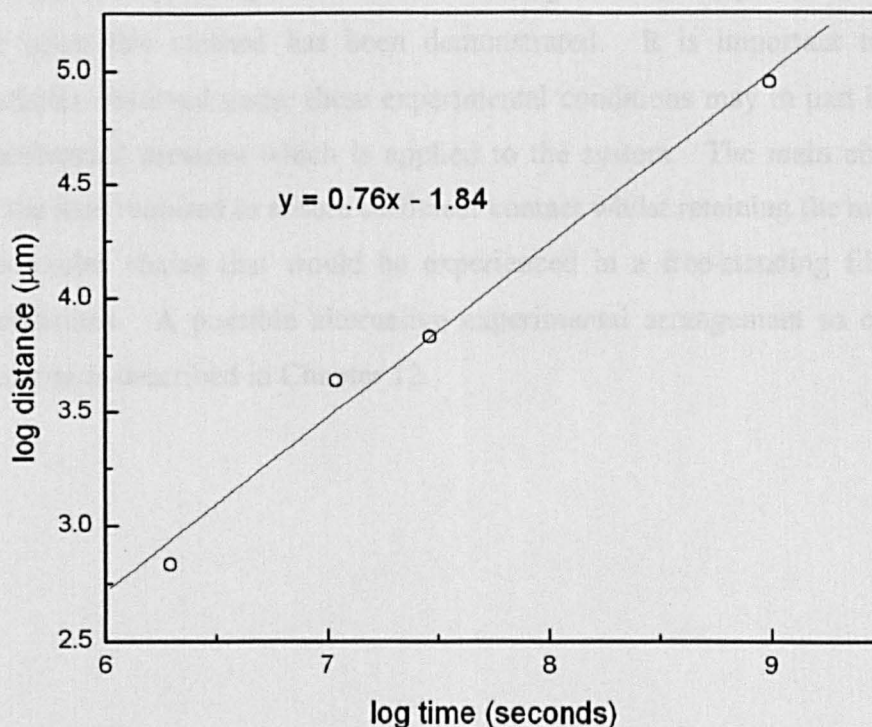


Figure 6.17. Plot of log distance vs. log time for CO<sub>2</sub> diffusing in PET at 75 bar and 40°C.

The available literature for CO<sub>2</sub> diffusion in PET under supercritical conditions reports observations of Fickian diffusion<sup>38,75</sup>. The anomalous diffusion mechanism obeyed by CO<sub>2</sub> in this approach suggests that the experimental system influences the diffusion of CO<sub>2</sub>. Additional experiments with PET have been conducted under various conditions

to explore the effect of temperature and pressure. However, the success of the experiments has been limited largely as a result of contact issues. Examples of PET samples (not included) have displayed CO<sub>2</sub> diffusion through the matrix but without showing morphological alterations, presumably due to the mechanical load imposed on the matrix. This issue poses significant experimental challenges to overcome which are described in more detail in the future work section of Chapter 12.

#### 6.3.4. CONCLUSIONS

This study represents the first example of investigating CO<sub>2</sub>-induced morphological alterations in PET using *in situ* ATR FTIR imaging. Using the preliminary data acquired it has been possible to evaluate the diffusion mechanism of CO<sub>2</sub>. Although the applied experimental set-up has inherent contact problems, the potential to extend and improve upon this method has been demonstrated. It is important to stress that characteristics observed under these experimental conditions may in part be due to the static mechanical pressure which is applied to the system. The main challenge is to balance the load required to ensure sufficient contact whilst retaining the mobility of the macromolecular chains that would be experienced in a free-standing film under the same conditions. A possible alternative experimental arrangement to overcome the contact issues is described in Chapter 12.

## **CHAPTER 7**

# **CONFOCAL RAMAN STUDY OF INDUSTRIALLY DYED PET FIBRES**

## **7. CONFOCAL RAMAN STUDY OF POLY(ETHYLENE TEREPHTHALATE) FIBRES DYED USING SUPERCRITICAL CARBON DIOXIDE**

### **7.1. INTRODUCTION**

The use of scCO<sub>2</sub> technology as a replacement for the traditional aqueous method for dyeing of PET is a commercially viable alternative that has grown in international interest since 1995.<sup>14</sup> The implementation of scCO<sub>2</sub> in the dyeing industry over the traditional aqueous method would result in a great gain in the rate of diffusion<sup>82</sup> and would offer further benefits by reducing the number of effluent streams and allowing the location of industry to areas where water supplies are limited.<sup>165</sup> Optimisation of the scCO<sub>2</sub> dyeing process requires knowledge of the dye mass transport through the polymer matrix. Methods used to investigate the scCO<sub>2</sub> dyeing of polymers include the film roll method<sup>82,83</sup> and the gravimetric approach,<sup>75</sup> as summarised in Table 3. These techniques measure the total dye uptake and are therefore devoid of information regarding the spatial distribution of dye throughout the sample geometry. CRM is particularly suited to investigating such distributions within polymers, as spectral information can be recorded as a function of depth within the sample, and hence the diffusion mechanism of the dye may be evaluated. The feasibility of CRM to investigate the dye concentration distribution in PET film processed with scCO<sub>2</sub> has been demonstrated.<sup>209</sup>

In this Chapter CRM is applied to PET fibres dyed under scCO<sub>2</sub> conditions which are of specific interest to the textile industry. The dye distribution in PET monofilaments is suited for this type of investigation due to their yarn size. Typical applications of the PET monofilaments used in this study are textile accessories such as zippers and velcro fastenings. The first dyeing results of such products from PA 6.6 in scCO<sub>2</sub> were published by Knittel et al.<sup>252</sup> in 1993, but detail regarding the dye distribution within the fibres was absent. In this context, fibres dyed on a laboratory scale for different periods of time have been investigated and the diffusion coefficient of the dye within the polymer estimated. The consequence of the dyeing process on the fibre morphology has also been evaluated, because changes in the crystallinity during dyeing can highly

influence the dye uptake of synthetic fibres and the diffusion coefficient of the dye in the polymer matrix.<sup>253</sup>

## 7.2. EXPERIMENTAL

PET monofilament fibres (Trevira® Monofil 900 S, Trevira, Bobingen, Germany) with a diameter of 0.4 mm were treated in scCO<sub>2</sub> with and without C.I. Disperse Yellow 23 (from Ciba Specialty Chemicals, Basle, Switzerland at a dye concentration of 5 % relating to the fabric weight) for 1, 2 and 3 hours. The fibres were placed in a stirrable perforated dyeing beam within a 400 ml high-pressure apparatus as described elsewhere.<sup>252</sup> The dye was placed into an aluminium tin covered with filter paper and placed at the bottom of the autoclave. The autoclave was filled with gaseous CO<sub>2</sub> at 45 bar and heated up to 130°C. To avoid dissolution of the dye as far as possible during the heating phase, the pressure was raised to 280 bar only when the treatment temperature was reached. 50x objectives (oil and dry) were used to measure all of the Raman spectra in this work. The immersion oil used had a refractive index of 1.515 (purchased from Cargille Laboratories Inc, Cedar Grove, NJ). All Raman spectra were recorded with a dispersive Renishaw 1000 confocal system as previously described.

## 7.3. RESULTS AND DISCUSSION

The chemical structure of Disperse Yellow 23 (DY23) is shown in Figure 7.1. The associated strong Raman activity of the dye is apparent in the 1360-1500 cm<sup>-1</sup> spectral region of the Raman spectra in Figure 7.2. Representative Raman spectra of the unprocessed fibre and fibres exposed at 280 bar and 130°C for 3 hours in the absence (B) and presence (C) of DY23 are presented. Spectrum D corresponds to pure DY23, (or more precisely DY23 interacting with the PET matrix), generated via spectral subtraction of spectrum B from C. The Raman signal originating from the dye is proportional to its concentration, and thus the spectra may be used to study the relative dye concentration, assessed by the integrated area of the band in the wavenumber range 1454-1475 cm<sup>-1</sup>.



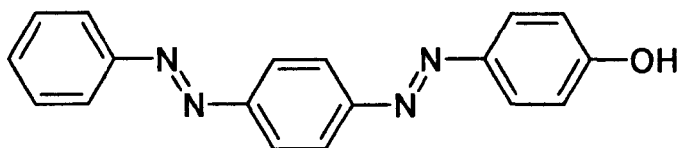


Figure 7.1. Chemical structure of Disperse Yellow 23.

The spectrum of the unprocessed fibre (A) shown in Figure 7.2 is characteristic of PET with a relatively high degree of crystallinity. This may be deduced from the spectral regions of the carbonyl band, the shoulder at  $1096\text{ cm}^{-1}$  and the band at  $1000\text{ cm}^{-1}$ . The band at  $1000\text{ cm}^{-1}$  corresponds to the *trans* conformation of the glycol unit and is indicative of the crystalline morphology (the *gauche* conformation is inherent to the amorphous domains of PET). The band at  $1117\text{ cm}^{-1}$  has a shoulder at  $1096\text{ cm}^{-1}$  that corresponds to the combination stretching vibration of the ester, glycol and ring unit of the *trans* configuration of the PET chain.

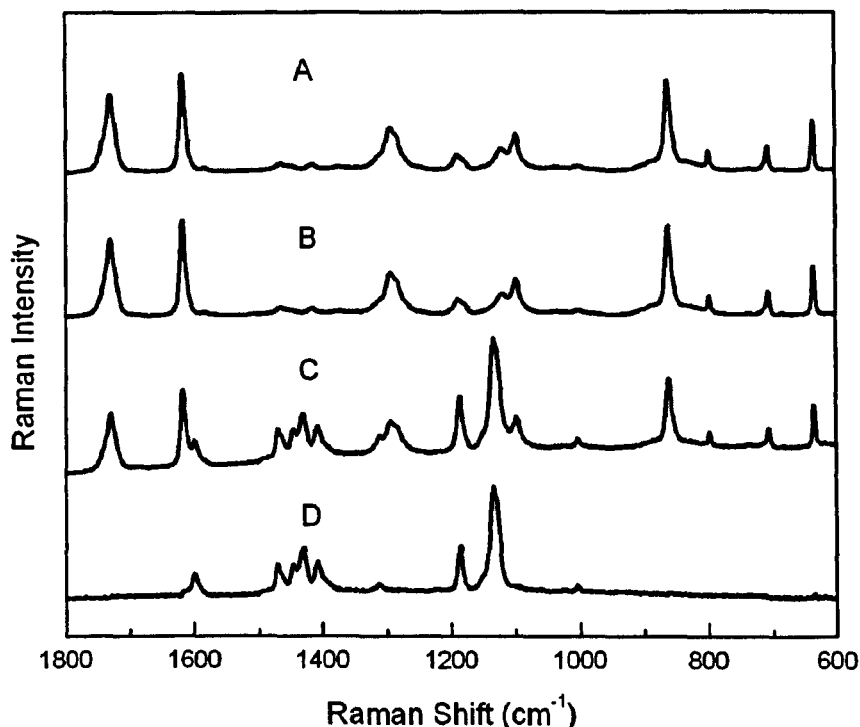


Figure 7.2. Raman spectra (acquired with a 50x dry objective in confocal mode) measured at the surface of the 0.4 mm fibres. Spectrum A corresponds to the unprocessed fibre, B and C following 3 hours exposure to  $\text{scCO}_2$  at 280 bar and  $130^\circ\text{C}$  in the absence and presence of Disperse yellow 23, respectively. Spectral subtraction of B from C was used to generate spectrum D which corresponds to Disperse Yellow 23.

However, both of the aforementioned bands can also occur in domains of amorphous PET that lack three-dimensional order. The carbonyl band of the unprocessed fibre has a FWHM (full width at half maximum) value of  $18\text{ cm}^{-1}$ , which compared to the amorphous form (ca.  $27\text{ cm}^{-1}$ ), corresponds to the morphology of semicrystalline PET with a relatively high degree of crystallinity. Following 3 hours exposure to  $\text{scCO}_2$  at 280 bar and  $130^\circ\text{C}$  (spectrum B) there were no changes to the spectral features associated with crystallinity. The carbonyl band does not significantly narrow for any of the dyeing times investigated, which reflects that the  $\text{scCO}_2$  processing does not lead to any increase in crystallinity at the fibre surface and provides evidence for the applicability of the carbonyl band to be used for dye concentration normalisation, as described in the following section. Additionally, DSC measurements were performed to detect structural changes in PET caused by the treatment in  $\text{scCO}_2$ . As seen in the Raman spectra, the DSC measurements did not show any differences in the DSC curves and the melting enthalpies of the pre-melting peak between the untreated,  $\text{scCO}_2$ -treated and dyed samples, even after a treatment for 6 h at  $130^\circ\text{C}$  at 280 bar in  $\text{scCO}_2$ .<sup>254</sup> This is consistent with the heat setting process performed on the fibres used for dyeing in the  $\text{scCO}_2$  and aqueous methods.

The dye concentration distribution in the polymer samples was investigated along the line normal to the fibre surface ( $z$ -direction). Raman depth profiles of the fibre dyed for 3 hours measured with the oil and dry objectives are shown in Figure 7.3. Spectra were collected at  $1\text{ }\mu\text{m}$  increments along the line normal to the fibre surface. In both the dry and oil data it can be seen that the concentration of the dye is not uniform as a function of depth, but decays in concentration from the surface to the core of the polymer, interpreted from the decrease of the dye bands relative to that of the polymer. There are two main features that differ between the depth profiles of the oil and dry approaches: an underestimation of the extent of the dye penetration in the case of the dry method and the decrease in intensity of all Raman bands with depth in the dry approach compared to the oil data. The Raman spectra from the dry data show a significant decay of the polymer bands over the initial  $100\text{ }\mu\text{m}$  depth, whereas the oil data does not show such a pronounced drop in intensity over this range. The decrease in refractive index mismatch when employing the immersion objective results in the reduction of refraction at the sample surface and, hence, minimises the optical aberrations associated with the enlargement and distortion of the focal volume with depth.

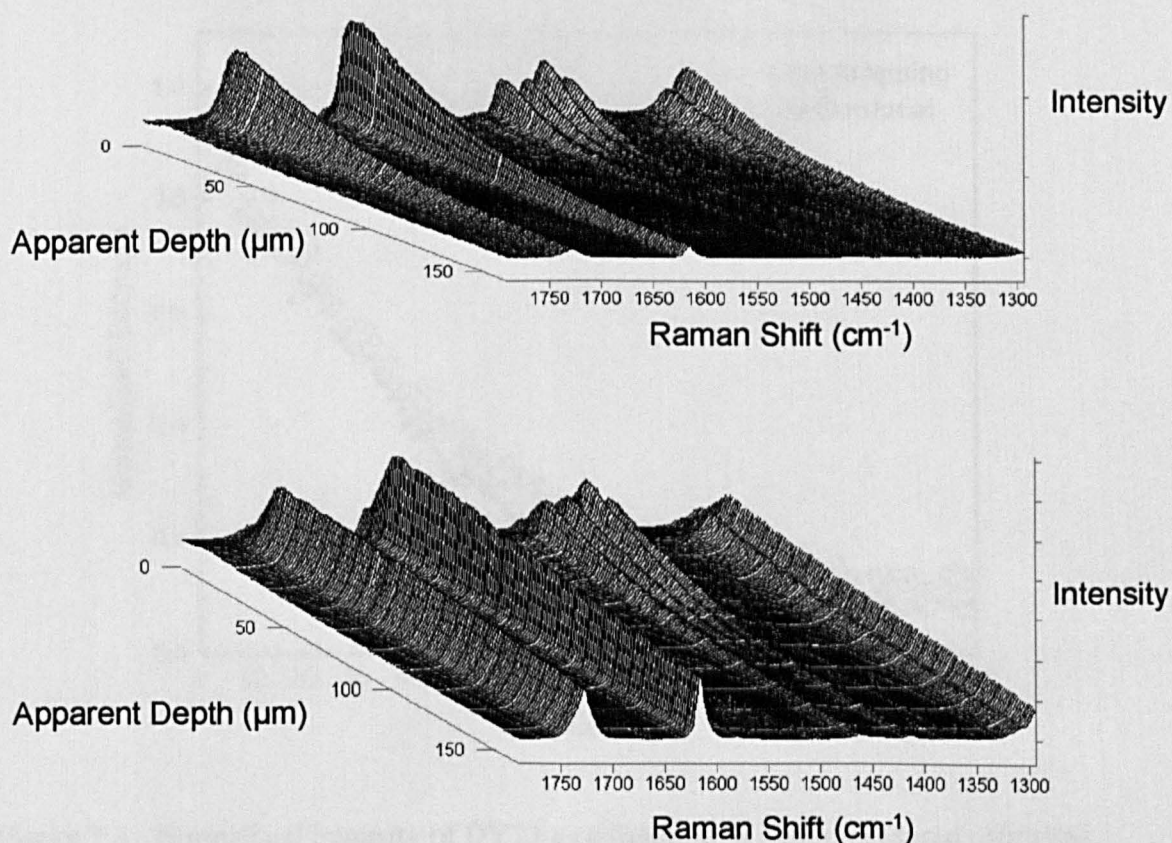


Figure 7.3. Confocal Raman depth profiles of the fibre dyed for 3 hours collected with the 50x dry objective (top) and 50x oil objective (bottom).

To visualise the relative distribution of DY23 as a function of depth, band normalisation is required and the carbonyl band was selected for this purpose. The Raman band corresponding to DY23 was integrated over the wavenumber range  $1454\text{--}1480\text{ cm}^{-1}$  and the carbonyl band between  $1700\text{--}1760\text{ cm}^{-1}$ . Peak area measurements were performed using the original baseline with the area under the peak integrated using a straight line that connected the aforementioned Raman shift values. The normalised dye intensity as a function of depth measured using the oil immersion confocal and line mapping approaches are presented in Figure 7.4. The line mapping results were measured along the radius of a cross-section of the dyed fibre.

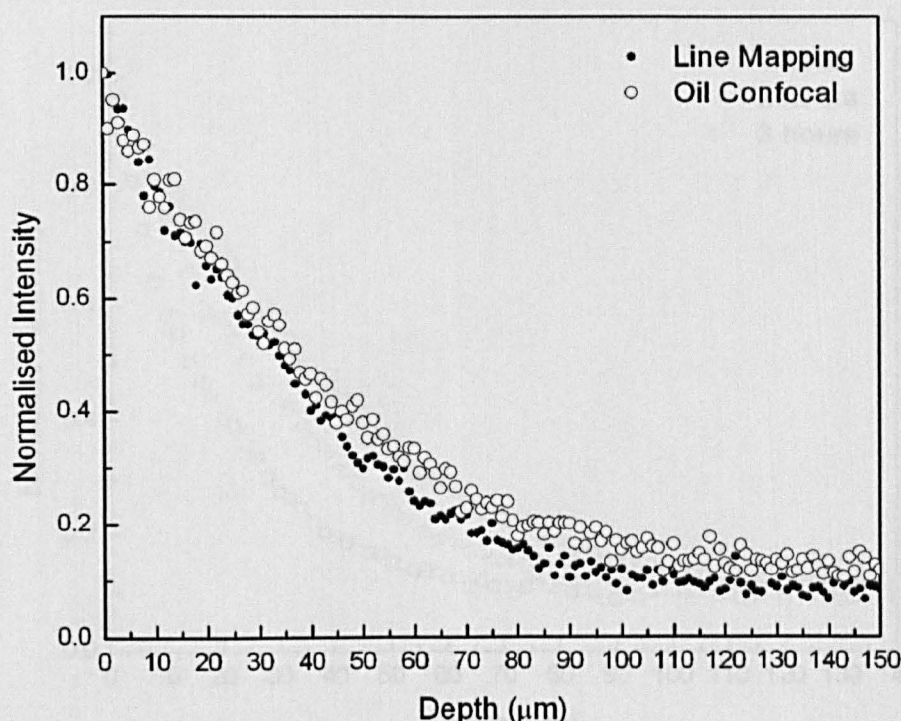


Figure 7.4. Normalised intensity of DY23 as a function of depth measured using the oil immersion confocal approach and line mapping measured along the radius of the microtomed fibre cross-section.

The high spatial resolution available with conventional line mapping is in the order of 1-2  $\mu\text{m}$ , which provides reference data to assess the confocality of the oil immersion approach. General agreement between the oil immersion data and line mapping is observed as a function of depth. At depths greater than 45  $\mu\text{m}$ , the oil data deviates from the line mapping data and slightly overestimates the concentration of dye at greater depths. This observation may be explained by the slight refractive index mismatch between the oil and the polymer combined with noise at greater depths. The relatively high degree of crystallinity present in the sample presents additional refractive index complications due to the presence of crystalline/amorphous boundaries. Orientation effects may also impart some variation in the carbonyl band intensity (used to normalise the dye signal) due to the partial polarisation of the laser beam. The orientation effects are likely to be different when z-sectioning the fibre compared to mapping along the radius of the cross-section.



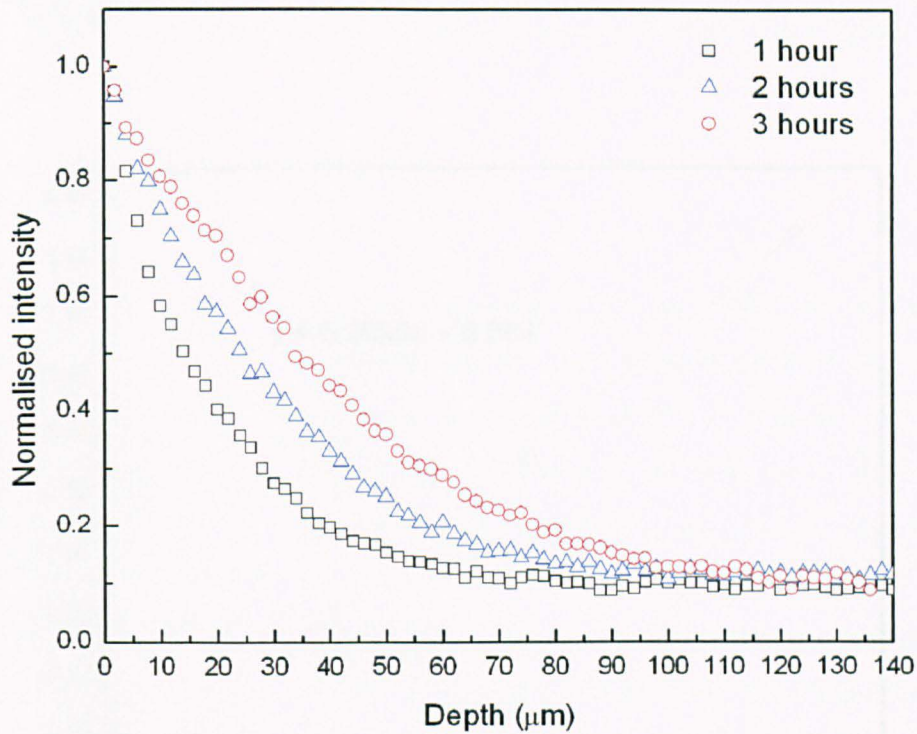


Figure 7.5. Normalised intensity of DY23 as a function of depth for fibres dyed for 1,2 and 3 hours measured using the oil immersion objective.

The normalised dye concentration gradients as a function of depth collected using the oil immersion objective are presented in Figure 7.5. The evolution of the concentration profile of DY23 as a function of time and space provides the required information to estimate the diffusion coefficient. A mathematical model to describe the diffusion in a cylinder where the direction of diffusion is only radial was presented by Crank.<sup>255</sup> In the case of Fickian diffusion the following equation can be applied:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{r^2}\right) \quad (7.1)$$

$M_t$  refers to the amount of dye absorbed,  $M_\infty$  the equilibrium amount absorbed,  $D$  the diffusion coefficient,  $r$  the radius of the non-swollen fibre, and  $t$  the sorption time. For short impregnation times, Equation 7.1 may be replaced with Equation 7.2.<sup>68</sup>



$$\frac{M_t}{M_\infty} = \frac{4}{r} \sqrt{\frac{Dt}{\pi}} \quad (7.2)$$

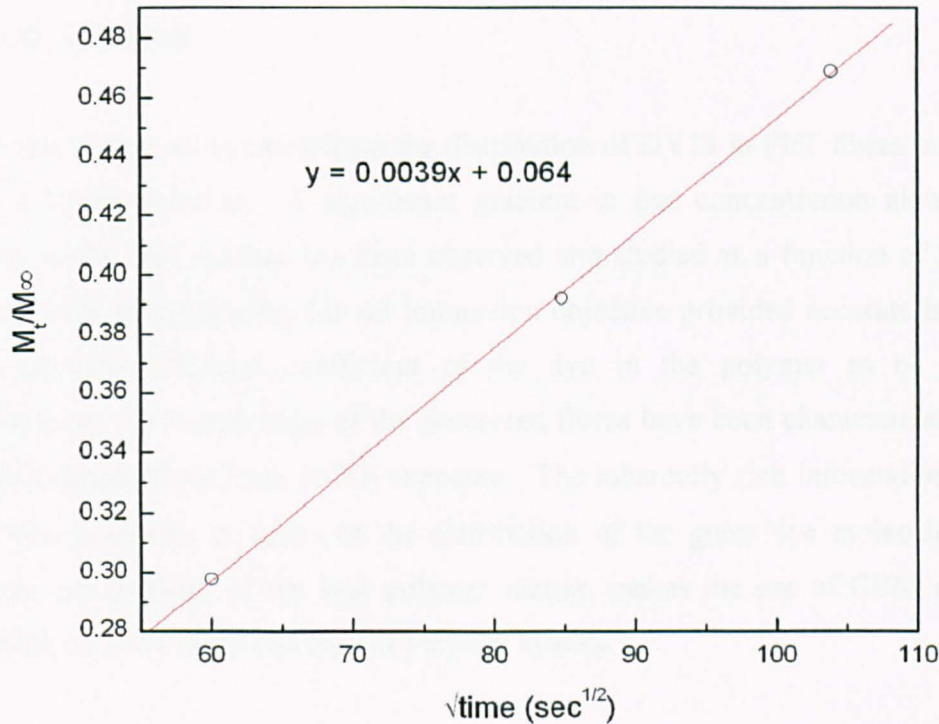


Figure 7.6. Plot of the normalised dye fraction vs. the square root of exposure time.

The values of  $M_t$  as a function of time were calculated from the integration of the area beneath the concentration profiles presented in Figure 7.5. The amount of dye sorbed at saturation, i.e.  $M_\infty$ , was assumed to correspond to the situation of constant concentration as a function of depth. The diffusion coefficient was estimated from the gradient of the plot shown in Figure 7.6 and the unswollen fibre radius. The linear plot is characteristics of Fickian diffusion which is expected as a result of the fast rate of polymer chain relaxation compared to the rate of dye diffusion at the conditions studied. The diffusion coefficient of DY23 in the PET fibres at the conditions studied is estimated at  $4.7 \times 10^{-13} \pm 1.11 \text{ m}^2\text{s}^{-1}$ . This value compares well with literature data reported by Sicardi et al.<sup>83</sup> who applied UV-vis spectroscopy to a disperse yellow/PET system processed using the film roll method, reporting a diffusion coefficient of  $1.5 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ . However, due to the processing conditions (110°C and 250 bar compared to 130°C and 280 bar used in this work), the difference in experimental procedure (Film

roll followed by UV-vis compared to non-invasive CRM) and the nature of yellow dye may not have been the same, a direct comparison of the results is not possible. Nonetheless, the potential of this approach to estimate the diffusion coefficient has been demonstrated.

#### 7.4. CONCLUSIONS

CRM has been used to investigate the distribution of DY23 in PET fibres impregnated from a scCO<sub>2</sub> solution. A significant gradient in dye concentration along the line normal to the fibre surface has been observed and studied as a function of time. The non-invasive analysis using the oil immersion objective provided accurate information to enable the diffusion coefficient of the dye in the polymer to be estimated. Furthermore, the morphology of the processed fibres have been characterised to assess possible implications from scCO<sub>2</sub> exposure. The inherently rich information available with this approach, in terms of the distribution of the guest dye molecules and the intrinsic morphology of the host polymer matrix, makes the use of CRM a powerful technique to investigate this type of polymer system.

