

ORIGINAL ARTICLE

Detection of melting point depression and crystallization of polycaprolactone (PCL) in scCO₂ by infrared spectroscopy

Catherine A Kelly¹, Katherine L Harrison², Gary A Leeke¹ and Mike J Jenkins²

The use of supercritical CO₂ to facilitate the processing of polymers is becoming increasingly popular. In light of this, it is important to understand the effect supercritical CO₂ has on these polymers especially in terms of glass transition temperature and melting point depression and the induction of crystallization. The aim of the current study is to use infrared spectroscopy to probe these properties. Plaques of polycaprolactone were exposed to supercritical CO₂ at a range of temperatures (41–60 °C) and pressures (0–200 bar). Examination of the carbonyl peak at 1720 cm⁻¹ at 41 °C while increasing the pressure shows a change in morphology at 100 bar, indicative of a melting point. This is a 22 °C reduction in the melting point compared with atmospheric pressure. Repetition of this experiment over a range of temperatures shows that the pressure required to induce melting reduces as the temperature is increased. Infrared spectroscopy is also used to observe the crystallization of polycaprolactone during the depressurization of CO₂.

Polymer Journal (2013) 45, 188–192; doi:10.1038/pj.2012.113; published online 6 June 2012

Keywords: IR; melting point depression; polycaprolactone; polymer; supercritical fluids

INTRODUCTION

The use of supercritical carbon dioxide (scCO₂) to facilitate polymer processing is widespread particularly in the production of scaffolds and particles for medical applications.^{1–3} scCO₂ is able to plasticize and liquefy polymers, at temperatures below the normal glass transition and melting temperatures, thereby allowing in some cases, the incorporation of thermally sensitive compounds.⁴ scCO₂ can also reduce the melt viscosity,⁵ change the polymer morphology by inducing crystallization⁶ and can be used to create foams.⁷

The plasticizing effect has been attributed to the ability of scCO₂ to dissolve within amorphous polymers whereupon it interacts with basic sites on the polymer chains.^{5,8} This is similar to Lewis-acid/base interactions and has been shown to occur between CO₂ and carbonyl groups.^{9,10} Such interactions reduce the intermolecular bonding between polymer chains and increase the mobility of the polymer segments,¹¹ leading to depressions of the glass transition temperature (T_g).¹² For example, it has been reported that the T_g of poly(ethylene terephthalate) can be lowered by as much as 40 °C in the presence of scCO₂.¹³

The role of scCO₂ in semicrystalline polymers is less understood. It is assumed that the gas molecules preferentially penetrate into the amorphous regions, where Lewis-acid/base interactions occur between the polymer and CO₂.⁹ This leads to a reduction in the chemical potential of the amorphous regions, driving the morphology

to a more amorphous state and therefore reducing the crystallinity. This results in a depression of the melting point.^{14–16} In addition, scCO₂ is known to weakly solvate the molecular segments of the polymer and behave as a molecular lubricant. It has been suggested that the presence of CO₂ at the surface of the polymer crystals enhances the mobility of the polymer molecules, reducing the effective time for the polymer molecules to reach a pure molten phase. These effects have been shown to reduce the melting point of polyethylene glycol by 9 °C at a pressure of ~240 bar.¹⁷

In addition to acting as a solvent to reduce the processing temperature of polymers, scCO₂ is also known to induce crystallization.⁶ Crystallization will occur in the amorphous regions of semi-crystalline polymers, when the operating temperature is above the T_g but below the melting temperature of the polymer. Upon heating a polymer above its T_g , there is a sharp increase in the mobility of the polymer chains, allowing the chains to rearrange into the more thermodynamically stable crystalline state.¹⁸ The crystallization temperature of numerous polymers have been seen to decrease in the presence of scCO₂.^{6,19,20} It is believed that the absorbed CO₂ increases the free volume of the amorphous regions as discussed above, enabling greater chain mobility than at ambient pressure. This allows the ordinarily rigid chains to rearrange into a more kinetically favored state at lower temperatures, forming lower free energy, crystalline structures.

¹School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, UK and ²School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, UK

Correspondence: Dr MJ Jenkins, School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham-B15 2TT, UK.

