

# Ring-Banded Spherulites in Poly( $\epsilon$ -caprolactone) Blended with Hydroxyethyl Cellulose Acetate as an Indication for Partial Miscibility

Q. XIAO,<sup>1</sup> S. YAN,<sup>1</sup> K. D. ROGAUSCH,<sup>1</sup> J. PETERMANN,<sup>1</sup> Y. HUANG<sup>2</sup>

<sup>1</sup> Institute of Materials Science, Department of Chemical Engineering, University of Dortmund, D-44221 Dortmund, Germany

<sup>2</sup> Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China

Received 12 May 2000; accepted 20 August 2000

**ABSTRACT:** The morphologies of poly( $\epsilon$ -caprolactone) (PCL) blends with hydroxyethyl cellulose acetate (HECA), a thermotropic liquid crystalline polymer (TLCP), were investigated by optical microscopy. It is demonstrated that when the pure PCL is crystallized from the melt, a spherulitic morphology arises with distinct Maltese crosses. With the addition of the HECA, the spherulites of the PCL/HECA blends show not only the Maltese crosses but also distinct extinction rings (i.e., a ring-banded spherulitic morphology). The average periodic distance of the extinction rings decreases drastically with the increase of the HECA content from 0.5 to 5 wt % in the mixture, whereas it decreases only slightly with the further increase of HECA. The periodicity of extinction rings is also influenced by the crystallization temperature. The formation of the ring-banded spherulites of PCL in PCL/HECA blends is explained in terms of stress-induced twisted lamellar crystallization and used as an indication of the molecular solubility of the HECA in the PCL. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1681–1686, 2001

**Key words:** poly( $\epsilon$ -caprolactone); hydroxyethyl cellulose acetate; blend; ring-banded spherulite

## INTRODUCTION

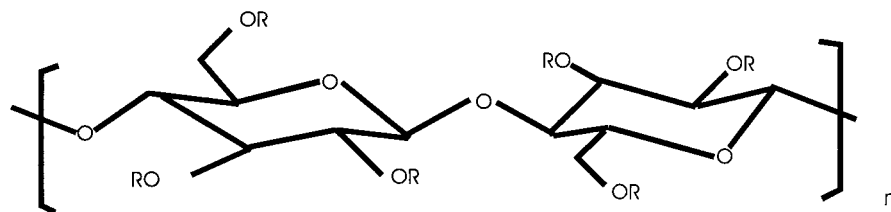
Maltese crosses and extinction rings are familiar phenomena of crystal spherulites in polymers under polarization optical microscopy. Whereas spherulites with distinct Maltese crosses are the commonly observed morphologies of most of the

semicrystalline polymers, only a few semicrystalline polymers [e.g., polyethylene,<sup>1</sup> polypropylene,<sup>1</sup> poly(ethylene terephthalate),<sup>2</sup> poly(propylene oxide),<sup>3</sup> and poly(hydroxybutyrate),<sup>3</sup>] can form spherulites not only with Maltese crosses but also with concentric extinction rings. The extinction rings, however, are often observed in miscible polymer-blend systems. For example, pure poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF), and poly( $\epsilon$ -caprolactone) (PCL) show spherulites without extinction rings, although blends of PEO with poly(methyl methacrylate) (PMMA),<sup>4</sup> PVDF with PMMA,<sup>5</sup> PVDF with poly(styrene-*co*-methyl methacrylate) (PS-PMMA),<sup>6</sup> and PCL with poly(vinyl chloride)

Correspondence to: J. Petermann (E-mail: petermann@chemietechnik.uni-dortmund.de)

Contract grant sponsor: Konrad-Adenauer-Stiftung; contract grant sponsor: Fonds der Chemischen Industrie (FCI); contract grant sponsor: Deutschen Forschungsgemeinschaft (DFG).

*Journal of Applied Polymer Science*, Vol. 80, 1681–1686 (2001)  
© 2001 John Wiley & Sons, Inc.



**Figure 1** The chemical structure of HECA.

(PVC)<sup>7,8</sup> exhibit spherulites not only with Maltese crosses but also with extinction rings.