## **CHAPTER 8**

# **IMPREGNATION OF POLY(ETHYLENE TEREPHTHALATE) FILM WITH DISPERSE RED 1**

## **8.1 DIFFUSION OF DISPERSE RED 1 IN POLY(ETHYLENE TEREPHTHALATE) FILMS IMPREGNATED FROM A SUPERCRITICAL CO<sub>2</sub> SOLUTION**

### **8.1.1 INTRODUCTION**

The application of CRM with an oil immersion objective to non-destructively assess the diffusion of a disperse dye in PET was demonstrated in Chapter 7. In this chapter, the approach is extended to a model polymer/dye system to generate data to which a comprehensive diffusion analysis may be performed. The textile industry relevant dye N-ethyl-N-hydroxyethyl-4-(4'-nitrophenylazo)phenylamine (Disperse Red 1) (DR1) was selected as the solute, and largely amorphous PET film (as used in the CO<sub>2</sub>-induced morphological study) was selected as the host matrix.

### **8.1.2. EXPERIMENTAL**

Custom built stainless steel high-pressure vessels were used to expose largely amorphous PET films to a scCO<sub>2</sub> solution of DR1 at isothermal and isobaric conditions. In each of the dyeing experiments a polymer film of approximate dimensions 4 mm x 4 mm x 0.23 mm was placed onto the metal gauze and sealed. The geometry of the film and the selected measurement position (central location) was such that only dye diffusing through the thickness of the film contributed to the measured profile. This experimental arrangement permits the study of diffusion in a uniaxial manner. All measurements were recorded using the dispersive Renishaw 1000 confocal Raman microscope as described previously.

### **8.1.3. RESULTS AND DISCUSSION**

The methodology to study the diffusion process using CRM was described in Chapter 7, involving the spectroscopic evaluation of the relative dye concentration as a function of depth in the dyed sample. Performing this evaluation requires the identification of bands attributed to DR1 in the Raman spectrum of DR1/PET film. This model system is ideally suited to be studied by Raman spectroscopy due to the large Raman cross-section of DR1 and hence the ability to detect its presence at very low concentrations.



The strong Raman response of DR1 is evident in several regions of the spectrum presented in Figure 8.1; of specific interest in this study is the 1300-1450  $\text{cm}^{-1}$  region. The spectral features present in this region are largely due to vibrational modes of the N=N and NO<sub>2</sub> groups of the DR1 molecules. The band corresponding to the NO<sub>2</sub> symmetric stretching mode of DR1<sup>50</sup> occurs at 1324-1450  $\text{cm}^{-1}$  and due to the low contribution from the polymer in this region, the band was selected to identify DR1 impregnated in PET. The area under the specific Raman band was integrated with respect to a baseline that connects the data points corresponding to the wavenumber limits of the integral ranges described. The Raman spectra presented in Figure 8.1 were measured in extended mode (600-1800  $\text{cm}^{-1}$ ). Depth profile measurements were recorded in static scan mode, centred at 1540  $\text{cm}^{-1}$ , with an acquisition time of 60 seconds per spectrum. A typical example of the Raman spectra as a function of depth acquired during a depth profile experiment using the 50x oil immersion objective are presented in Figure 8.2 from which component depth profiles may be generated.

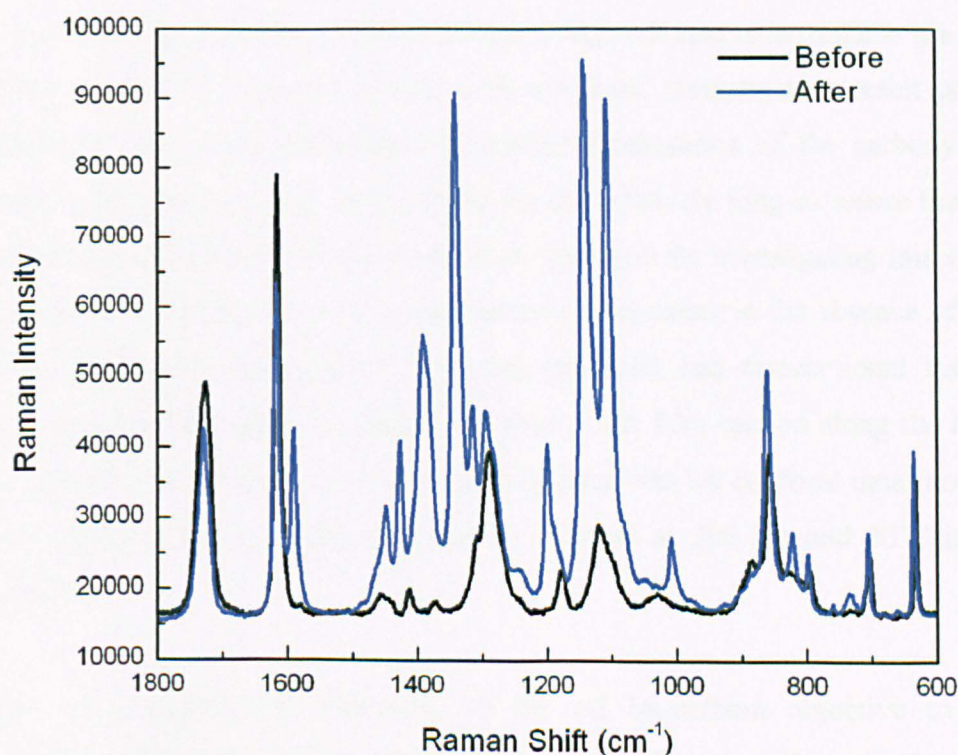


Figure 8.1. Raman spectra of largely amorphous PET film before (black) and following exposure to scCO<sub>2</sub> solution containing DR1 at 200 bar and 60°C for 48 hours (blue).



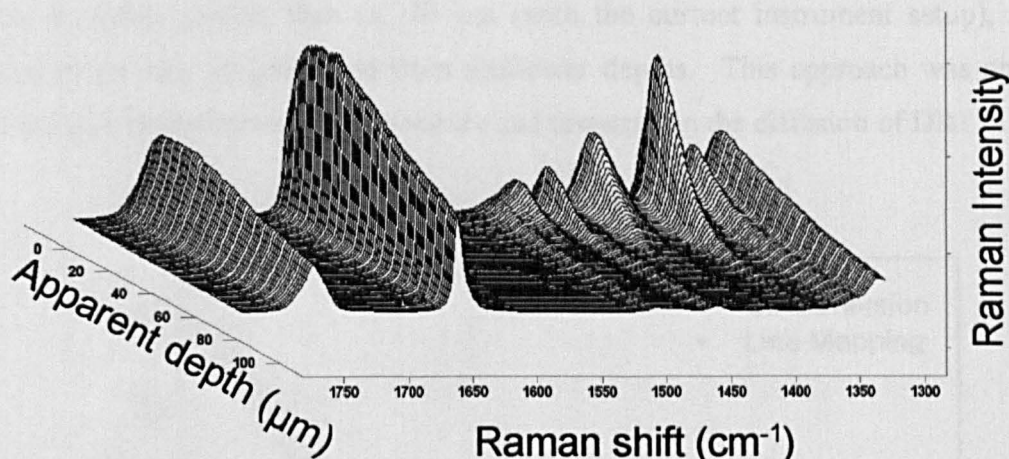


Figure 8.2. Typical example of Raman spectra acquired during depth profiling of PET film impregnated with DR1 from a scCO<sub>2</sub> solution.

The carbonyl band of PET (1700-1760 cm<sup>-1</sup>) was selected to normalise the DR1 band because changes in crystallinity (the carbonyl band narrows as a result of increased crystallinity due to the reduction of possible orientations of the carbonyl group in relation to the ring system) were uniform for the relatively long exposure times studied. The limit of reliability of the oil immersion approach for investigating this system may be assessed by comparison with measurements undertaken in the absence of refraction. A cross-section of the polymer film was prepared and conventional Raman point mapping performed along the central position of the film section along the line normal to the surface. A comparison of line mapping data with oil confocal data (normalised to unity) measured for a sample exposed for 5 hours at 200 bar and 80°C is shown in Figure 8.3.

Figure 8.3 confirms the reliability of the oil immersion objective to study the distribution of DR1 to a depth of ca. 70 μm, after which the oil confocal data deviates from the reference (line mapping) data. As previously described, the combination of noise in the measured spectra and the slight mismatch between the refractive index of the oil and the polymer (PET = 1.58 compared to the immersion oil = 1.515) attribute to the observed overestimation of DR1 concentration at depth greater than ca. 70 μm. This

feature has been observed for other examples of CRM studies of PET dyed from a supercritical solution.<sup>209,254</sup> Nevertheless, despite the inaccuracy of the oil immersion data at depths greater than ca. 70  $\mu\text{m}$  (with the current instrument setup), accurate information may be generated from shallower depths. This approach was applied to investigate the influence of temperature and pressure on the diffusion of DR1 in PET.

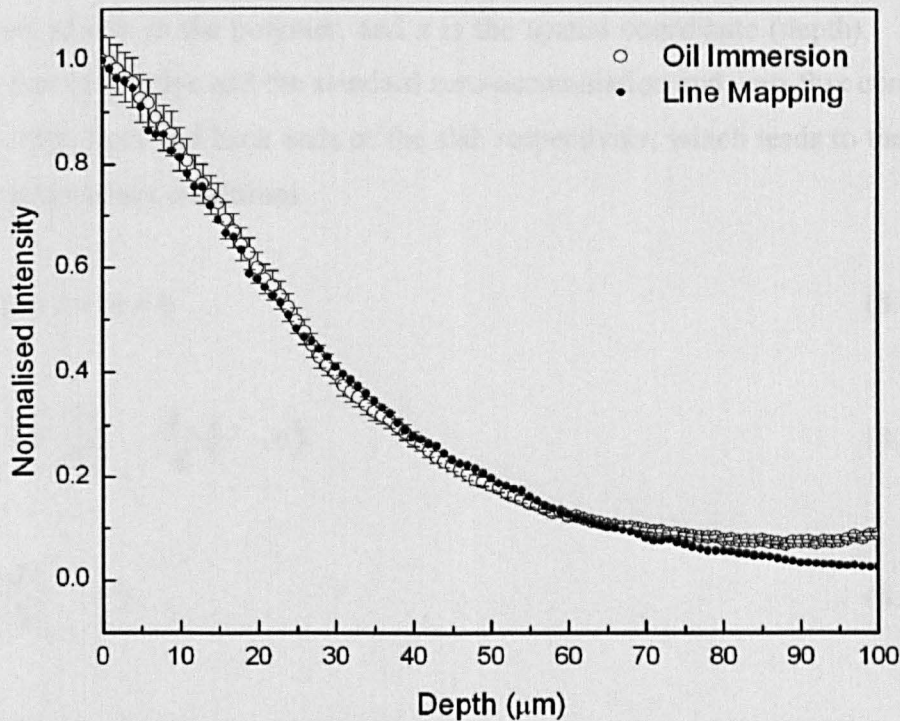


Figure 8.3. Normalised DR1 profiles measured using the oil immersion confocal approach and conventional line mapping of the microtomed film cross-section. The sample was exposed to a  $\text{scCO}_2$ /DR1 solution for 5 hours at 200 bar and  $80^\circ\text{C}$ .

The concentration-depth profiles measured for various times at the described conditions are presented in Figures 8.4a-c. Overlaid are the computed plots generated from a model formulated on the following basis:

The one-dimensional transient Fickian diffusion of dye molecules within an isotropic polymer slab is described by the partial differential equation

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial x^2} \quad (8.1)$$

where  $c$  is the concentration of dye in the polymer,  $t$  is time,  $D'$  is the diffusion coefficient of dye in the polymer, and  $x$  is the spatial coordinate (depth). The slab is initially free of any dye and the standard zero-accumulation and zero-flux conditions are applied at the front and back ends of the slab respectively, which leads to the following initial and boundary conditions:

$$c(x, t = 0) = 0 \quad (8.2a)$$

$$-D' \frac{\partial c}{\partial x} \bigg|_{x=0} = \frac{k_m}{K} (c^* - c) \quad (8.2b)$$

$$\frac{\partial c}{\partial x} \bigg|_{x=L} = 0 \quad (8.2c)$$

where  $L$  is the thickness of the slab,  $k_m$  is a mass-transfer coefficient,  $K$  is the equilibrium partitioning coefficient, and  $c^* = K c_f$  is the dye concentration in the polymer that would be in equilibrium with the surrounding fluid phase with dye concentration  $c_f$ . Equation 8.1 with initial and boundary conditions 8.2a-c was solved numerically using the method of lines, with second-order finite difference discretisation in the spatial domain. Before numerical solution, a normalised concentration  $c'$  was introduced by scaling  $c$  by the equilibrium concentration  $c^*$ , i.e.

$$c' \equiv c/c^* \text{ so that } c' \in \langle 0, 1 \rangle.$$

There are two *a priori* unknown parameters: the diffusion coefficient  $D'$  and the reduced mass-transfer coefficient  $k'_m \equiv k_m/K$ . Both  $D'$  and  $k'_m$  were regarded as adjustable parameters and their values determined from experimental data, i.e. the normalised intensity profiles of dye in the polymer  $c^{ex}(x, t)$  at a specific time interval,



measured as described in the experimental section. The values of  $D^s$  and  $k'_m$  were determined by minimisation of the global error between the experimental and computed concentration profiles for each impregnation time, i.e. by solving the optimisation problem

$$\min_{k'_m, D^s} \sum_x (c^{ex}(x, t) - c'(x, t))^2 \quad (8.3)$$

where  $c'(x, t)$  denotes the normalised concentration profiles obtained computationally by numerical solution of Equation 8.1 and the sum denotes summation across all spatial discretisation points. Although the experimental data points were nominally taken at spatial coordinates with 1  $\mu\text{m}$  increments, they actually represent average values over the depth resolution achievable. Therefore, before performing the summation in Equation 8.3, the computational profiles were also transformed by calculating a moving spatial average over the depth resolution, selected as 4  $\mu\text{m}$ .

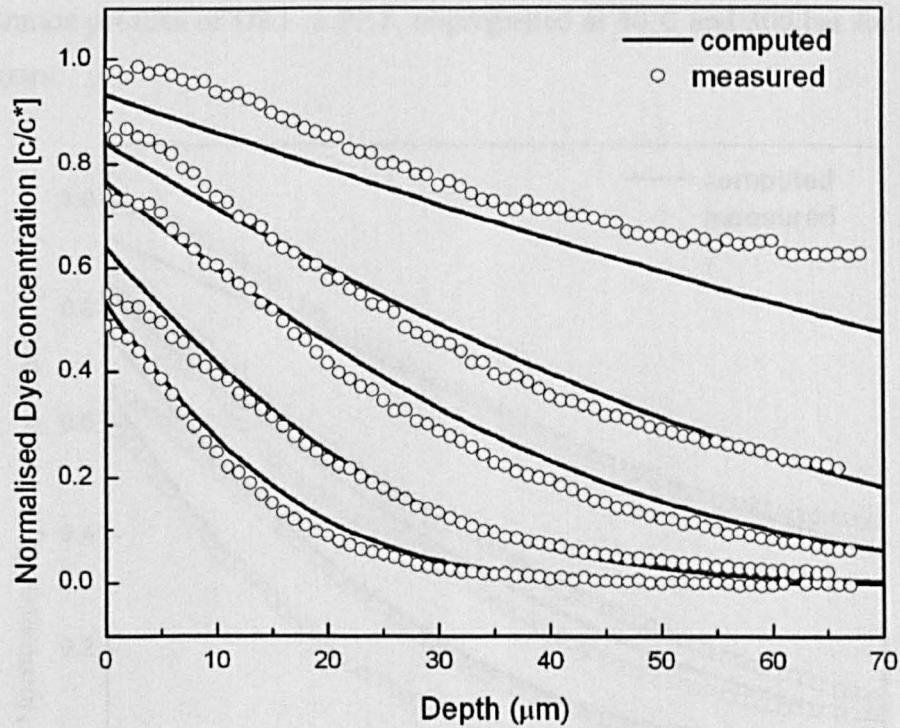


Figure 8.4a. Measured and computed (using optimised  $k'_m$  and  $D^s$ ) normalised concentration profiles of DR1 in PET, impregnated at 60°C and 200 bar for 5, 10, 25, 50 and 168 hours.

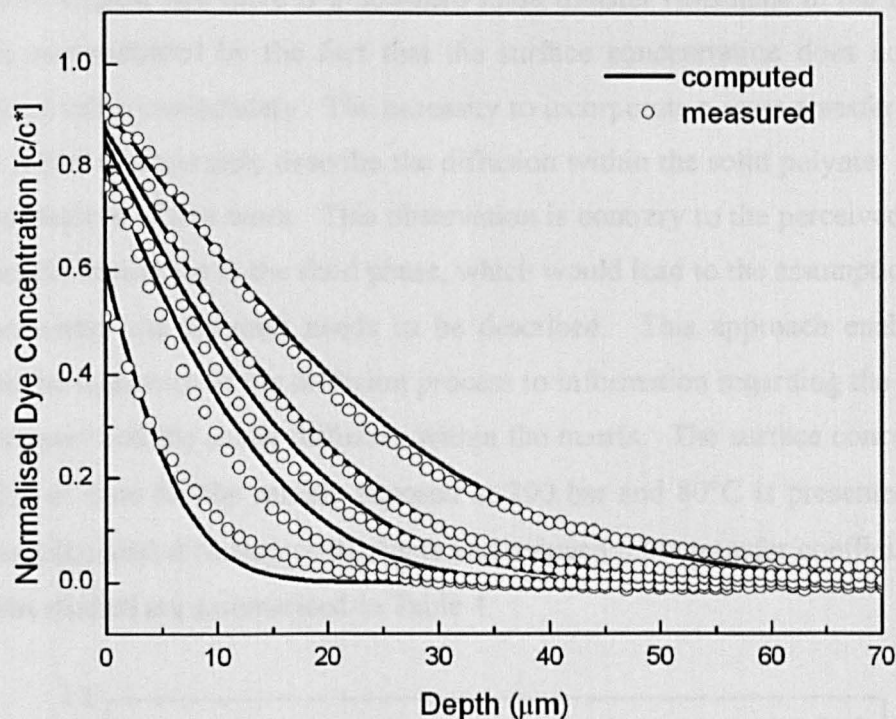


Figure 8.4b. Measured and computed (using optimised  $k'_m$  and  $D^s$ ) normalised concentration profiles of DR1 in PET, impregnated at 60°C and 300 bar for 0.5, 2, 3, 4 and 7 hours.

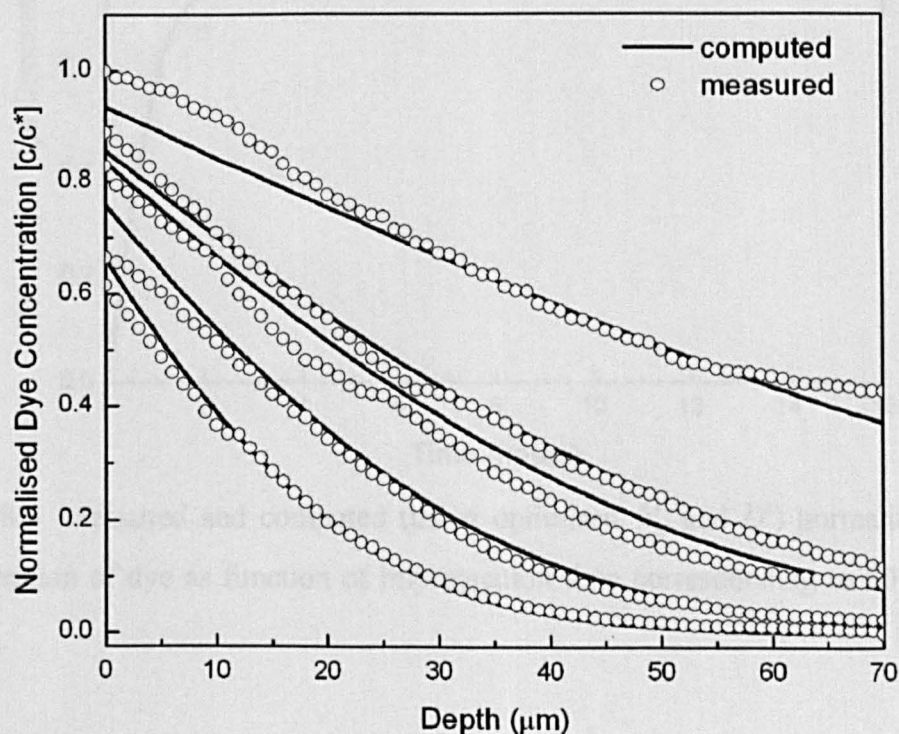


Figure 8.4c. Measured and computed (using optimised  $k'_m$  and  $D^s$ ) normalised concentration profiles of DR1 in PET, impregnated at 80°C and 200 bar for 1, 2, 4, 5 and 15 hours.



The results suggest that there is a non-zero mass transfer resistance in the fluid phase, which is demonstrated by the fact that the surface concentration does not reach its equilibrium value immediately. The necessity to incorporate a mass-transfer coefficient into the model to accurately describe the diffusion within the solid polymer phase is an important feature of this work. This observation is contrary to the perceived negligible mass-transfer resistance in the fluid phase, which would lead to the assumption that only diffusion within the polymer needs to be described. This approach enables one to delineate the dynamics of the diffusion process to information regarding the fluid phase mass transport and the solute diffusion within the matrix. The surface concentration as a function of time for the sample exposed at 200 bar and 80°C is presented in Figure 8.5. The calculated diffusion coefficients and reduced mass transfer coefficients for the conditions studied are summarised in Table 4.

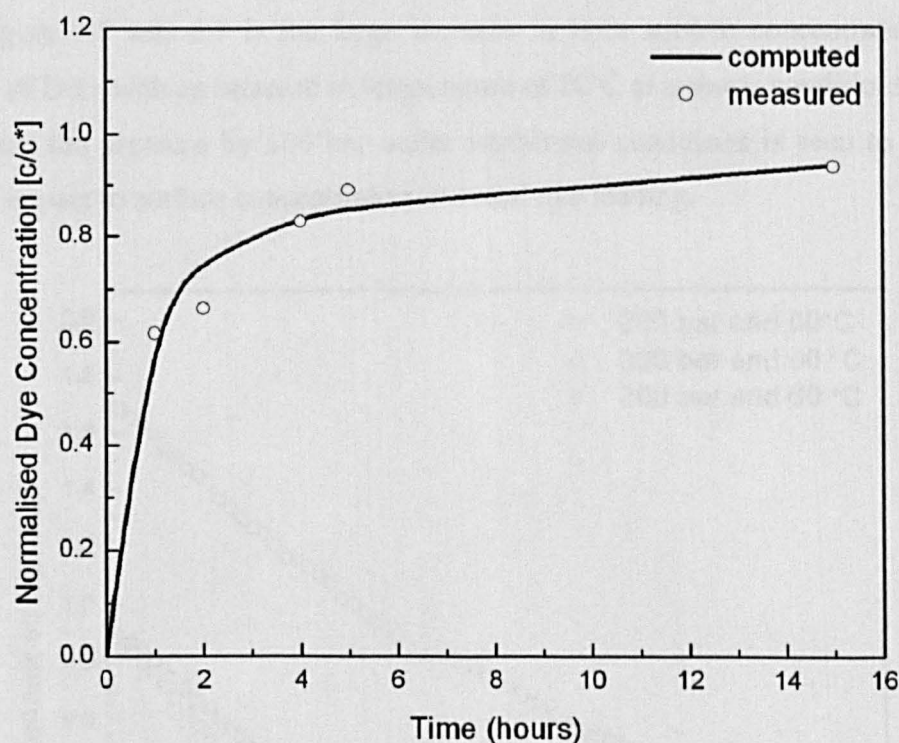


Figure 8.5. Measured and computed (using optimised  $k'_m$  and  $D^s$ ) normalised surface concentration of dye as function of impregnation time corresponding to 80°C and 200 bar.

Table 4. Diffusion and mass transfer coefficients evaluated from computed profiles

| Temp (°C) | Pressure (bar) | Diffusion coefficient ( $m^2s^{-1}$ ) | Mass transport coefficient ( $ms^{-1}$ ) |
|-----------|----------------|---------------------------------------|------------------------------------------|
| 60        | 200            | $9.44 \pm 1.06 \times 10^{-15}$       | $5.55 \pm 1.08 \times 10^{-10}$          |
| 80        | 200            | $6.88 \pm 1.01 \times 10^{-14}$       | $6.39 \pm 1.19 \times 10^{-9}$           |
| 60        | 300            | $1.49 \pm 1.11 \times 10^{-14}$       | $5.01 \pm 1.07 \times 10^{-9}$           |

A comparison of the normalised DR1 concentration-depth profiles for PET exposed for 5 hours at 200 bar and 60°C, 200 bar and 80°C, and 300 bar and 60°C is presented in Figure 8.6. The associated raw Raman spectra from which the normalised plots were generated are shown in Figure 8.7. The differences between the profile shapes are discussed in the following section and related to the conditions within the polymer matrix and the fluid phase as a consequence of the operating conditions. Apparent in both Figure 8.6 and 8.7 is the large increase in both surface concentration and the loading of DR1 with an increase in temperature of 20°C at isobaric conditions (200 bar). Increasing the pressure by 100 bar under isothermal conditions is seen to have a far smaller impact to surface concentration and total dye loading.

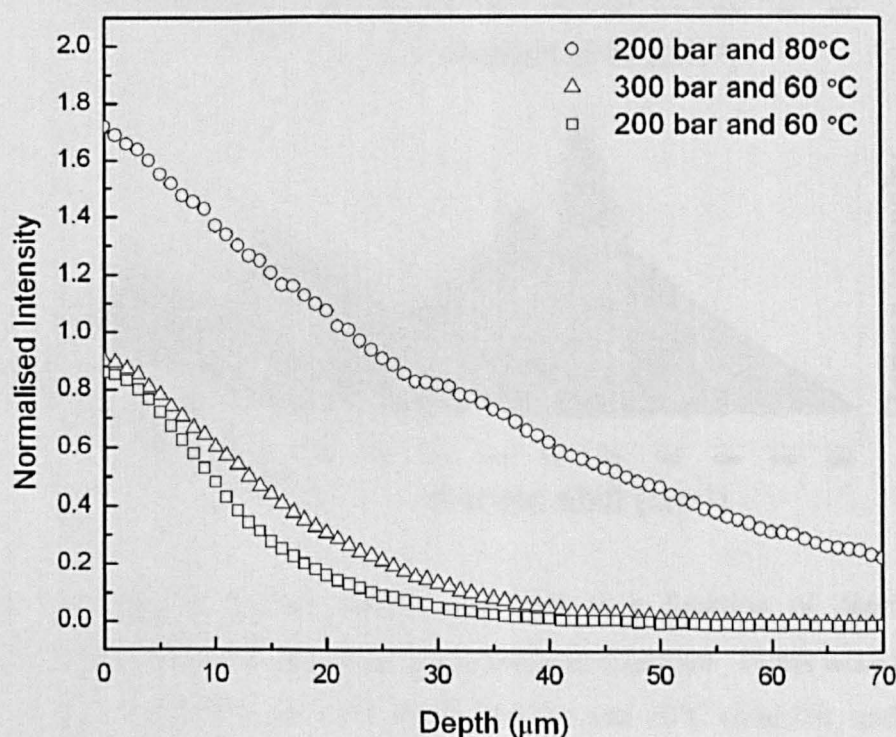


Figure 8.6. Normalised DR1 profiles measured using the oil immersion confocal Raman approach corresponding to films exposed for 5 hours at 200 bar and 60°C, 200 bar and 80°C, and 300 bar and 60°C.



