The ring-banded spherulite structure of poly(ε-caprolactone) in its miscible mixtures with poly(styrene-*co*-acrylonitrile)

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The structure of the PCL spherulite in poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile) (PCL/SAN) blends was investigated by optical microscopy and small angle light scattering. The spherulite structure with a Maltese cross has been observed in pure PCL. Similar PCL/SAN blends exhibited not only spherulites with a Maltese cross, but also distinct extinction rings. The H_v light scattering pattern especially caused diffraction rings in PCL/SAN blends but not in pure PCL. The spherical symmetry of spherulite PCL becomes more incomplete and the twist of the lamella becomes more irregular with increasing SAN content. It is found that the spherulite structure of PCL/SAN blends is dependent on the crystallization temperature and the concentration of SAN in PCL/SAN blends.

(**Keywords: poly(ε-caprolactone); spherulite; mixture**)

INTRODUCTION

In miscible polymer blends, the crystallization of a constituent polymer is an important origin of the morphology formation. The crystallization usually brings about the development of spherulite structure in the mixtures. It is very interesting to compare the spherulite structure of the pure polymer with that of the polymer blends. The mixtures of poly(ε-caprolactone) with poly(vinyl chloride) (PCL/PVC)[1] and poly(ethylene oxide) with poly(methyl methacrylate) (PEO/PMMA)[2] have been studied. In the PCL/PVC blends, the PCL spherulites are composed of lamellae radiating from the spherulite centre and twisting regularly. With increasing PVC, the texture of the spherulites becomes coarser and more open. In the PEO/PMMA blends, the blend films are completely filled with PEO spherulites and no separated domains of PMMA are observed up to 40 wt% of PMMA. The blends with higher PMMA content show islands of crystalline PEO within a matrix of PMMA. Large amorphous regions coexist with less developed PEO spherulites. In this study, the structure of the PCL spherulite in PCL/poly(styrene-*co*-acrylonitrile) (SAN) blends was studied by optical microscopy and small angle light scattering.

EXPERIMENTAL

The PCL was purchased from Polysciences Inc. (USA). The weight average molecular weight, M_w, and number average molecular weight, M_n, determined by gel permeation chromatography (g.p.c.) are 101 000 and 50 600, respectively. Their ratio $\alpha = 2.00$. The melting temperature of PCL was ~60°C. The SAN was synthesized by radical copolymerization of styrene with acrylonitrile monomer. SAN is an amorphous polymer and was found, by element nitrogen analysis, to include 24 wt% acrylonitrile. The M_w and M_n are 487 000 and 145 000 by g.p.c. and their ratio $\alpha = 3.36$.

The samples of pure PCL and PCL/SAN blends were prepared by mixing in CH_2Cl_2 solution. The composition of PCL/SAN (wt/wt) mixtures was 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50. A dilute solution (1% wt/wt) was stirred continuously for 24 h at room temperature. Films were cast on a glass microscope slide and held in a vacuum at 40°C for 48 h.

PCL/SAN blends were molten at 80°C for 7 h, and then were cooled slowly to 40°C at a rate of 0.16°C min^{-1}, and crystallized at 40°C for 3 days. The temperature of crystallization was controlled by circulating water in a thermostat.

RESULTS AND DISCUSSION

Figure 1 shows the cross-polarized optical photomicrographs of PCL/SAN blends. The birefringent spherulite structure of pure PCL was observed. The spherulites have been truncated by impingement and displayed a Maltese cross. Similar spherulites could be observed in PCL/SAN blends. As well as birefringent spherulites with a Maltese cross, a distinct pattern of extinction rings, which are absent in pure PCL, are apparent in the blends. Furthermore, from *Figure 1* it can be seen that the texture of the spherulites becomes increasingly open, coarser, and more irregular and the width of the extinction ring decreases with increasing amounts of SAN (*Figure 2*).