E-mail: m.j.jenkins@bham.ac.uk

Received 13 February 2012; revised 26 April 2012; accepted 6 May 2012; published online 6 June 2012

The real-time conformational and structural changes that occur during scCO_2 processing can be investigated by infrared spectroscopy (IR). Previous studies have shown that, as melting and crystallization occurs in polymers, the intensities of some functional group bands change and can also shift in frequency.^{21,22} This frequency shift has been attributed to morphological changes between the amorphous and crystalline states.

We have previously shown that IR can be used to determine the melting point and crystallization temperatures of polycaprolactone (PCL) with a good correlation to differential scanning calorimetry.²³ In this paper, we expand on this knowledge to determine the morphological changes experienced by PCL during scCO_2 processing. IR studies are used to investigate the melting point depression of PCL caused by the addition of CO_2 and the crystallization behavior upon venting.

MATERIALS AND METHODS

Materials

Polycaprolactone (CAPA 6800) (M_w 120 kDa; PDI 2.82) was supplied in pellet form by Solvay Interlox Ltd (Warrington, UK) and used as received. CP grade CO_2 (99.995% CO_2) was provided by BOC (Birmingham, UK).

Preparation of PCL plaques

Plaques of PCL were prepared using a Moore E1127 hydraulic hot press (George E. Moore & Sons Ltd, Birmingham, UK). The pellets (7 g) were compression-moulded at 150 °C using a load of 10 kN. The resulting plaques (100 mm \times 100 mm \times 1 mm) were then quenched by an ice/water bath and warmed to room temperature to create a known thermal history. The moulded polymer plaques were cut into 10 mm \times 10 mm \times 1 mm samples and stored at ambient conditions, in sealed containers, before analysis.

Infrared spectroscopy

Changes to the IR spectra of PCL with CO_2 pressure were monitored with a Nicolet 860 IR (ThermoScientific, Hemel Hemstead, UK) coupled to a Golden Gate ATR supercritical fluid analyser (Specac, Slough, UK) (Figure 1). The high-pressure cell (1 μm^3) was fitted with two 1/16" tubes to allow the introduction and venting of CO_2 . The temperature of the cell was controlled and monitored by a heater control unit (Specac, Slough, UK) with an accuracy of ± 0.1 °C. The pressure was measured using a Bourdon gauge (Budenberg, Manchester, UK) with an accuracy of ± 4 bar.

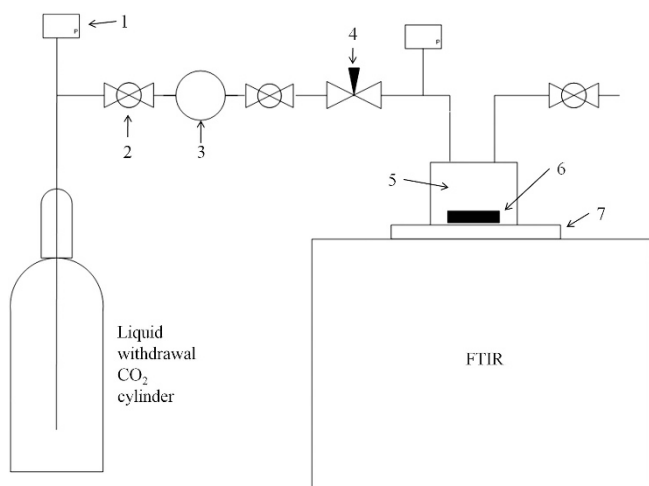


Figure 1 Diagram illustrating the high-pressure IR system: 1. pressure gauge; 2. ball valve; 3. high-pressure pump; 4. flow control valve; 5. high-pressure cell; 6. polymer sample and 7. heated plate.

Variation in the IR spectra of PCL with increasing pressure, at a series of isothermal temperatures, was investigated. Briefly, a PCL plaque was placed into the preheated cell. The temperature then remained constant while the pressure was varied from 0 to a maximum of 200 bar, in 10 bar increments. Samples were allowed to stabilize in the CO_2 environment for 10 min at each pressure before being scanned 200 times at a resolution of 2 cm^{-1} . Isothermal measurements were taken at 41, 46, 51, 56 and 60 °C and the variation in peak intensity of both the amorphous and crystalline carbonyl bands (~ 1720 cm^{-1}) were recorded as a function of pressure.

