

NOTES

## Spherulite Structure in Compatible Mixtures of Poly( $\epsilon$ -caprolactone) and Poly(vinyl chloride)

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In compatible polymer blends, crystallization of a constituent polymer is an important origin of the morphology formation. The crystallization usually brings about the development of the spherulite structure in the system. The comparison of the spherulite structure in polymer blends with that in pure polymers leads to the fact that the structure changes significantly with increasing the non-crystalline component in the system. Stein *et al.*, for example, investigated<sup>1,2</sup> the spherulite structure of poly( $\epsilon$ -caprolactone) (PCL) in the compatible blend of PCL and poly(vinyl chloride) (PVC) and found qualitatively that the alternating period of the extinction ring in the PCL spherulite increased proportionally with increasing the PCL component.

In this study, the detailed structure of the PCL spherulite in PCL/PVC blends was observed, and parameters characterizing the spherulite structure were evaluated quantitatively as a function of PCL composition in the blend.

### EXPERIMENTAL

#### *Materials and Sample Preparation*

The poly( $\epsilon$ -caprolactone) (PCL) obtained from Scientific Polymer Products, Inc. was fractionated with a benzene/*n*-heptane sys-

tem.<sup>3</sup> The weight average molecular weight  $\bar{M}_w$ , and its ratio,  $\bar{M}_w/\bar{M}_n$ , to number average molecular weight  $\bar{M}_n$ , determined by gel permeation chromatography were 27,400 and 1.59, respectively. The melting temperature of PCL,  $T_m$ , was about 60°C. The PVC supplied from Aldrich Chemical Co., Inc. was fractionated with a tetrahydrofuran (THF)/water system.<sup>4</sup> The values of  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  were 114,000 and 1.56, respectively.

The samples of pure PCL and PCL/PVC blends with various PCL compositions,  $\phi_{PCL}$ , were prepared by casting from THF solution onto a glass plate and evaporating THF at about 100°C for 12 h. The thickness of the sample thus prepared for the microscopic observation was about 0.03 mm. The sample had been maintained at a temperature above  $T_m$  until use, because once the PCL crystallized, a trace of the spherulite did not disappear even if the sample was melted at the temperature above  $T_m$ .

#### *Microscopic Observation and the Structure Analysis*

The spherulite of PCL was observed by an optical microscope with a hot stage. The temperature of this hot stage was controlled by circulating water with constant temperature. The temperature fluctuation of the sample was

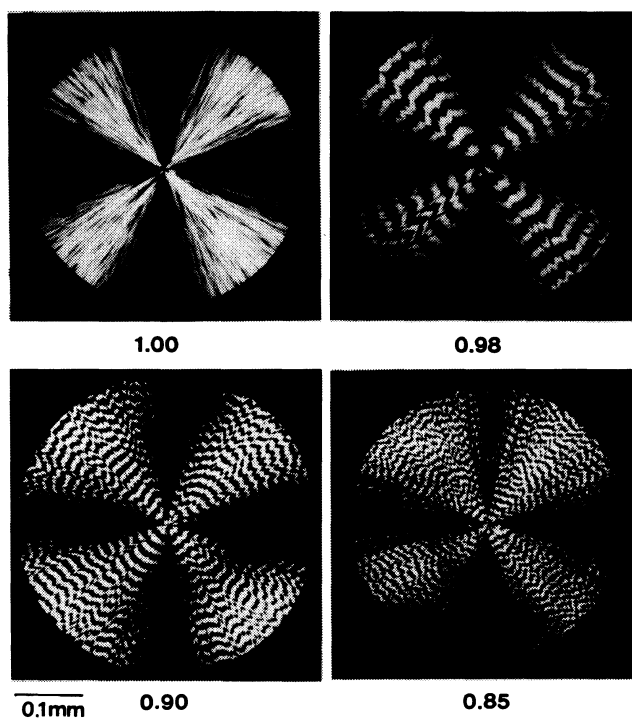
within 0.2°C throughout the experiment. The blends containing 50–100 wt% PCL were crystallized at 38.0°C. For the blend with  $\phi_{\text{PCL}}=0.95$ , the crystallization at  $T_c=42.7$ , 40.5, and 34.3°C was also carried out to investigate the  $T_c$  dependence of the spherulite structure. The sample was cooled down to  $T_c$  within a minute from the molten state. The spherulite was photographed between crossed polarizers to analyze the structure with the aid of computer. The radial average width of the extinction ring, that is, the alternating period of the black and white circles, and its distribution were evaluated as a function of  $\phi_{\text{PCL}}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the spherulite structure crystallized at 38°C in the blends with  $\phi_{\text{PCL}}=0.85$ , 0.90, 0.98, and 1.00. Similar spherulite structure could be observed for the blends with