The H_v and V_v patterns of the PCL/SAN blends from light scattering were studied using photographic apparatus. (H_v patterns are obtained when the polarizer in the incident beam is vertical and the analyser in the scattered beam is horizontal, and V_v patterns are obtained when the polarizer and the analyser are both vertical.) A typical example of an H_v pattern is given in *Figure 3*. The H_v pattern of pure PCL shows a four-leaf clover pattern and maximum intensity occurs at an azimuthal angle of multiples of 45°. This pattern is

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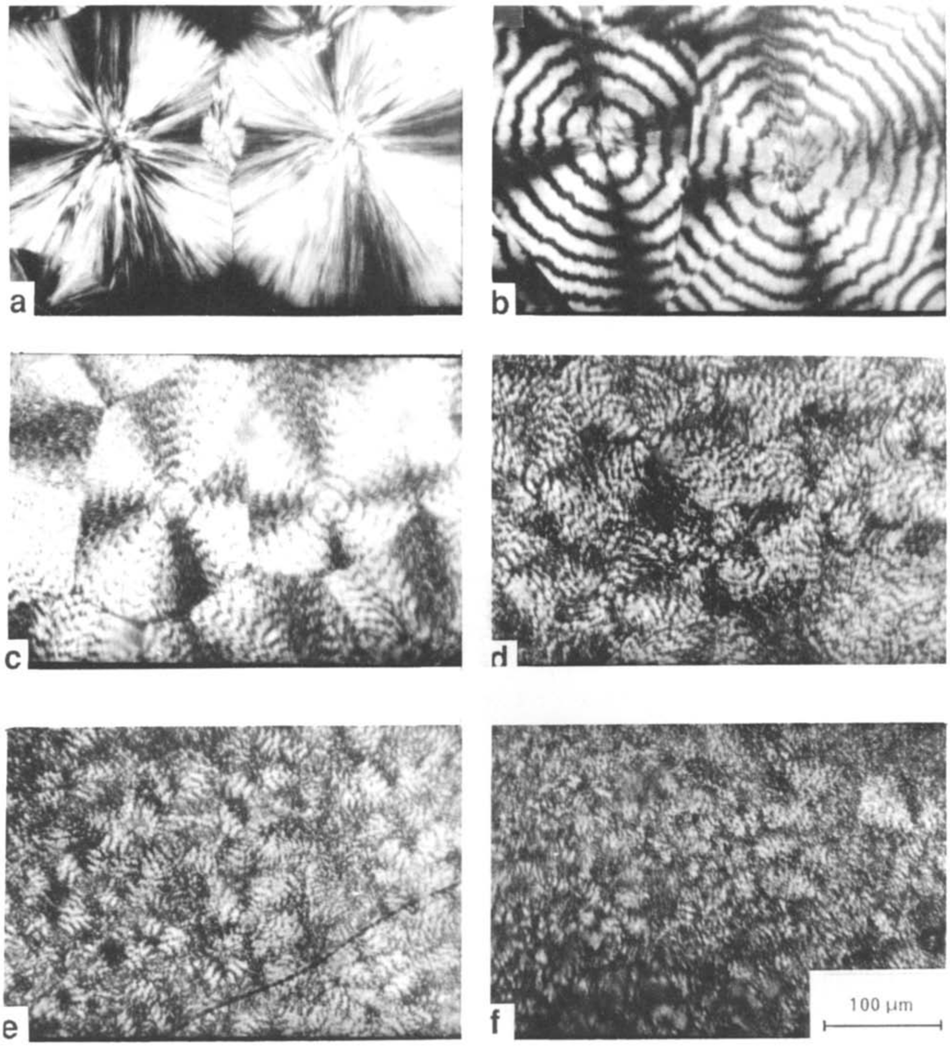

Figure 1 Polarized light micrographs of PCL/SAN blends with different compositions crystallized at 40°C for 3 days from melting at 80°C for 7 h and then cooled slowly to 40°C at a rate of 0.16°C min^{-1}: (a) 100% PCL; (b) 90/10 PCL/SAN; (c) 80/20 PCL/SAN; (d) 70/30 PCL/SAN; (e) 60/40 PCL/SAN; (f) 50/50 PCL/SAN