Crystallization induced by the venting of CO_2 at 41 °C was also evaluated. Spectra were taken every 2 s throughout the experiment, to generate a real-time profile of the conformation changes. Spectra were initially taken for 1 min prior to CO_2 being delivered to the cell. scCO_2 was then introduced to give a pressure of 160 bar, and spectra were recorded over a 1-min period. The cell was subsequently vented to atmospheric pressure over 5 min and the recording of the spectra continued for a further 4 min to ensure the complete removal of the CO_2 . Background spectra in the presence of CO_2 were also run and subtracted from the sample spectra.

RESULTS AND DISCUSSION

The IR spectra of polymers are sensitive to the local molecular environment and, as a result, can be used to distinguish between crystalline and amorphous morphologies. PCL displays three distinct regions in its spectrum (Figure 2). The two absorbances at ~ 2930 and 2850 cm^{-1} have been attributed to the asymmetric and symmetric stretching modes of the CH_2 groups in the gauche conformation, while the peak at 2906 cm^{-1} corresponds to the stretching vibration of the trans conformation.²⁴ PCL also displays a large peak at 1720 cm^{-1} , containing a shoulder at 1735 cm^{-1} , which is typical of the stretching vibration of free bonded carbonyls. The major peak is characteristic of a crystalline conformation, whereas the shoulder indicates an amorphous structure.^{25,26} The remaining region to note is that of the C–O stretch at 1500 – 1000 cm^{-1} . Although the main peak appears at 1200 cm^{-1} , it is the peak at 1100 cm^{-1} (circled) that provides conformation information about the morphology. This peak is characteristic of the C–O stretching vibration in gauche conformations and contains a shoulder at 1095 cm^{-1} that denotes the trans conformation.²²

Previously, we have successfully probed the region at 1720 – 1735 cm^{-1} , to observe the conformational changes that occur as PCL melts and subsequently recrystallizes.²⁴ It was therefore

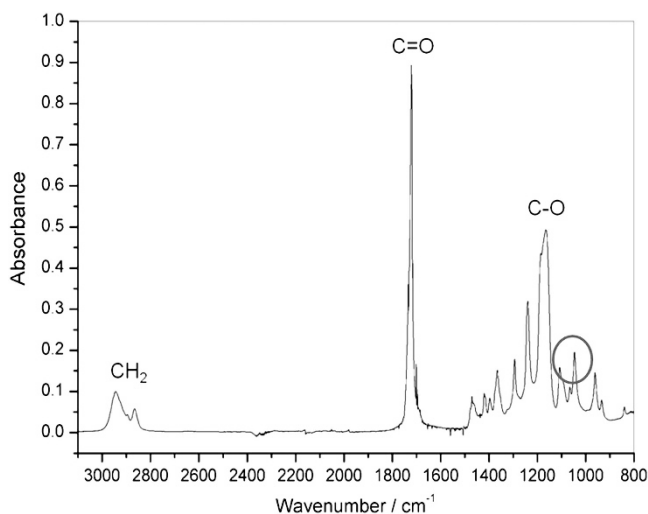


Figure 2 IR spectra of PCL highlighting the primary components.

postulated that CO₂-induced melting of PCL could also be detected. Plaques of PCL were placed inside the cell and subjected to 41 °C. The CO₂ pressure was increased from atmospheric pressure to 200 bar in 10 bar increments while continuously recording the IR spectra.

It was found that the characteristic conformational changes within the carbonyl region ($\sim 1720\text{--}1735\text{ cm}^{-1}$), previously associated with melting,²³ were observed as the CO₂ pressure increased (Figure 3). At atmospheric and low CO₂ pressures, a peak is observed at 1720 cm^{-1} indicative of a crystalline morphology. However, as the pressure is increased, the intensity of this peak reduces and the shoulder at 1735 cm^{-1} , indicative of an amorphous structure, becomes more prominent. Because the temperature remained constant throughout the experiment, this melting phenomena is a result of the pressure increase alone. Furthermore, PCL melts at $62\text{ }^{\circ}\text{C}$ ²³ under ambient pressures; however, in the presence of supercritical CO₂, melting is observed at $41\text{ }^{\circ}\text{C}$. The gaseous nature of CO₂ enables it to diffuse into the amorphous regions of the polymer chains. It undergoes Lewis acid/base interactions with the chains disrupting the intermolecular forces and, as a result, increasing the mobility of the chains. This reduces the chemical potential of the amorphous regions, shifting the equilibrium towards an amorphous morphology and thereby reducing the crystallinity of PCL.¹⁶ As the pressure is raised, and consequently the density of the CO₂ increased, the free volume difference between the polymer and CO₂ decreases causing the solvent power of the fluid to increase.¹⁸ As a result, the entropy of mixing becomes more positive thereby allowing a greater concentration of CO₂ to be absorbed into the polymer. This lowers the chemical potential of the amorphous morphology further leading to PCL displaying melting behavior.

