PII: S0032-3861(97)10248-8

*Polymer* Vol. 39 No. 17, pp. 4175–4179, 1998
© 1998 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

# Crystallization of a linear aliphatic polyester from solution in supercritical carbon dioxide

**J. Stejny*, A.F. Whitfield, G.M. Pritchard and M.J. Hill**
*H.H. Wills Physics Laboratory, University of Bristol, Bristol, BS8 1TL UK*

*(Received 30 October 1997)*

Poly(decamethylene sebacate) was crystallized from solution in supercritical carbon dioxide in a high pressure optical cell. Turbidity measurements were used to monitor the crystallization process and to determine the polymer solubility as a function of temperature and pressure. The morphology of the crystals obtained was studied by transmission electron microscopy. The polymer crystallized in the form of long ribbon-like lamellae with their aspect ratios dependent on the crystallization conditions. The ribbon-like morphology of the crystals and their electron diffraction pattern are different from those found previously from crystals of this polyester grown from conventional solvents, which indicates that the lateral packing of polyester chains in the ribbon-like lamellae is not of the polyethylene type observed in conventionally grown crystals. This is in agreement with the expectation that crystallization from supercritical fluids can achieve a wider range of crystallization conditions than crystallization from a single conventional liquid. © 1998 Published by Elsevier Science Ltd. All rights reserved.

**(Keywords: aliphatic polyester; crystallization; supercritical carbon dioxide)**

## *Introduction*

When a gas at a temperature higher than its critical point temperature, $T_c$, is isothermally compressed the density will increase continuously, reaching a liquid-like density at pressures higher than its critical pressure, $p_c$. The increase in density is accompanied by a large increase in the solvent power of the fluid[1,2]. By decreasing the pressure, the solvent properties of a supercritical fluid at a constant temperature can, therefore, be smoothly changed from those of a good solvent to those of a complete non-solvent. This contrasts with the behaviour of liquids which are little affected by pressure; a change in temperature is required to alter their solvent power. In the crystallization of a solute from a liquid the crystallization temperature and the supercooling are interdependent, thus it is difficult to study their individual effects. In previous investigations[3], chemically different compounds were used as solvents in order to separate the effect of crystallization temperature and supercooling, but this is not fully satisfactory because any change in solvent introduces a new variable. However, the control of the solvent power of the supercritical fluids by pressure provides an opportunity to study the effects of crystallization temperature and supersaturation separately, using a single solvent. Another advantage of supercritical solvents is that their pressure and associated solvent power can be changed much faster than the solvent power of single conventional solvents where the change is obtained by altering the temperature. This makes it possible to achieve very high supersaturations, otherwise unobtainable in large volumes of rapidly crystallizing solutions.

The main condition for a supercritical fluid (SCF) to be considered as a solvent for polymer crystallization studies is that its critical temperature has to be below the melting temperature of the polymer so that the polymer can crystallize from it. However, it should not be too low, otherwise inconveniently high pressures would be needed to achieve a liquid-like density, hence, a fluid of good solvent power. As the solubility of a particular polymer-solvent pair depends on the intermolecular forces, the chemical structure of the solvent should be similar to that of the polymer. These requirements limit considerably the choice of suitable SCF solvent–polymer pairs. It has been found that the most commonly used SCF solvent, carbon dioxide ($T_c = 31$°C, $p_c = 7.375$ MPa), is a good solvent for linear aliphatic polyesters[4]. The present paper reports preliminary experiments on the crystallization of poly(decamethylene sebacate) from supercritical carbon dioxide.

## *Experimental*

*Materials.* Poly(decamethylene sebacate), also known as polyester 10,10, was prepared by condensation of sebacoyl chloride with decamethylene glycol as described previously[5]. The number-average molecular weight was measured as 10 600 by vapour pressure osmometry.

In order to facilitate the dissolution of the polyester in the supercritical carbon dioxide it was found necessary to have the polymer in a highly dispersed form. This was achieved by crystallizing the polyester from 0.1% solution in *tert*-butyl alcohol at 30°C followed by freeze-drying the crystal suspension by sublimation of the solvent in a vacuum. This procedure gave a loosely packed aggregate consisting of hexagonal shaped lamellar crystals similar to those obtained previously[5].