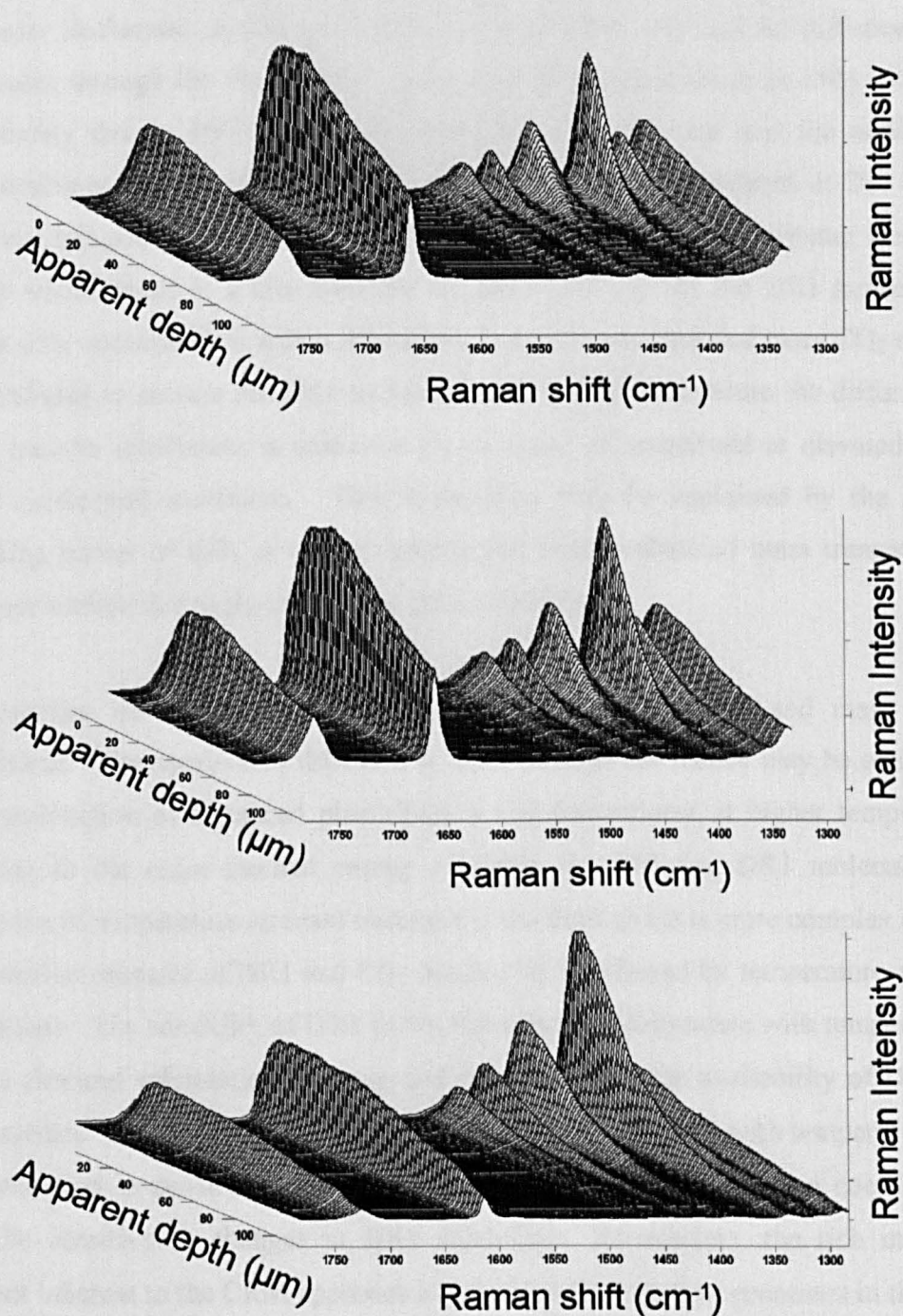


Figure 8.7. Confocal Raman spectra measured as a function of depth at 1  $\mu\text{m}$  increments in the z-direction using the oil immersion objective. Films were exposed for 5 hours to  $\text{CO}_2$  at 200 bar and 60°C (top), 300 bar and 60°C (middle), and 200 bar at 80°C (bottom).

Table 4 indicates that the diffusion coefficient and mass transfer coefficient are dependent on both temperature and pressure. The increase in pressure from 200 to 300 bar under isothermal conditions is shown to moderately enhance the diffusion of DR1 molecules through the PET matrix. The moderate enhancement in DR1 diffusion is presumably due to PET being well above its  $T_g$  at 200 bar and the additional  $T_g$  suppression at 300 bar does not differ significantly to the conditions at 200 bar. The observed behaviour may be explained by a possible increase in polymer free-volume which would result in a less hindered diffusion pathway for the DR1 molecules. At higher  $\text{CO}_2$  concentration within the matrix, it may be possible that more  $\text{CO}_2$  molecules are available to solvate the DR1 molecules and possibly accelerate the diffusion. The mass transfer coefficient is enhanced by an order of magnitude at elevated pressure under isothermal conditions. This observation may be explained by the enhanced solvating power of  $\text{CO}_2$  at higher density and hence enhanced mass transport to the polymer surface due to the increase in DR1 solubility.

Temperature has a greater effect on the diffusion coefficient and mass transport coefficient. The accelerated diffusion of DR1 through the matrix may be explained by the combination of enhanced plasticisation and free-volume at higher temperature in addition to the extra thermal energy available for diffusing DR1 molecules. The influence of temperature on mass transport in the fluid phase is more complex due to the sublimation pressure of DR1 and  $\text{CO}_2$  density being affected by temperature at isobaric conditions. The solubility of DR1 in the fluid phase will increase with temperature due to the elevated sublimation pressure and hence increase the availability of DR1 at the film surface. However, the solvating power of  $\text{CO}_2$  is reduced with temperature due to the reduction in density with temperature. Furthermore, the partition coefficient will also be sensitive to changes in DR1 solubility. Nonetheless, the rich information content inherent to the CRM approach has enabled the transport processes in this system to be assessed and studied as a function of temperature and pressure.

From a practical point of view it would be important to know whether the quality of the dyeing process (i.e., the perceived colour of the dyed polymer) is related to the surface concentration or to an aggregate amount of dye present in a sub-surface layer of the polymer film. The integral amount of dye present in the 70  $\mu\text{m}$  sub-surface layer after different impregnation times (film impregnated at 200 bar and 80°C) is plotted in Figure

8.8 (each data point in Fig 8.8 was obtained as the surface area below the profile from Figure 8.4c for the corresponding time).

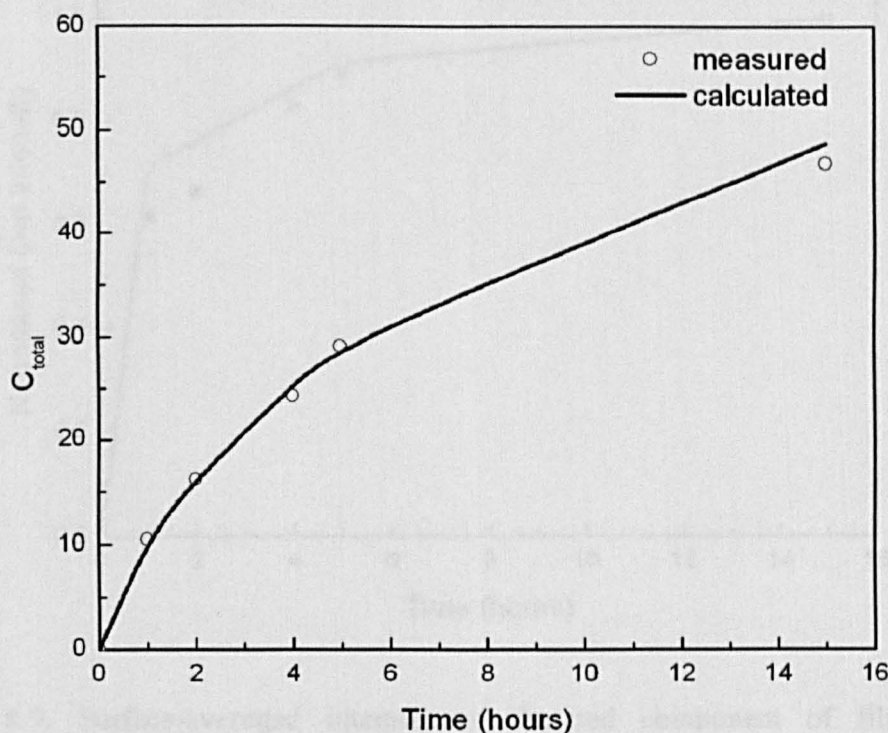


Figure 8.8. Aggregate amount of dye present in the 70  $\mu\text{m}$  sub-surface layer of the polymer sample impregnated at 200 bar and 80°C as function of impregnation time.

A colorimetry analysis of the dyed polymer samples has been performed; digital images of the polymer samples were taken and the average intensity of the red component after an RGB-split has been evaluated using a public-domain image analysis software ImageJ. The normalised intensity values obtained by optical analysis and those obtained by Raman spectroscopy as function of impregnation time are shown in Figure 8.9. The shape of the curve is similar to that plotted in Figure 8.5, indicating that the surface concentration of the dye rather than the aggregate amount is the key factor controlling the perceived colour quality of a dyed thin polymer films.



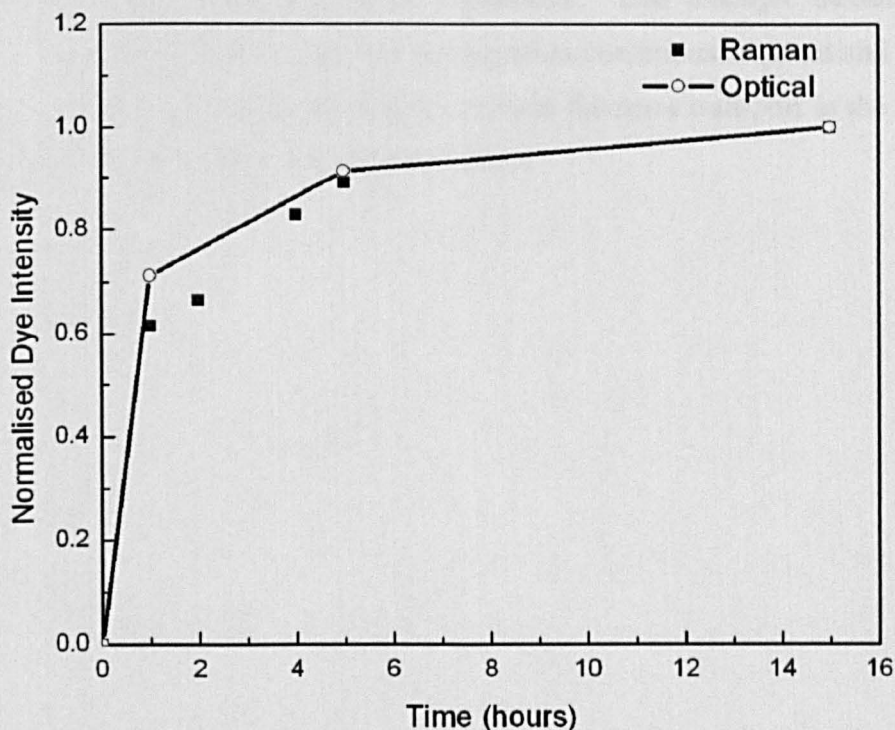


Figure 8.9. Surface-averaged intensity of the red component of film samples impregnated at 200 bar and 80°C as a function of impregnation time, evaluated from digital images of polymer samples.

#### 8.1.4. CONCLUSIONS

The combination of CRM and modelling has proved particularly suitable to elucidate the impregnation of polymeric material from a  $\text{scCO}_2$  solution. The diffusion coefficient of DR1 in PET has been obtained directly from the raw Raman spectra of dyed polymer samples measured non-invasively. The quantitative data generated from the depth profiles of dye in the polymer provided a reliable dataset for modelling the diffusion process. A Fickian diffusion model was used to evaluate the Raman spectroscopic data and calculate the diffusion coefficient for DR1 in PET. This approach represents a very useful tool to quantitatively study diffusion in polymer systems in a non-destructive manner when mechanical sectioning might result in an adjustment to the polymer morphology or the distribution of components in the matrix. Moreover, the valuable information gained from studying time dependence of the

surface concentration provides valuable information relating to the mass transport processes occurring under supercritical conditions. This example demonstrates the potential of this approach to guide the impregnation conditions required and investigate the influence of the processing parameters on both the mass transport in the fluid phase and the diffusion of the solute through the matrix.

## **8.2. CONFOCAL RAMAN MICROSCOPY OF PET FILM IMPREGNATED WITH 2 DISPERSE DYES**

### **8.2.1. INTRODUCTION**

The suitability of CRM with the oil immersion objective to study the impregnation of PET impregnated with DY23 and DR1 has been demonstrated in the preceding chapters. The need to impregnate the matrix with a mixture of components may be required to achieve performance optimisation and lead to a desired synergism of the colours. Investigating the diffusion behaviour of the individual components is important due to the potentially large differences between solute behaviour depending on the specific structural characteristics of the molecule. The use of UV-vis has been applied to investigate a 2 dye system<sup>80</sup> (DR1 and 3-(ethyl-N-(2-hydroxyethyl)amoni-4'-nitroazobenzene)) by studying changes through the entire thickness of the PMMA film. That work revealed that the interaction between the solutes in the dye mixture may influence the diffusion behaviour relative to single dye systems. However, the overlap present in the UV absorption peaks between these two dyes inhibited the resolution of the individual dye diffusion characteristics. The importance of the diffusion of complex mixtures may be significant in the design of materials for advanced applications.

On this basis, CRM is applied to investigate the distribution of two dyes simultaneously impregnated into PET film from a scCO<sub>2</sub> solution mixture. The characteristic Raman spectra associated with the individual dye molecules should permit the respective distributions to be studied. In principle, this approach should offer advantages over the UV-vis method due to the ability to simultaneously spatially resolve the distribution of each of the dyes based on their characteristic Raman spectra.

### **8.2.2. EXPERIMENTAL**

PET film was exposed to an excess of both dyes for 15 hours at 200 bar and 80°C. Equal proportions of DR1 and DY23 (ca. 5 mg of each dye) were mixed and placed into the bottom of the high-pressure vessel. The same sample preparation procedure

described previously was followed to prepare the impregnated sample and all Raman measurements were recorded using the Renishaw system.

### 8.2.3. RESULTS AND DISCUSSION

Raman spectra corresponding to PET film impregnated with DR1 and a PET fibre impregnated with DY23 in the 1320-1500  $\text{cm}^{-1}$  spectral range are presented in Figure 8.10. The presence of the disperse dyes is apparent in this region: the bands at ca. 1340  $\text{cm}^{-1}$  and 1455  $\text{cm}^{-1}$  correspond to DR1 and DY23 respectively. These bands are absent from significant mutual overlap indicating that it should be possible to study their distribution using the univariate analysis adopted in the previous sections i.e. plotting the normalised intensity of each of the aforementioned bands as a function of depth.

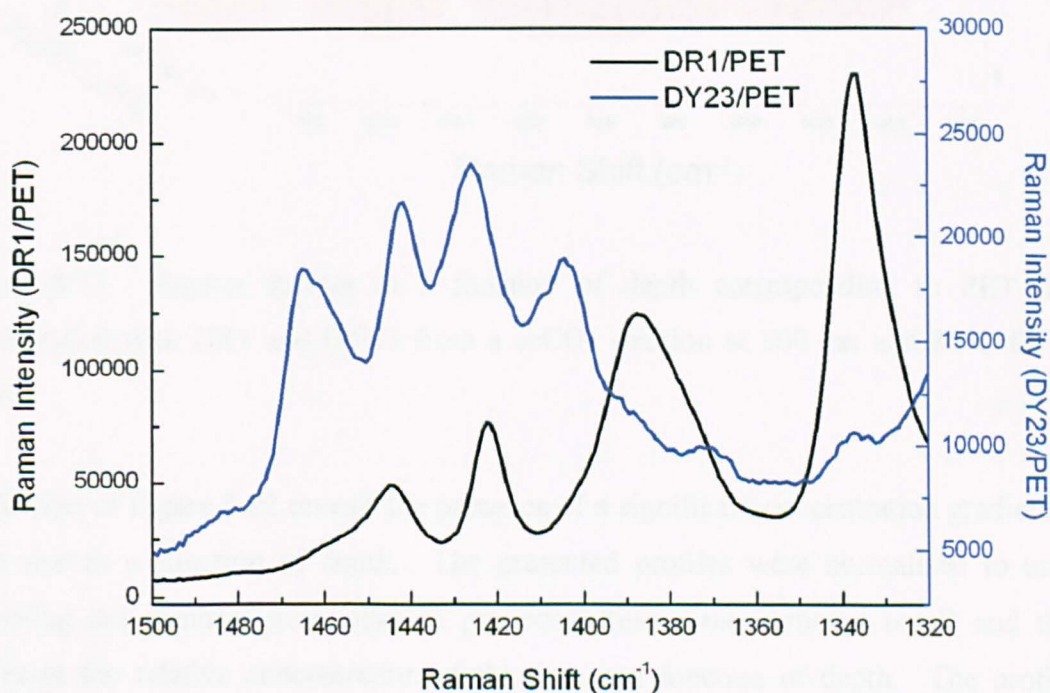


Figure 8.10. Raman spectra corresponding to DR1 (black) and DY23 (blue) impregnated into PET from a  $\text{scCO}_2$  solution.

The oil immersion approach was used to obtain depth profile of the impregnated film at 1  $\mu\text{m}$  increments along the line normal to the surface. The resultant Raman spectra as a function of depth are presented in Figure 8.11. As expected, the bands attributed to the dyes decay more rapidly than the polymer bands as the laser focuses deeper into the



polymer, indicative of a dye concentration gradient along the line normal to the film surface. To visualise the relative concentrations of both dyes as a function of depth, the respective normalised integrated intensities are plotted in Figure 8.12. The bands corresponding to DR1 and DY23 were integrated between  $1324\text{--}1358\text{ cm}^{-1}$  and  $1454\text{--}1475\text{ cm}^{-1}$  respectively. Both bands were normalised using the carbonyl band ( $1700\text{--}1760\text{ cm}^{-1}$ ) of PET.

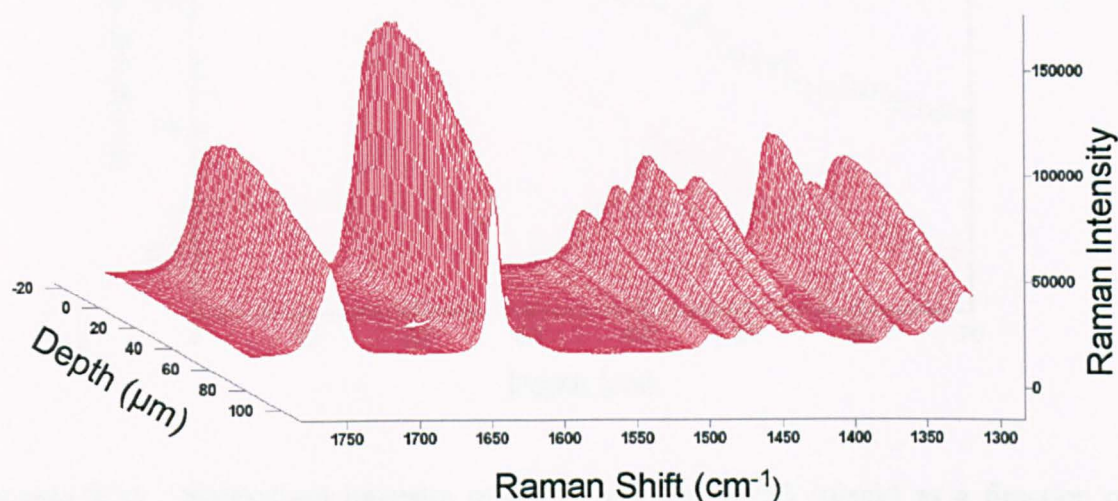


Figure 8.11. Raman spectra as a function of depth corresponding to PET film impregnated with DR1 and DY23 from a  $\text{scCO}_2$  solution at 200 bar and  $80^\circ\text{C}$  for 15 hours.

Inspection of Figure 8.12 reveals the presence of a significant concentration gradient of each dye as a function of depth. The presented profiles were normalised to unity following the standard normalisation procedure (using the carbonyl band) and thus represent the relative concentration of the dye as a function of depth. The profiles suggest that the diffusion of DY23 is greater than DR1, as seen by the shallower concentration profile exhibited by DY23 which displays a greater relative concentration of DY23 at subsurface location in the film. The apparent noise in the DY23 profile is likely to be a consequence of the relatively low integrated intensity of the selected band and thus its sensitivity to noise is enhanced compared to the DR1 band. Regardless of the apparent noise in the data, significant differences between the two profiles are observed as a consequence of the diffusion behaviour through the swollen matrix.



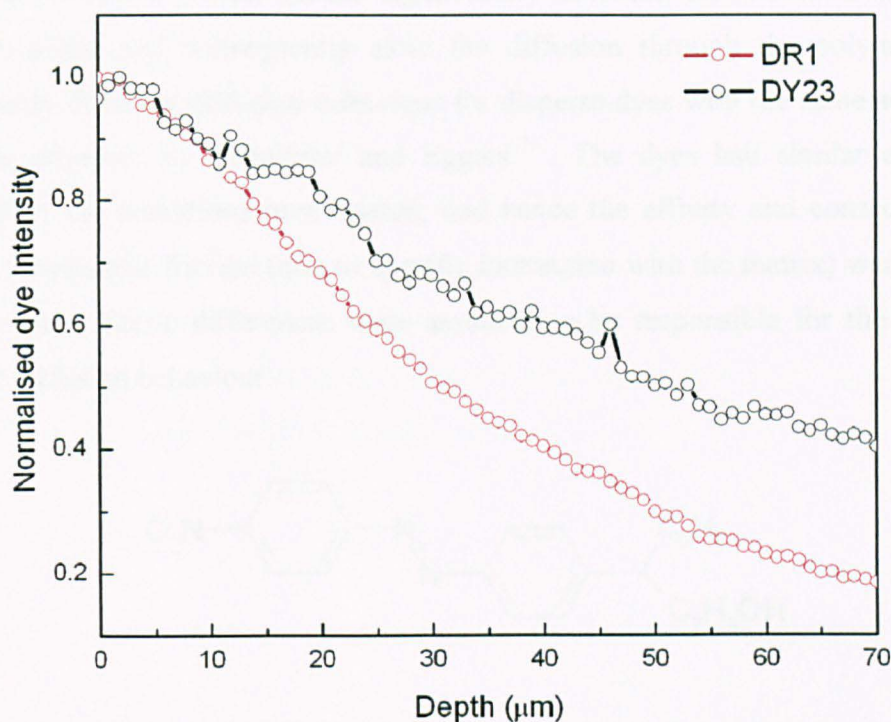


Figure 8.12. Normalised intensity of DR1 (red) and DY23 (black) as a function of depth measured using the oil immersion confocal approach. The sample was exposed to a  $\text{scCO}_2$ /DR1/DY23 solution for 15 hours at 200 bar and 80°C.

The chemical structures of DR1 and DY23 are presented in Figure 8.13. As previously mentioned, both are azo dyes which accounts for the associated large Raman cross-section and hence the ability to detect them at low concentrations. The importance of intermolecular interactions, e.g. hydrogen bonding between the diffusing solute and the polymer matrix, has been identified to play an important role on the observed diffusion characteristics. The resistance to diffusion by the specific interaction between the solute and the matrix has been termed “molecular friction”.<sup>81</sup> Although both dye molecules have the presence of an OH functionality, the proton donating ability of the DR1 proton is stronger and hence a stronger H-bond with the polymer matrix is expected. The consequence of this stronger interaction can be expected to result in a greater degree of “molecular friction” and hence slower diffusion through the matrix. Steric factors may also influence the diffusion properties; the aliphatic chains of DR1 (314 Mw) may cause resistance to diffusion compared to the linear DY23 (302 Mw) molecules which also

have a lower molecular weight. It may also be possible for dimerisation of the DR1 molecules to occur, which would significantly increase the effective size of the diffusion solute and consequently slow the diffusion through the polymer matrix. Significantly different diffusion behaviour for disperse dyes with the same solubility in PET was observed by Schnitzler and Eggers.<sup>75</sup> The dyes had similar equilibrium solubility at the conditions investigated, and hence the affinity and consequently the degree of molecular friction (due to specific interaction with the matrix) were expected to be similar. Steric differences were assumed to be responsible for the drastically different diffusion behaviour.

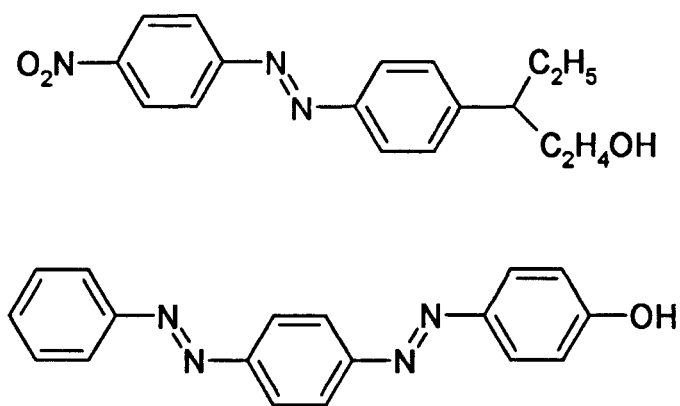


Figure 8.13. Chemical structures of DR1 (top) and DY23 (bottom)

The partial overlap of the band corresponding to DY23/PET at ca. 1455 cm<sup>-1</sup> with the DR1/PET spectrum shown in Figure 8.10 may lead to artefacts in the univariate analysis performed, i.e. the depth profiles may not be solely contributed from the respective dyes. Multivariate analysis enables all of the spectral information to be used for the identification of a specific component, rather than just a defined spectral region. A classical least square (CLS) analysis of the dataset has been performed to assess the suitability of the univariate analysis implemented in this system with partial spectral overlap of some spectral bands of the solutes. The amounts of the individual components as a function of depth were derived from the Raman depth profile data set using the CLS approach. In this approach, the spectra in the depth profiling data set were reproduced from the spectra of the components, known to be present in the sample, i.e. spectra of PET film impregnated with DR1, PET film impregnated with DY23, immersion oil and pure PET film. The best fit (least squares) linear combination



of these components was calculated for each spectrum as a function of depth, described in Equation 8.4.

$$\text{Sample spectrum} = \alpha * \text{spectrum 1} + \beta * \text{spectrum 2} + \gamma * \text{spectrum 3 etc.} \quad (8.4)$$

The factors that were found to produce the best fit (one factor per pure component per sample spectrum) are a measure of the amount of the particular pure component at a specific depth. The CLS profiles (factors of DR1 and DY23 as a function of depth) presented in Figure 8.14 were normalised to unity and overlaid with the normalised profiles generated using the univariate approach.

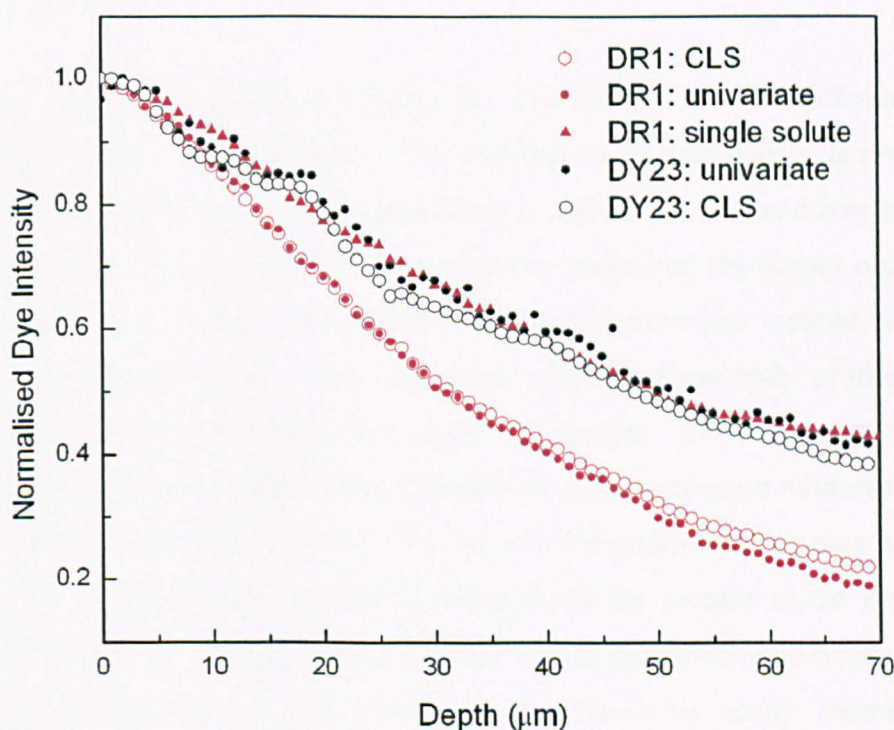


Figure 8.14. Comparison of normalised concentration profiles generated via CLS (open circles) and univariate (closed circles) analysis. The corresponding profile of DR1 impregnated in the absence of DY23 is included.

