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Density fluctuations: the nucleation event in isotactic polypropylene crystallization

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The present study was undertaken to investigate the mechanism for primary nucleation in polymer crystallization. Previous studies in this area have not been conclusive. Experiments on polypropylene with long induction times, studied by small- and wide-angle X-ray scattering (SAXS and WAXS), reveal the onset of long-range ordering prior to crystal growth. Rapid crystallizations studied by melt extrusion indicate the development of well-resolved oriented SAXS patterns associated with long-range order before the development of crystalline peaks in the WAXS region. The experimental results suggest pre-nucleation density fluctuations play an integral role in nucleation of polymer crystallization. © 1998 Elsevier Science Ltd. All rights reserved.

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Polymer processing relies on the shaping of molten material in either moulds or dies and the stabilization of the shape produced by crystallization[1]. During crystallization, a microstructure develops which can control the mechanical and aesthetic properties of the polymer. To produce more useful materials, it is essential to understand and predict this process. Despite the maturity and market penetration of the polymer industry, one aspect of polymer processing, nucleation, is little understood. Whereas the growth of polymer crystals is well established in literature, and there are reliable theories to predict the kinetics of crystallization, understanding of the initiation or nucleation step remains somewhat of a mystery. The available theories are complicated and somewhat unphysical[2–7]. There is good reason for this: experimental access to the nucleation step is very difficult, whereas studies of crystal growth are simple enough to be used in undergraduate laboratory classes[8]. This work aims to show that a process similar to spinodal decomposition, with a non-conserved order parameter, plays an integral role in initiating crystallization in polymers.

Crystallization involves phase separation into crystalline and amorphous regions. Phase separation can be divided into two classes, depending on whether the order parameter (i.e. concentration) is conserved or not. An example of phase separation with a conserved order parameter is liquid–liquid phase separation in a polymer blend. Crystallization involves a transformation from wholly amorphous to partially crystalline and the order parameter (volume fraction of crystals) is obviously not conserved.

Currently the main mechanism proposed to explain the initiation step in polymer crystallization is classical nucleation followed by growth[2–4] or a 2-D growth process[5–7]. Nucleation and growth involves the spontaneous formation of fragments of the more stable phase (crystal nuclei). The formation of these nuclei generates an imbalance in the system, which advances the growth process directly once an energy barrier has been overcome, as illustrated schematically in *Figure 1a*, for nucleation and growth with a non-conserved order parameter and consequently no depletion layer.

Phase separation in polymer systems below a stability limit is known to follow spinodal decomposition[9]. In this case, spinodal decomposition involves two regions of polymer, one having the appropriate polymer chain conformation for crystallization and the other which becomes the amorphous region present in all semicrystalline polymers. These two phases will have subtly different energy densities and will tend to separate, there being a continuous transformation through slightly more ordered regions, as illustrated in *Figure 1b*, for spinodal decomposition with a non-conserved order parameter. In spinodal decomposition there is no thermodynamic barrier to phase separation, and diffusion occurs from regions of low to regions of high concentration (so-called uphill diffusion) which advances the growth process. Decomposition occurs below the stability limit and the amplitude of the density oscillations increases to form eventually crystal nuclei.

An examination of the morphological changes that take place in polymers during crystallization will afford information crucial to our understanding of the process. These changes occur at the molecular level; small-angle X-ray scattering (SAXS) can probe long-range order changes, while wide-angle X-ray scattering (WAXS) can monitor changes at the polymer segment level. For the nucleation and growth mechanism, WAXS growth should occur from isolated crystallites prior to interference scattering in SAXS because crystals are present from the beginning of the ordering process. If, however, spinodal