*Apparatus.* The crystallization of the polyester from solution in SCF carbon dioxide was carried out in a high pressure optical cell (*Figure 1*) immersed in a temperature controlled water bath. The pressure and the volume of the cell chamber were controlled by a piston separating the SCF solution from a hydraulic pressure generator. The pressure and the temperature of the solution were monitored by a pressure transducer and a thermocouple respectively; the bottom outlet of the cell was connected to a carbon dioxide cylinder and a rotary vacuum pump. The crystallization

---

* To whom correspondence should be addressed

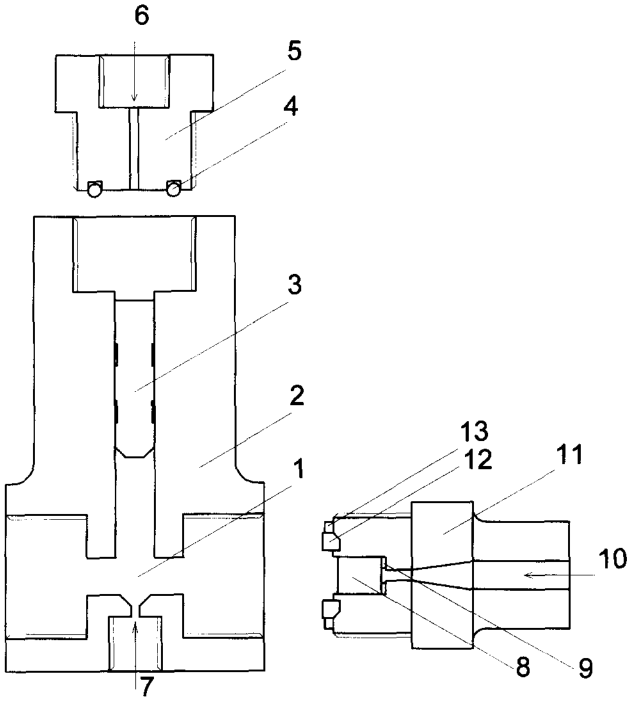

**Figure 1** Exploded view of the high pressure optical cell. (1) Main chamber. (2) Main body. (3) PTFE piston. (4) O-ring seal. (5) Top flange. (6) High pressure oil inlet. (7) Carbon dioxide inlet. (8) Sapphire window. (9) PTFE seal. (10) Optical path. (11) Window holder. (12) PTFE seal. (13) Phosphor–bronze ring. Two identical window holder assemblies (11) are screwed into the opposite sides of the main body (2)

process was monitored optically, by measuring the turbidity of the solution in the cell according to the method used by Organ and Keller[6]. A HeNe laser was used as the light source, and the light intensity of the beam after passing through the cell was recorded by a photodiode. The temperature, pressure and light level data were collected electronically.

*Crystallization procedure.* A known weight of freeze-dried polyester single crystals was placed in the cell, the cell was assembled and evacuated with the rotary vacuum pump, and carbon dioxide from a cylinder was recondensed into it. The cell was held at a temperature above 55°C and pressure above 41 MPa (6000 psi) for 1 h, in order to dissolve the polymer. The temperature of the cell was then changed to the required crystallization temperature and the crystallization was started by reducing the pressure of the solution. Changes in pressure and in turbidity were monitored and recorded during the crystallization. Blank experiments, following the same procedure but without the polymer charge, were carried out to check that the system remained in the supercritical state. The crystals were recovered from the cell by allowing the contents to flow under a low pressure difference into a cylinder pressurised with carbon dioxide. The cylinder was cooled to below −80°C, the frozen mass was removed and immersed into a container filled with cold ethanol, and the carbon dioxide was then allowed to sublime off at atmospheric pressure. This procedure prevented mechanical damage to the crystals, which could have occurred if the cell were emptied through a needle valve using a high pressure difference.

*Transmission electron microscopy.* Crystals were deposited from suspension in ethanol onto carbon-coated grids and then shadowed with Pt/Pd for examination in a Philips 301 TEM operating at 80 kV.

