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The formation of ring-banded spherulites of poly(ϵ-caprolactone) in its miscible mixtures with poly(styrene-co-acrylonitrile)

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Ring-banded spherulites in polymer blends of poly(ϵ-caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN) were investigated by optical microscopy equipped with a digital image analysis system. PCL/SAN blends exhibit not only spherulites with a Maltese cross, but also distinct extinction rings. The periodic distance of rings changes with blend ratio and crystallization temperature and was plotted as a function of the undercooling and overall mobility of the mixtures, respectively. It was found that the overall mobility of chain segments in the mixtures could be mainly attributed to the origin of the formation of ring-banded spherulites. It was believed that for the first time a quantitative experimental result was obtained about the relationship of periodic distance of rings and the overall mobility of the mixtures. This relationship may be useful to explain the formation mechanism of ring-banded spherulites in polymer blends or even in homopolymers in the future. © 1977 Elsevier Science Ltd.

(Keywords: ring-banded spherulites; poly(ϵ-caprolactone); overall mobility)

Introduction

In miscible polymer blends, crystallization of one polymer constituent is an important origin of morphology formation [1,2]. The most common growth form observed is termed 'spherulite'. This form consists of radial arrays of predominantly chain folded crystals which are lamellae. Sometimes, under crossed polarizers, spherulites of the blends exhibit not only a Maltese cross but also distinct extinction rings, which are named 'ring-banded spherulites'. For examples, in the mixtures of poly (vinylidene fluoride) (PVF$_2$) with poly(methyl methacrylate).

PMMA, or with poly (styrene-co-methylmethacrylate) (PS-PMMA) or poly(methyl acrylate) (PMA) and of poly(ϵ-caprolactone) (PCL) with poly(vinyl chloride) (PVC), or with poly(styrene-co-acrylonitrile) (SAN), ring-banded spherulites have been observed [3–7].

Ring-banded spherulites in homopolymers such as polyethylene and polypropylene were studied by Keith and Padden [8]. They concluded that the ring-banded structure is formed by axial twisting of lamellae under the influence of surface stress and cooperative arrangement of twisted crystallites. An additional mechanism for the formation of highly regular ring-banded spherulites in miscible polymer blends was also suggested [9]. The coherence of this texture throughout the whole spherulite is really astonishing, where the orientations of all crystallites are well-determined and exactly correlated, on length scales of some μm. However, the mechanism leading to this peculiar texture has not been clarified yet. The most important characterization of ring-banded spherulites is the periodic distance of distinct extinction rings. It is thought that this important parameter may be related to the formation mechanism of ring-banded spherulites. In the literature, this parameter has mostly been evaluated as a function of the composition of crystallizable or noncrystallizable component [6,7,9,10]. A common conclusion is that the periodic distance of rings decreases on increasing the noncrystallizable component. Nevertheless, very little explanation has been given for this phenomenon.

In this investigation, the detailed structure of ring-banded spherulites in PCL/SAN mixtures during isothermal crystallization process was observed by optical microscopy equipped with a digital image analysis system. The changes of periodic distance of rings with different blends ratio and crystallization temperature were studied. For the first time, the influence of the undercooling and the overall mobility of the mixtures on the periodic distance of rings was discussed.

Experimental

The PCL was purchased from Polysciences Inc. (USA). The Mw and Mn determined by gel permeation chromatography (GPC) are 22,000 and 11,300, respectively. Their ratio is 1.93. The melting temperature of PCL is about 60°C from DSC measurement, and the glass transition temperature was −60°C from DSC measurement. The SAN with 25 wt% AN content was also supplied by Polysciences. The Mw and Mn are 197,000 and 106,000 by GPC and their ratio is 1.86. The T_g of SAN is about 105°C measured by DSC. The PCL/SAN blends were prepared by mixing in CH_2Cl_2. A dilute solution (5% wt/wt) was stirred continuously at 25°C for 24 h. The thin films were casted on a clean cover glass and held in a vacuum oven at 40°C for 3 days. A polarizing optical microscope (XPT-7, made in Nanjin Jianan Optical Electronic Co. Ltd) equipped with a MINTRON CCD camera (MTV 1881EX, made in Taiwan) was used to observe the isothermal crystallization process of PCL/SAN blends. Two homemade microscope hot stages were used, with temperatures controlled to ±0.1°C. The films with a free surface upwards were first melted on one hot stage at 80°C for 5 h, then were rapidly