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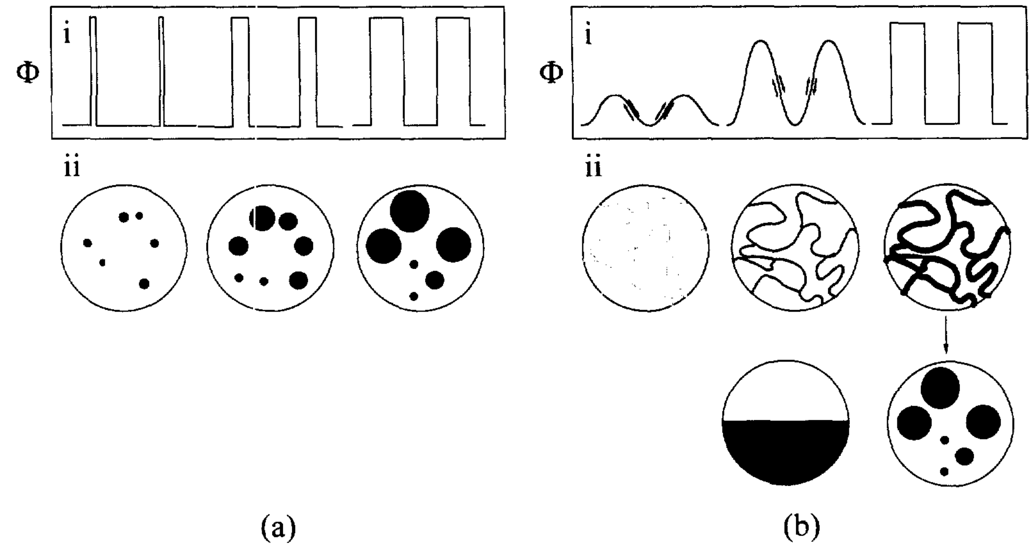

Figure 1 (a) Schematic illustration of phase separation by the nucleation and growth mechanism: (i) one-dimensional evolution of concentration profiles; (ii) two-dimensional representation of the resultant phase structure. (b) Schematic illustration of phase separation by spinodal decomposition: (i) one-dimensional evolution of concentration profiles; (ii) two-dimensional representation of the resultant phase structure. In both cases the order parameter is not conserved. [Φ - volume fraction]

decomposition plays a major role, development of a SAXS pattern due to density fluctuations should occur prior to any WAXS from crystals because there is a continuous transformation of the partially ordered phase through slightly more ordered states rather than building a crystalline structure instantaneously, as discussed by Strobl[10].

In order to separate nucleation from growth, two types of experiments have been performed on polypropylene (M_w = 520 000 g mol^{-1}, M_n = 117 000 g mol^{-1}). Slow crystallizations with long induction times have been studied by simultaneous SAXS and WAXS (see *Figure 2a* for time resolved data for SAXS and WAXS) [11]. These experiments show a clear development of a SAXS peak, due to electron density fluctuations, prior to the presence of crystals identified by WAXS. The peak area *versus* time data in *Figure 2b* were extracted from the data in *Figure 2a* and show unequivocally that the SAXS peak grows before the WAXS peak. Similar behaviour has been reported for a semi-rigid polymer poly(ethylene-terephthalate) crystallized by heating from an amorphous glassy state[12–15].

The scattering data have been analysed in the formalism described by Cahn and Hilliard[16,17] and *Figure 3* shows data from polypropylene at 418 K where we could estimate both the dominant length scale $L \approx 175$ Å and the effective co-operative diffusion coefficient $D_{\mathrm{eff}} = -0.34$ Å^2 s^{-1}. There was a precrystallization induction period of 400 s and the last 200 s of this showed density fluctuations by SAXS. By conducting these experiments at a series of temperatures, the stability limit could be found at 438 ± 5 K by extrapolation of D_{eff} to zero.

The stability limit is the temperature below which polypropylene spontaneously separates into two phases, one of which is rich in polymer segments of the appropriate chain conformation to crystallize (trans–gauche arrangement of the carbon backbone in isotactic polypropylene[18]) and the other is depleted in polymer segments with the appropriate chain conformation to crystallize and is concentrated in sequences near entanglements and other defects which cannot crystallize. The stability limit is 6 K below the measured melting point for polypropylene with a long spacing of 140 Å and 25 K below the thermodynamic melting point of isotactic polypropylene[19,20]. Once WAXS from crystals (atomic order on the 1 Å scale) was observed, the kinetics reverted to those of nucleation and growth. This type of behaviour has also been observed in PET by Kaji and co-workers[12–15] and in PEEK by Ezquerra and co-workers[21].

Rapid crystallizations were studied by SAXS and WAXS during melt extrusion of a tape. Previous SAXS/WAXS studies on polymer extrusion have concentrated on the growth and orientation of crystals[22]. Extrusion of tape or fibre is a steady-state process where the crystallization time increases down the spin-line. This allowed long data collection times (minutes) for very short crystallization times (milliseconds). Prior to the development of crystals, well resolved, oriented small-angle patterns could be observed with length scales (50–200 Å) and intensities that grew down the spin-line. *Figure 4* shows the scattering patterns collected during extrusion of the same grade of polypropylene, together with a schematic diagram of the proposed density modulations at regular intervals down the spinline.