## *Results and discussion*

*Figure 2a* shows typical experimental data; the pressure changes and corresponding development of the turbidity are shown for a crystallization using SCF carbon dioxide as the solvent. This is compared with the development of turbidity (*Figure 2b*) observed during an isothermal crystallization of the same polyester from the conventional solvent 2-butanol. It is clear from the turbidity measurements that crystallization from SFC carbon dioxide is much faster than crystallization from 2-butanol.

An interesting feature shown in *Figure 2a* (but not in *Figure 2b*) is the increase in the intensity of transmitted light observed about 45 s after the large initial drop in the intensity (which indicates the onset of the crystallization process). This increase is a consequence of the rapid sedimentation of the crystals occuring in the cell reducing the number of light scattering solid particles in the beam path. The sedimentation of polyester crystals is also observed when 2-butanol is used as a solvent (*Figure 2b*), however, it is very much slower due to the smaller difference in density between the crystals and 2-butanol and the higher viscosity of 2-butanol as compared with the carbon dioxide fluid.

The values of pressure and temperature at the onset of the turbidity were used to construct phase diagrams for solutions of the polyester in SCF carbon dioxide (method of isopleths[7]). A typical phase diagram, constructed for a solution concentration of approximately 0.1%, is shown in *Figure 3*. The polymer will precipitate when the conditions of the system are changed from the single phase region (region 1) to the two phase region (region 2). It is interesting to note that the polymer precipitates at constant pressure when the temperature is increased; this effect can be explained by the fact that the density, and hence the solvent power of the SCF, decreases as the temperature increases when the pressure is held constant.

The morphologies of the crystals obtained were studied by transmission electron microscopy. Three different types of crystals were found: highly extended ribbon-like lamellae (*Figure 4a*); dendrites (*Figure 4b*) and a few, approximately equidimensional, irregular shape lamellae. The crystallization conditions and the types of crystals obtained are summarized in *Table 1*. The irregular shape lamellae were similar in lateral size to the hexagonal lamellae obtained from conventional solvents in previous work[5] (*Figure 4c*), so it seems likely that the irregular lamellae are the partially dissolved and annealed remnants of the original charge of polymer. However, highly extended ribbons have not been observed in conventional solution crystallization of this polyester and are specific to the crystallization from the SFC carbon dioxide. The maximum length of the ribbons, obtained at the crystallization temperature of 31.2°C, was well over 100 μm (*Figure 4a*), but the ribbon length decreased as the crystallization temperature was increased from 31.2 to 53.5°C. Ribbon crystals were not observed at the crystallization temperature of 55°C but dendrites were found instead, nucleated on small spherical particles (*Figure 4b*). These results suggest that a liquid–liquid separation into polymer rich droplets, suspended in a polymer poor phase, occurred initially. This was followed by the crystallization where the crystalline polymer contained in the droplets nucleated the growth of the dendrites.