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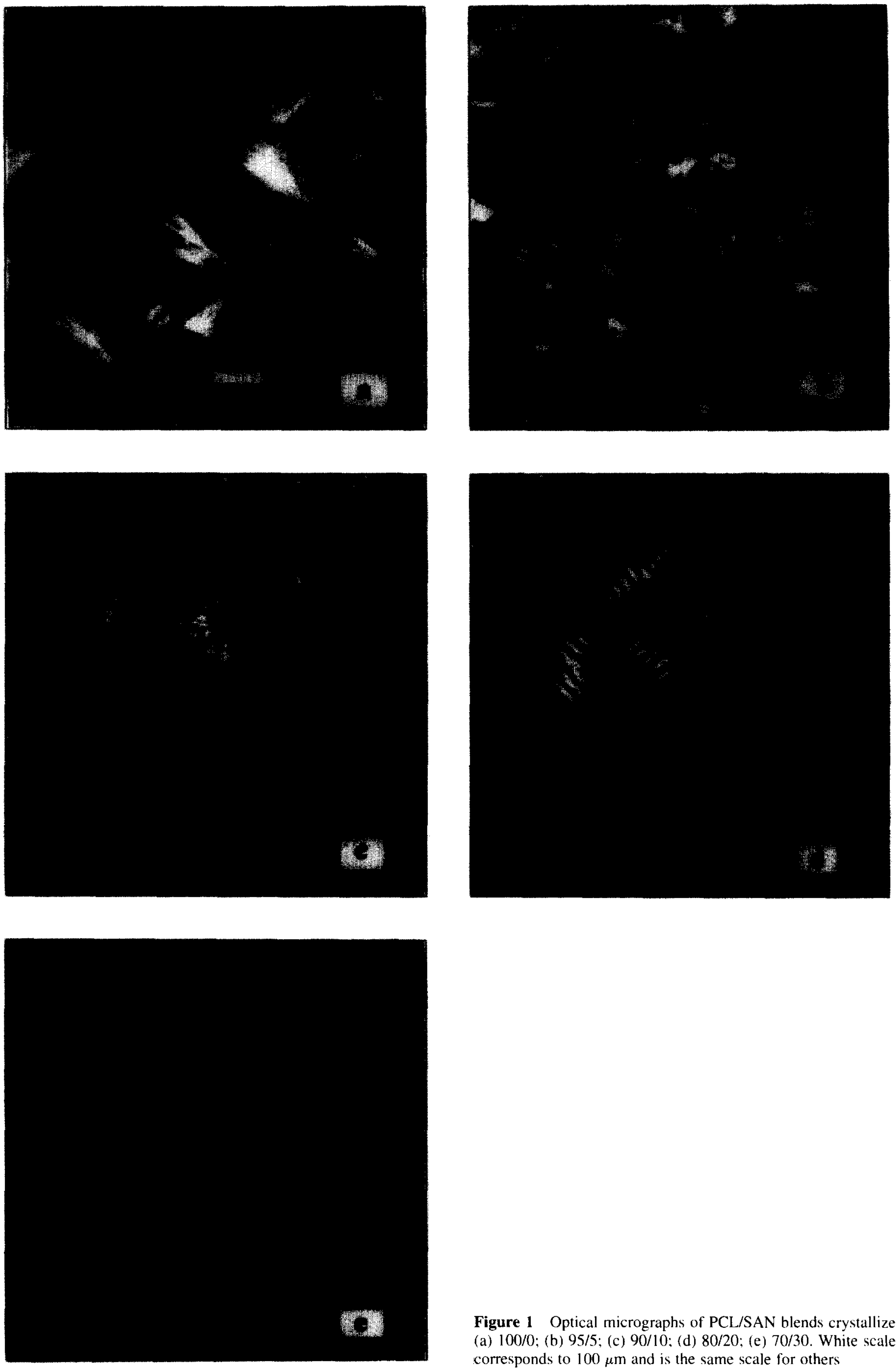