These early patterns had the shape associated with spinodal decomposition. The orientation observed in the scattering is caused by coupling of density fluctuations with the slight elongational flow-field (the take-up speed was approximately twice the extrusion speed). Once crystallization had been observed in the wide-angle region, the shape of the small-angle pattern changed from that characteristic of sinusoidal density fluctuations to that typical of lamellar crystals. Since the elongational flow was weak, the crystallization process dominated and only weakly anisotropic crystals were produced.

The combination of modern X-ray techniques has allowed us to study the previously inaccessible process of nucleation. These experiments, quiescent time-resolved SAXS/WAXS and extrusion, suggest that a process that strongly resembles spinodal decomposition of chain segments with different average conformations is the

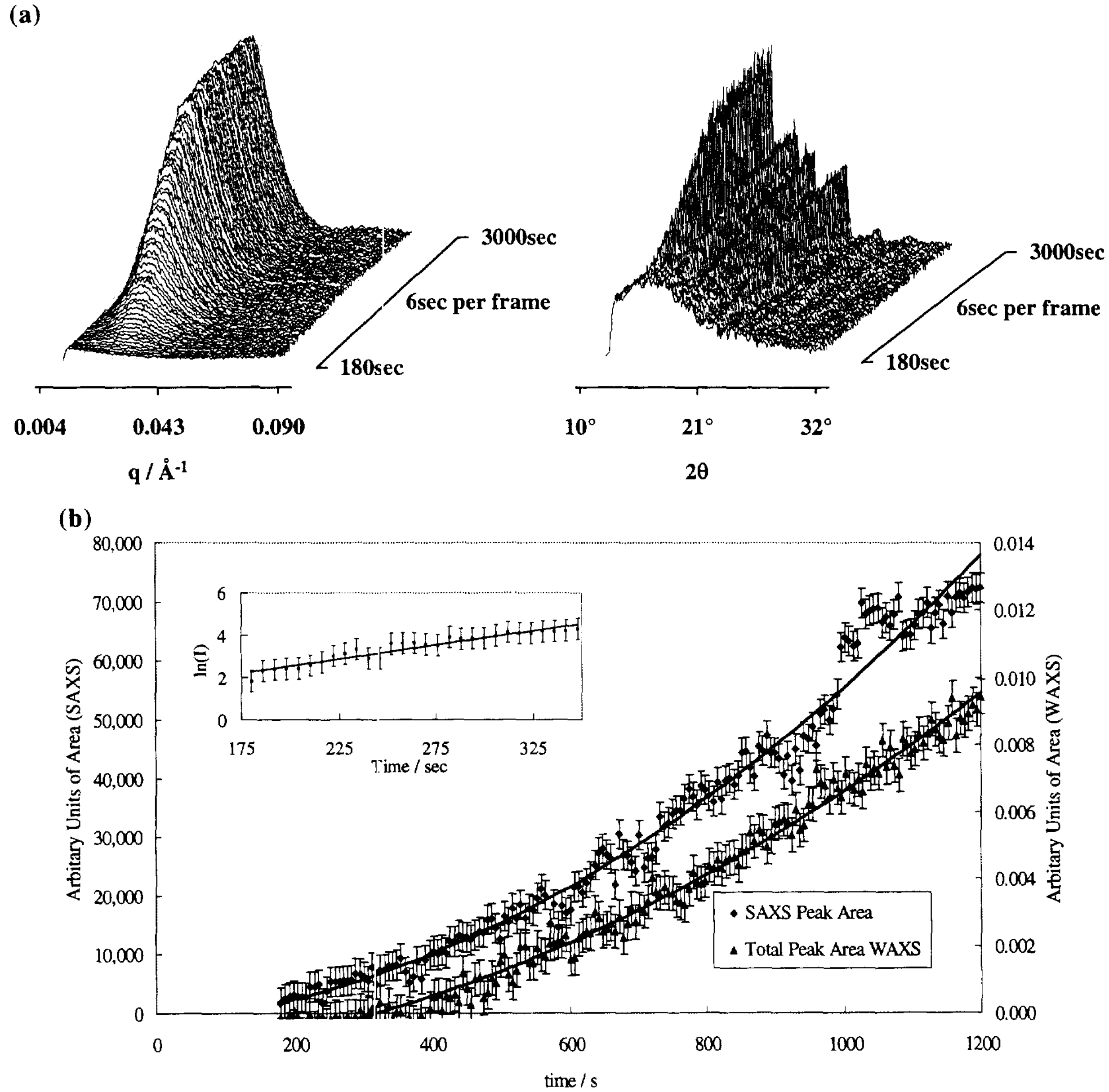

Figure 2 (a) Time resolved Lorentz corrected SAXS intensity data, $I(q)*q^2$, *versus* q, taken during the crystallization of isotactic polypropylene at 145°C together with its complimentary WAXS data. (b) Calculated peak area data for SAXS and WAXS results taken during the crystallization of isotactic polypropylene at 145°C, the inset is the initial part of the SAXS data plotted in the Cahn-Hilliard form of the peak intensity, $\log I(q^*)$, *versus* time, t

nucleation step in polymer crystallization. That polymer crystallization occurs with phase separation is in no doubt; at the end of the process regions of well-ordered crystalline polymer coexist with regions of disordered polymer in a layered morphology (lamellae). Sequences that can be oriented with the right conformation and incorporated into the crystal separate from sequences near entanglements and other defects which cannot crystallize and can only be part of the amorphous regions. The transformation from the disordered phase to the better ordered partially crystalline phase proceeds continuously passing through a sequence of slightly more ordered states rather than building up a crystalline state instantaneously. A mechanism of continuous transformation could be consistent with a fast homogeneous nucleation process. Polymer crystallization, like any other phase separation, is kinetically controlled. The structure formed is the one with the highest growth rate. Once a crystallite is formed, it has a lateral growth rate much higher than that of the fluctuations and so dominates (we have measured the spherulitic growth rate of polypropylene by optical microscopy). In this case the growth mechanism of semi-crystalline polymer sperulites takes over because the lateral growth rate of crystals ($0.5\,\mu\mathrm{m s}^{-1}$) is 10^4 faster than the growth rate of the fluctuations ($0.35\,\text{Å}^2\,\mathrm{s}^{-1}$).

The combination of the steady-state extrusion and the high intensity, synchrotron X-ray source allows nucleation phenomena to be observed. If the results we have described are substantiated with further work, the less well understood part of nucleation and growth theory, that is nucleation, could have a proper explanation and be predictable. Furthermore our method to study stability limits in phase transitions in polymers could have wide implications for condensed matter physics.