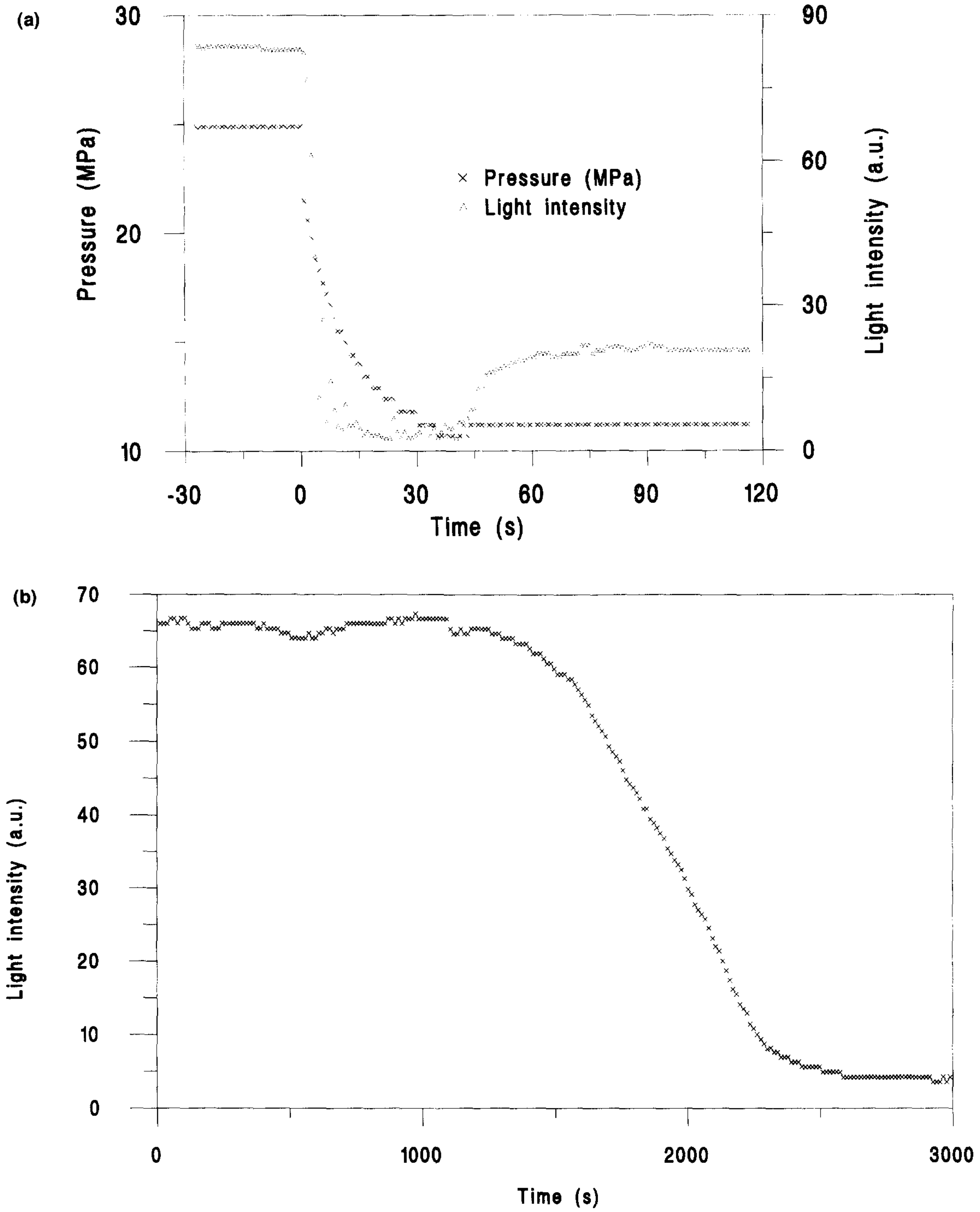

**Figure 2** (a) Variation of the pressure and turbidity (expressed as the light intensity of transmitted beam in arbitrary units (a.u.)) with time during the crystallization of 0.1% solution of poly(decamethylene sebacate) from SCF carbon dioxide. (b) Variation of turbidity (expressed as the light intensity of transmitted beam in arbitrary units (a.u.)) with time during the crystallization of 0.1% solution of poly(decamethylene sebacate) from 2-butanol

**Table 1** Crystallization conditions and the morphology of the crystals of poly(decamethylene sebacate) crystallized from its solution (0.1% approx.) in SCF carbon dioxide

| Temperature (°C) | Initial pressure (MPa (psi)) | Final pressure (MPa (psi)) | Crystal morphology |
|---|---|---|---|
| 31.2 | 31.0 (4500) | 9.0 (1 300) | Ribbon-like lamellae |
| 42.0 | 36.5 (5300) | 11.0 (1 600) | Ribbon-like lamellae |
| 53.5 | 51.0 (7400) | 12.4 (1 800) | Ribbon-like lamellae |
| 55.0 | 68.9 (10 000) | 31.0 (4 500) | Dendrites |