Another interesting point to note is that a shift in the absorbance wavenumber is observed in the amorphous conformation as the pressure is increased but not in the crystalline morphology. This shows that CO₂ diffusion is limited to the amorphous regions and does not enter the crystal lattice.

This isothermal experiment was repeated for a range of temperatures to observe how the melting point depression of PCL in the presence of scCO₂ varied. The overlapping of the two carbonyl peaks prevented measurement of the absorbance of the crystalline peak

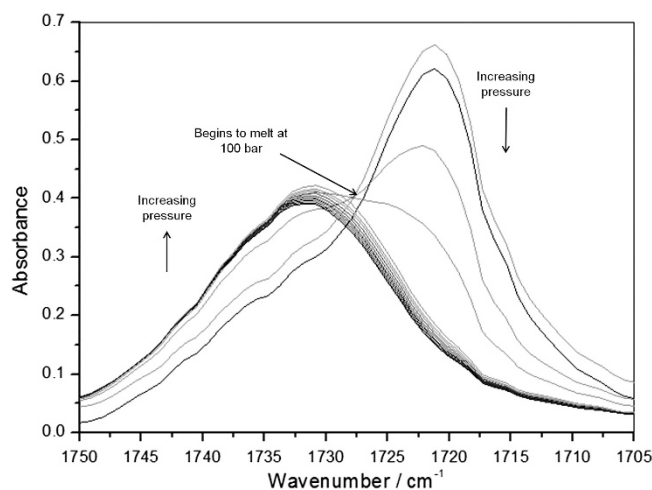


Figure 3 Characteristic conformation changes observed in the presence of scCO₂ at $41\text{ }^{\circ}\text{C}$. On raising the pressure to 200 bar in 10 bar increments, the peak at 1720 cm^{-1} decreases whereas the shoulder at 1735 cm^{-1} increases illustrating the transition from a crystalline morphology to an amorphous one.

following melting.²³ As a result, the pressure required to melt the material was taken as the point where the crystalline peak could no longer be resolved, that is, in this case, at $41\text{ }^{\circ}\text{C}$ at a pressure of 100 bar (Figure 3). The results (Figure 4) show that the CO₂ pressure required to melt PCL decreases as the temperature is raised with a 70-bar reduction observed on heating the polymer by $19\text{ }^{\circ}\text{C}$. An increase in temperature results in a concomitant increase in chain mobility, and, therefore, less CO₂ is needed to induce melting. Such a reduction of the polymer melting temperature has important implications, because it allows the viscosity of the polymer to be significantly decreased without additional heating. This has already enabled therapeutic agents such as proteins to be incorporated into polymers without degrading or denaturing.³

It is also interesting to note that, under the conditions adopted in this experiment, the CO₂ was not supercritical over the entire temperature and pressure range (Table 1). Despite this, the PCL melting point was still reduced on the addition of CO₂. This is because, at high temperatures, there is greater chain mobility which enables CO₂ to penetrate the amorphous phases of polymers at lower pressures.

The ability of CO₂ to induce crystallization is generally known.¹⁸ An excess of thermodynamic free energy within the system, owing to the presence of CO₂, drives the polymer chains from a disordered liquid phase into an ordered crystal phase. The onset of crystallization can therefore be generated by initiating a change in the thermodynamic state of the system by either lowering the temperature below a critical (crystallization) value or by supersaturation of the system through the venting of CO₂.