Figure 1 Optical micrographs of PCL/SAN blends crystallized at 40°C. (a) 100/0; (b) 95/5; (c) 90/10; (d) 80/20; (e) 70/30. White scale bar in (a) corresponds to 100 μm and is the same scale for others

transported to another hot stage controlled at crystallization temperature (T_c). The structures of growing spherulites were followed by taking the digital images at appropriate intervals of time with a image processor (VCIC 2.0, homemade). The resolution of the measurement was 0.033 s. The periodic distance of rings was analyzed by using a image software XQF-7 IMAGE ANALYSIS SYSTEM (produced in Nanjin Jianan Optical Electronic Co. Ltd).

Results and discussion

Figure 1 shows the cross-polarized optical micrographs of the spherulites in pure PCL and PCL/SAN blends crystallized at 40°C. The birefringent spherulites structure of pure PCL was observed, which are truncated by impingement and displayes a Maltese cross. For PCL/SAN mixtures, besides birefringence of spherulites with a Maltese cross, a distinct pattern of extinction rings, absent in pure PCL, is apparent. The average value of periodic distances of extinction rings decreases with increasing content of SAN component and the ring becomes irregular with increasing crystallization temperature. The spherulites were analyzed by digitizing the pattern of the structure. *Figure 2* shows the composition dependence of the periodic distance of extinction rings ρ, which increases with decreasing SAN composition in the mixture. This result agrees qualitatively with the observation of the spherulites in polymer mixtures of PCL/PVC and PCL/SAN [9,10]. The values of ρ, however, increase dominantly as the content of SAN approaches to zero. The spherulite of pure PCL seems to correspond to that with a $\rho = \infty$.

The periodicity of the rings varies with crystallization temperature. *Figure 3* shows the periodic distance of extinction rings as a function of crystallization temperature for different blend ratios. It can be seen that the periodic distance increases with crystallization temperature. This result is different from that of reference [7], wherein a linear relationship between the periodic distance and crystallization temperature was observed. The reason may be that the compositions of the mixtures used in reference [7] are different from that of ours.

The most comprehensive study on the ring-banded spherulite structures in homopolymers such as polyethylene has been published by Keith and Padden [8]. The proposed basic mechanism leading to the ring pattern is axial twisting in lamellae under the influence of surface stress, and cooperative arrangement of twisted crystallites. And these conclusions have been simply used to explain the formation of ring-banded spherulites in the mixtures. However, how the mechanism leads to this peculiar texture has not been clarified yet. In our opinion, the formation of ring-banded spherulites in polymer mixtures is connected with the crystallization kinetics. There is no obvious relationship between the radial growth rates and the periodic distances of the ring-banded spherulites for the PCL/SAN mixtures, because the radial growth rate deponds upon both the rate of transport of the crystallizable segments across the liquid–solid interface (related to the T_g of the mixtures) and the free energy of critical nucleus formation on the crystal surface (related to the undercoolings). However, in next discussion, we will show that the periodic distances of ring-banded spherulites have a inherent relationship with the mobility of the segments in mixtures. In the study of crystallization kinetics of PCL/SAN blends, it has been shown that the glass transition temperature of the mixture has a predominant influence on crystallization kinetics of PCL/SAN mixtures [11]. In the crystallization process, it is clear that T_g is a very important parameter which has a significant influence on the transport of the crystallizable segments across the liquid–solid interface. In fact, this transport deals specifically with the local mobility of the segments, due to the interconnectivity of the polymer molecule, segments of the chain not crystallizing will be forced to undergo motions and, thus, will be affected by the overall mobility in the mixture. Therefore it is the overall mobility in the mixture that will be affected significantly by the T_g of the mixture. The specific interaction between the components of PCL and SAN in the mixtures will alter the mobility of both the crystallizable and noncrystallizable components significantly through the amorphous component with a higher T_g, SAN, involved. The overall mobility may be simply represented as the difference between the crystallization temperature, T_c, and the glass transition temperature, T_g, of the mixtures. *Figure 4* shows the periodic distance of extinction rings plotted as a function of the parameter T_c–T_g, which represents the overall mobility of the mixtures. For PCL/SAN blends, the T_g of the mixtures could be calculated according to the Fox equation and was