Good correlation between the CLS and univariate approaches is observed. The noise apparent in the DY23 univariate profile is reduced in the CLS approach due to the increased information content used to generate the data. Nevertheless, the univariate

analysis is seen to provide an adequate measure of the relative dye fraction as a function of depth, in spite of the partial overlap of the individual dye species.

Comparison of the DR1 profile measured in the absence of DY23 under the same conditions reveals significantly different diffusion behaviour. The presence of the mixture of dyes is seen to suppress the diffusion of DR1 compared to that in absence of DY23. Due to the diffusion of DY23 apparently occurring at a greater rate than DR1 (when a mixture of dyes are diffusing), the available free-volume for the DR1 molecules to diffuse through will be limited by the presence of the DY23 molecule and hence reduce the effective diffusion of DR1.

#### **8.6.4. CONCLUSIONS**

CRM has been applied to investigate the distribution of two different azo-dyes impregnated from a scCO<sub>2</sub> solution. The distribution of both dyes was revealed from the depth profile information, assessed using a univariate and multivariate analysis. Good agreement was found for both approaches, indicating the partial overlap of the dye spectra did not hamper the effectiveness of the univariate method to reveal the distribution of each dye. The measured concentration-depth profiles revealed differences in the diffusion behaviour of the dye species. This study demonstrates the suitability of CRM to investigate the diffusion of multicomponent mixtures in polymer impregnated from a scCO<sub>2</sub> solution. The use of multivariate analysis may be applied to the data set when heavily overlapping components are present in the system. This approach will help to evaluate potential differences in the diffusion characteristics of the constituent components of the mixture. This feasibility study demonstrates the possibility to perform a diffusion analysis following the generic approach presented in section 8.1. The time dependence of the surface concentration of each of the components will also reveal information regarding the mass transfer characteristics of each of the components in the fluid phase, providing valuable information for modelling purposes.



## **CHAPTER 9**

# **APPLICATION OF CRM TO OTHER POLYMER SYSTEMS IMPREGNATED FROM A $\text{scCO}_2$ SOLUTION**

## 9.1 IMPREGNATION OF SYNDIOTACTIC POLYSTYRENE WITH DR1 FROM A SUPERCRITICAL CO<sub>2</sub> SOLUTION

### 9.1.1. INTRODUCTION

The feasibility of extending the generic approach established to study the distribution of disperse dye in an alternative semicrystalline polymer matrix is explored. The matrix under study is syndiotactic polystyrene (sPS), which significant research efforts have been invested to elucidate the complex morphological behaviour and its gamut of polymorphs.<sup>55,256,257</sup> The CO<sub>2</sub>-induced morphological alterations in sPS were summarised in Chapter 3.2.3 where evidence for the formation of the helical  $\gamma$  crystalline form of sPS was described.<sup>56</sup> The study of the distribution of DR1 impregnated from a scCO<sub>2</sub> solution using CRM is described in the following section. A comparison of the impregnation behaviour of PET and sPS is also included.

### 9.1.2. EXPERIMENTAL

*Syndiotactic Polystyrene Film Preparation:* A sPS pellet was sandwiched between two glass slides and heated to a temperature of ca. 270°C in a heat press. The polymer was held at this temperature for 5 minutes and then quenched in ice water. The resultant film was ca. 130  $\mu\text{m}$  in thickness and spectroscopically determined to be largely amorphous. The high-pressure rig assembly and exposure procedure was the same as that used in the previous section. Films of PET and sPS were placed into a high-pressure vessel with an excess of DR1 and loaded with 300 bar of CO<sub>2</sub> and held at 60°C for 5 hours. Raman measurements were performed using the previously described Renishaw 1000 confocal system.

### 9.1.3. RESULTS AND DISCUSSION

Following depressurisation, the two films had strikingly different appearances: PET a deep red colour, and sPS a light yellow/orange. Raman surface spectra corresponding to the impregnated PET and sPS films are presented in Figure 9.1, also included is the

Raman spectrum of sPS following exposure in the absence of dye. The presence of DR1 is apparent at Raman shift values occurring at ca. 1400, 1340, 1140 and 1100  $\text{cm}^{-1}$ . Inspection of the associated intensity scales (black for DR1/PET and blue for DR1/sPS) reveals that the bands corresponding to DR1/PET are ca. 5x the intensity of the corresponding DR1/sPS bands. Although one cannot quantitatively determine relative concentrations from this observation, it does provide qualitative support for the visual appearance of the films.

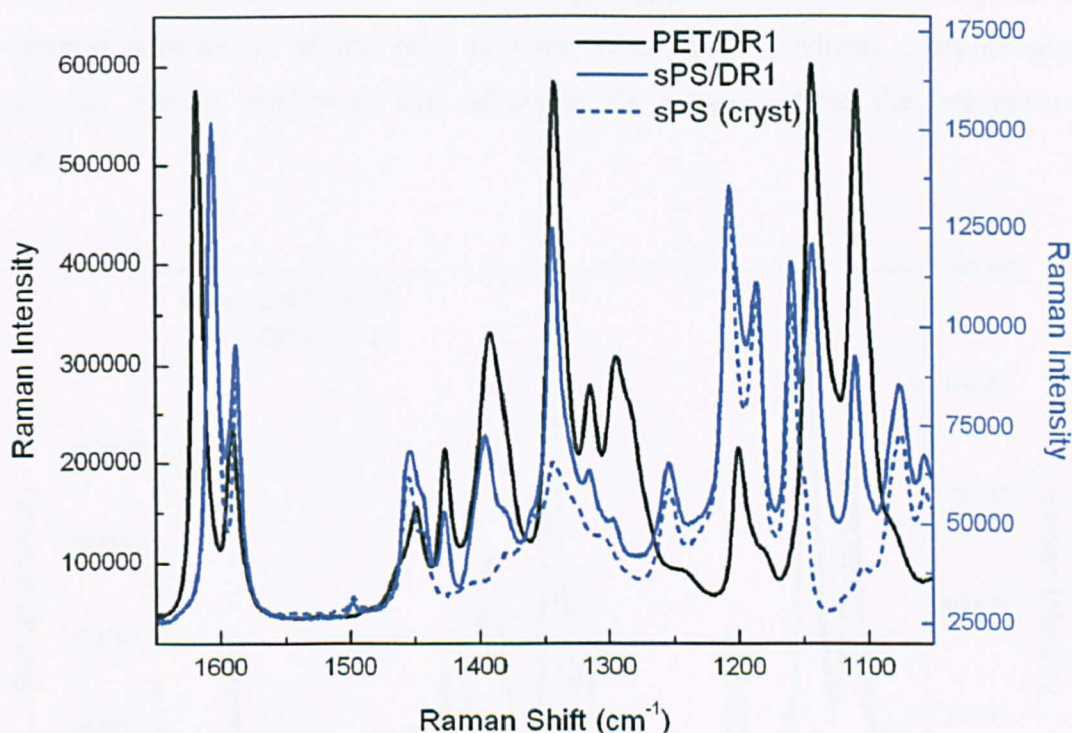


Figure 9.1. Raman spectra measured at the surface of PET and sPS films exposed to a  $\text{scCO}_2$ /DR1 solution at 300 bar and 60°C for 5 hours. The blue dotted trace corresponds to sPS film exposed to  $\text{scCO}_2$  in the absence of dye for 5 hours, sPS film dyed with DR1 (blue solid trace), and PET dyed with DR1 (black).

Conventionally one would apply a normalisation procedure to enable a qualitative comparison between samples. However, this is not the case when comparing two different polymer systems, due to the observed intensity being affected by many factors other than simply the concentration and laser power.<sup>184</sup> Although it is not possible to



compare the relative DR1 concentrations, the specific interaction between DR1 molecules and the polymer matrix may be interpreted from differences in the DR1 spectrum. The affinity of DR1 to the polymer, which drives the partitioning between the fluid phase and the matrix, is partly due to the interaction with functionalities on the macromolecular chains. This enables one to gain a molecular level insight into the affinity differences between the two systems and thus direct evidence for the relative DR1 uptake. Assessing the interaction requires the spectrum of DR1 interacting with the polymer matrix to be generated without the overlap from the spectrum of polymer, possible via spectral subtraction. The spectra presented in Figure 9.2 were generated via spectral subtraction of the pure polymer (due to CO<sub>2</sub>-induced morphological changes the spectra used were that of crystalline samples) from the impregnated polymer.

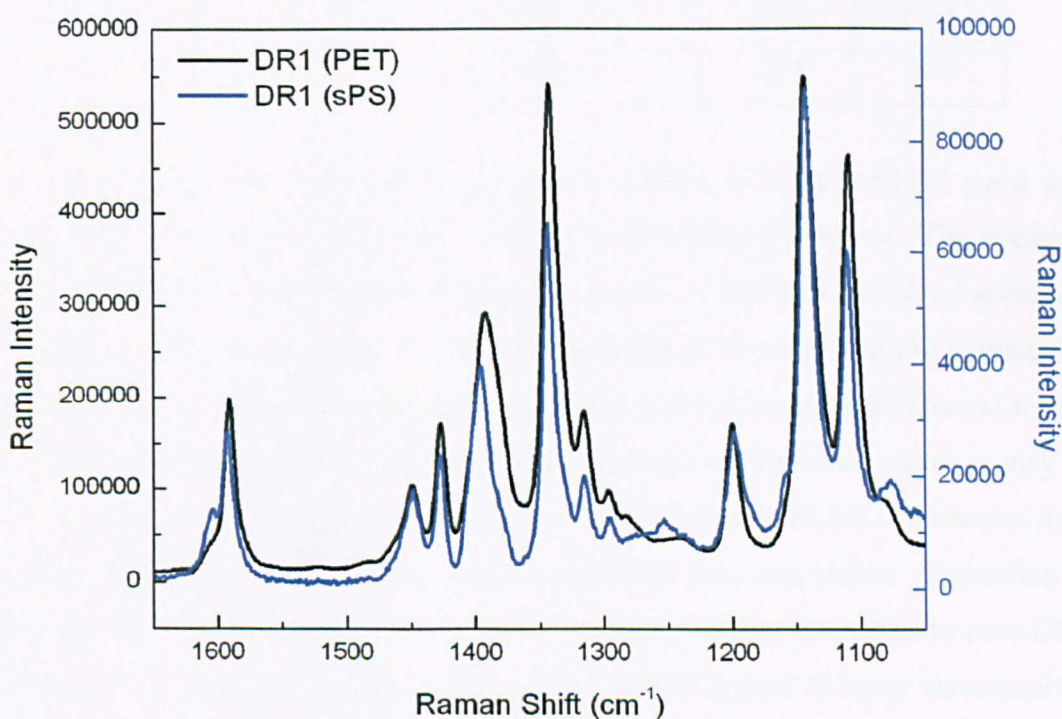


Figure 9.2. Raman spectra corresponding to DR1 interacting with PET (black) and sPS (blue). Spectra were generated via spectral subtraction of the polymer exposed in the absence of dye from the impregnated polymer.

Differences are apparent in the spectra presented in Figure 9.2; both band shape and position differ for DR1 in each of the polymers. Although the band shifts observed are



in the order of a few wavenumbers, spectra were measured in confocal mode with a nominal spectral resolution of  $1\text{ cm}^{-1}$ . Band assignments for pure DR1 powder<sup>258</sup> and the values measured in this work are summarised in Table 5. The evidence for interaction may be implied by the extent that a spectral band is “red shifted” from its position in the absence of interaction with the matrix. A red shift usually corresponds to an attractive interaction, with a greater shift indicative of strength. Additionally, changes in band shape may also be used to interpret the specific nature of the interaction.

Table 5. DR1 band assignment<sup>258</sup> and band positions measured in this work.

| Wavenumber ( $\text{cm}^{-1}$ ) | Assignment (pure DR1)        | DR1/PET | DR1/sPS |
|---------------------------------|------------------------------|---------|---------|
| 1104                            | $\nu \text{ } \phi\text{-N}$ | 1108    | 1110    |
| 1331                            | $\nu_s \text{ NO}_2$         | 1341    | 1343    |
| 1390                            | $\nu \text{ N=N}$            | 1391    | 1395    |
| 1585                            | $\omega \text{ C=C phenyl}$  | 1591    | 1593    |

If one is only to consider the chemical structures of the host matrix and the guest dye, the differences in affinity are obvious on the basis of hydrogen bonding. The chemical structure of the sPS matrix shown in Figure 9.3 is seen to lack basic carbonyl groups to participate in hydrogen bonding; only weak interaction of the dye with the  $\pi$ -system is possible. Hence the lower DR1 uptake is due to the reduced interaction potential for the dye in sPS compared to PET. Additional differences between the two matrices may be due to the higher crystalline fraction possible in sPS and hence the DR1 molecules have a smaller available polymer volume fraction in which they can reside. Inspection of Table 5 reveals that the bands of DR1 occur at shifted positions compared to pure DR1. The bands in the spectrum corresponding to DR1 in PET appear at lower wavenumbers and hence are red shifted from the positions of DR1 in sPS. The observed shifts are in the order of a few wavenumbers and may be explained by a possibly stronger interaction occurring between DR1 molecules in PET than in sPS. Several of the PET/DR1 spectral bands shown in Figure 9.2 display broader features compared to the corresponding sPS/DR1 feature. Band broadening can be explained by the distribution of relative orientations of the DR1 molecules at the interaction sites.

Furthermore, the presence of two possible interaction sites in PET (carbonyl and phenyl  $\pi$ -system) may contribute to band broadening. These observations provide some substantiating evidence for the visual appearance of the films. One would anticipate that the diffusion through sPS would be less hindered than in PET as a result of the weaker interactions present in the dynamic system.

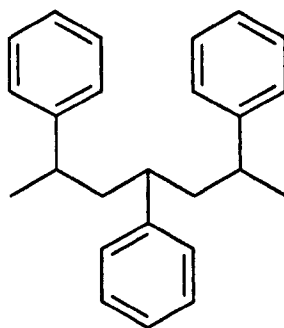


Figure 9.3. Chemical structure of sPS

In hope of substantiating the interaction of DR1 with each of the polymers, FTIR spectroscopy was applied. Specifically, microtomed film sections were analysed using single point FTIR transmission microscopy. An aperture was utilised to restrict the measurement to the surface of the sample where the dye was in the greatest concentration. Spectral subtraction of the surface measurement from the bulk polymer (measured at the centre of the film section) was performed to reveal information about the  $\nu(\text{O-H})$  band of the DR1 molecules interacting with the polymer. Unfortunately, the  $\nu(\text{O-H})$  band of DR1 in PET was too weak due to the low concentration of DR1 impregnated into the polymer and was not observable for sPS. This did not allow direct comparison of position of the  $\nu(\text{O-H})$  band of DR1 in two polymers to assess differences in interaction.

In an identical manner to PET, DR1 profiles in sPS have been generated for samples exposed to a  $\text{scCO}_2/\text{PET}$  solution at 300 bar and 60°C. The resultant profiles, measured using the oil approach and conventional line mapping are presented in Figure 9.4. A collection time of 120 seconds was employed to record spectra at each depth, recorded in static scan mode, centred at 1240  $\text{cm}^{-1}$ , with 100 % laser power. The normalisation of DR1 was performed using the band of sPS at ca. 1000  $\text{cm}^{-1}$ . Under these conditions

the signal to noise of spectra was poor at depths of ca. 20  $\mu\text{m}$  which significantly limits the success of the oil immersion approach to study the distribution of DR1 at relatively shallow depths. Due to the limited reliable sampling depth of the sPS/DR1 system using the oil immersion approach, line mapping has been applied to measure the DR1 distribution. The normalised DR1 concentration-depth profiles for various exposure times are presented in Figure 9.5, demonstrating the possibility to study the distribution of DR1 in sPS, albeit in a destructive manner.

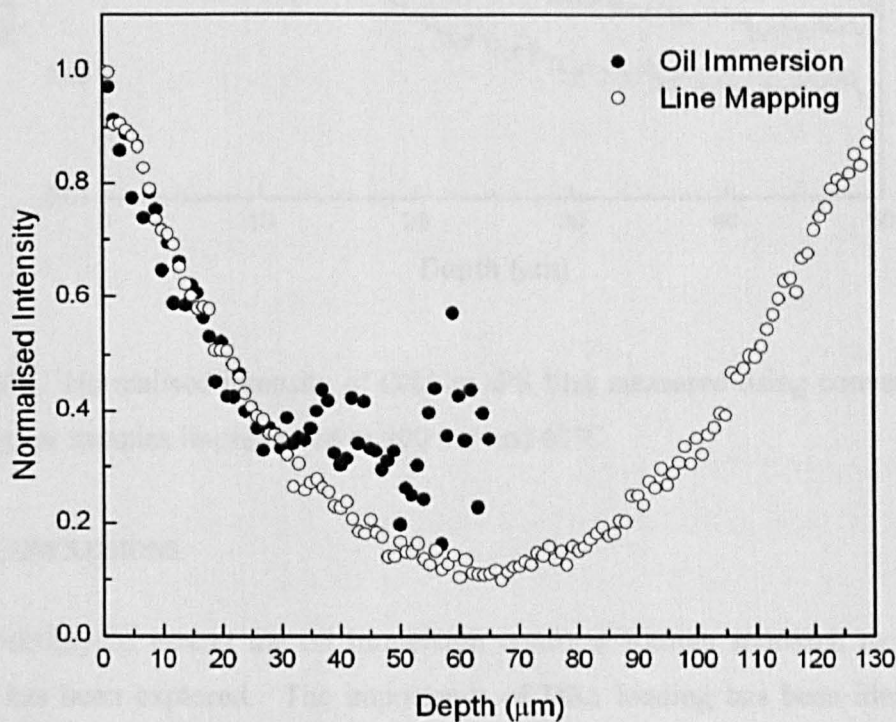


Figure 9.4. Comparison of the depth profiles of the distribution of DR1 in sPS film impregnated for 5 hours at 300 bar and 60°C obtained using the oil immersion approach and conventional line mapping along the line normal to the surface of the microtomed cross-section.



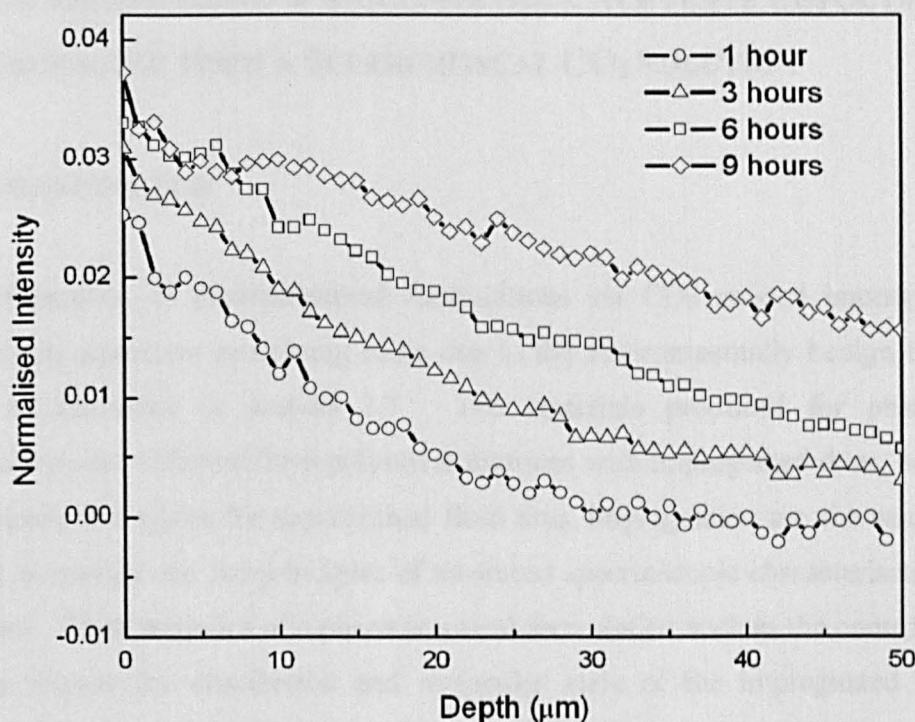


Figure 9.5. Normalised intensity of DR1 in sPS film measured using conventional line mapping for samples impregnated at 300 bar and 60°C.

#### 9.1.4. CONCLUSIONS

The feasibility to extend the oil immersion confocal Raman approach to a DR1/sPS system has been explored. The importance of DR1 loading has been identified as a critical parameter for successful depth profiling due to the associated low Raman signal at low concentrations. This requirement will be central to the extension of this approach to any guest/host system. Nonetheless, the destructive application of conventional line mapping was shown to be suitable to study the distribution of DR1 in sPS. A qualitative comparison of the interaction strength between DR1/PET and DR1/sPS has been undertaken via spectral subtraction of Raman spectra. The section demonstrates the possibility of studying the relative interaction strength of the solute with the matrix in addition to the distribution of the solute.



## 9.2. IMPREGNATION OF A BIOCOMPATIBLE ACRYLATE COPOLYMER WITH IBUPROFEN FROM A SUPERCRITICAL CO<sub>2</sub> SOLUTION

### 9.2.1. INTRODUCTION

The preparation of pharmaceutical formulations via CO<sub>2</sub>-assisted impregnation is a particularly attractive processing route due to the environmentally benign character of CO<sub>2</sub>, as discussed in section 3.7. The materials produced for pharmaceutical applications are different from polymeric matrices with impregnated dyes, however, the engineering principles for supercritical fluid drug impregnation are the same as in the dyeing processes and the principles of advanced spectroscopic characterisation are also the same. Characteristics of a pharmaceutical formulation such as the controlled release profile require the distribution and molecular state of the impregnated drug to be defined in order to interrelate observed dissolution characteristics. With this information at the engineer's disposal, the optimal design of formulations is possible. The applicability of CRM to characterise polymers processed with CO<sub>2</sub> has been established in the preceding chapters where a generic methodology to study the distribution of Raman-active chemical species as a function of depth was described. This chapter extends that approach to investigate the distribution of pharmaceutically relevant drug molecules in a biocompatible polymer matrix.

A biocompatible acrylate copolymer, poly(methylmethacrylate-co-ethylhexylacrylate-co-ethyleneglycoldimethacrylate) or P(MMA–EHA–EGDMA), was selected as the host polymer because it has been identified as a possible matrix for controlled release in ophthalmic applications.<sup>259</sup> Ibuprofen was selected as the model active pharmaceutical ingredient as shown in Figure 9.6. The matrix used in this example has a low  $T_g$  (–4°C) and is rubbery at ambient conditions, hence CO<sub>2</sub> is not required to plasticise the matrix but does result in significant swelling.<sup>259</sup> The solubility of ibuprofen in CO<sub>2</sub> at the conditions studied in this example<sup>260</sup> is ca. 10<sup>–3</sup> M, which is significantly greater than DR1 at 10<sup>–6</sup> M. This chapter explores the suitability of CRM and transmission FTIR imaging to investigate the distribution of drugs impregnated into a rubbery polymer from a scCO<sub>2</sub> solution.

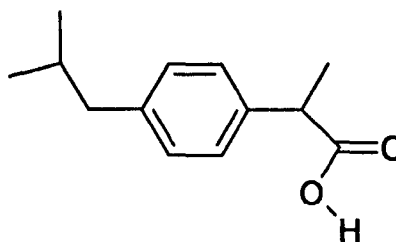


Figure 9.6. Chemical structure of Ibuprofen

### 9.2.2. EXPERIMENTAL

The high-pressure experimental arrangement employed was the same as that used throughout this thesis. The film samples were ca. 500  $\mu\text{m}$  in thickness and cut into ca. 5 x 5 mm<sup>2</sup> sections. Excess ibuprofen was placed into the bottom of the high-pressure vessel and the film section was placed onto the metal gauze, separating the polymer from the solid drug. The vessel was placed into a water bath at 40°C and loaded with CO<sub>2</sub> to 100 bar. Once the desired exposure time had elapsed, the vessel was depressurised. The impregnated film sample was cut in half at the central position and one half cryogenically sectioned. The sectioning procedure required the sample to be embedded in epoxy due to the low  $T_g$  of the matrix. Cryogenic sectioning was performed at -80°C to prepare sections of ca. 5  $\mu\text{m}$  thickness. The remaining half was retained for CRM z-sectioning. All Raman and IR measurements were performed on the system previously described in section 6.1.2 and 6.2.2 respectively.

### 9.2.3. RESULTS AND DISCUSSION

*Transmission FTIR imaging:* The FTIR transmission image (266 x 266  $\mu\text{m}^2$ ) of the 5  $\mu\text{m}$  thick impregnated section is presented in Figure 9.7. The image was generated based on the distribution of the integrated absorbance of the band corresponding to ibuprofen (1500–1527 cm<sup>-1</sup>). Inspection of Figure 9.7 reveals that the distribution of ibuprofen is localised at the surfaces of the film section. The thickness of the surface layer occupied by ibuprofen molecules is seen to be approximately equal along the edges of the sample. At approximately midway along the bottom film surface there is a region that is significantly thicker than the surrounding areas (indicated by line b). To visualise the concentration gradient of ibuprofen along the two lines (labelled a and b in

Figure 9.7), integrated absorbance values corresponding to ibuprofen have been extracted for the pixel positions that span the lines. Data were extracted for 10 lines, centred at the positions indicated and an average value was calculated to improve the signal to noise. The absorbance values of ibuprofen as a function of distance from the film surface are presented in Figure 9.8.

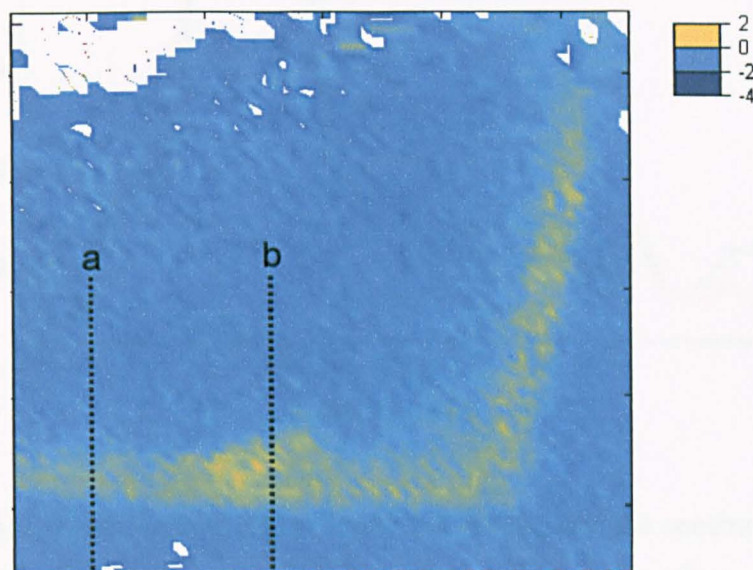


Figure 9.7. Transmission FTIR image corresponding to the distribution of ibuprofen in P(MMA–EHA–EGDMA), impregnated from a  $\text{scCO}_2$  solution for 30 minutes at 100 bar and  $40^\circ\text{C}$ . The dotted lines (a and b) correspond to the extracted profiles presented in Figure 9.8.