The blends of PCL with thermoplastic polymers were intensively investigated in recent years, not only because it is a biodegradable material,<sup>9,10</sup> but also because its blends can form ring-banded spherulitic morphologies. For instance, blends of PCL with PVC,<sup>7,8,11–13</sup> poly(ethylene terephthalate- $\epsilon$ -caprolactone),<sup>14</sup> poly(butylene terephthalate- $\epsilon$ -caprolactone),<sup>14</sup> poly(styrene-*co*-acrylonitrile) (SAN),<sup>15–19</sup> or poly(butadiene-*co*-caprolactone)<sup>20</sup> are well investigated. The common characteristics of those blends are that the second components are all amorphous polymers and molecularly miscible with PCL in the melt. Until now only a few investigations of blends of PCL and thermotropic liquid crystalline or/and semicrystalline polymers were published.<sup>21</sup>

The purpose of this study is to present some experimental results of PCL blends with a thermotropic liquid crystalline polymer [i.e., hydroxyethyl cellulose acetate (HECA)] with respect to their miscibilities and spherulitic morphologies.

## EXPERIMENTAL

### Materials and Sample Preparation

Hydroxyethyl cellulose acetate (HECA),  $M_w = 151,000$  g/mol and polydispersity  $\approx 2.32$ , was prepared by Prof. Huang at Guangzhou Institute of Chemistry, Chinese Academy of Sciences. The synthesis is described elsewhere.<sup>22</sup> Figure 1 shows its chemical structure. The degree of its esterification, calculated from the content of oxygen, is about 2.6–3.0 wt %.

A commercial-grade poly( $\epsilon$ -caprolactone) (PCL; Aldrich-Chemie Gesellschaft mbH, Germany), with molecular weight  $M_w = 65,000$  g/mol, poly-

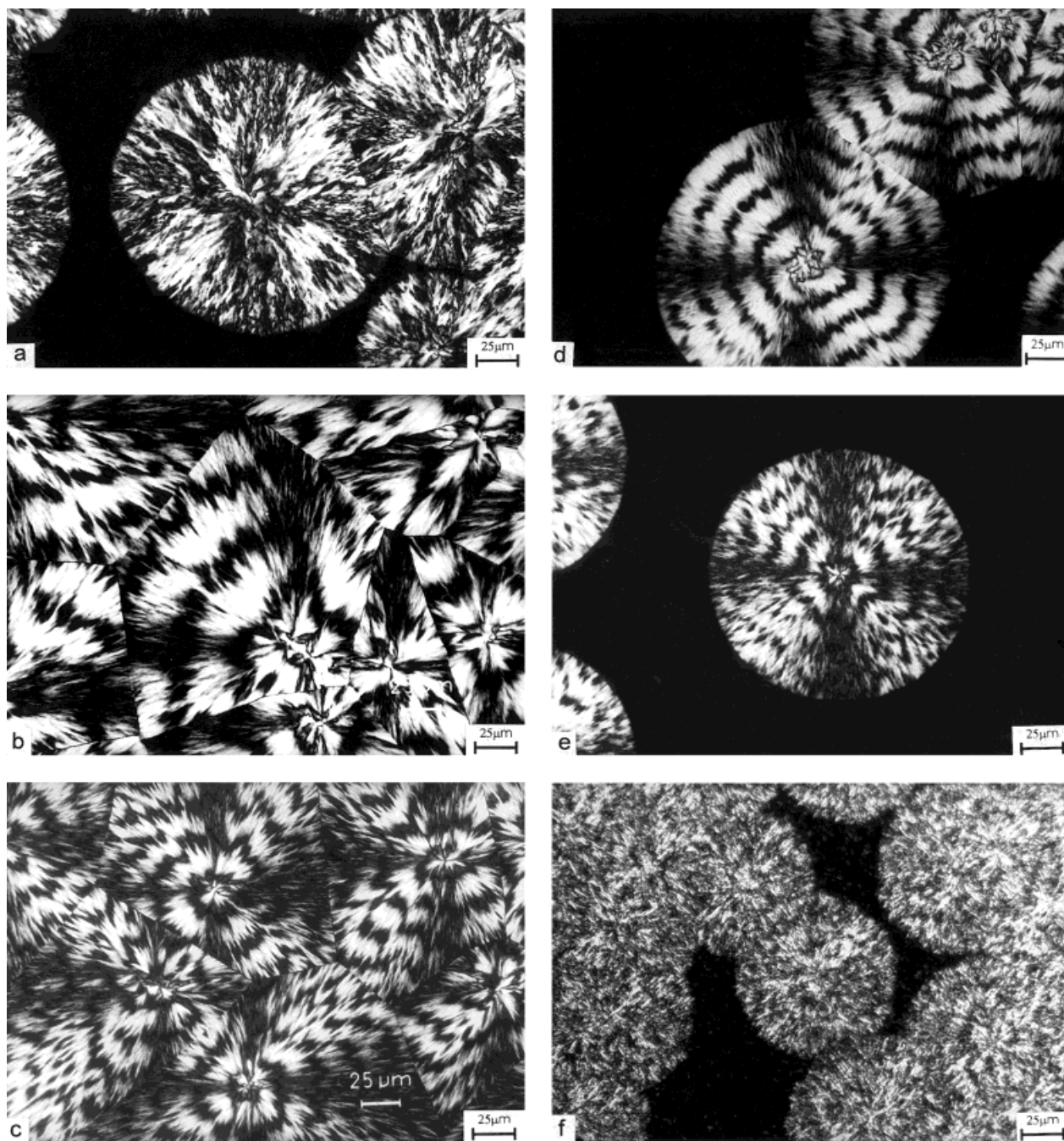
dispersity 1.53, and melting point 60°C, was used as the thermoplastic polymer matrix.