same  $\phi_{\text{PCL}}$  irrespective of the crystallization temperature investigated. The spherulite formed in the blends with  $0.99 > \phi_{\text{PCL}} > 0.70$  has a Maltese cross and a distinct pattern of the extinction rings, whereas that in pure PCL has no extinction ring. The average width of the extinction ring decreases and the ring becomes more irregular with decreasing  $\phi_{\text{PCL}}$ . This irregularity of the extinction ring leads to the structure beyond recognition of the ring for the blends with  $\phi_{\text{PCL}} < 0.70$  as expected from Figure 1. The spherulite was analyzed by digitalizing the pattern of the structure. The number  $n_i$  of the width  $l_i$  of the extinction ring was counted radially from the center of the spherulite. Two average widths of the extinction ring,  $L (= \sum n_i l_i / \sum n_i)$  and  $L' (= \sum n_i l_i^2 / \sum n_i l_i)$ , were calculated. The distribution of the ring width  $\sigma$  was defined as  $\sigma = L'/L$ .

Figure 2 shows the composition dependence of the width of the extinction rings  $L$  and  $L'$ ,



**Figure 1.** Spherulite structure of PCL in pure PCL and PCL/PVC blends crystallized at 38°C. The numeral stands for PCL composition.

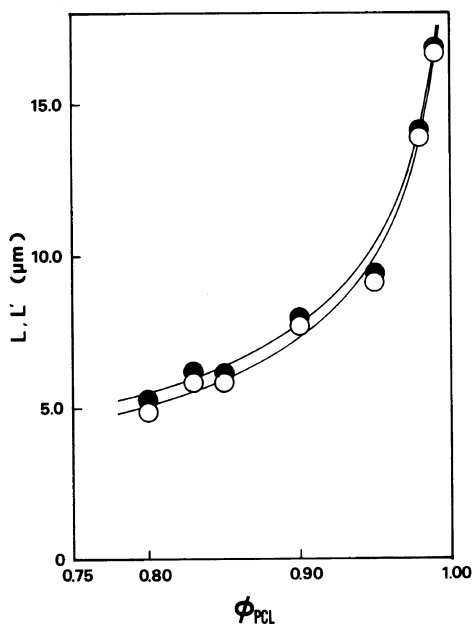


Figure 2. The width of the extinction ring as a function of  $\phi_{PCL}$ :  $\circ$ ,  $L$  ( $=\sum n_i l_i / \sum n_i$ );  $\bullet$ ,  $L'$  ( $=\sum n_i l_i^2 / \sum n_i l_i$ ).

which decrease with decreasing PCL composition in the blend. This result agrees qualitatively with the observation of Khambatta *et al.*<sup>1</sup> carried out for the same system. The values of  $L$  and  $L'$ , however, increase dominantly as  $\phi_{PCL}$  approaches to unity. The spherulite of pure PCL seems to correspond to that with  $L = \infty$ . Figure 3 shows the distribution of the width of the extinction ring, which increases with decreasing  $\phi_{PCL}$ .

The extinction ring is ascribed to the twist of the lamella structure of PCL.<sup>5</sup> Therefore present result means that the interval of the twist becomes shorter and the spherical symmetry of the spherulite becomes more incomplete with decreasing  $\phi_{PCL}$ . On the microscopic observation, there is an extreme difference in the spherulite structure between pure PCL and the blend with  $\phi_{PCL} = 0.99$ , that is, the spherulite in pure PCL does not have any twist of the lamella. Our preliminary result of small angle X-ray scattering measurement showed, however, that there was no large difference in the

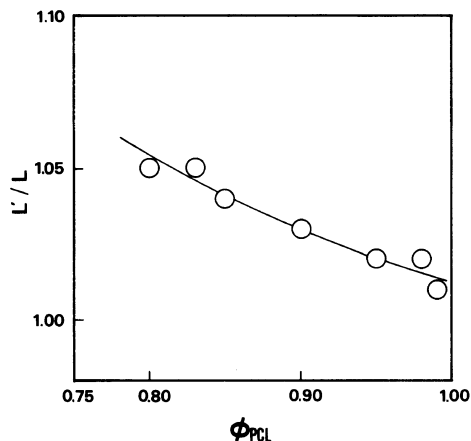


Figure 3. The distribution of the width of the extinction ring  $\sigma$  ( $=L'/L$ ).

thickness of the lamella and the amorphous layer, indicating that the appearance of the extinction ring in the spherulite of the blend does not simply correlate to the structure with the magnitude of the crystallite size. The crystallization rate of PCL in the blend may be responsible for the formation of the extinction ring in the spherulite structure of the blend.<sup>6</sup>

In summary, the spherulite structure with a Maltese cross and distinct extinction rings could be observed in PCL/PVC blends with  $0.70 < \phi_{PCL} < 0.99$ , whereas no extinction ring could be observed in pure PCL and blends with  $\phi_{PCL} < 0.70$  at any crystallization temperature. The width of the extinction ring  $L$  increased dominantly as  $\phi_{PCL}$  approached to unity. The distribution of  $L$  increased slowly with decreasing  $\phi_{PCL}$ .

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