The extracted profiles reveal the presence of a significant gradient in ibuprofen which is not apparent from the image. The relatively thick region of ibuprofen-rich polymer shown in the image surface region (Figure 9.7) is confirmed in the extracted profile corresponding to profile b. The reason for the enhanced penetration at this localised region may be due to inhomogeneity in the polymer matrix in terms of local density or the presence of pores which would reduce the effective diffusion path length and hence lead to an apparent increase in penetration depth. This exemplifies the importance of FTIR imaging to visualise the sample with a relatively large field of view to enable such anomalies to be identified.

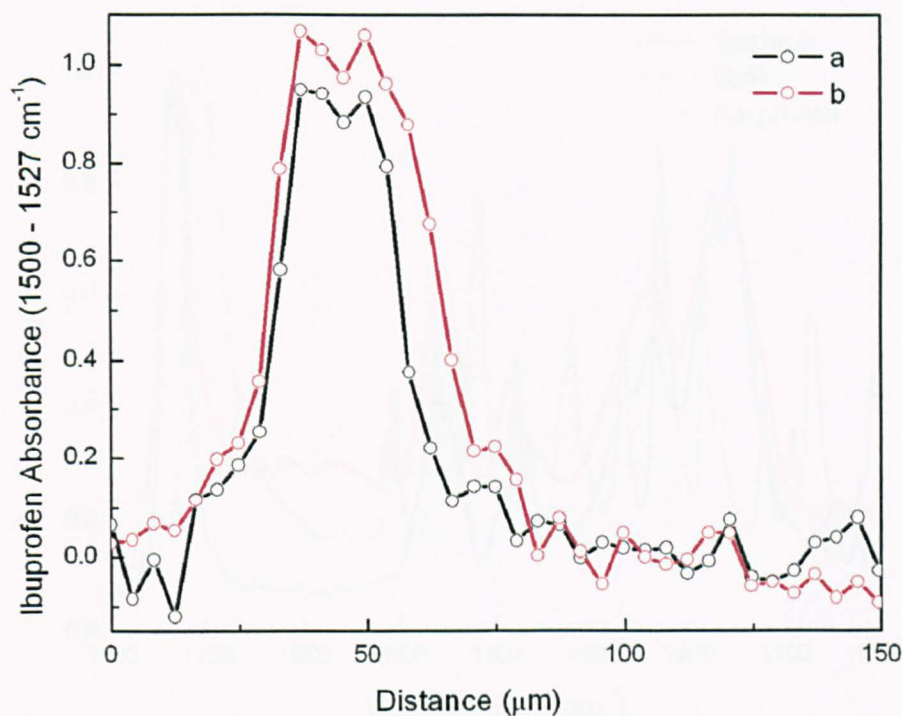


Figure 9.8. Absorbance values of the ibuprofen band from the spectra extracted along the lines (a and b indicated on Figure 9.7.) normal to the film surface. Each data point represents an average value for 10 neighbouring lines.

FTIR spectra extracted from the surface and bulk regions of the transmission image, and the ATR FTIR spectrum of pure ibuprofen are presented in Figure 9.9. Inspection of the spectrum extracted from the surface (black) reveals the characteristic ibuprofen absorbance at ca.  $1510\text{ cm}^{-1}$ . The carbonyl region of the extracted spectra potentially offers a probe to assess molecular interactions between the hydroxyl group of ibuprofen molecules and the carbonyl oxygen of the polymer.<sup>25</sup> Hydrogen bonding would result in a red shift of the carbonyl band of the polymer to a lower wavenumber. Small differences are apparent in the carbonyl region of the bulk and surface extracted spectra, but interpretation is complicated by the absorption of the carbonyl and of ibuprofen.



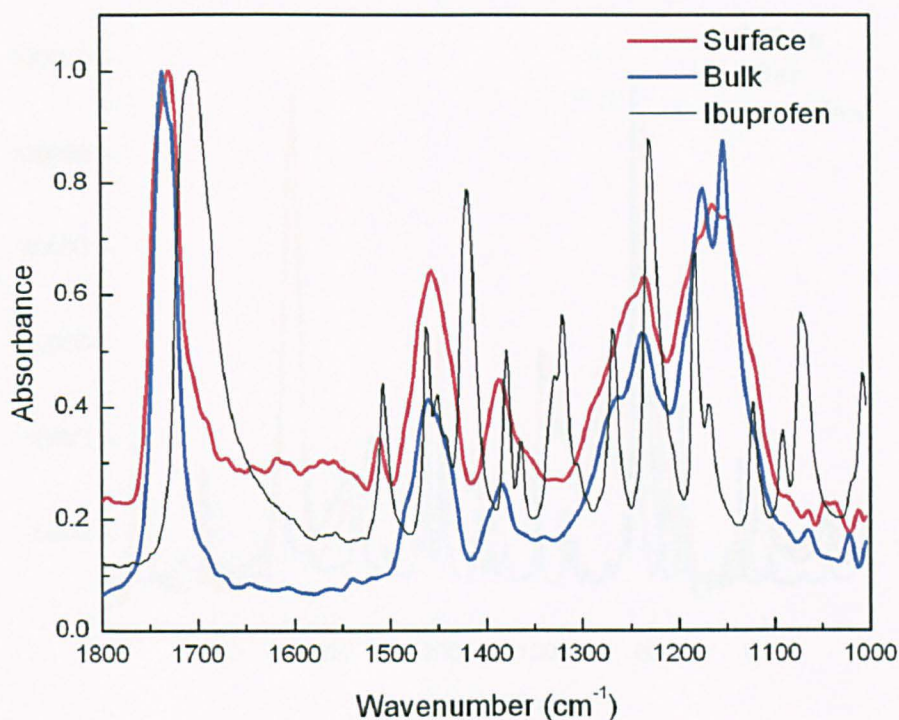


Figure 9.9. FTIR spectra extracted from the surface (red) and the bulk (blue) regions of the transmission FTIR image. The ATR FTIR spectrum of pure ibuprofen is also included (black).

*Raman mapping:* Raman spectra corresponding to the surface of polymer film before and after 3 hours exposure to the  $\text{scCO}_2$ /ibuprofen solution at 100 bar and  $40^\circ\text{C}$ , and pure ibuprofen are presented in Figure 9.10. The processed film shows the presence of impregnated ibuprofen as indicated by the several bands of ibuprofen in the spectrum. The ibuprofen band at  $\text{ca. } 1620 \text{ cm}^{-1}$  and the bands in the  $1180\text{--}1220 \text{ cm}^{-1}$  region do not overlap with the polymer bands and thus represent potential features to identify the presence of ibuprofen.

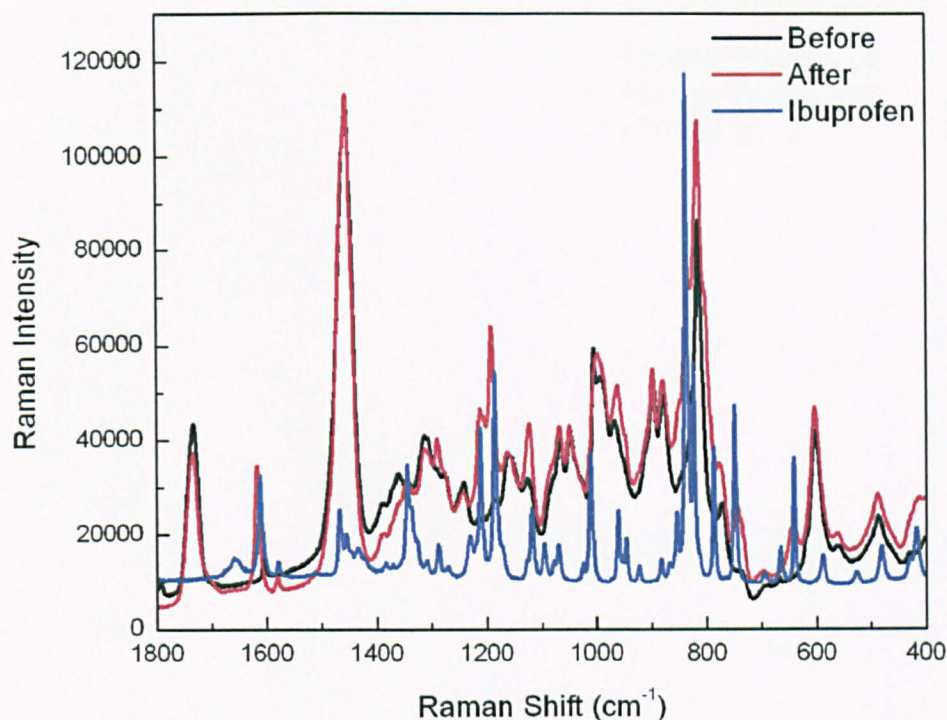


Figure 9.10. Raman spectra of pure ibuprofen, pure polymer and the impregnated film.

Raman point mapping was performed along the line normal to the film surface of the microtomed section. The integrated intensity of ibuprofen (1180-1220 cm<sup>-1</sup>) was normalised using the integrated intensity of the polymer band (1420-1490 cm<sup>-1</sup>) as a function of position from the film surface. The extracted profiles measured using FTIR imaging and Raman mapping (2 positions) are plotted in Figure 9.11. The presence of a drop in surface concentration is apparent in the profiles measured by the independent techniques. This feature is not due to the presence of a surface region of solid drug, as determined by examination of the spectra which show the presence of polymer with impregnated ibuprofen. The drop in drug concentration at the subsurface region may be due to possible damage caused during the sectioning process, known as striations.<sup>224</sup>



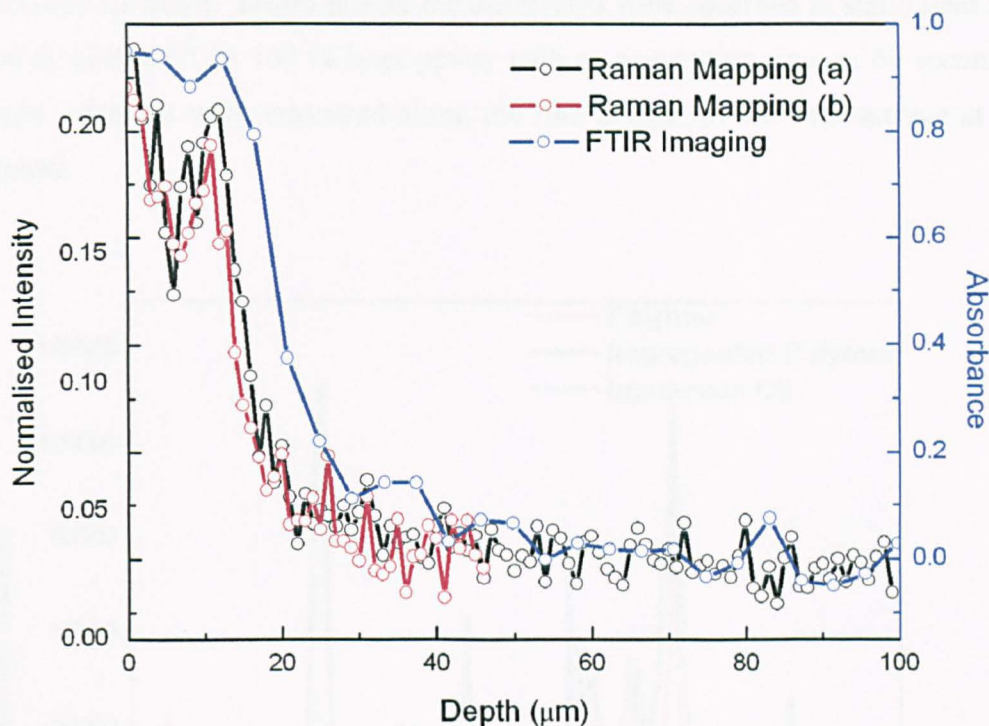


Figure 9.11. Overlay of ibuprofen concentration gradient measured by Raman mapping and FTIR imaging of 5  $\mu\text{m}$  microtomed section.

The superior spatial resolution of Raman mapping (1-2  $\mu\text{m}$ ) compared to transmission FTIR imaging (ca. 20  $\mu\text{m}$ ) may explain the difference in extracted profiles. The depth corresponding to the absorbance value falling to ca. 25 % of the maximum is used to define the depth that ibuprofen molecules reside. This corresponds to a value of 20  $\mu\text{m}$  and 24  $\mu\text{m}$  for Raman mapping and FTIR imaging respectively. The spatial resolution of the two techniques is possibly responsible for the discrepancy. The overestimated depth of penetration of ibuprofen in the FTIR imaging data is most likely due to the inferior spatial resolution.

*Confocal Raman microscopy:* Raman spectra corresponding to P(MMA–EHA–EGDMA) before and after exposure to the  $\text{scCO}_2$ /ibuprofen solution, and the immersion oil are presented in Figure 9.12. Spectral overlap is apparent in several potential regions to study the presence of impregnated ibuprofen. The spectral region between 1180-1220  $\text{cm}^{-1}$  has the least amount of overlap and hence was selected to identify ibuprofen

as a function of depth. Depth profile measurements were recorded in static scan mode, centred at  $1240\text{ cm}^{-1}$ , at 100 % laser power with an acquisition time of 60 seconds per spectrum. Spectra were measured along the line normal to the film surface at  $1\text{ }\mu\text{m}$  increments.

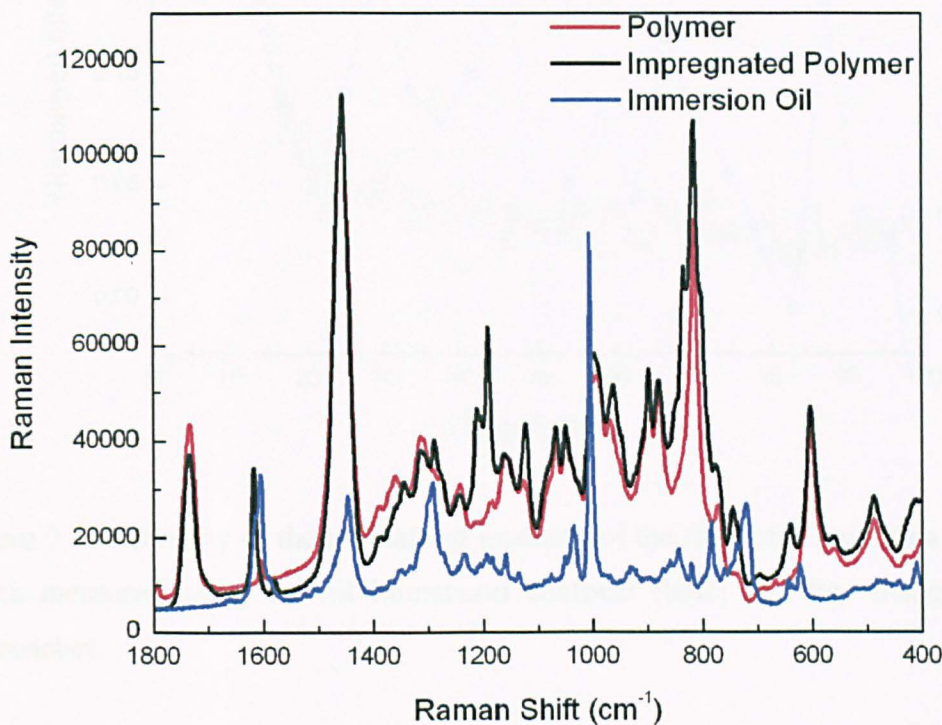


Figure 9.12. Raman spectra of P(MMA–EHA–EGDMA) before and after exposure to the  $\text{scCO}_2$ /ibuprofen solution at 100 bar and  $40^\circ\text{C}$  for 30 minutes; the spectrum of the immersion oil used for depth profiling is also shown.

Unfortunately, the signal to noise in the Raman spectra measured in preliminary oil immersion depth profile measurements was poor, especially when focussing deep within the sample. The normalised ibuprofen profiles as a function of depth for the oil immersion CRM and Raman mapping data are presented in Figure 9.13. Although a decrease in ibuprofen concentration that decays from a maximum at the surface of the film is apparent, the noise in the data does not enable a quantitative analysis to be performed.



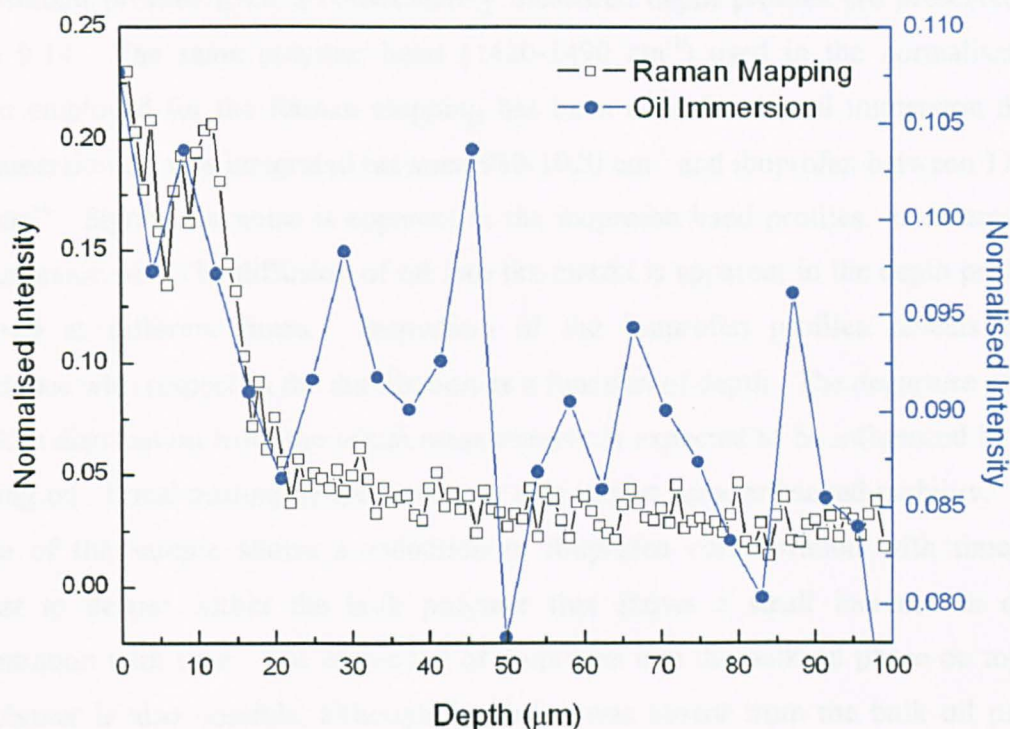


Figure 9.13. Overlay of the normalised intensity of the ibuprofen band as a function of depth measured using the oil immersion confocal (blue) and line mapping (black) approaches.

When subsequent depth profile measurements were performed on the same sample the presence of Raman bands belonging to the immersion oil were observed deep within the matrix. This is indicative of oil diffusing through the polymer during the time-scale of the measurement. The low  $T_g$  of the polymer ( $-4^\circ\text{C}$ ) combined with the presence of potentially plasticising ibuprofen molecules permits the diffusion of oil molecules through the plasticised matrix. The presence of pores in the polymer may potentially enhance the diffusion of oil through the matrix. Due to the relatively weak basic carbonyl group of the polymer, ibuprofen molecules are likely to weakly interact with the matrix and hence their distribution may be altered by the diffusion of oil through the matrix. To investigate the influence of oil on the distribution of the impregnated ibuprofen molecules, three consecutive depth profiles were measured to study the distribution of oil and possible changes in the ibuprofen concentration gradient.

The resultant profiles from 3 consecutively measured depth profiles are presented in Figure 9.14. The same polymer band ( $1420\text{--}1490\text{ cm}^{-1}$ ) used in the normalisation method employed for the Raman mapping has been used for the oil immersion data. The immersion oil was integrated between  $980\text{--}1020\text{ cm}^{-1}$  and ibuprofen between  $1180\text{--}1220\text{ cm}^{-1}$ . Significant noise is apparent in the ibuprofen band profiles, in contrast to the immersion oil. The diffusion of oil into the matrix is apparent in the depth profiles measured at different times. Inspection of the ibuprofen profiles reveals time dependence with respect to the distribution as a function of depth. The departure of the ibuprofen distribution from the initial measurement is expected to be influenced by the diffusing oil. Local heating by the laser may also impart some enhanced mobility. The surface of the sample shows a reduction in ibuprofen concentration with time, in contrast to deeper within the bulk polymer that shows a small increase in drug concentration with time. The extraction of ibuprofen into the bulk oil phase on top of the polymer is also possible, although ibuprofen was absent from the bulk oil phase Raman spectra (not included). Due to the noise in the ibuprofen data, quantitative analysis is not possible, but qualitatively, it is possible to observe a change in ibuprofen distribution as a function of depth.

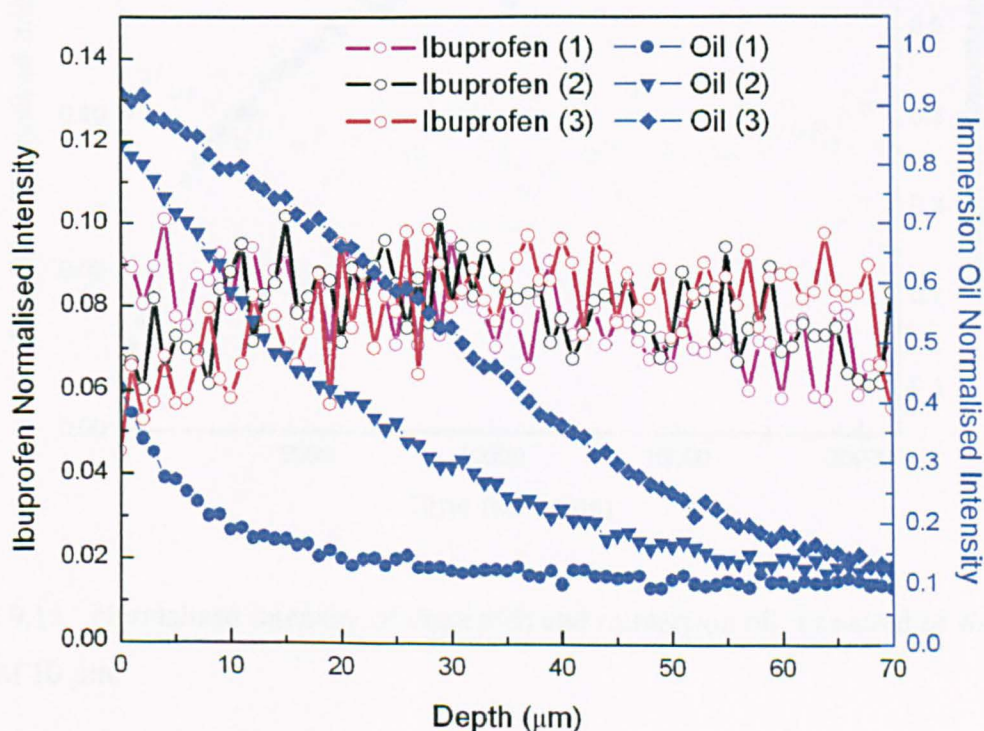


Figure 9.14. Overlay of the normalised bands of ibuprofen and oil as a function of depth for three independent, consecutively measured depth profiles.



The suitability of oil immersion CRM to study this low  $T_g$  polymer system is limited due to the diffusion of the oil. Rapid acquisition times would possibly enable the distribution of ibuprofen to be measured prior to the arrival of diffusing oil. However, the drug used requires long acquisition times to achieve adequate signal to noise. The influence of the immersion oil on the system was investigated *in situ* by measuring multiple spectra at the same location during the diffusion of oil, and hence the study of a dynamic system has been performed. Oil was applied to the top of the film (as would be conducted in any oil immersion measurement) and the laser focussed to a depth of 10  $\mu\text{m}$  below the surface. Raman spectra were recorded as a function time at that point and the band of the immersion oil (at ca.  $1000\text{ cm}^{-1}$ ) and the ibuprofen band were studied. The normalised intensity (using the aforementioned  $1420\text{--}1490\text{ cm}^{-1}$  band) of ibuprofen and immersion oil as a function of time are presented in Figure 9.15.

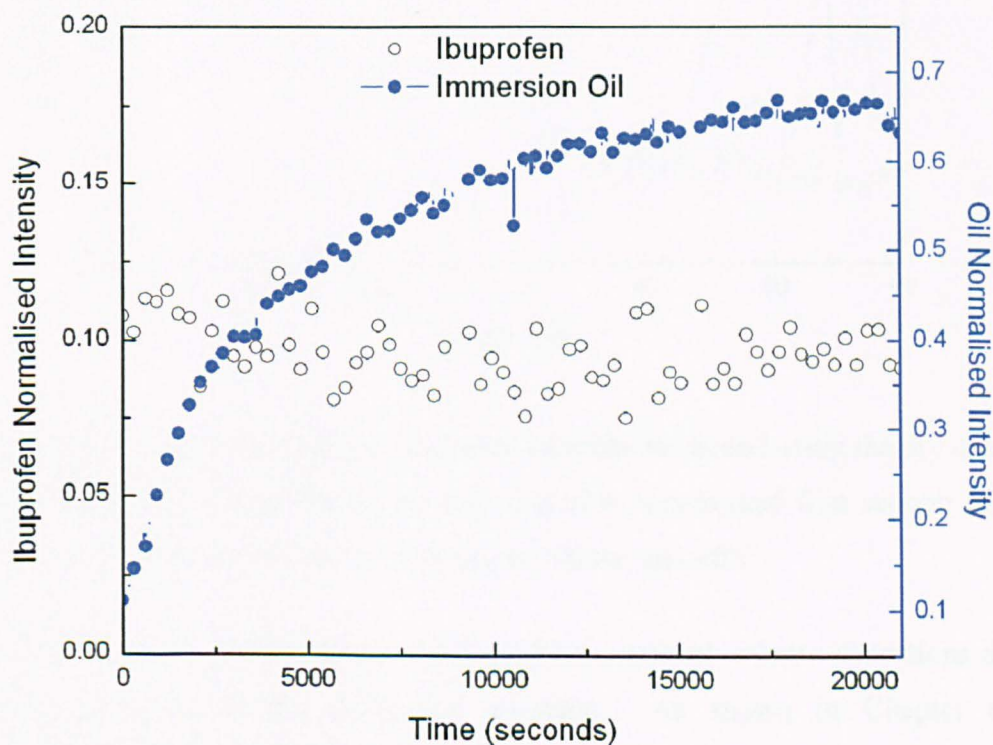


Figure 9.15. Normalised intensity of ibuprofen and immersion oil measured *in situ* at a depth of 10  $\mu\text{m}$ .

The *in situ* results confirm the diffusion of oil and the consequential change in ibuprofen concentration as a function of time, presumably being entrained in the diffusing oil. These measurements confirm the unsuitability of the oil immersion technique to study this polymer/drug system, but exemplify the possibility to study the diffusion of oil through the matrix.

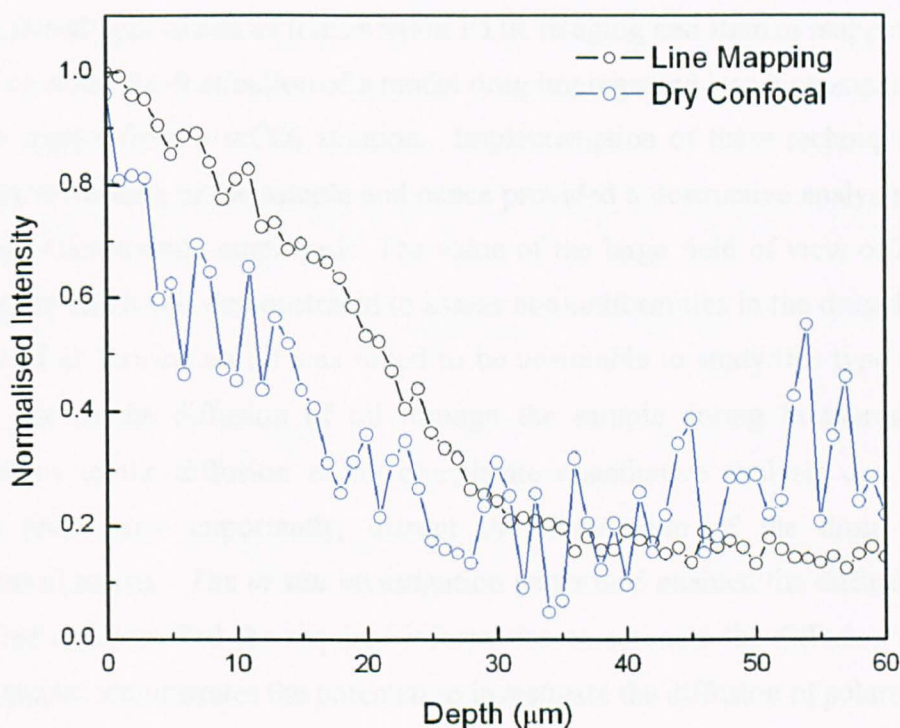


Figure 9.16. Overlay of normalised ibuprofen intensity measured using the dry confocal approach (blue) and conventional line mapping of a microtomed film section (black). The sample was impregnated for 40 minutes at 100 bar and 40°C.