PCL/HECA blends with contents of HECA of 0.5, 1, 2, 5, 10, 20, 30, 40, and 50 wt %, respectively, were used in this study. Pure HECA was studied by Prof. Huang.<sup>22</sup> For the optical microscope observations, the samples of pure PCL and PCL/HECA blends were prepared by casting a 3 wt % acetone solution of the corresponding polymer blends onto clean glass slides. After evaporation of the acetone at room temperature for 24 h in a vacuum oven, thin polymer films with the thickness of about 30  $\mu\text{m}$  were used directly for optical microscopic observations.

The morphologies of the obtained polymer samples were examined under crossed polarized light in a Leica optical microscope equipped with a hot stage. The temperature fluctuation of the sample was within 0.5°C throughout the experiments. The blends were heated to a temperature of 90°C and subsequently cooled within 1 min to the crystallization temperatures  $T_c$ . For studying the influence of HECA on the morphology of PCL, the pure PCL as well as the blends were all crystallized at 50°C. To check the crystallization temperature dependence on the structure of PCL/HECA blends, the blend with  $\phi_{\text{HECA}} = 5$  wt % was used as the example and crystallized at  $T_c = 45, 47, 49, 51, 53, 55, \text{ and } 57^\circ\text{C}$ , respectively.

## RESULTS AND DISCUSSION

The sequence 2(a)–2(f) of optical micrographs in Figure 2 shows spherulites in pure PCL and selected PCL/HECA blends with  $\phi_{\text{HECA}} = 2, 5, 10, 20, \text{ and } 50$  wt % crystallized at 50°C. The spherulites of pure PCL display a Maltese cross, although it is less well pronounced than that by

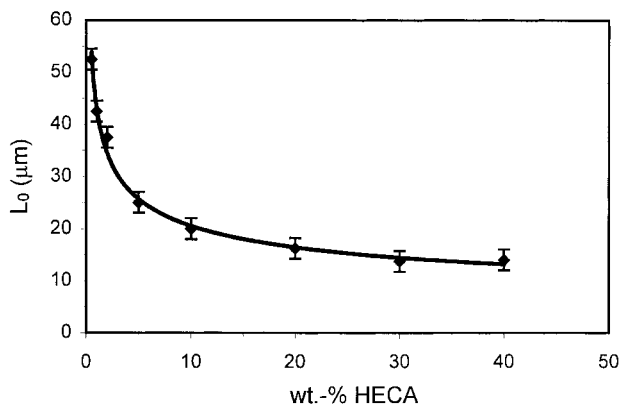


**Figure 2** Optical micrographs of spherulitic structure of PCL in HECA/PCL blends crystallized at 50°C. The PCL/HECA compositions are (a) 100/0, (b) 98/2, (c) 95/5, (d) 90/10, (e) 80/20, and (f) 50/50 (wt%).