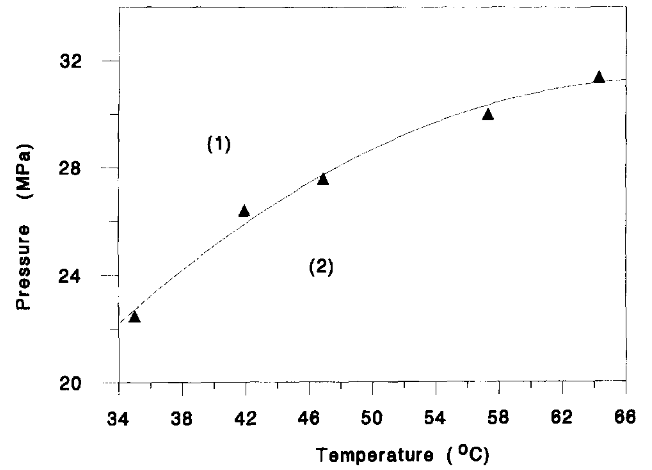

**Figure 3** Phase diagram for 0.1% solution of poly(decamethylene sebacate) in SCF carbon dioxide. The curve separates the single phase region (1) from the two phase region (2)

The electron diffraction pattern of the irregularly shaped lamellae is identical with the patterns obtained from the hexagonal lamellae crystallized from conventional solvents (*Figure 4c* inset). It corresponds to the reciprocal lattice section plane perpendicular to the chain direction and agrees with the accepted crystal structure of the polyester 10,10 with parameters $a' = a\sin\beta$ of 5 Å and $b$ of 7.4 Å[8]. However, the pattern obtained from the ribbon lamellae (*Figure 4a* inset) is different. It does not correspond to the accepted unit cell but it fits a rectangular net with the dimensions of 9.46 Å and 4.20 Å. This result suggests that both the morphology of the crystals and the packing of the polyester chains are controlled by the crystallization process. It is known that the chain packing in linear aliphatic polyesters depends on the spacial frequency of ester groups along the alkane chain. As expected, the packing of polyester chains with a low frequency of ester groups along the chain is the same as in polyethylene with the chains fully extended in planar conformation. With increasing frequency of ester groups the planar conformation becomes less stable and the chains eventually assume a 'kinked' conformation resulting in a different lateral packing. Liau and Boyd[9] have calculated the energies associated with different conformations and packings for a series of six aliphatic polyesters of which polyester 6,10 had the lowest frequency of ester groups. Their results show that the polyethylene type planar chain packing is the more stable form for polyester 6,10, and therefore such packing should be even more stable for polyester 10,10. We suggest that the reason for the energetically less favourable packing obtained during the rapid crystallization from SCF solutions is that the chains remain 'frozen' in their energetically less favourable conformations in a local energy minimum and do not have time to pack into the most energetically favourable structure.