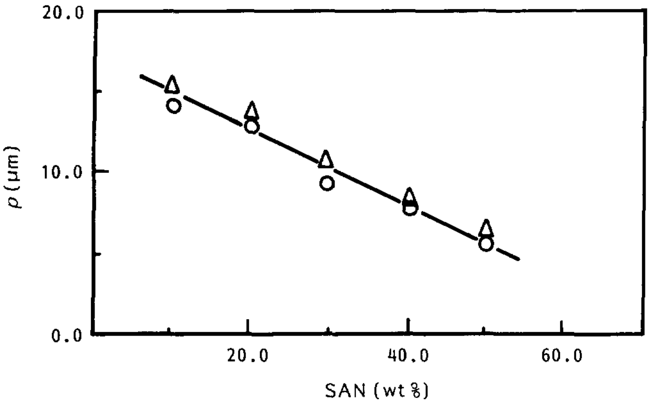

Figure 2 Periodicity of helicoidal crystal orientation within spherulites of blends as a function of weight fraction of SAN: (△) light scattering; (○) optical microscopy

characteristic of a normal spherulite structure. The H_v scattering of PCL/SAN blends has a similar pattern, but the diffraction rings with maximum intensity were observed at an azimuthal angle of 45°. The diffraction ring becomes diffused with increasing SAN. In *Figure 4*, the V_v scattering pattern of pure PCL has a maximum intensity in the polarization direction, but the V_v pattern of PCL/SAN mixtures has a diffraction ring in the horizontal direction.

The extinction ring in optical microscopy and the diffraction ring in the light scattering pattern are ascribed to the twist of the lamella structure of PCL[3,4], that is, the helicoidal orientation of crystals within the spherulites[5]. The periodicity of orientation p (ring spacing) was calculated from the positions of the ring scattering maxima, which are attributed to ring spacings. The apparent ring spacing was estimated using the following relationship:

$$\lambda = 2p \sin\left(\frac{\theta_{\max}}{2}\right)$$

where λ is the wavelength (6328 Å) of incident He–Ne laser light. The periodicity p calculated in this way is plotted against SAN weight fraction in *Figure 2*. It decreases in a regular manner with SAN content. Values deduced from the light scattering pattern agree well with those determined by optical microscopy.

From the microscopic observations and light scattering patterns, the difference between the spherulite structure of pure PCL and the PCL/SAN mixture is apparent, that is, the spherulite in PCL/SAN mixtures consists of

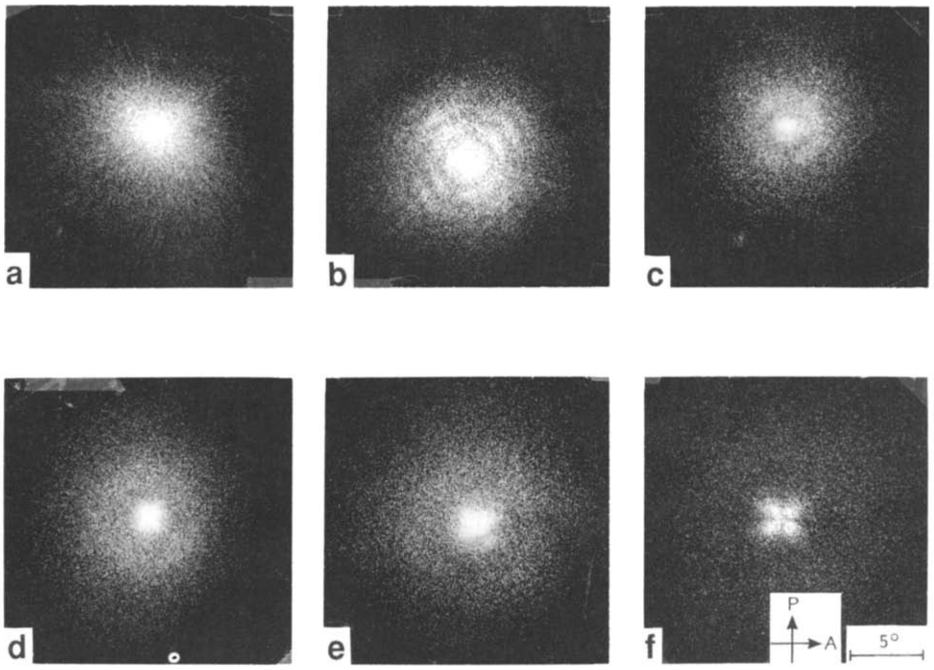

Figure 3 H_v light scattering patterns of PCL/SAN blends with different compositions crystallized at 40°C for 3 days from melting 80°C for 7 h and then cooled slowly to 40°C at a rate of 0.16°C min^{-1}. (a)–(f) as in *Figure 1*