The ability of CO₂ to crystallize PCL was investigated using IR. Spectra were recorded as PCL was exposed to CO₂ and subsequently vented. Initially, the carbonyl band at 1720 cm^{-1} was observed indicating the presence of a crystalline morphology in the solid state. Upon introducing 160 bar CO₂, this peak shifted to 1735 cm^{-1} , indicative of an amorphous morphology, which shows that melting has occurred (Figure 5). This shift in peak wavenumber is not created by the CO₂ gas alone, as this displays a sharp peak 2300 cm^{-1} . On venting, PCL originally retained its amorphous nature, but as the pressure reduced further, it recrystallized. The spectra were recorded

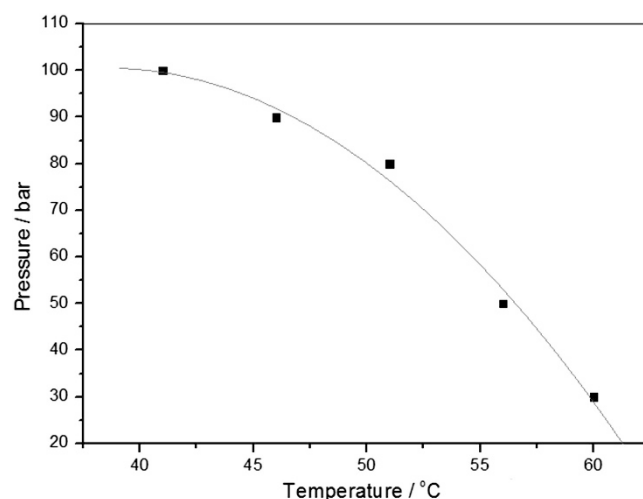
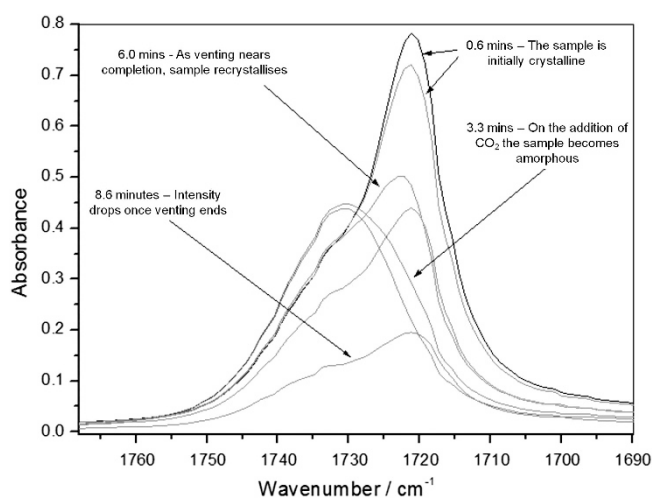


Figure 4 Pressure required to melt PCL at a range of isothermal temperatures. As the temperature of the system is increased, the pressure required to melt PCL reduces.

Table 1 Phase of CO₂ required to melt PCL at a range of temperatures and pressures

Temperature / °C	Pressure / bar	CO ₂ Density ²⁷ / g cm ⁻³	Phase
41	100	0.61	Supercritical
46	90	0.32	Supercritical
51	80	0.22	Supercritical
55	50	0.10	Vapour
60	30	0.05	Vapour


Figure 5 Pressurization and venting of CO₂ at 41 °C. PCL is initially crystalline; however, it becomes amorphous when 160 bar CO₂ is added. During the venting of CO₂, the sample initially stays amorphous and becomes crystalline as the venting nears completion (at ~10 bar CO₂).

for an additional 4 min following venting to ensure the complete removal of CO₂. During this time, PCL retained its crystalline nature. The addition of CO₂ plasticizes the amorphous regions of semicrystalline PCL. The increased mobility afforded by the chains following plasticization allows the amorphous regions to adopt a more kinetically favorable crystalline form. Upon venting, the more ordered configuration results in induced crystallization and concomitant changes in the morphology.¹²

This behavior follows the classical thermodynamics concept of nucleation described by Gibbs and extended to polymers by Turnbull and Fisher²⁸ (Equation 1):

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where ΔG is the Gibbs free energy, ΔH is the enthalpy change, T is the temperature, and ΔS is the entropy change.