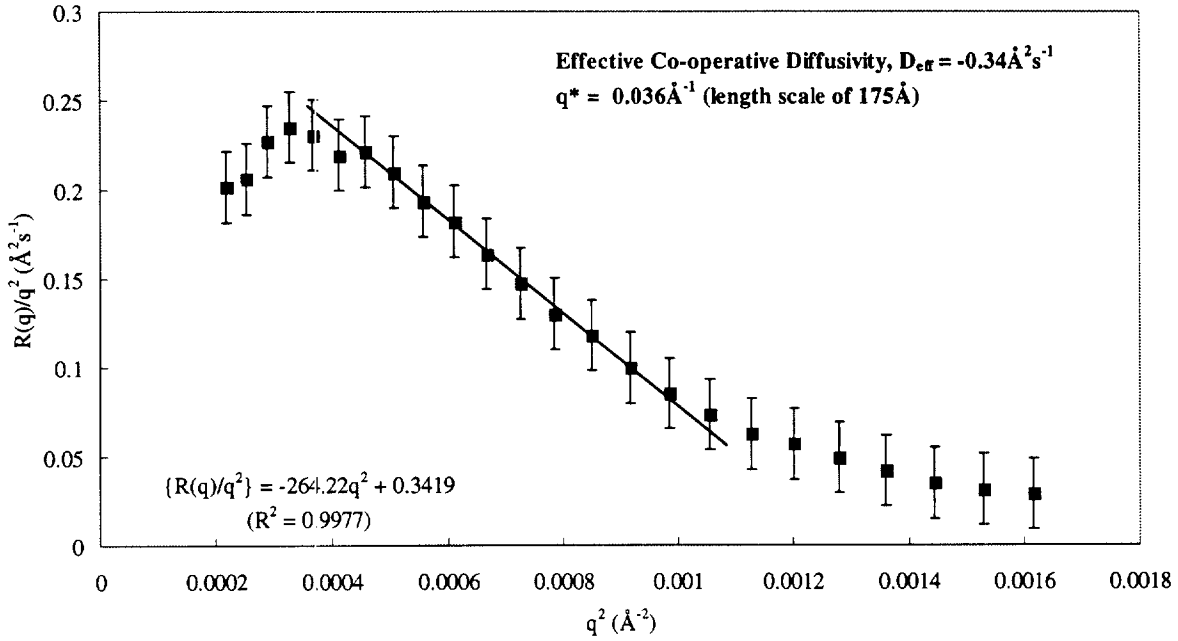

Figure 3 Scattering results are obtained from a crystallization experiment for polypropylene at 145°C. The data are then analysed as per the Cahn-Hilliard's formalism where the $R(q)/q^2$ values are calculated from an examination of $\ln I(q)$ *versus* time, t, for all data. The effective co-operative diffusivity is obtained by extrapolation of the $R(q)/q^2$ *versus* q^2 data plot to $q^2 = 0$