crystallization at lower temperatures. For PCL/HECA mixtures with  $0.5 \text{ wt } \% < \phi_{\text{HECA}} < 40 \text{ wt } \%$ , in addition to the Maltese cross a distinct pattern of the extinction rings can also be observed. In the 50/50 PCL/HECA blend it is difficult to identify the Maltese cross and the extinction rings. It can be seen that the textures of the

spherulites become increasingly open, coarser, and more irregular with increasing amount of HECA. The average value of the periodic distance of extinction rings ( $L_0$ ) decreases with increasing content of the HECA component in the mixture. Figure 3 shows the composition dependence of the periodic distance of the extinction rings  $L_0$ , which





**Figure 3** The periodic distance of the extinction ring ( $L_0$ ) as a function of  $\Phi_{\text{HECA}}$ .

decreases strongly as the HECA composition increases from 0.5 to 5 wt %. When the content of the HECA component is above 5 wt % in the mixture, the  $L_0$ 's decrease only very slightly with further increase of the HECA amount. The ring pattern of the spherulites of pure PCL seems to correspond to that with  $L_0 = \infty$ .

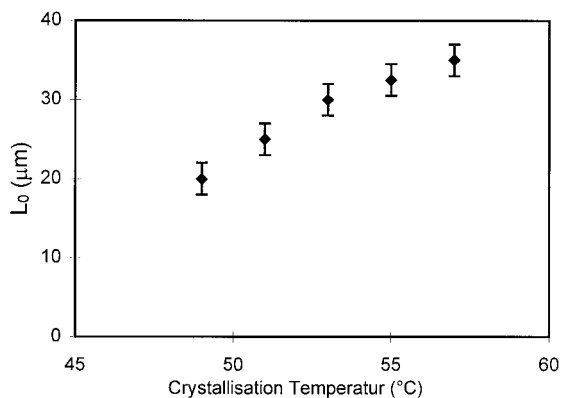
Figure 4 shows the distances of the periodic extinction rings as a function of crystallization temperature ( $T_c$ : 49 to 57°C) for 95/5 PCL/HECA. It can be seen that the periodic distance of the extinction rings increases with increasing crystallization temperature. The temperature range of the observation of ring-banded pattern is limited as a result of the fact that, when  $T_c$  is close to  $T_m$  (60°C), separations of the rings become comparable to the spherulite diameter and make the observation of the ringed structure difficult, whereas at low  $T_c$  the number of spherulites increases and their diameter decreases. Hence, it becomes difficult to observe several extinction rings within a single spherulite.

Similar phenomena of the development of extinction rings were observed in other blends of PCL with other thermoplastic polymers at lower crystallization temperatures (<50°C). According to Keith and Padden,<sup>13</sup> Nojima et al.,<sup>20</sup> and Defieuw et al.,<sup>23</sup> distinct ring patterns can be observed only in a blend system, which exhibits molecular compatibility, and when the spherulitic growth rate is higher than the diffusibility of the solute macromolecules in the melt.<sup>23</sup> Keith et al.<sup>13</sup>, for example, did not observe the ring-banded spherulites in phase-separated systems.

Concerning the origin of the formation of the ring pattern in PCL blends, Wang et al.<sup>19</sup> found in PCL/SAN blend systems that the distance of the

extinction rings depends on the difference between the crystallization temperature ( $T_c$ ) and the respective glass-transition temperature ( $T_g$ ), which is a function of the blend concentration. They were able to construct a master curve (ring distance versus  $T_c - T_g$ ). Obviously this fact does not hold for the PCL/HECA blends because all the blends with different concentrations possess roughly the same  $T_g$  (about -60°C for PCL). This means that, at the same crystallization temperature, their chain segments have about the same mobility and should display the same periodic distance of extinction rings, which is obviously not the case as seen in Figure 3.