At the melting point, the Gibbs free energy is zero and therefore the system is stable. However, below this temperature a system will spontaneously seek to minimize its free energy by undergoing crystallization.²⁹ This is also true during supercritical CO₂ processing. scCO₂ acts as a solvent and plasticizes the amorphous regions of PCL causing chain mobility similar to melting. When CO₂ is vented, fluctuations in the melt viscosity can overcome the Gibbs free energy barrier to nucleation and phase transformation begins when the free energy of crystallization becomes negative. This initially causes the formation of sub-critical nuclei by way of positive free energy of crystallization. The nuclei then grow spontaneously to the crystal size with an associated free energy, and a crystalline phase ensues.

CONCLUSIONS

IR spectroscopy is a powerful tool for detecting local molecular environments and has revealed the conformational changes of PCL in the presence of CO₂ and upon depressurization. This work has highlighted the ability of CO₂ to penetrate into the amorphous regions of semi-crystalline polymers and induce melting below the atmospheric melting temperature. The results show that the melting point decreases as the CO₂ pressure, and therefore density, are increased with the melting point being depressed by over 20 °C at 100 bar. Increasing the temperature of the polymer also reduces the pressure required to induce melting. IR has also shown the crystallization of PCL following the removal of CO₂.

- 1 Woods, H.M., Silva, M.M.C.G., Nouvel, C., Shakesheff, K.M. & Howdle, S.M. Materials processing in supercritical carbon dioxide: surfactants, polymers and biomaterials. *J. Mater. Chem.* **14**, 1663–1678 (2005).
- 2 Cooper, A.I. Polymer synthesis and processing using supercritical carbon dioxide. *J. Mater. Chem.* **10**, 207–234 (2000).
- 3 Jordan, F., Naylor, A., Kelly, C.A., Howdle, S.M., Lewis, A. & Illum, L. Sustained release hGH microsphere formulation produced by a novel supercritical fluid technology: *In vivo* studies. *J. Control. Release* **141**, 153–160 (2010).
- 4 Kikic, I., Vecchione, F., Alessi, P., Cortesi, A., Eva, F. & Elvassore, N. Polymer plasticization using supercritical carbon dioxide: Experiment and modeling. *Ind. Eng. Chem. Res.* **13**, 3022–3029 (2003).
- 5 Tai, H., Upton, C.E., White, L.J., Pini, R., Storti, G., Mazzotti, M., Shakesheff, K.M. & Howdle, S.M. Studies on the interactions of CO₂ with biodegradable poly(DL-lactic acid) and poly(lactic acid-co-glycolic acid) copolymers using high pressure ATR-IR and high pressure rheology. *Polymer* **51**, 1425–1431 (2010).
- 6 Liao, X., Wang, J., Li, G. & He, J.S. Effect of supercritical carbon dioxide on the crystallization and melting behavior of linear bisphenol A polycarbonate. *J. Polym. Sci. Pol. Phys.* **42**, 280–285 (2004).
- 7 Zhu, X.H., Lee, L.Y., Jackson, J.S.H., Tong, Y.W. & Wang, C.H. Characterization of porous poly(D,L-Lactic-co-glycolic acid) sponges fabricated by supercritical CO₂ gas-foaming method as a scaffold for three-dimensional growth of hep3B cells. *Biotechnol. Bioeng.* **100**, 998–1009 (2008).
- 8 Leeke, G.A., Cai, J.G. & Jenkins, M. Solubility of supercritical carbon dioxide in polycaprolactone (CAPA 6800) at 313 and 333 K. *J. Chem. Eng. Data* **51**, 1877–1879 (2006).
- 9 Kazarian, S.G., Vincent, M.F., Bright, F.V., Liotta, C.L. & Eckert, C.A. Specific intermolecular interaction of carbon dioxide with polymers. *J. Am. Chem. Soc.* **118**, 1729–1736 (1996).
- 10 Shieh, Y.T. & Liu, K.H. The effect of carbonyl group on sorption of CO₂ in glassy polymers. *J. Supercrit. Fluids* **25**, 261–268 (2003).
- 11 Alessi, P., Cortesi, A., Kikic, I. & Vecchione, F. Plasticization of polymers with supercritical carbon dioxide: Experimental determination of glass-transition temperatures. *J. Appl. Polym. Sci.* **88**, 2189–2193 (2003).
- 12 Kazarian, S.G., Brantley, N.H. & Eckert, C.A. Applications of vibrational spectroscopy to characterize poly(ethylene terephthalate) processed with supercritical CO₂. *Vib. Spec.* **19**, 277–283 (1999).
- 13 Shieh, Y.T., Su, J.H., Manivannan, G., Lee, P.H.C., Sawan, S.P. & Spall, W.D. Interaction of supercritical carbon dioxide with polymers.2. Amorphous polymers. *J. Appl. Polym. Sci.* **59**, 707–717 (1996).
- 14 Lian, Z.Y., Epstein, S.A., Blenk, C.W. & Shine, A.D. Carbon dioxide-induced melting point depression of biodegradable semicrystalline polymers. *J. Supercrit. Fluids* **39**, 107–117 (2006).
- 15 Shieh, Y.T., Su, J.H., Manivannan, G., Lee, P.H.C., Sawan, S.P. & Spall, W.D. Interaction of supercritical carbon dioxide with polymers.1. Crystalline polymers. *J. Appl. Polym. Sci.* **59**, 695–705 (1996).
- 16 Shenoy, S.L., Fujiwara, T. & Wynne, K.J. Quantifying supercritical CO₂ dilation of poly(vinylidene fluoride) and poly(vinylidene fluoride-co-hexafluoro-propylene) utilizing a linear variable differential transducer: Plasticisation and melting behavior. *Macromol. Symp.* **201**, 171–178 (2003).
- 17 Weidner, E., Wiesmet, V., Knez, Z. & Skerget, M. Phase equilibrium (solid-liquid-gas) in polyethyleneglycol-carbon dioxide systems. *J. Supercrit. Fluids* **10**, 139–147 (1997).
- 18 Beckman, E. & Porter, R.S. Crystallisation of bisphenol A polycarbonate induced by supercritical carbon dioxide. *J. Polym. Sci. Pol. Phys.* **25**, 1511–1517 (1987).
- 19 Kishimoto, Y. & Ishii, R. Differential scanning calorimetry of isotactic polypropene at high CO₂ pressures. *Polymer* **41**, 3483–3485 (2000).
- 20 Handa, Y.P., Roovers, J. & Wang, F. Effect of thermal annealing and supercritical fluids on the crystallization behavior of methyl-substituted poly(aryl ether ether ketone). *Macromolecules* **27**, 5511–5516 (1994).
- 21 Jiang, Y., Gu, Q., Li, L., Shen, D.Y., Jin, X.G., Lei, Y.G. & Chan, C.M. Structural changes during isothermal crystallization of a poly(bisphenol A-co-decane ether) polymer. *Polymer* **43**, 5615–5621 (2002).