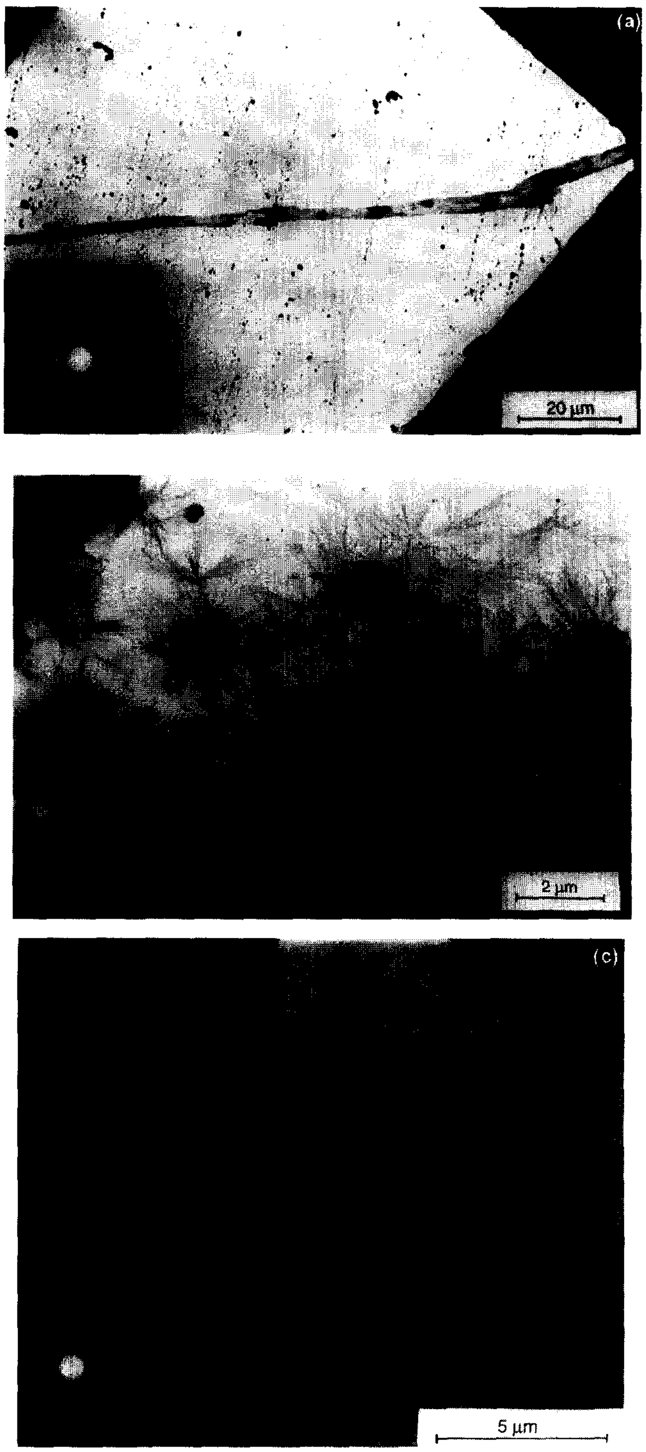

**Figure 4** Transmission electron micrographs of poly(decamethylene sebacate) crystals. (a) A ribbon-like poly(decamethylene sebacate) lamella grown at 31.2°C from solution in SCF carbon dioxide. The electron diffraction pattern, oriented with the crystal, is shown in the inset. (b) Dendrites of poly(decamethylene sebacate) grown at 55°C from solution in SCF carbon dioxide. (c) A poly(decamethylene sebacate) lamella grown at 25.5°C from solution in 2-butanol. The electron diffraction pattern, oriented with the crystal, is shown in the inset

### *Conclusions*

From these preliminary experiments we may conclude that the crystallization of polymers from SCF solvents allows us to examine the effect of crystallization conditions, such as temperature and supersaturation, separately using the same solvent. The rapid change of solvent power, controlled by the change of pressure, makes it possible to achieve crystallization conditions which are unobtainable in conventional solvents. These conditions can give rise to the ribbon-like morphology and chain packing in the lamellar crystals of polyester 10,10 which are markedly different from the morphology and the chain packing found in crystals grown from conventional solvents.

## *References*

1. Eckert, A. E., Knutson, B. L. and Debenedetti, P. G., *Nature*, 1996, **383**, 313.
2. McHugh, M. A. and Krukonis, V. J., in *Encyclopedia of Polymer Science and Engineering*, vol. 16, eds H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges. Wiley-Interscience, New York, 1986, pp. 368–399.
3. Organ, S. J. and Keller, A., *J. Mater. Sci.*, 1985, **20**, 1571, 1586, 1602.
4. Lele, A. K. and Shine, A. D., *Polymer Preprints*, 1990, **31**(1), 677.
5. Girolamo, M., Keller, A. and Stejny, J., *Makromol. Chem.*, 1975, **176**, 1489.
6. Organ, S. J. and Keller, A., *J. Polym. Sci., Polym. Phys. Edn*, 1986, **24**, 2319.
7. Colman, E. J., Condo, P. D., Tan, L. Y. and Ehrlich, P., *Polymer Preprints*, 1990, **31**(1), 675.
8. Fuller, C. S. and Frosch, C. J., *J. Am. Chem. Soc.*, 1939, **61**, 2575.
9. Liau, Wen-Bin and Boyd, R. H., *Macromolecules*, 1990, **23**, 1531.