The mechanisms leading to the extinction rings in spherulites are still under discussion and not yet clarified. It is even suggested that different reasons for different polymers may lead to the twisting.<sup>24</sup> A number of authors have attempted to explain the extinction phenomenon in terms of either preferred crystal orientation (Schuur<sup>25</sup>) or "rhythmic crystallization" (Keith and Padden<sup>26</sup>). As for the origin of the twisted lamellae by crystallization from melt, the most comprehensive studies on the ring-banded spherulite structures in homopolymers, such as polyethylene, were published by Lustiger and colleagues<sup>27</sup> and by Keith and Padden.<sup>1</sup> They suggested that the extinction rings of the banded spherulites are caused by a radially oriented assembly of continuous helicoidally twisted lamellae. Keith and Padden<sup>1</sup> further explained that the twist of the polymer lamellae results from the surface stresses created by the congested molecular packing of the emerging polymer chains from the crystal surface on the amorphous side of the crystal-



**Figure 4** Variation of periodic distance of extinction ring ( $L_0$ ) with crystallization temperature of a 95/5 (wt%) PCL/HECA blend.

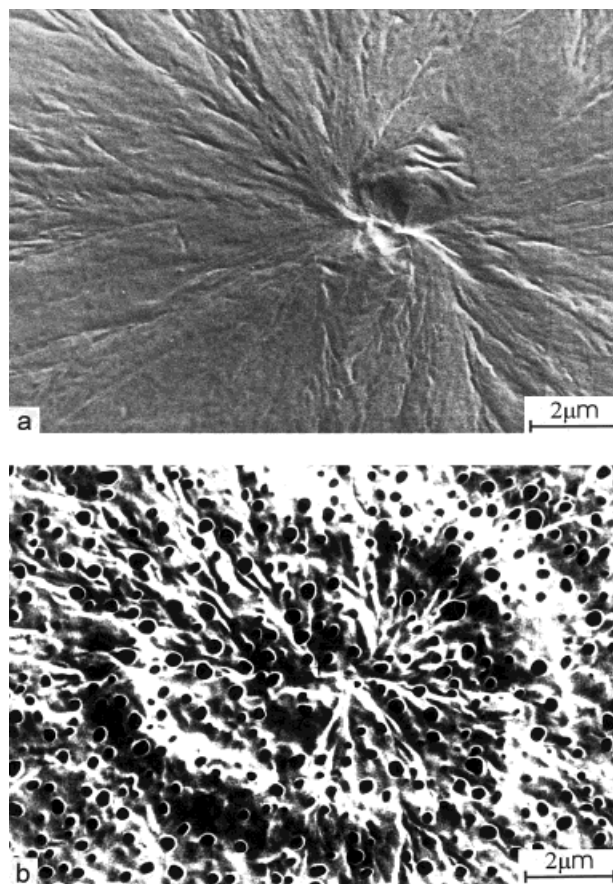
line–amorphous phase boundary. During the crystallization of the semicrystalline component, the blended amorphous polymer chains are rejected from the crystal lamellae. In this way a congestion of the molecular packing in the amorphous interlamellar phase is expected, enhancing the surface stresses and, consequently, leading to lamellar twisting.

In initial investigations it was suggested that PCL/HECA blends were an immiscible system, considering that the HECA is a thermotropic liquid–crystalline polymer with rigid chain segments, whereas the PCL consists of flexible chain segments. Additionally, the thermal measurements of the  $T_g$ 's of the blends by DSC did not give any significant indication of a miscibility. But scanning electron microscopic (SEM) investigation of the PCL/HECA blends showed that the HECA component cannot be identified when its content in the blends is less than 5 wt %, whereas a two-phase structure is clearly seen when its content is more than 5 wt %. Figure 5(a) and (b) show SEM micrographs of 98/2 and 70/30 PCL/HECA blends, respectively, which were etched by a selective solvent (acetone/water). In Figure 5(a) there are no HECA domains in the PCL matrix. However, in Figure 5(b) the dark areas indicate the HECA domains that were washed out by the selective solvent.

The observation that no separated HECA phase can be seen in the PCL/HECA sample with HECA concentration < 5 wt % indicates that for small amounts the HECA is molecular dispersed in the PCL matrix. This is in accordance with ring-banded spherulite observations, in which the distances between the extinction rings strongly depend on the HECA content for concentrations less than about 5 wt %. The fact that no remarkable changes in the glass-transition temperature ( $T_g$ ) were detected may be the result of the fact that the  $T_g$  measurements in a DSC are not precise enough to detect small changes, which would be expected in the blends with low HECA concentration.