- 22 Nalawade, S.P., Picchioni, F., Janssen, L., Grijpma, D.W. & Feijen, J. Investigation of the interaction of CO₂ with poly(L-lactide), poly(DL-lactide) and poly(epsilon-caprolactone) using FTIR spectroscopy. *J. Appl. Polym. Sci.* **109**, 3376–3381 (2008).
- 23 Murphy, S., Leeke, G. & Jenkins, M.A. Comparison of the use of FTIR spectroscopy with DSC in the characterisation of melting and crystallisation in polycaprolactone. *J. Therm. Anal. Calorim.* **105**, 251–257 (2011).
- 24 Kimura, F., Kimura, T., Sugisaki, A., Komatsu, M., Sata, H. & Ito, E. FTIR spectroscopic study on crystallization process of poly(ethylene-2,6-naphthalate). *J. Polym. Sci. Pol. Phys.* **35**, 2741–2747 (1997).
- 25 Coleman, M.M. & Zarian, J. Fourier-transform infrared studies of polymer blends.2. Poly(epsilon caprolactone)-poly(vinyl chloride) system. *J. Polym. Sci. Part B Pol. Phys.* **17**, 837–850 (1979).
- 26 He, Y. & Inoue, Y.. Novel FTIR method for determining the crystallinity of poly(epsilon-caprolactone). *Polym. Int.* **49**, 623–626 (2000).
- 27 <http://webbook.nist.gov/chemistry/> accessed (November 2011).
- 28 Turnbull, D. Kinetics of heterogeneous nucleation. *J. Chem. Phys.* **18**, 198–203 (1950).
- 29 Long, Y., Shanks, R.A. & Stachurski, Z.H. Kinetics of polymer crystallisation. *Prog. Polym. Sci.* **20**, 651–701 (1995).