Depth profiling using a dry objective suffers from confocal volume distortions due to refraction occurring at the air/surface interface. As shown in Chapter 6 the morphological distribution in PET measured using the dry confocal approach was approximately half the true value. Measured profiles obtained using the dry (metallurgical) confocal approach and line mapping for a sample exposed for 40 minutes at 100 bar and 40°C are presented in Figure 9.16. Although noise is apparent in the confocal profile measured using the dry objective, the underestimation is seen to be



approximately half of the line mapping data. From this non-destructive measurement with the dry objective, one may estimate the “true” depth of penetration. However, it should be noted that success of this estimation is dependent upon the specific distribution in the sample and the refractive indices of the constituent components.

#### 9.4. CONCLUSIONS

The combined application of transmission FTIR imaging and Raman mapping has been utilised to study the distribution of a model drug impregnated into biocompatible low  $T_g$  polymer matrix from a  $scCO_2$  solution. Implementation of these techniques required specialist sectioning of the sample and hence provided a destructive analysis due to the cryogenic microtoming employed. The value of the large field of view offered by the imaging approach was demonstrated to assess non-uniformities in the drug distribution. The use of an immersion oil was found to be unsuitable to study this type of polymer system due to the diffusion of oil through the sample during measurement. The implications to the diffusion of oil complicate quantitative analysis due to spectral overlap and, more importantly, disrupt the distribution of the drug within the impregnated matrix. The *in situ* investigation performed enabled the diffusion of oil to be studied and provided the required information to estimate the diffusion coefficient. This example demonstrates the potential to investigate the diffusion of solutes through a polymeric matrix. This form of analysis has been reported in the literature for molecules diffusing through a membrane,<sup>215</sup> the correction for refractive index was however not addressed.

## **CHAPTER 10**

# **HIGH-PRESSURE CO<sub>2</sub>-ENHANCED POLYMER INTERDIFFUSION STUDIED WITH *IN SITU* ATR FTIR SPECTROSCOPIC IMAGING**

## 10. HIGH-PRESSURE CO<sub>2</sub>-ENHANCED POLYMER INTERDIFFUSION STUDIED WITH IN SITU ATR FTIR SPECTROSCOPIC IMAGING

### 10.1. INTRODUCTION

The favourable interaction of high-pressure CO<sub>2</sub> with glassy and semicrystalline polymers permits the processing applications described in Chapter 3. The plasticising effect leads to the reduction in polymer viscosity<sup>114,261</sup> and interfacial tension reduction which facilitates the enhanced blending of polymers.<sup>134,262</sup> The benefits that CO<sub>2</sub> provides in these examples may be anticipated to extend to enhancing/accelerating the interdiffusion in miscible polymer systems as a direct consequence of plasticisation and viscosity reduction of the polymer components. Because of the experimental challenges, studies of polymer interdiffusion facilitated by high-pressure CO<sub>2</sub> are limited. Recent examples include the study of low-temperature reactive coupling at polymer-polymer interfaces<sup>263</sup> and density fluctuations in thin polymer films<sup>264</sup> subjected to scCO<sub>2</sub>. It should be noted that relevant studies of organic solvent enhanced diffusion of polymers have also been reported recently.<sup>265</sup> Knowledge of the CO<sub>2</sub>-enhanced interdiffusion in a polymer blend aids the full understanding of this novel processing route and therefore provides the required knowledge to adopt and optimise the technology. Previous attempts to study polymer interdiffusion under high-pressure CO<sub>2</sub> involved rheology, light scattering and neutron reflectivity.

This study utilises *in situ* ATR FTIR imaging to evaluate the effect of high-pressure CO<sub>2</sub> on the interdiffusion of a polymer system. To assess the validity of this *in situ* imaging approach to study the phenomena, a model system is selected where polymer interdiffusion induced by heat has been reported in the literature. The interdiffusion of poly(ethylene glycol) (PEG) and polyvinylpyrrolidone (PVP) has received much attention in the polymeric and pharmaceutical communities due to the importance in pharmaceutical formulations.<sup>25</sup> Blends of PVP-PEG are used for the preparation of skin patches due to their good adhesive properties with the surface of the skin and the ability to control the diffusion of released drug molecules. The interdiffusion of these polymers, formation of a homogeneous blend and possible phase separation are important phenomenon for optimal design of materials based on these polymers. The

effect of molecular weight on the diffusion characteristics of both polymers have been highlighted in studies where interdiffusion was induced by heat and studied via optical wedge microinterferometry.<sup>266</sup> This *in situ* high-pressure study of interdiffusion in the PEG-PVP system via ATR FTIR spectroscopic imaging is the first example of the application of this powerful imaging approach to polymer interdiffusion facilitated by high-pressure or supercritical CO<sub>2</sub>.

## 10.2. EXPERIMENTAL

*Polymer interface preparation:* PVP (K15, 10000 Mw), PEG 1500 and PEG 600 were purchased from Sigma and used as received without further treatment. The chemical structures of PVP and PEG are shown in Figure 10.1. A film of PVP with 20 wt% of PEG 1500 was created by co-dissolving in ethanol followed by casting directly onto the diamond ATR crystal which was heated to 90°C. The necessity for the inclusion of PEG is to ensure good contact between the PVP and the diamond ATR crystal following the evaporation of ethanol. A similar film preparation method was utilised in the related study.<sup>266</sup> After ca. 25 minutes following polymer solution deposition, a scalpel was used to remove half of the polymer film along the central line across the diamond. The sample was held at 90°C until all of the ethanol had evaporated, the level of which was monitored via FTIR spectroscopy. Once all of the ethanol was removed, which typically took ca. 45 minutes, PEG was placed onto the remaining half of the diamond. Intimate and uniform contact between PVP and PEG at the interface was easily achieved for PEG 600 since it is a liquid at room temperature. For PEG 1500, which is a solid at ambient conditions, heat was applied to melt the PEG at ca. 70°C resulting in good contact between the solid PVP and liquid PEG phases. All experiments were prepared using approximately the same quantity of each polymer, enabling a fair comparison to be made between experiments. At the point of contact between the polymers, the film thickness was approximately identical which enables one to study uniaxial diffusion by eliminating potential diffusion from the top of one of the polymer phases.



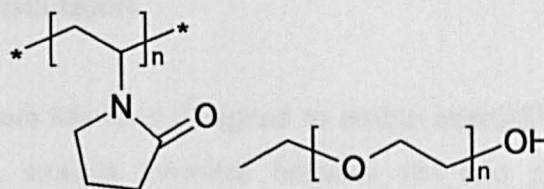


Figure 10.1. Chemical structure of PVP (left) and PEG (right)

**High-pressure apparatus:** The miniature cell used in this study is the same as that described in section 5.2; the principle of using this cell for polymer interdiffusion is shown schematically in Figure 10.2. The absence of fragile windows and the small volume of the cell result in an inherently safe design. The cell is sealed with a polytetrafluoroethylene (PTFE) spacer against the diamond support plate and is held in position using the gate of the accessory. The temperature in the high-pressure cell can be adjusted using the temperature control unit and was maintained at 35°C for all experiments so that it was above the critical temperature of CO<sub>2</sub>. Once thermal equilibrium was reached, the cell was slowly loaded with CO<sub>2</sub> (99% purity provided by BOC) using an ISCO model 500D syringe pump. Cell pressurisation was typically completed within 1 minute and the system pressure was monitored during the pressurisation stage and throughout the course of the experiment using a digital pressure transducer. Once the required pressure was reached, the image acquisition procedure was initiated which served as time zero for the interdiffusion experiments.

**FTIR imaging:** FTIR images were measured using the same instrumentation described in section 6.3.2. Images were recorded using 5 coadditions with a spectral resolution of 8 cm<sup>-1</sup> which took ca. 3 minutes to acquire an image.

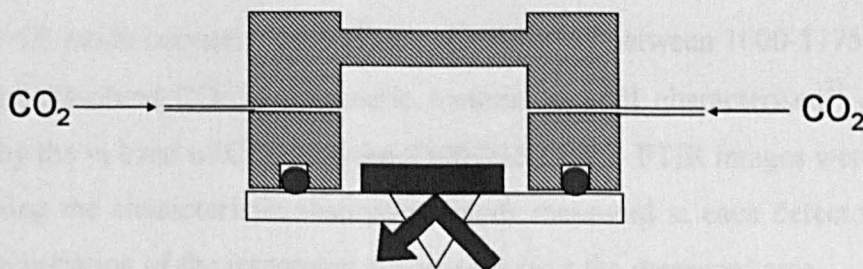


Figure 10.2. Schematic diagram of high-pressure cell.

### 10.3. RESULTS AND DISCUSSION

The experimental system has been designed to enable interdiffusion to be studied in a uniaxial manner. A straight interface between the two polymers was prepared approximately at the central location of the diamond which, when imaged, extends vertically from the bottom of the image. The interdiffusion occurring in the polymer system is therefore observed along the horizontal plane of the image. The studied length scales are dictated by the spatial resolution of ca. 15  $\mu\text{m}$  available with ATR FTIR imaging using this particular set-up.<sup>236</sup> This is significantly greater than the scales studied by neutron reflectivity and thus, later stages of interdiffusion are studied with ATR FTIR imaging. The intrinsic vibrational modes associated with the functional groups present on the polymer backbone provide the basis for FTIR spectroscopy to differentiate and characterise polymers. To study the spatial distribution of the components in this ternary system, FTIR spectra of the individual components have to be compared to select suitable spectral bands corresponding to a particular component. The FPA detector provides spatial discrimination and hence images are generated based on the distribution of the integrated absorbance of a specific spectral band, corresponding to either of the components in this ternary PVP/PEG/CO<sub>2</sub> system.

ATR FTIR spectra of PVP and PEG 600 are presented in Figure 10.3 which reveal several regions that are absent from mutual spectral overlap. As mentioned in the experimental section, PEG 1500 is added to mildly plasticise PVP. The small quantity of PEG 1500 (20 wt%) in the bulk PVP is detected and characterised by the absorbance in the 1020-1170  $\text{cm}^{-1}$  region. Pure PEG 1500 is a semicrystalline polymer at 35°C, but a specific interaction occurring between the chains of dispersed PEG and chains of PVP inhibits the formation of PEG crystallites, which is signified by the lack of crystalline PEG absorption at 1060  $\text{cm}^{-1}$ .<sup>267</sup> The presence of PVP was identified by the absorbance of the  $\nu(\text{C=O})$  mode between 1600-1720  $\text{cm}^{-1}$  and PEG between 1000-1175  $\text{cm}^{-1}$ . The spectrum of dissolved CO<sub>2</sub> in polymeric material is well characterised<sup>37</sup> and can be identified by the  $\nu_3$  band of CO<sub>2</sub> between 2300-2350  $\text{cm}^{-1}$ . FTIR images were generated by integrating the characteristic absorption bands measured at each detector pixel and plotting the variation of the integrated absorbance over the measured area.

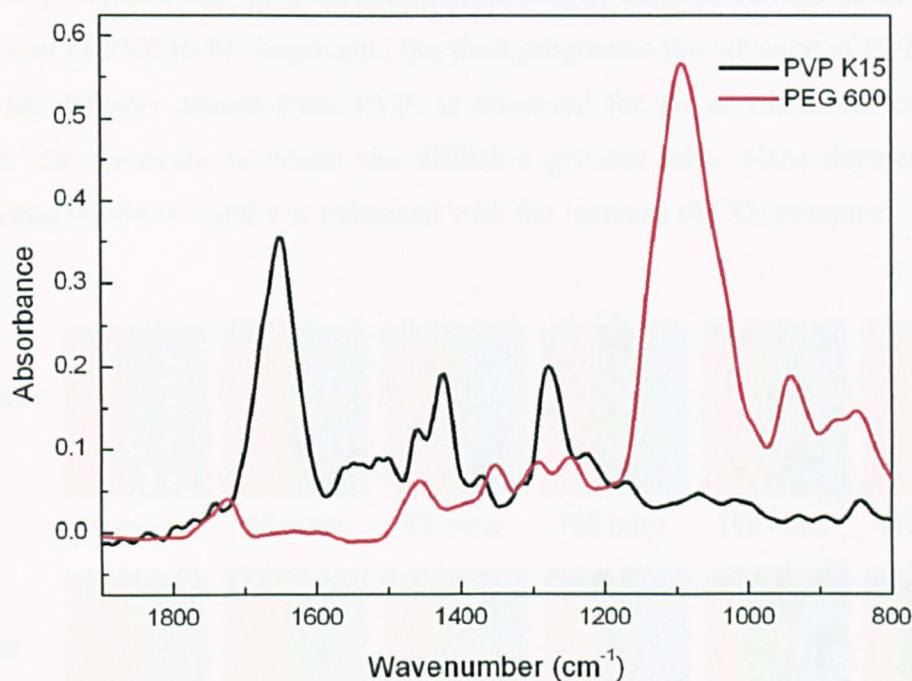


Figure 10.3. ATR FTIR spectra of PVP K15 (black) and PEG 600 (red) measured with 8 cm<sup>-1</sup> spectral resolution

ATR FTIR images corresponding to PVP in contact with PEG 600 in the absence of CO<sub>2</sub>, at 40 and 80 bar are presented in Figure 10.4. The images correspond to an area of ca. 820 x 1140 μm<sup>2</sup>, as determined in a previous study,<sup>236</sup> and are accompanied by a scale bar which associates the colour used in the images with the integrated absorbance. The initial distribution of the two polymers (0 minutes) is seen to consist of the two polymers in contact with a sharp, straight interface which typifies all experiments that have been performed. PVP is seen to occupy the left side of the image, interpreted by the high intensity of the red/pink colour in this region. The right side of the image is initially absent from PVP and is composed entirely of PEG 600. Inspection of the images reveals a cluster of low intensity pixels in the top left hand corner which appear out of place when one considers the intensity of the surrounding pixels. These correspond to bad pixels that are no longer active due to delamination of the detector elements and were consequently not included in the analysis. In the series of images conducted in the absence of CO<sub>2</sub>, PVP is in the solid state in contact with liquid PEG 600 and hence the diffusion process occurs at a glassy/liquid interface and can be



viewed as the dissolution of PVP in PEG. Once this interface was formed, the image acquisition procedure was initiated with measurements taken at various times to enable the diffusion of PVP to be visualised. As time progresses the advance of PVP into the PEG phase, initially absent from PVP, is observed for all of the series of images. However, the timescale in which the diffusion process takes place depends on the experimental conditions and it is enhanced with the increase of CO<sub>2</sub> pressure.

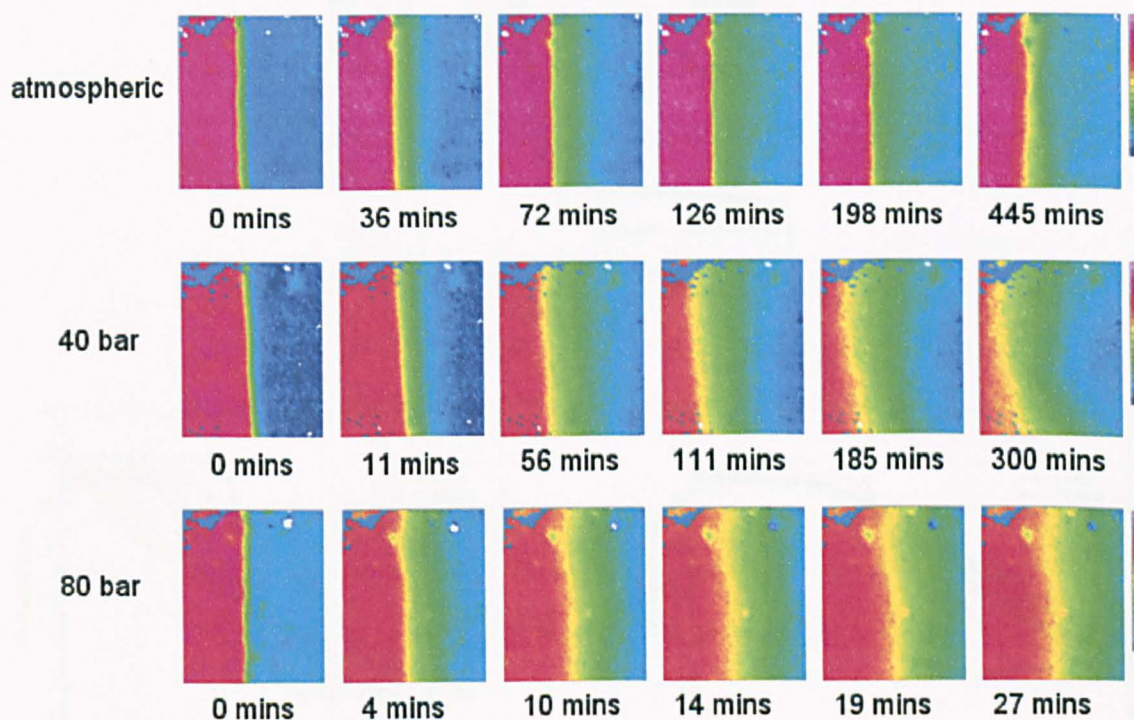


Figure 10.4. ATR FTIR images corresponding to PVP in contact with PEG 600 as a function of time at various pressures. The images are based on the distribution of the integrated absorbance of the  $\nu(\text{C}=\text{O})$  band of PVP.

An analysis has been performed to quantify the effect of CO<sub>2</sub> pressure at accelerating the polymer interdiffusion. The diffusion analysis requires the evolution of the spatial concentration profile of one of the polymers as a function of time to be studied. The measured images provide component concentrations in the time and spatial dimension which is required to assess the diffusion behaviour. The arrangement of the polymer interface on the diamond ATR crystal facilitates the study of a specific components concentration profile along the line that intersects the interface perpendicularly. The evolution of the concentration distribution of a specific component is achieved by



extracting the integrated absorbance values for a row of pixels that span this line. This process was repeated for 5 consecutive lines and an average value calculated for each pixel position along the line to improve signal to noise. A selection of the concentration-distance profiles extracted from the imaging data are presented in Figures 10.5 and reflect the relative concentration of PVP as a function of time.

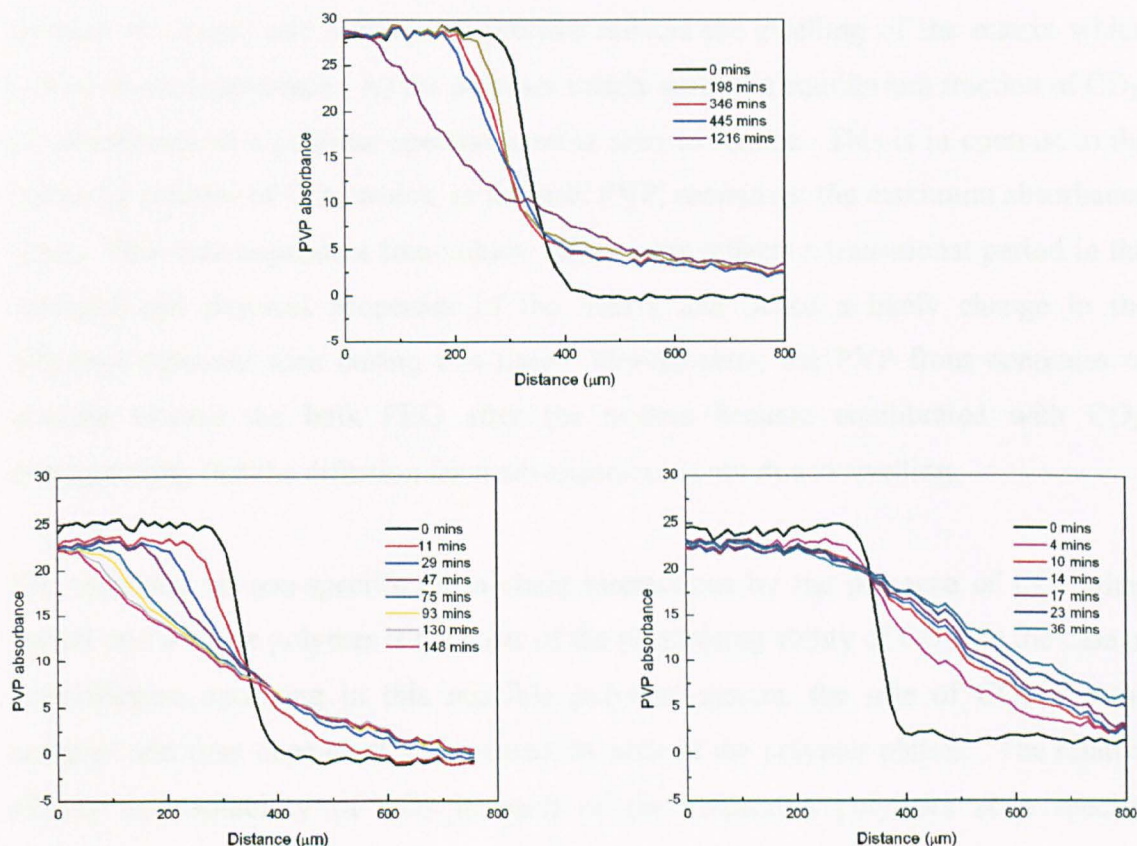


Figure 10.5. Extracted PVP concentration-distance profiles in contact with PEG 600 in the absence of CO<sub>2</sub> (top), at 40 bar (bottom left) and 80 bar (bottom right). Each profile represents an average signal from 5 consecutive lines that intersect the interface perpendicularly.

Figure 10.5 (no CO<sub>2</sub>) represents a situation whereby the PVP and PEG are diffusing within each other at an approximately equal rate and mutual diffusion acts to remove the inhomogeneity in the polymer system. The diffusion of glassy PVP into the liquid PEG is presumably facilitated by the act of PEG plasticising the PVP at the interfacial area which increases the mobility of the PVP macromolecules, thus enabling the diffusion (dissolution) of PVP. The relatively low molecular weight of PEG leads to the idea of

PEG diffusing through the bulk PVP on the basis of steric arguments. The sorption of CO<sub>2</sub> into the polymer matrix and the associated swelling is pronounced in the absorbance maximum of the concentration profiles (40 and 80 bar). The principles of quantitative determination of polymer swelling from *in situ* ATR measurements were described for the case of conventional FTIR spectroscopy and they remain the same in the case of ATR FTIR imaging.<sup>234</sup> The reduction in absorbance in the bulk PVP between the initial and subsequent profiles reflects the swelling of the matrix which exhibits time dependence. As the polymer matrix sorbs the equilibrium fraction of CO<sub>2</sub>, the absorbance of a polymer spectral band is seen to reduce. This is in contrast to the system in absence of CO<sub>2</sub>, which, in the bulk PVP, remains at the maximum absorbance value. This time dependent free-volume adjustment reflects a transitional period in the chemical and physical properties of the matrix and hence a likely change in the diffusion characteristics during this time. Nevertheless, the PVP front continues to advance toward the bulk PEG after the system became equilibrated with CO<sub>2</sub>, demonstrating that the diffusion front advancement is not due to swelling.

The reduction of non-specific chain-chain interactions by the presence of CO<sub>2</sub> when sorbed into a single polymer is the basis of the plasticising ability of CO<sub>2</sub>. In the case of interdiffusion occurring in this miscible polymer system, the role of CO<sub>2</sub> is more complex and time dependent with respect to each of the polymer phases. The relative affinity and solubility of CO<sub>2</sub> in each of the respective polymers at a specific temperature and pressure condition will dictate the rate at which the maximum weight fraction of dissolved CO<sub>2</sub> is approached. This translates into a difference in degree of swelling and extent of viscosity reduction between the polymer entities, which is also dependent on the molecular weight of the polymers. The diffusion behaviour displayed in a specific ternary system is complex. Prior to the acquisition of the first image in an interdiffusion experimental series, the polymer phases are contacted in the absence of CO<sub>2</sub>, followed by a pressurisation stage. The initial contact time of the polymer phases represents the initiation of the diffusion process between the polymer phases. The extent that diffusion occurs across the interface is determined by the molecular state of the polymer (i.e. amorphous or crystalline), molecular weight, degree of interaction, concentration of available polymer to maintain the concentration gradient and other factors such as temperature. During the initial stages of diffusion the cell is

loaded with CO<sub>2</sub> to the required pressure. CO<sub>2</sub> molecules diffuse into both of the polymer phases and into the miscible region of diffused polymer (depending on the speed of the diffusion process in the absence of CO<sub>2</sub>). As the concentration of dissolved CO<sub>2</sub> molecules increases to the pressure specific equilibrium value, the swelling of the matrices will increase to a maximum value. It should be noted that the relative affinity of CO<sub>2</sub> for each of the polymers will result in favourable sorption into a specific matrix and consequently the free-volume of a specific polymer will reach its maximum value at a greater rate, as shown in Figure 10.6. The distribution of all three components measured for PEG 600 in contact with PVP at 40 bar are shown in the series of images presented. Inspection of Figure 10.6 reveals that each of the polymer phases is seen to diffuse into the bulk of the other phase, thus confirming the phenomena of interdiffusion. The concentration of CO<sub>2</sub> in PEG is shown to have reached its maximum value in the first image. However, in the PVP phase the CO<sub>2</sub> concentration does not reach the equilibrium fraction until some time after the absorbance of CO<sub>2</sub> in PEG reached its maximum value, which is associated with slower diffusion of CO<sub>2</sub> through the glassy PVP matrix. In addition to the difference in rate of CO<sub>2</sub> sorption, the equilibrium concentration of dissolved CO<sub>2</sub> differs between the polymers.

A qualitative comparison of the extent of swelling induced by the presence of dissolved CO<sub>2</sub> molecules as a function of pressure is possible with *in situ* ATR spectroscopy.<sup>234</sup> The known depth of penetration (thus the effective pathlength) of the evanescent field provides a means to measure the sample density. The increase in free-volume associated with the plasticisation of the matrix decreases the concentration of polymer probed, which is reflected in the absolute absorbance in the polymer spectrum. Inspection of the images measured in the presence of CO<sub>2</sub> in Figure 10.4 and the maximum absorbance values in the concentration plots in Figures 10.5 reveal a decreased absorbance of PVP at 40 and 80 bar relative to atmospheric pressure (no CO<sub>2</sub>).