## CONCLUSIONS

The influence of blending a LCP (hydroxyethyl cellulose acetate) on the morphologies of poly( $\epsilon$ -caprolactone) (PCL) has been investigated. It is found that the “Maltese cross” spherulites of the pure PCL are changed into a ring-banded structure by blending. From the observations that the



**Figure 5** Scanning electronic micrograph of PCL/HECA, after HECA component was washed out with a selective solvent (Acetone/Water). (a) 98/2, (b) 70/30 (wt%).

distance between extinction rings strongly decreases up to a concentration of about 5 wt % HECA, it is concluded that the system PCL/HECA possesses a partial miscibility of about 5%. This is confirmed by SEM investigations of etched samples.

The financial support of the Konrad-Adenauer-Stiftung, the Fonds der Chemischen Industrie (FCI), and der Deutschen Forschungsgemeinschaft (DFG) is gratefully acknowledged.

## REFERENCES

1. Keith, H. D.; Padder, F. J., Jr. *Polymer* 1984, 25, 28.
2. Keller, A. *J Polym Sci* 1955, 17, 291.
3. Singfield, K. L.; Hobbs, J. K.; Keller, A. *J Crystal Growth* 1998, 183, 683.

4. Martuscelli, E.; Silvestre, C.; Addonizio, M. L.; Ametino, L. *Makromol Chem* 1986, 187, 1557.
5. Saito, H.; Stuhn, B. *Macromolecules* 1994, 27, 216.
6. Braun, D.; Jacobs, M.; Hellmann, G. P. *Polymer* 1994, 35, 706.
7. Khambatta, F. B.; Warner, F.; Russell, T.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1976, 14, 1391.
8. Ong, C. J.; Price, F. P. *J Polym Sci Polym Symp* 1978, 63, 45.
9. Potts, J. E.; Clendinning, R. A. M.; Ackart, W. B.; Niegisch, W. D. in *Polymer Science and Technology: Polymers and Ecological Problems*, Vol. 3; Guillet, J., Ed.; Plenum Press: New York, 1973.
10. Kolleske, J. V. *Polymer Blends*; Academic Press: New York, 1978; Chapter 22, pp 369–389.
11. Nojima, S.; Tsutsui, H.; Mruskihara, M.; Kosaka, W.; Kato, N.; Ashida, T. *Polym J* 1986, 18, 451.
12. Nojima, S.; Watanaba, K.; Zheng, Z.; Ashida, T. *Polym J* 1988, 20, 823.
13. Keith, H. D.; Padden, F. J., Jr.; Russell, T. P. *Macromolecules* 1989, 22, 666.
14. Ma, D. Z.; Xu, X.; Luo, X. L.; Toshio, N. *Polymer* 1997, 38, 1131.
15. Keith, H. D.; Padden, F. J., Jr. *Macromolecules* 1989, 22, 267.
16. Li, W.; Yan, R. J.; Jiang, B. Z. *Polymer* 1992, 33, 889.
17. Kummerlöve, C.; Kammer, H. W. *Polym Networks Blends* 1995, 5, 131.
18. Schulze, K.; Kressler, J.; Kammer, H. W. *Polymer* 1993, 34, 3704.
19. Wang, Z. G.; Wang, X. H.; Yu, D. H.; Jiang, B. Z. *Polymer* 1997, 38, 5897.
20. Nojima, S.; Wang, D.; Ashida, T. *Polym J* 1991, 23, 1473.
21. Taesler, C.; Petermann, J.; Kricheldorf, H. R. *Innovations Mater Res* 1996, 1, 89.
22. Huang, Y. *J Appl Polym Sci* 1994, 51, 1979.
23. Defieuw, G.; Groeninckx, G.; Reynaers, H. *Polym Commun* 1989, 30, 267.
24. Keith, H. D.; Padden, F. J., Jr. *Macromolecules* 1996, 29, 7776.
25. Schuur, G. *J Polym Sci* 1953, 11, 385.
26. Keith, H. D.; Padden, F. J., Jr. *J Polym Sci* 1958, 31, 415.
27. Lustiger, A.; Lotz, B.; Duff, T. S. *J Polym Sci Part B Polym Phys* 1989, 27, 561.