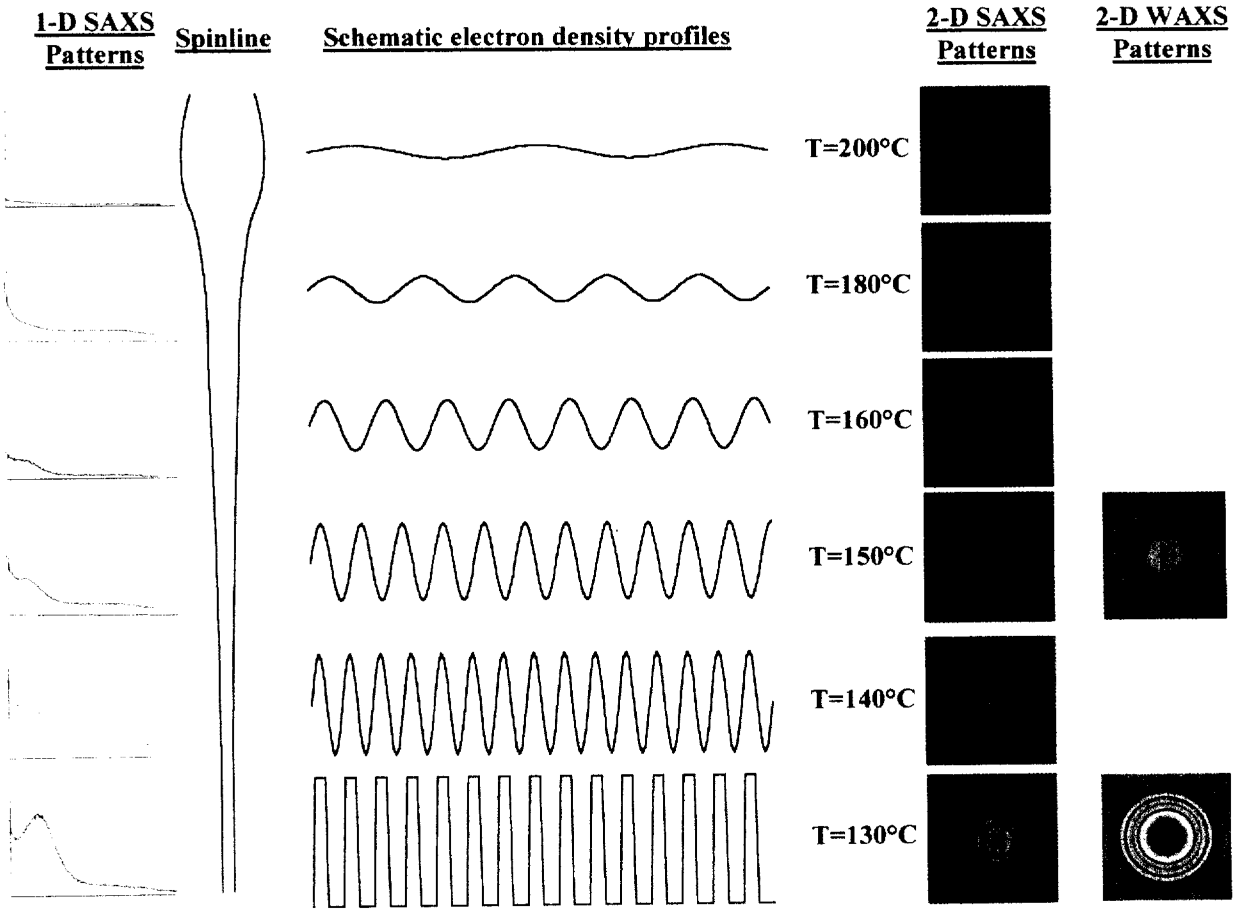

Figure 4 Data taken during extrusion of isotactic polypropylene with a low wind-up speed are shown alongside a schematic of proposed density modulation and the shape of the extrudate. The X-ray beam impinges on the tape and the scattered X-rays are collected by either two 2-D wire chamber detectors or a single 2-D wire chamber to collect the SAXS data and an image plate to collect the WAXS data. To reduce air scatter, a vacuum chamber is inserted between the sample and the SAXS detector. Close to the die head tear-shaped scattering features are observed in 2-D SAXS with only an amorphous halo in 2-D WAXS. At the furthest position from the die head, when crystallization starts, isotropic rings from crystals can be seen in SAXS and in the WAXS. The one-dimensional SAXS patterns are obtained by horizontal integration of a vertical section through the two-dimensional data and are shown to indicate the movement of the SAXS peak to larger values of q with the onset of crystal growth. The density modulation is a sketch and does not imply a perfectly alternating 'top-hat' function for the polymer at $T = 130°C$

REFERENCES

1. Crawford, R. J. and Roy, J., *Plastics Engineering*, 3rd edn. Pergamon Press, Oxford, 1987.
2. Lauritzen, J. I. and Hoffman, J. D., *J. Res. Natl. Bur. Stand. Sect. A.*, 1960, **64**, 73.
3. Hoffman, J. D., Lauritzen, J. I., Passaglia, E., Ross, G., Frohlen, L. J. and Weeks, J. J., *Kolloid. Z. Poly.*, 1969, **231**, 564.
4. Hoffman, J. D., Davis, G. T. and Lauritzen, J. I., *Treatise on Solid State Chemistry*. Plenum, New York, 1976.