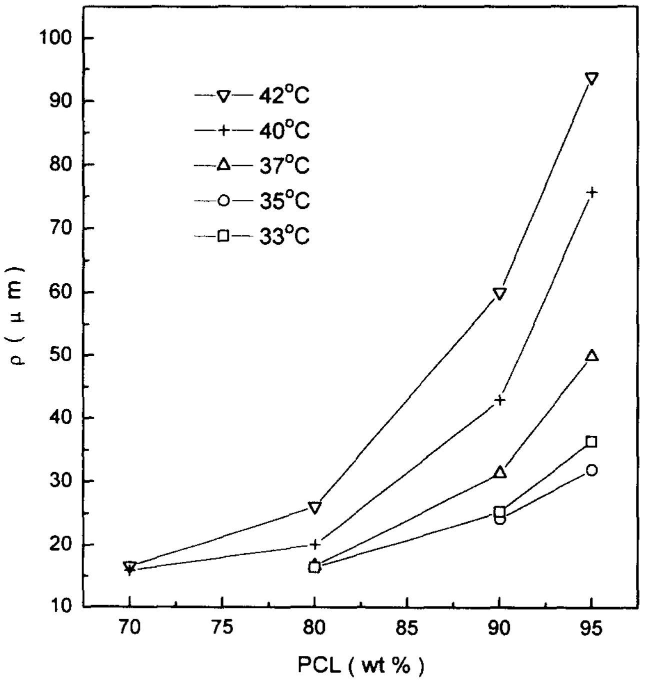

Figure 2 Variation of periodic distance of extinction rings with blend composition for PCL/SAN mixtures

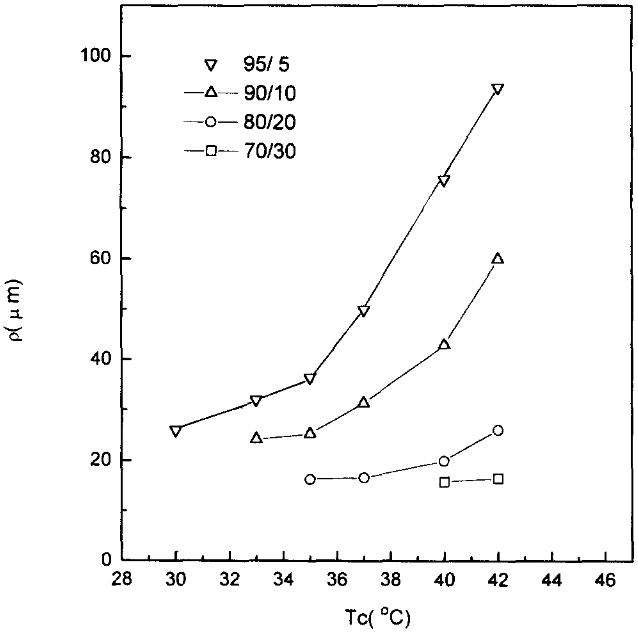

Figure 3 Variation of periodic distance of extinction rings with crystallization temperature for PCL/SAN mixtures