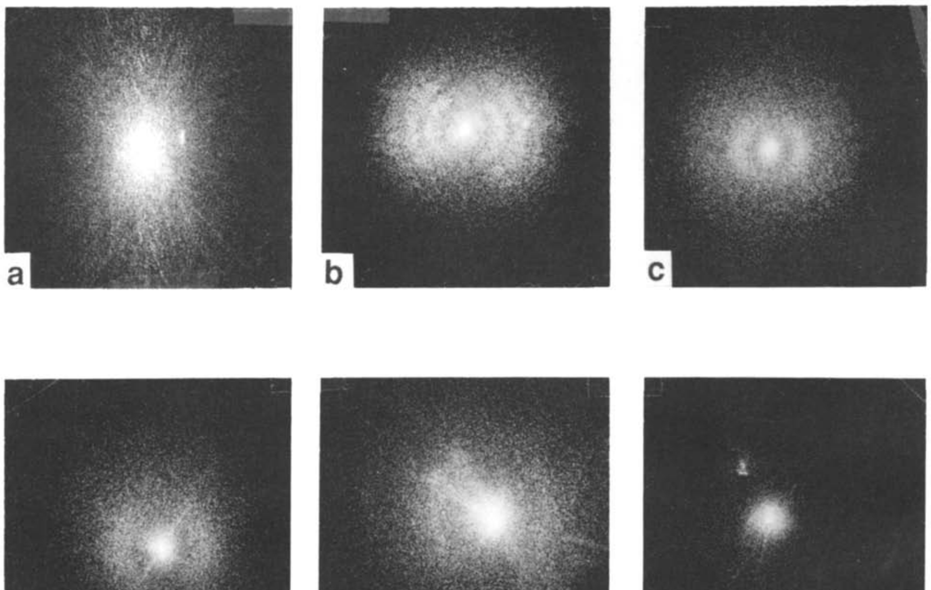

Figure 4 V_v light scattering patterns of PCL/SAN blends with different compositions crystallized at 40°C for 3 days from melting 80°C for 7 h and then cooled slowly to 40°C at a rate of 0.16°C min^{-1}. (a)–(f) as in *Figure 1*

twisted lamella of PCL. It is known that the formation of ring-banded spherulites normally depends on the rate of growth. Ring-banded spherulites are formed at a slow growth rate and at a temperature near the melting point, not at a fast growth rate near the temperature of maximum crystallization rate (T_{max}) or at a slow growth rate near the glass transition temperature (T_g)[6,7]. Such dependence was observed for poly(ethylene terephthalate) and polyethylene. In our case, the influence of crystallization temperature on the PCL spherulites in PCL/SAN mixtures has been observed.

According to Keith and Padden[8], the twisted crystallization results from stress setting up during crystallization, which probably occurs within disordered fold surfaces of polymer crystals. For PCL/SAN mixtures, the morphology has been examined by small angle X-ray scattering[9]. It has been demonstrated that the PCL lamellar structure is affected by the presence of

SAN, and suggested that SAN is included within the spherulites but confined in interlamellar regions. This lamellar structure consists of PCL lamellae separated by amorphous regions containing PCL and SAN. The rejection of SAN with high T_g from crystalline lamellae to interlamellar amorphous region will give rise to stress on the lamellar surface and result in twist of lamellae during crystallization. If this is the case, the stress should be larger for higher SAN fraction and the twist period should be shorter, just as shown experimentally.

In summary, the spherulite structure with a Maltese cross and distinct extinction rings can be observed in PCL/SAN blends, but not in pure PCL. Meanwhile, the diffraction rings appear in the H_v and V_v light scattering pattern of PCL/SAN blends. The spherical symmetry of spherulite PCL becomes more incomplete and the twist of the lamella becomes more irregular. However, it is interesting to note that the change in spherulite structure in PCL/SAN blends relates not only to crystallization temperature, but also to the concentration of the amorphous polymer SAN in PCL/SAN blends.

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