5. Petermann, J., Gohil, R. M., Schultz, J. M., Hendricks, R. W. and Lin, J. S., *J. Polym. Sci. Polym. Phys.*, 1982, **20**, 523.
6. Sadler, D. M., *Polymer. Comm.*, 1986, **27**, 140.
7. Sadler, D. M., *Polymer*, 1987, **28**, 1440.
8. Young, R. J. and Lovell, P. A., *Introduction to Polymers*, 2nd edn. Chapman and Hall, London, 1991.
9. Binder, K., *Materials Science and Technology*, Vol. 5, *Phase Transitions*. VCH Publishers, Weinheim, 1993.
10. Strobl, G., *The Physics of Polymers*. Springer, Berlin, 1996, p. 173.
11. Bras, W., Derbyshire, G. E., Ryan, A. J., Mant, G. R., Felton, A., Lewis, R. A., Hall, C. J. and Greaves, G. N., *Nucl. Instrum. Meth. Phys. Res.*, 1993, **A326**, 587.
12. Imai, M., Kaji, K., Kanaya, T. and Sakai, Y., *Phys. Rev. B. Condensed Matter*, 1995, **52**, 12696.
13. Imai, M., Mori, T., Mizukami, K., Kaji, K. and Kanaya, T., *Polymer*, 1992, **33**, 4451.
14. Imai, M., Mori, K., Mizukami, T., Kaji, K. and Kanaya, T., *Polymer*, 1992, **33**, 4457.
15. Imai, M., Kaji, K. and Kanaya, T., *Macromolecules*, 1994, **27**, 7103.
16. Cahn, J. W. and Hilliard, J. E., *J. Chem. Phys.*, 1958, **28**, 258.
17. Cahn, J. W., *J. Chem. Phys.*, 1965, **42**, 93.
18. Natta, G. and Corradini, P., *Nuovo Cimento Suppl.*, 1960, **15**, 40.
19. Monasse, B. and Haudin, J. M., *Colloid and Polymer Science*, 1985, **263**, 822.
20. Fatou, J. G., *European Polymer Journal*, 1971, **7**, 1057.
21. Ezquerra, T. A., López-Cabarcos, E., Hsiao, B. S. and Baltà-Calleja, F. J., *Phys. Rev. E. Brief Reports*, 1996, **54**, 989.
22. Cakmak, M., Teitge, A., Zachmann, H. G. and White, J. L., *J. Polym. Sci., Part B; Polymer Physics*, 1993, **31**, 371.