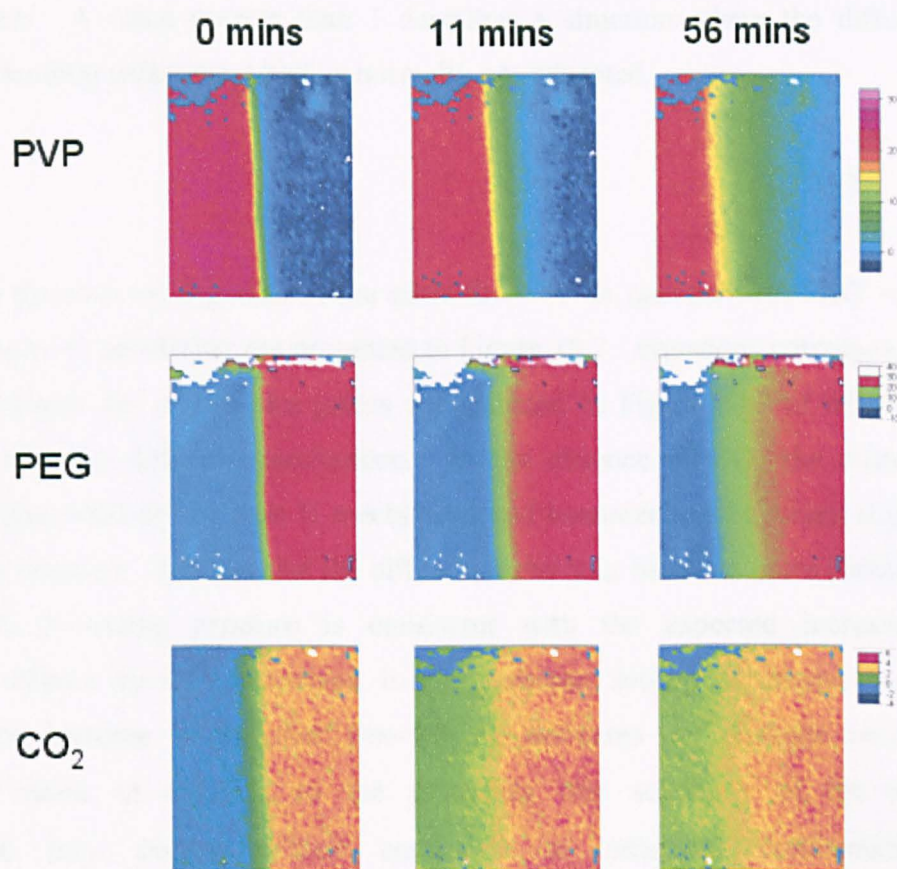


Figure 10.6. ATR FTIR images of PVP in contact with PEG 600 at 40 bar corresponding to PVP (top), PEG (middle) and dissolved CO<sub>2</sub> (bottom). For a specific time all of the images were generated from the same measurement using the distribution of the characteristic spectral feature associated with each component.

One may assess the role of CO<sub>2</sub> on the interdiffusion profiles by examining the diffusion mechanism obeyed by the system. Determining the diffusion mechanism is commonly achieved using the power law shown in Equation 10.1 where  $d$  is the position of the front (for 1-D diffusion) after a given time  $t$  and  $A$  is a proportionality factor. Elucidation of the diffusion mechanism is possible through evaluation of the gradient of a plot of logarithm distance vs. logarithm time. The distance refers to the diffusing front of the polymer, which has been defined as the position where the concentration of PVP falls to ca. 75 % of the maximum value. A gradient of 0.5 describes Fickian/case I diffusion in contrast to a value of 1 which corresponds to case II diffusion. Anomalous diffusion occurs when the gradient of the regression line of the measured points has an



alternative value. A value greater than 1 describes a situation where the diffusion process is accelerating with time which is normally not expected.

$$d = At^a \quad (10.1)$$

The logarithm distance vs. logarithm time plots for PVP in contact with PEG in the absence of CO<sub>2</sub>, at 40 and 80 bar are presented in Figure 10.7. Equations corresponding to the specific linear fits of the data points are included in Figure 10.7 of which the gradients describe the diffusion mechanism. In the absence of CO<sub>2</sub> the diffusion mechanism is described by the case II mechanism and becomes more Fickian (case I) with increasing pressure. The fact that the diffusion behaviour becomes more Fickian in character with increasing pressure is consistent with the expected increase in plasticisation offered by CO<sub>2</sub> dissolved in the polymer system at greater weight fractions. The increase in polymer free-volume increases the distance between neighbouring chains in addition to the proximity that segments of the same macromolecule may occupy which contribute to enhanced conformational mobility/relaxation. Under such conditions the time scale for conformational adjustment is small in comparison with the characteristic timescale for diffusion which results in a Deborah number significantly lower than 1 and hence Fickian diffusion occurs.<sup>255</sup> The transition from a case II to case I mechanism is a consequence of free-volume/chain mobility alterations.

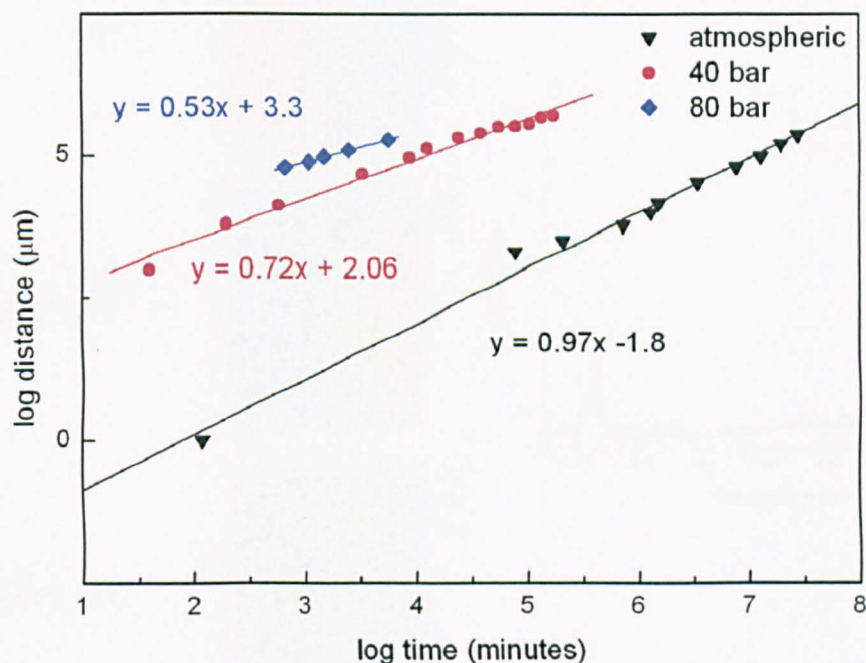


Figure 10.7. Plot of logarithm distance vs. logarithm time for PVP in contact with PEG 600 in the absence of CO<sub>2</sub>, at 40 and 80 bar. The distance of the PVP corresponds to the position on the concentration profile where the absorbance falls to ca. 75% of its maximum value. The gradient of the linear regression is indicative of the diffusion mechanism.

The same analysis procedure was performed on the imaging data sets for PVP in contact with PEG 1500. PEG 1500 has a semicrystalline morphology and when in contact with PVP at 35°C did not undergo any observable interdiffusion after 100 hours. However, exposure of the same system to CO<sub>2</sub> results in significant interdiffusion and thus CO<sub>2</sub> not only accelerates the process, but actually facilitates its occurrence. CO<sub>2</sub> is able to initiate interdiffusion by lowering the melting temperature of the PEG crystallites<sup>173,268</sup> and thus mimicking the effect of heat. The nature of CO<sub>2</sub> sorption into the PEG matrix is depicted in Figure 10.8 where PEG 1500 in contact with PVP at 40 bar measured directly after the pressurisation procedure was complete.

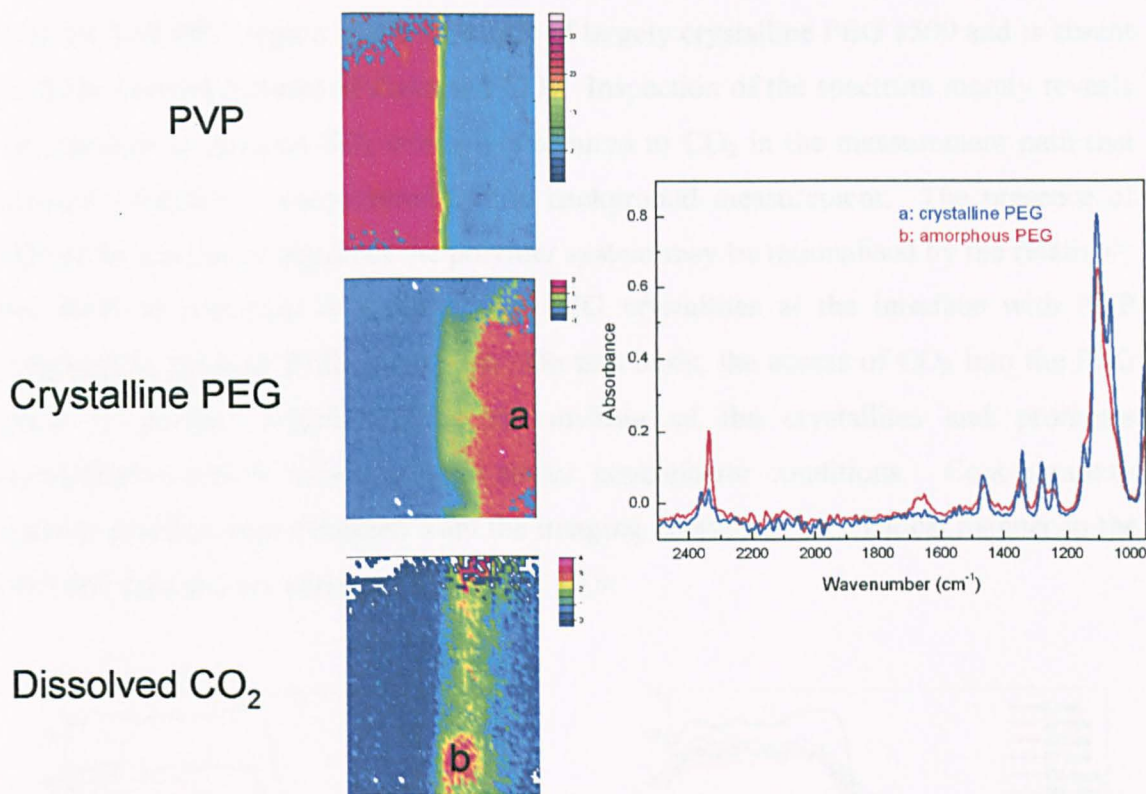


Figure 10.8. ATR FTIR images corresponding to PVP in contact with PEG 1500 at 40 bar of CO<sub>2</sub> shortly after pressurisation. All of the images were generated from the same measurement and integrated for each of the three components. The spectra shown were extracted from the two positions labelled (a and b).

All three images, measured once the cell was pressurised with CO<sub>2</sub>, were generated from the same measurement, but different characteristic absorption bands were used to represent the distribution of PVP, crystalline PEG and dissolved CO<sub>2</sub>. CO<sub>2</sub> is found to reside mostly within the PEG domain close to the polymer interfacial region. The initial absence of CO<sub>2</sub> in the bulk PVP is related to the relative affinity of CO<sub>2</sub> to the polymer entities and the time required to reach the area of polymer adjacent to the diamond. The CO<sub>2</sub> distribution coincides with the distribution of largely amorphous PEG which is evident in the spectrum extracted from the interfacial region (labelled b on image). The PEG in that region displays spectral features characteristic of amorphous PEG in addition to the presence of dissolved CO<sub>2</sub> molecules. This provides evidence that the relatively high CO<sub>2</sub> concentration in this region is not attributed to a void in the polymer system that is simply filled with the surrounding CO<sub>2</sub>, but reflects CO<sub>2</sub> molecules that are dissolved within the largely amorphous polymer matrix. The spectrum extracted



from the bulk PEG region is characteristic of largely crystalline PEG 1500 and is absent from the spectral features of dissolved CO<sub>2</sub>. Inspection of the spectrum merely reveals the presence of gaseous CO<sub>2</sub> which is attributed to CO<sub>2</sub> in the measurement path that was not completely compensated by the background measurement. The presence of CO<sub>2</sub> at the interfacial region of the polymer system may be rationalised by the relatively low level of structural integrity of the PEG crystallites at the interface with PVP compared to the bulk PEG crystallites. On this basis, the access of CO<sub>2</sub> into the PEG phase is possible which enables the melting of the crystallites and promotes interdiffusion which is not possible under atmospheric conditions. Concentration-distance profiles were extracted from the imaging datasets in an identical manner to the PEG 600 data and are presented in Figures 10.9.

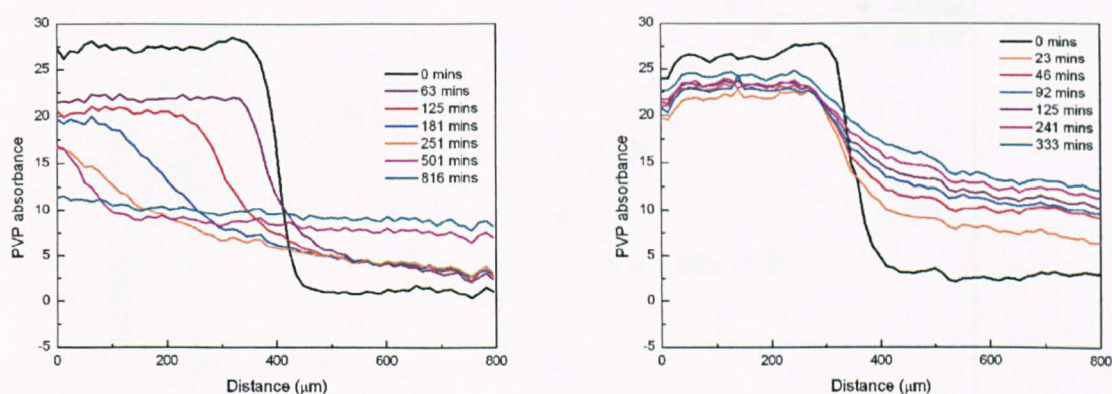


Figure 10.9. Extracted PVP concentration-distance profiles in contact with PEG 1500 at 40 bar (left) and 80 bar (right). Each profile represents an average signal from 5 consecutive lines that intersect the interface perpendicularly.

Figure 10.10 shows that the plot of the logarithm of diffusion front distance vs logarithm of time (Log distance-Log time) at 40 bar has a gradient greater than 1 which implies the diffusion increases in speed as a function time. A possible explanation for this behaviour is due to the dramatic changes in the free-volume of the PEG during the transition in morphology from crystalline to amorphous. The density of the PEG crystallites are relatively high<sup>269</sup> which corresponds to a low degree of free-volume. As the crystallites melt due to the sorption of CO<sub>2</sub>, the free-volume increases in a time dependent manner due to the kinetics of the morphological transition which accompanies crystallite melting combined with the diffusion of CO<sub>2</sub> through the



polymer. This is a plausible explanation for the diffusion mechanism. At 80 bar the diffusion mechanism does not show an increase in speed, presumably due to the rapid melting of the crystallites at higher pressure. The fact that case II behaviour is observed may be explained by the molecular weight of PEG 1500. The amount of chain entanglement in the bulk PEG 1500 will be considerably greater than in the lower molecular weight PEG even in the presence of CO<sub>2</sub>. The advance of PVP into the bulk PEG requires the coordinated movement of PEG macromolecules to accommodate the passage of PVP, which is likely to be more hampered at higher molecular weights and thus the time scale for conformational change is likely to be greater.

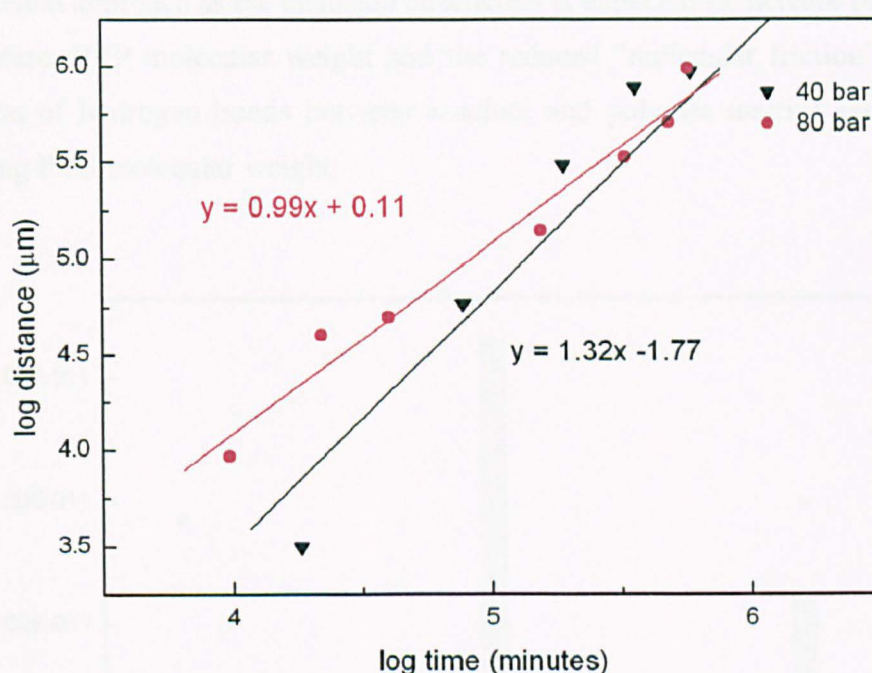


Figure 10.10. Plot of logarithm distance vs. logarithm time for PVP in contact with PEG 1500 subjected to 40 and 80 bar of CO<sub>2</sub>. The distance of the PVP corresponds to the position on the concentration profile where the absorbance falls to ca. 75% of its maximum value. The gradient of the linear regression is indicative of the diffusion mechanism.

For one-dimensional Fickian diffusion, a plot of the distance moved by the PVP front vs. square root of time provides the required information to calculate the diffusion coefficient from the experimental data. The diffusion mechanism values (1 = case II and 0.5 = case I) calculated are summarised in Figure 10.11. The diffusion coefficient

for those systems which obey case I and case II mechanisms have been calculated and presented in Figure 10.11. In all cases the presence of CO<sub>2</sub> accelerates the interdiffusion relative to the reference data of PEG 600 under atmospheric conditions. Increasing the CO<sub>2</sub> pressure is seen to accelerate the interdiffusion, demonstrating the opportunity to “tune” the interdiffusion process. The validity of this approach may be assessed through a comparison of the calculated diffusion coefficient in the absence of CO<sub>2</sub> with a literature value. Bairamov et al.<sup>270</sup> studied the interdiffusion of PVP (K17-molecular weight is 9000) in contact with PEG 400 at 25°C and reported a diffusion coefficient of  $6.6 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ . The value calculated in this work for PVP (K15) in contact with PEG 600 at 35°C of  $5.2 \times 10^{-13} \pm 0.5 \text{ m}^2\text{s}^{-1}$  provides confidence in this experimental approach as the diffusion coefficient is expected to increase on the basis of temperature, PVP molecular weight and the reduced “molecular friction” (relating to formation of hydrogen bonds between a solute and polymer matrix) associated with increasing PEG molecular weight.

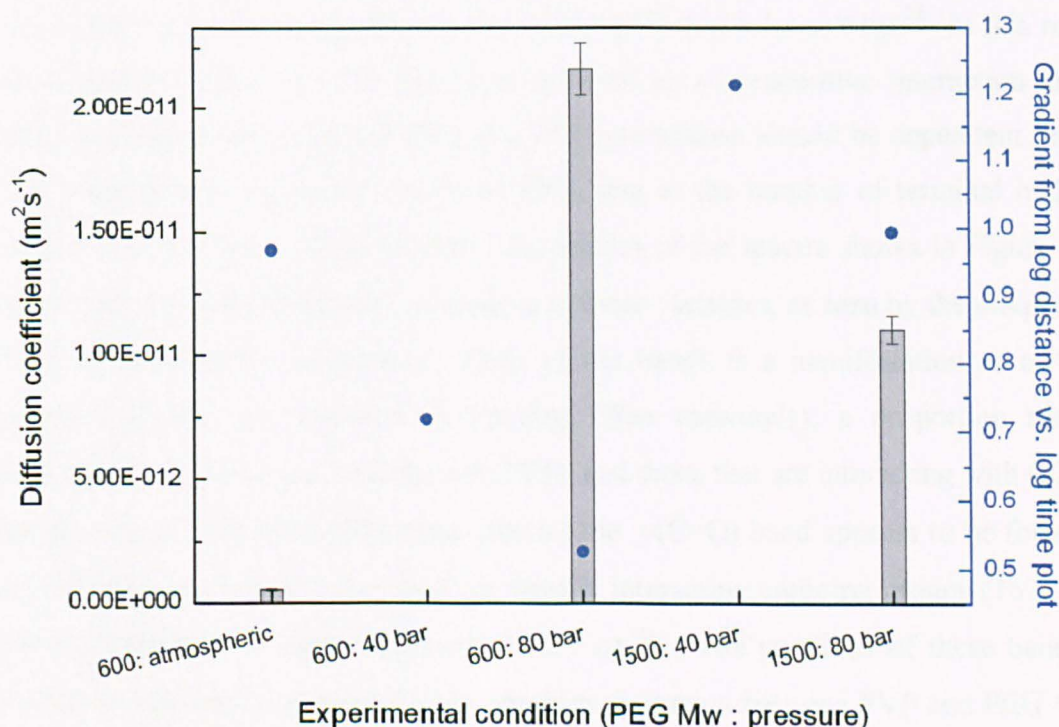


Figure 10.11. Summary of diffusion coefficients (grey bars) and exponents of log distance vs. log time plot (characteristic of diffusion mechanism) for each experimental condition.



*Specific intermolecular interactions.* The advantage of FTIR spectroscopy is the ability to examine the system at the molecular level and hence evaluate intermolecular interactions. Such an analysis allows one to relate the observed bulk diffusion characteristics with intermolecular interactions occurring in the ternary system. This analysis focuses on the  $\nu(\text{C=O})$  of PVP, due to the involvement of the oxygen atom of the carbonyl group of PVP in hydrogen bonding with the terminal OH groups of PEG.<sup>25</sup> The presence of the hydrogen bonding results in the shift of the  $\nu(\text{C=O})$  band to a lower-wavenumber region.

To assess the strength of interaction occurring between the polymers, spectra containing all three components of the system have been extracted from the interfacial area. The  $\nu(\text{C=O})$  region corresponding to spectra extracted from the interfacial regions of images that were measured after the equilibrium concentration of CO<sub>2</sub> had been achieved are shown in Figure 10.12. The observed changes in the spectral features of the  $\nu(\text{C=O})$  band are due to contributions from hydrogen bonding and weak Lewis acid-base interactions with CO<sub>2</sub> molecules, as demonstrated in a similar system.<sup>25</sup> In this respect the carbonyl oxygen of PVP can be considered as a competitive interaction site, at which a stoichiometric ratio of PEG and CO<sub>2</sub> interactions should be dependent on both CO<sub>2</sub> pressure and molecular weight of PEG, due to the number of terminal hydroxyl groups a consequence of this variable. Inspection of the spectra shown in Figure 10.12 reveals that the  $\nu(\text{C=O})$  indeed is sensitive to these variables, as seen by the unique band shape under different conditions. Each of the bands is a manifestation of carbonyl groups that are: not involved in bonding (free carbonyls); a proportion that are participating in hydrogen bonding with PEG; and those that are interacting with CO<sub>2</sub>. In the absence of CO<sub>2</sub> (PEG 600: atmospheric) the  $\nu(\text{C=O})$  band appears to be formed of two features, presumably the “free” or weakly interacting carbonyl groups (1671 cm<sup>-1</sup>) and the hydrogen bonded component (1656 cm<sup>-1</sup>). The positions of these bands are consistent with those reported for the complex formation between PVP and PEG 400 in the absence of CO<sub>2</sub>.<sup>271,272</sup> At this condition, the spectrum shows the largest contribution from the hydrogen bonded carbonyls. This confirms that the amount of hydrogen bonding is greater with PEG 600 compared to 1500 as a result of the number of the terminal hydroxyl functionalities available. In the presence of CO<sub>2</sub>, the relative ratio of the two components changes, which may be attributed to the competition of CO<sub>2</sub>

interacting with the carbonyl group of the PVP molecules. The number of hydrogen bonded carbonyl groups is reduced at greater pressure, indicated by the reduction in the absorption band ( $1656\text{ cm}^{-1}$ ) as a function of increasing pressure (80 bar shows the lowest degree of hydrogen bonding). This is molecular level evidence for the origin of the observed increase in diffusion coefficient of PEG 600 with increasing CO<sub>2</sub> pressure, as not only does the increase in free-volume act to accelerate the transport by “molecular lubrication”, but additionally the degree of “molecular friction” occurring between the polymeric components via H-bonding is reduced. As expected, the changes of the  $\nu(\text{C=O})$  bands shown for PEG 1500 confirm that the extent of hydrogen bonding is significantly reduced in comparison with PEG 600.

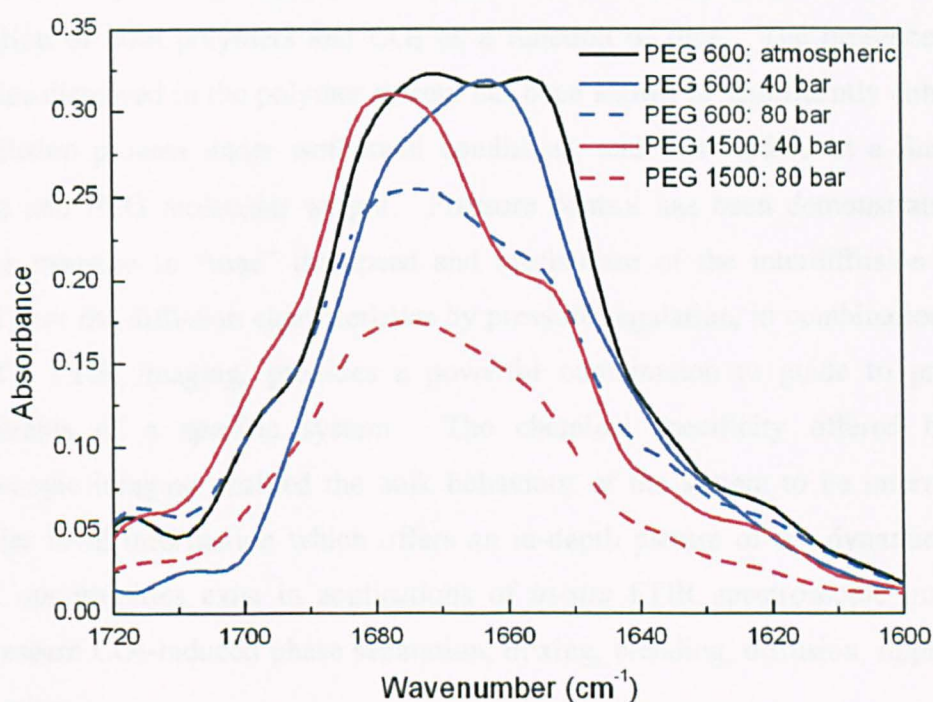


Figure 10.12. ATR FTIR spectra of PVP in the  $\nu(\text{C=O})$  region extracted from the interfacial region with PEG for the experimental conditions indicated.

The reduction of “molecular friction” present may enable the progression of PEG 1500 in a less hindered manner than 600 which interacts with PVP more strongly. This is not observed at 80 bar due to the carbonyl groups being sufficiently shielded by CO<sub>2</sub>, and hence PEG diffuses at a significantly accelerated rate in addition to the reduction of chain entanglement. This highlights the importance of considering both the molecular



dimensions of the components of the system and the strength of the interaction. The effect of CO<sub>2</sub>-enhanced diffusion of PEG in PVP is similar to that observed for the enhancement of diffusion of dyes in other glassy polymers,<sup>81</sup> however, it is the first time that this effect was related to polymer interdiffusion which was visualised with spectroscopic imaging.

#### 10.4. CONCLUSIONS

The application of *in situ* ATR FTIR spectroscopic imaging to investigate the interdiffusion process in a miscible polymer system (PVP/PEG) in the presence of high-pressure and supercritical CO<sub>2</sub> has been realised. This chemical imaging approach enabled the study of a dynamic system *in situ* and to simultaneously measure the spatial distribution of both polymers and CO<sub>2</sub> as a function of time. The presence of CO<sub>2</sub> molecules dissolved in the polymer system has been shown to significantly enhance the interdiffusion process under isothermal conditions, and was studied as a function of pressure and PEG molecular weight. Pressure control has been demonstrated as an effective measure to “tune” the speed and mechanism of the interdiffusion process. Control over the diffusion characteristics by pressure regulation, in combination with *in situ* ATR FTIR imaging, provides a powerful combination to guide to processing requirements of a specific system. The chemical specificity offered by FTIR spectroscopic imaging enabled the bulk behaviour of the system to be interrelated to molecular level information which offers an in-depth picture of the dynamic system. Further opportunities exist in applications of *in-situ* FTIR spectroscopic imaging to high-pressure CO<sub>2</sub>-induced phase separation, mixing, blending, diffusion, impregnation and foaming.