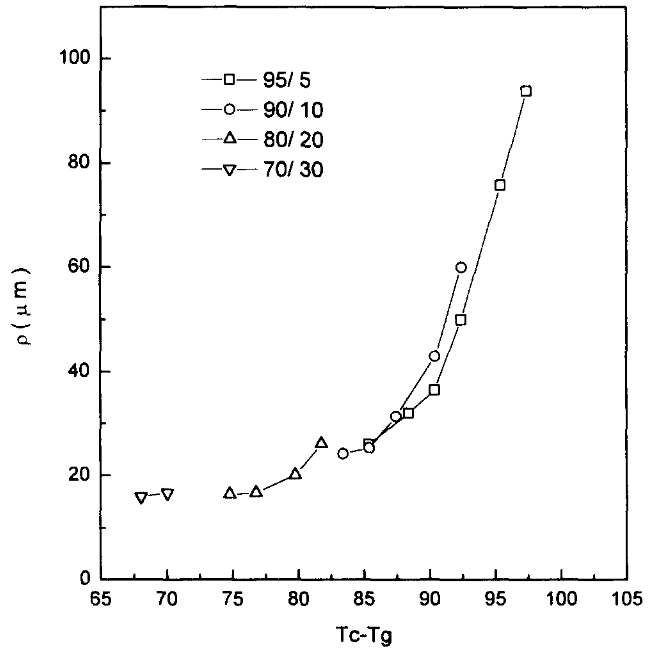

Figure 4 The periodic distance of extinction rings as a function of T_c–T_g for PCL/SAN mixtures with different blend ratios

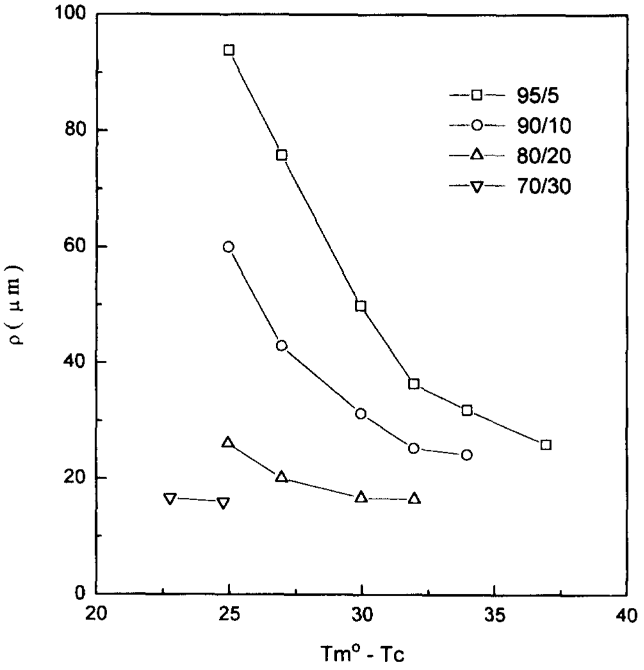

Figure 5 The periodic distance of extinction rings as a function of T_m°–T_c for PCL/SAN mixtures with different blend ratios

Table 1 Values of T_g and the equilibrium melting point T_m° of the mixtures

PCL/SAN	T_g (°C)	T_m (°C)
100/0	−60 ± 1	67 ± 1
95/5	−55 ± 1	67 ± 1
90/10	−50 ± 1	67 ± 1
80/20	−40 ± 1	66 ± 1
70/30	−28 ± 1	65 ± 1

contained in *Table 1* because experimental measurements on PCL blends conformed its validity [12–14].

The periodic distances of the ring-banded spherulites of the mixtures with different blends ratios fall on one master curve as shown in *Figure 4*. This infers that the periodic distances of ring-banded spherulites have a inherent relationship with the mobility of the segments in mixtures. For the first time, the influence of T_g has been demonstrated quantitatively and clearly. In future, in the investigation of the formation mechanism of ring-banded spherulites, the T_g of the mixtures will be emphasized.