## **CHAPTER 11**

# **ATR FTIR IMAGING OF CO<sub>2</sub>-INDUCED POLYMER BLEND PHASE SEPARATION**

## 11. ATR FTIR IMAGING OF CO<sub>2</sub>-INDUCED POLYMER BLEND PHASE SEPARATION

### 11.1. INTRODUCTION

This chapter explores distribution of components in a binary polymer blend system during exposure to high-pressure CO<sub>2</sub> using *in situ* ATR FTIR imaging. The success of exploiting the favourable processing capabilities of CO<sub>2</sub> requires a detailed understanding of the phase behaviour and the associated processing window. The function of CO<sub>2</sub> to adjust the phase behaviour in polymer blend systems was introduced in section 3.4. The critical temperature identifies the conditions where a polymer system becomes miscible and hence defines the processing window. The presence of CO<sub>2</sub> in UCST polymer blends has shown to enhance blend miscibility.<sup>157</sup> Conversely, the effect of CO<sub>2</sub> sorption in LCST blends acts to depress the lower critical solution temperatures of the polymer system.<sup>159</sup> These characteristics lead to comparisons of CO<sub>2</sub> sorption with the effect of heating the system. ATR FTIR imaging offers substantially more information than visual observations of cloud points.<sup>273</sup> In systems of suitable domain size, ATR imaging enables the size of the polymer domains to be assessed and the morphology of the system to be scrutinized. Knowledge of the phase behaviour of polymer blends in the presence of high-pressure or scCO<sub>2</sub> is vital to optimise the processing conditions when the use of scCO<sub>2</sub> polymer processing technology is desired.

The pharmaceutical industry presents an ideal sector for scCO<sub>2</sub> technology impact. Therefore, the system chosen to study effect of high-pressure CO<sub>2</sub> on phase behaviour involves biodegradable polymers of interest for pharmaceutical applications. The polymer system investigated is a blend of poly( $\epsilon$ -caprolactone) and poly(D,L-lactide-co-glycolic acid). *In situ* ATR FTIR imaging is applied to study the phase separation in this PCL/PLGA system during exposure to high-pressure CO<sub>2</sub>.

## 11.2. EXPERIMENTAL

Poly(D,L-lactic-co-glycolic acid) (PLGA) ( $M_w = 90,000$ - $126,000$ ) was purchased from Birmingham Polymers Inc. (Alabama, USA) and Poly(caprolactone) (PCL) ( $M_w = 114,000$ ) was purchased from Sigma Aldrich. The chemical structures of PLGA and PCL are presented in Figure 11.1. A solution of PCL (30 wt%)/PLGA in chloroform was prepared and cast directly onto the diamond at 40°C. The blend composition selected was identified from a study performed by Sung et al.<sup>274</sup> who investigated phase separation as a function of temperature and composition. The composition selected was shown to result in a suitable domain size for the spatial resolution of this ATR imaging approach. The ATR cell and pressure rig described in section 5.2 was used for this investigation.

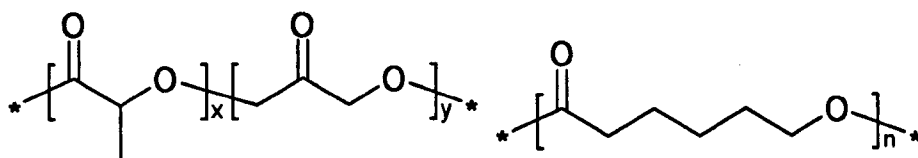


Figure 11.1. Chemical structure of PLGA (left) and PCL (right).

Fourier transform infrared images were collected using a 64 x 64 focal plane array (FPA) detector through the diamond ATR accessory in a macro chamber with a step scan spectrometer as previously described. Spectra were recorded using 5 coadditions with a spectral resolution of 8 cm<sup>-1</sup> which took ca. 3 minutes to acquire an image.

## 11.3. RESULTS AND DISCUSSION

ATR FTIR spectra of the pure polymers are presented in Figure 11.2. Spectral overlap hinders the selection of a region that is contributed solely from either of the polymers. The 1732-1800 and 1226-1253 cm<sup>-1</sup> spectral region were used to study the distribution of PLGA and PCL respectively. Spectral differences were present in the C-H stretching mode region, however, the signal was not sufficient to generate images of adequate quality.



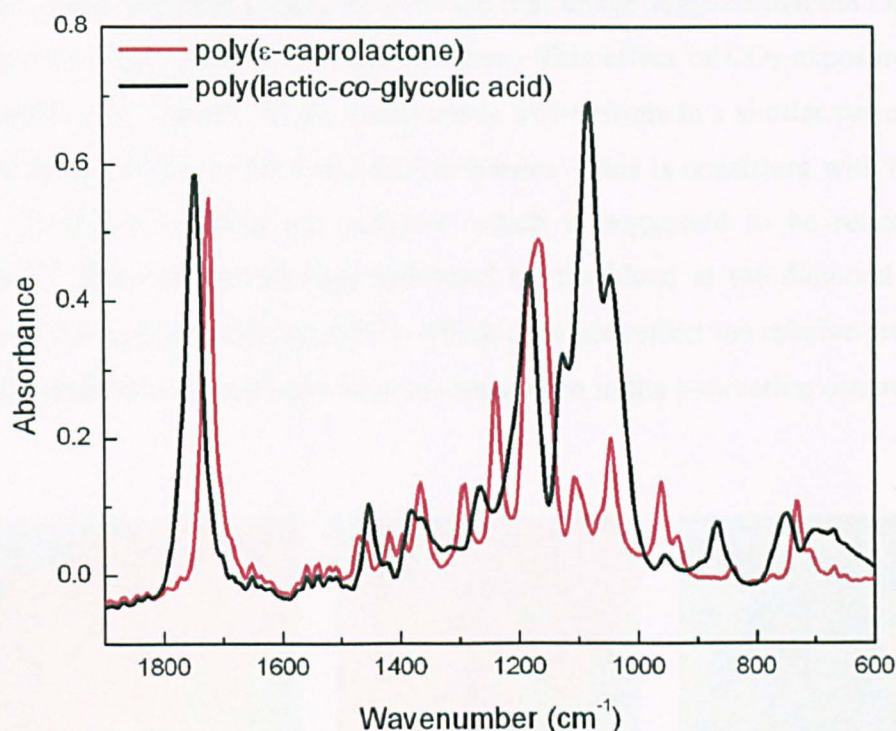


Figure 11.2. ATR FTIR spectra corresponding to PCL (black) and PLGA (red)

The series of images of the PCL/PLGA blend presented in Figure 11.3 are based on the distribution of PLGA. In the first image (measured in the absence of CO<sub>2</sub>) the distribution of PLGA appears almost homogeneous in the field of view. Although not entirely homogeneous, the exposure to 60 bar of CO<sub>2</sub> results in phase separation of the blend where a departure from the initial distribution is observed. The contrast in the images provides a measure of the approximate dimensions of the polymer domains in the x-y plane but offers no information regarding the height or z-dimension of the domain geometry. The architecture of the blend is seen to pass through a transitional morphology (after 12 minutes) consisting of relatively small domains of PCL dispersed within the PLGA matrix. Further separation forms the morphology presented in the image measured following 51 minutes after the addition of CO<sub>2</sub>, showing isolated PLGA domains of various dimensions. The largest domains are circular with a diameter of ca. 300  $\mu\text{m}$ . It should be noted that this morphology was apparent, with minor differences, after 23 minutes CO<sub>2</sub> exposure (not included). The observed behaviour of the polymer blend system is indicative of a LCST system where an increase in temperature, or in this case increase of CO<sub>2</sub> pressure, results in phase separation.



The partial phase separation apparent from the first image suggests that the LCST of the system is lower than 40°C at this composition. This effect of CO<sub>2</sub> exposure has been rationalised by the disparity in the components free-volume in a similar system<sup>34</sup> due to relative affinity of CO<sub>2</sub> to the individual polymers. This is consistent with the relative number of carbonyl groups per polymer which is suggested to be related to CO<sub>2</sub> solubility.<sup>239</sup> The final morphology exhibited by the blend at the diamond surface is seen to predominantly comprise of PCL which does not reflect the relative proportion of the blend composition, implying that some separation in the z-direction occurred.

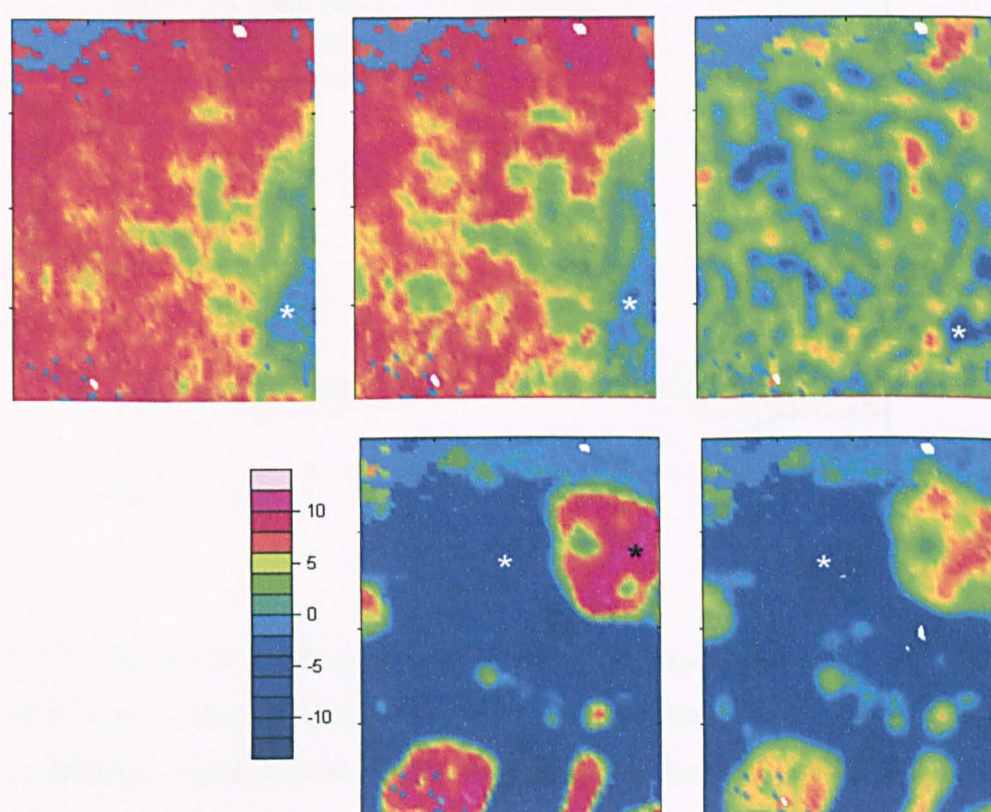


Figure 11.3. ATR FTIR images reflecting the distribution of the integrated absorbance of the spectral band indicative of PLGA. The images correspond to (clockwise from top left image) the system in the absence of CO<sub>2</sub>, 3 minutes after pressurisation to 60 bar, 12 minutes, 51 minutes and after depressurisation.

The composition of the PCL-rich domains has been assessed by extracting FTIR spectra from the regions of low PLGA absorbance (indicated by a white asterisk) from the ATR FTIR images. Inspection of the extracted spectra presented in Figure 11.4 enables the relative fraction of PCL and PLGA in the measured layer adjacent to the diamond crystal to be assessed.

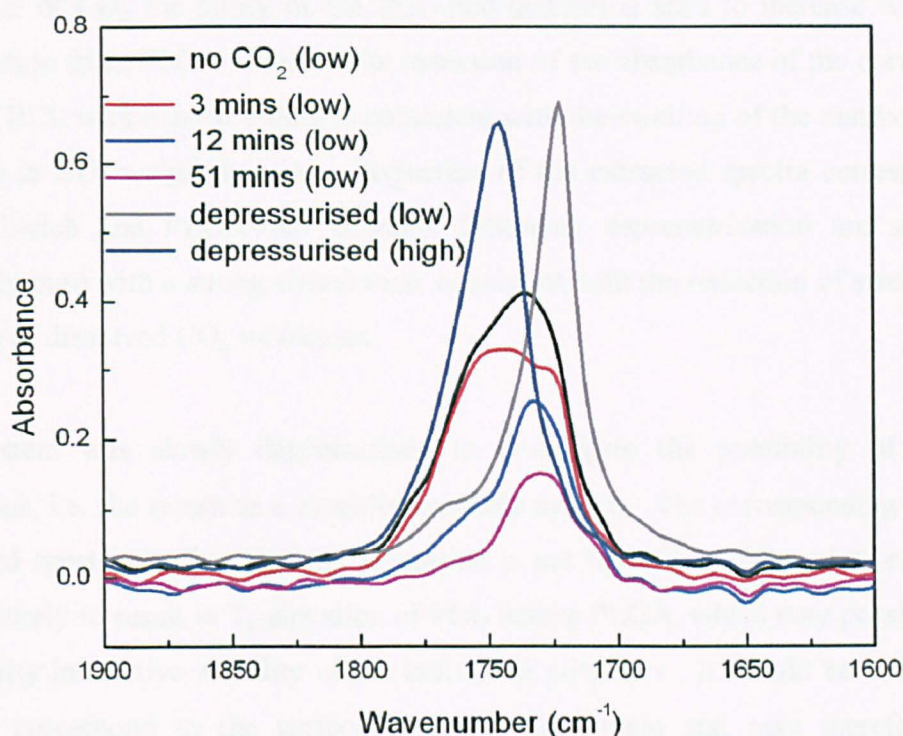


Figure 11.4. Extracted FTIR spectra in the  $\nu(\text{C}=\text{O})$  region from the blue positions indicated by white asterisks in the ATR FTIR images presented in the Fig. 11.2. The spectrum labelled depressurised (high) was extracted from the PLGA rich domain indicated by the black asterisk.

Prior to exposure to CO<sub>2</sub>, the PCL-rich domain is seen to comprise of a mixture of both polymers and thus full phase separation is not apparent. The greater contribution of the lower wavenumber component of the broad band at ca. 1735 cm<sup>-1</sup> is indicative of a higher concentration of PCL in the mixture. Following 3 minutes exposure to CO<sub>2</sub>, the absorbance decreases due to swelling by CO<sub>2</sub> and changes to the band shape are apparent. The  $\nu(\text{C}=\text{O})$  region consists of contributions from the bands corresponding to



the “free” polymer carbonyl groups, polymer-polymer interacting carbonyl groups and polymer-CO<sub>2</sub> interacting carbonyl groups. The apparent increase from the higher-wavenumber contribution in the spectrum shown in red (3 mins (low)) may be due to the relatively greater number of CO<sub>2</sub> molecules interacting with PLGA. The greater number of carbonyl groups per monomer unit would result in a red shift for the  $\nu(\text{C=O})$  band of PLGA, which may explain the observed band shape. After 12 minutes exposure to 60 bar of CO<sub>2</sub> the purity of the PCL-rich domain is seen to increase whereby the contribution from PLGA is less. The reduction of the absorbance of the corresponding band of PCL with exposure time is consistent with the swelling of the matrix due to the increase in CO<sub>2</sub> weight fraction. Inspection of the extracted spectra corresponding to the PCL-rich and PLGA-rich domains following depressurisation are seen to be relatively pure with a strong absorbance, consistent with the reduction of swelling in the absence of dissolved CO<sub>2</sub> molecules.

The system was slowly depressurised to investigate the possibility of reversible behaviour, i.e. the return to a partially miscible system. The corresponding image and extracted spectra confirm that the separation is not reversible. The relative affinity of CO<sub>2</sub> is likely to result in  $T_g$  elevation of PCL before PLGA, which may possibly lead to a disparity in relative mobility of the individual polymers. It should be noted that the images correspond to the surface layer of the sample and may therefore not be representative of the bulk material, especially the unrestrained surface of the polymer system.

#### 11.4. CONCLUSIONS

The behaviour of a PCL/PLGA polymer blend in the presence of high-pressure CO<sub>2</sub> has been investigated using *in situ* ATR FTIR imaging. The departure from the initial spatial distribution of the two components of the partially miscible polymer system was visualised at various times to study the phase separation. The phase separation was shown to occur through an intermediate morphology, consisting of small PCL domains dispersed within a PLGA matrix. The final blend morphology consisted of isolated PLGA domains, ca. 300  $\mu\text{m}$  in diameter, dispersed within a PCL matrix.



This feasibility study demonstrates the promise of this *in situ* imaging approach to investigate the dynamics of phase separation induced by high-pressure CO<sub>2</sub> in this LCST system. A further study would require the influence of temperature, pressure, polymer molecular weight and polydispersity to be investigated. This form of analysis would enable the processing window for the system to be defined at various compositions and thus enable process optimisation.

## **CHAPTER 12**

# **GENERAL CONCLUSIONS AND FUTURE WORK**

## 12.1 GENERAL CONCLUSIONS

The results presented in this thesis contribute towards the advance in understanding of polymer processing with high-pressure and  $\text{scCO}_2$  in three main areas:  $\text{CO}_2$ -induced morphological alterations in semicrystalline polymers, impregnation of polymeric material with doping solutes and the interdiffusion of miscible polymer systems in the presence of  $\text{CO}_2$ . The general strategy employed to deliver the objectives detailed in section 1.2 was the application of advanced vibrational spectroscopy to reveal the distribution of chemical species in the polymeric materials in order to elucidate key features of the  $\text{CO}_2$  processing route. The chemical specificity inherent to the spectroscopic methods employed has enabled quantitative and qualitative measurements to be performed and thus the distribution of components has been studied with molecular level insight. In the following section the main findings of this research are summarised in line with the project objectives.

The processing of semicrystalline polymers with  $\text{CO}_2$  was one of the main focuses of this research.  $\text{CO}_2$ -induced morphological alterations in PET have been investigated using a combination of CRM, Raman mapping and transmission FTIR imaging. The presence of a significant morphological gradient in PET as a function of depth normal to the film surface was revealed. The application of the oil immersion objective for CRM measurements proved to be highly successful to study the distribution of  $\text{CO}_2$ -modified PET in a non-destructive manner. The reliability of the oil immersion CRM approach was validated using conventional Raman point mapping and transmission FTIR imaging of polymer film cross-sections, providing substantiating support for the formation of a morphological gradient with a relatively large field of view. The influence of exposure time, temperature and pressure on the evolution of the morphological gradient was studied. The ability to tailor the morphology of the surface region in PET film by manipulation of the processing conditions was demonstrated.

Practical implications to the surface layer modification of the polymer morphology, whilst leaving the bulk material unchanged, may result in enhanced barrier properties. The importance of gas permeability in PET is of high industrial interest due to the application of PET in the carbonated beverage industry. In applications where the

required change in permeability may be obtained through surface modification, CO<sub>2</sub> processing enables the minimum amount of material to be modified by controlling CO<sub>2</sub> diffusion through the polymer. The required conditions for this level of customisation/morphological tailoring may be guided using CRM with the oil immersion objective.

For the first time, the combination of the oil immersion objective with CRM was applied to study the impregnation of solutes from a scCO<sub>2</sub> solution. PET films impregnated with azo-dye (DR1) from a scCO<sub>2</sub> solution were studied using CRM to generate concentration profiles of DR1 in the polymer as a function of time and space. A one-dimensional Fickian diffusion analysis was performed on this model system generating quantitative information regarding the diffusion coefficient of the dye in the polymer as a function of temperature and pressure. Details of the mass transfer characteristics within the fluid phase were also established via analysis of the spatially resolved dye distribution data, highlighting the advantages of the non-destructive CRM approach over total mass uptake measurements. The ability to study the impregnation of a multi-component solute system was demonstrated for PET impregnated with 2 disperse dyes from a scCO<sub>2</sub> solution. The chemical specificity of Raman spectroscopy enabled the distribution of both dyes to be resolved simultaneously as a function of depth. Multivariate analysis of the depth profile data using the classical least squares approach was presented, indicating the potential to investigate the diffusion of solutes with heavily overlapping spectral bands.

The applicability of the CRM approach to investigate the distribution of solutes impregnated in other polymer systems was also explored. The impregnation of syndiotactic polystyrene with DR1 revealed the challenges associated with studying polymers with a very low dye loading. Nonetheless, the distribution of impregnated dye was readily available by mapping along the microtomed cross-section. Comparison of the dye loading in PET and sPS films impregnated under identical conditions was related to possible differences in the strength of interaction between the dye and these two polymers. The suitability of the oil immersion CRM approach was also investigated to study the distribution of a model drug impregnated into a low-T<sub>g</sub> polymer matrix. The system exposed significant limitations due to the migration of the immersion oil through the sample during the measurement. In consequence, contamination of the



sample occurred and hence the non-destructive benefits associated with the technique were lost. Moreover, the distribution of the impregnated solute was disrupted, presumably due to entrainment in the diffusing oil. However, the combination of transmission FTIR imaging and Raman mapping of microtomed samples provided a complementary analysis of the sample, albeit in a destructive manner.

The *in situ* investigation of polymeric materials in the presence of high-pressure and scCO<sub>2</sub> was studied using ATR FTIR imaging. The main focus of this approach was the study of a miscible PVP/PEG system. For the first time, the use of ATR FTIR imaging has been applied to visualise the dynamics of polymer interdiffusion subjected to high-pressure CO<sub>2</sub>. The ability to visualise each of the components in the ternary system enabled the diffusion mechanism to be explored as a function of polymer molecular weight and CO<sub>2</sub> pressure. The opportunity to control the diffusion mechanism and the diffusion coefficient with CO<sub>2</sub> pressure was demonstrated, exemplifying the “tuneable” control offered when employing CO<sub>2</sub> technology. The observed diffusion characteristics obeyed by the system were substantiated by assessing the  $\nu(\text{C}=\text{O})$  region of extracted FTIR spectra which served as probe of the relative interaction strength between the components in the ternary system. This chemical specific detail is valuable for the interpretation of the macroscopic properties of a dynamic system. The feasibility to apply ATR FTIR *in situ* imaging to study CO<sub>2</sub>-induced crystallisation in PET and the example of the phase separation in a LCST polymer blend was also demonstrated. The ATR FTIR imaging approach has enormous potential for investigating the influence of CO<sub>2</sub> on other polymer systems in a quantitative manner. Applying the experimental approaches described in this thesis may permit the elucidation of the influence of processing conditions on other specific systems with a molecular level insight.

In summary, the chemical specificity combined with the spatially resolved sampling capability offered by the advanced vibrational spectroscopic techniques employed has enabled key features of the CO<sub>2</sub> processing route to be elucidated. The results presented highlight the “tuneable” nature of CO<sub>2</sub> processing and the suitability of the specific techniques employed to investigate the systems. The application of advanced spectroscopic techniques has provided valuable information on the chemical and physical characteristics of the processed polymeric materials, and exemplified generic methodologies to investigate CO<sub>2</sub>-processed systems.

## 12.2 FUTURE WORK

In the following section suggestions are made for future investigations based on the work presented in this thesis. Examples of CO<sub>2</sub> processed polymeric material that would benefit from advanced spectroscopic analysis are detailed. Recommendations for future developments are suggested for particular systems where the generic approaches established in this work may be applied. Possible technical improvements/adaptations to overcome the experimental challenges experienced are outlined.

The implementation of CRM during the design and testing of impregnated polymeric materials will be extremely valuable due to the rich information content that can be derived in relation to the mass transport properties of the process. The non-invasive depth profile measurements yield information to guide the design of the material to achieve the required solute distribution and loading level. The morphological sensitivity of the technique offers the potential to assess the molecular state of the impregnated solute and morphology of the matrix and thus molecular level assessment of the sample is possible. The ability to study accurately the sample in a non-destructive manner is desirable when working with a limited amount of material so that subsequent analysis by different techniques is possible or even additional processing steps may be performed after which it may be measured again. In general, CRM would be suited to investigate polymers with a non-uniform distribution of impregnated solutes including multi-component dye systems, flavours, fragrances and pesticides. The study of samples with possible skin-core structural differences could also be suitable with CRM. The characterisation of polymers extruded under high-pressure CO<sub>2</sub> would establish the homogeneity of the samples thereby investigating the possible implication of wall effects.

Advanced polymer systems for use in pharmaceutical formulations and biomaterial application would be ideal candidates for CRM study. The preparation of these materials will involve the impregnation of a biocompatible polymer matrix with the desired release properties with drugs, nutrients, hormones and growth factors or a multi-component mixture of solutes. The precise nature of the processing route will be dependent on the final application of the material e.g. scaffolds for tissue engineering

prepared via foaming. The performance of the material will be measured in terms of satiating the demand of the growing culture/tissue and will be highly dependent on the distribution and release of the impregnated solutes. The application of CRM to probe the diffusion and distribution of the impregnated solutes should yield valuable information to be interpreted together with the material performance data to optimise the design of the polymer system. Furthermore, the potential to establish the morphology of the host matrix and the active solute is valuable information to inter-relate the performance of the material and to provide information to guide the selection of the necessary processing conditions. Analysis of the time dependence of the surface concentration should provide an effective measure of the mass transport characteristics of the CO<sub>2</sub> fluid phase. This information could be used to investigate the influence of a co-solvent on the fluid phase mass transport properties. Furthermore, CRM could be used to establish the extent of solvent diffusion within the matrix and to correlate it with the solute diffusion. This method would determine the suitability of operating with a co-solvent in line with the material specification and requirements and thus ensuring the performance and reproducibility of these advanced CO<sub>2</sub> processed polymer systems.

The potential of the *in situ* ATR FTIR imaging approach to investigate the diffusion of CO<sub>2</sub> and the ensuing morphological implications in PET was demonstrated in section 6.3. The desire to realise this experimental approach stems from the valuable information that would be available for quantitative analysis and the elucidation of the dynamics of CO<sub>2</sub>-induced morphological behaviour. The main experimental limitation identified was the application of the required contact load. Both the uniformity and magnitude of the force need to be controlled in a measurable and reproducible manner to successfully study the CO<sub>2</sub>-induced phenomena. As previously described, the load must satisfy the contact required to ensure that CO<sub>2</sub> does not leak into the diamond/PET interface whilst not acting to inhibit the mobility of polymer chains normally available in a free-standing film. A possible approach would be the use of a piezoelectric drive to apply the load directly to the polymer film surface in a calibrated manner. The success of this approach should enable the study of various film thicknesses and the influence of temperature, pressure and load on the dynamic system to be elucidated. The realisation of this approach would have tremendous potential for applications such as the diffusion of multi-component gases, the influence of co-solvents and the impregnation of

polymeric matrices with doping solutes. The ability to simultaneously visualise the distribution of the various chemical species in the system and their intrinsic morphology would yield valuable data for modelling purposes.

Further investigations of CO<sub>2</sub>-induced phase separation using a combination of *in situ* ATR FTIR imaging and Raman microscopy would be a powerful arrangement to determine how representative the FTIR image, measured at the diamond surface, is of the phase separated system. A sapphire window would permit the investigation of the “upper” surface through the fluid phase. The implementation of Raman global imaging or point mapping would enable the morphology of the polymer blend to be assessed. Comparison of the distribution measured by ATR imaging and Raman microscopy would determine the possible influence of the ATR crystal on the observed distribution and potentially lead to a complementary analysis of the dynamics of CO<sub>2</sub>-induced phase separation.

Finally, the area of high-throughput technology would be extremely valuable for the development of scCO<sub>2</sub> technology to enable rapid screening of many samples simultaneously. The power of ATR imaging to screen many samples arranged on the crystal in an array fashion has been demonstrated.<sup>239</sup> This approach may possibly be applied to materials processed with scCO<sub>2</sub> to allow the influence of experimental variables to be elucidated along a property gradient e.g. morphology, molecular weight, polydispersity etc. The realisation of this technology will enable the variables required for material and product optimisation to be identified rapidly.



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