In the crystallization process, the undercooling is another factor which affects the spherulite structures. For comparison with the influence of the overall mobility in the mixtures, the periodic distance of extinction rings was plotted as a function of the undercoolings, represented by the parameter T_m—T_c, where T_m° is the equilibrium melting point of the mixtures. For miscible polymer–polymer mixtures, as shown by Nishi and Wang, the Flory-Huggins theory predicts that the equilibrium melting point of the mixture, $T_{m,eq}$ will be lower than that of the pure material, T_m° such that [15]

$$\frac{1}{T_{m,eq}} = \frac{1}{T_m^\circ} - \frac{RV_{2u}}{\Delta h_u V_{1u}}\chi(1-\theta_2)^2 \qquad (1)$$

where Δh_u is the heat of fusion per mole of monomer of the crystallizable component with volume fraction ϕ_2 of the crystallizable component at a temperature T, V_{iu} is the molar volume of component i, and χ is the Flory-Huggins interaction parameter. The equilibrium melting point of the mixtures were calculated by using equation (1) and list in *Table 1*.

The plot is displayed in *Figure 5*. It can be seen that the variation of periodic distance of extinction rings in *Figure 5* is similar to that in *Figure 3*. The higher the crystallization temperatures, that is the lower the undercoolings, the wider the periodic distance of extinction rings. From *Figures 4 and 5*, it is thought that the undercoolings affect the apparent pattern of ring-banded spherulite structures and the overall mobility of the mixtures in crystallization process is the origin of the formation of ring-banded spherulites. In future research we wish to deal in great detail with the physical meanings of the observed results in *Figure 4*.

Conclusion

The PCL/SAN blends exhibited not only spherulites with a Maltese cross, but also distinct extinction rings. The periodic distance of rings changes with blend ratio and crystallization temperature. The periodic distance of rings was plotted as a function of the undercooling and the overall mobility of the mixtures, respectively. It was interesting to find that the periodic distances of the ring-banded spherulites with different blends ratios fall on one master curve when plotted as a function of the overall mobility of the mixtures. It was concluded that the overall mobility of the chain segments mainly controls the formation of ring-banded spherulites. For the first time a quantitative experimental result was obtained concerning the relationship of the periodic distance of rings and the overall mobility of the mixtures. This relationship may be useful to explain the formation mechanism of ring-banded spherulites in polymer blends or even in homopolymers in future.

Acknowledgements

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References

1. Stein, R. S., Khambatta, F. B., Warner, F. P., Russell, T., Escala, A. and Balizer, E., *J. Polym. Sci., Polym. Symp.*, 1978, **63**, 313.
2. Balijepalli, S. and Schultz, J. M., *Macromolecules*, 1996, **29**, 2095.
3. Braun, D., Jacobs, M. and Hellmann, G. P., *Polymer*, 1994, **35**, 706.
4. Saito, H. and Stuhn, B., *Macromolecules*, 1994, **27**, 216.
5. Khambatta, F. B., Warner, F. P., Russell, T. and Stein, R. S., *J. Polym. Sci., Polym. Phys. Edn*, 1976, **14**, 139.
6. Li, W., Yan, R. J. and Jiang, B. Z., *Polymer*, 1992, **33**, 889.
7. Kummerlowe, C. and Kammer, H. W., *Polym. Networks Blends*, 1995, **5**, 131.
8. Keith, H. D. and Padden, F. J., *Polymer*, 1984, **25**, 28.
9. Schulze, K., Kressler, J. and Kammer, H. W., *Polymer*, 1993, **34**, 3704.
10. Nojima, S., Watanabe, K., Zheng, Z. Y. and Ashida, T., *Polymer*, 1988, **20**, 823.
11. Wang, Z.G. and Jiang, B.Z. *Macromolecules*, in press.
12. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
13. Kressler, J., Svoboda, P. and Inoue, T., *Polymer*, 1993, **34**, 3225.
14. Koleske, J. V. and Lundberg, R. D., *Polymer*, 1969, **7**, 795.
15. Nishi, T. and Wang, T. T., *Macromolecules*, 1975, **8**, 909.