

THE FORMATION OF SUPERMOLECULAR POLYCAPROLACTONE (PCL) SPHERULITES IN POLYSTYRENE-POLYBUTADIENE-PCL (PS-*b*-PB-*b*-PCL) SEMICRYSTALLINE BLOCK COPOLYMERS

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Abstract

The morphological behavior of polystyrene (PS), polybutadiene (PB), and polycaprolactone (PCL) semicrystalline block copolymers as a function of annealing conditions is discussed. For this study, both bulk and thin films of (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5} were cast from toluene solution and the morphologies were examined using transmission electron microscopy (TEM) and polarized light microscopy (PLM). The morphology of either as-cast or annealed bulk (1 mm) specimens is a lamellar-cylindrical morphology having PB cylinders at the interphase boundaries. The block copolymer thin film (5-10 μm) from fast solvent evaporation also shows a lamellar-cylindrical microphase-separated morphology without the formation of visible PCL spherulites using PLM. After the formation of the well-defined PCL spherulites by annealing, the micromorphology is no longer lamellar-cylindrical but instead the PCL lamellar crystals dominate the system.

Introduction

The self-organization of amorphous block copolymers into ordered microstructures has been extensively studied and reviewed (1-2). In the case where one block is semi-crystalline, however, much less is known about controlling the microstructure, and the interplay between the microphase separation temperature, crystallization temperature and the glass transition behavior becomes important (3-9). These materials have the innate potential to function as nanocomposites, if crystallization within the microphase separated structure occurs. In addition to local microstructure, the formation of supermolecular spherulitic structure via crystallization strongly affects ultimate mechanical properties in semi-crystalline polymers. It is well known that homopolymers tend to reject impurities and low molecular weight material during spherulitic crystallization, and the boundaries between adjacent spherulites are often the weak point in mechanical performance (10-11). Recent attempts to overcome this in polypropylene have been achieved by

adding a copolymer that can co-crystallize with the polypropylene, even after it is rejected to the spherulite boundaries, resulting in a reinforced, toughened material (11). A similar reinforcement mechanism might be possible in semi-crystalline block copolymers, where the attached amorphous component is of sufficiently high molecular weight to be entangled between spherulites. Although spherulites have been seen in semi-crystalline block copolymer thin films (4-7), a model to explain the coexistence of the microphase separated and spherulitic morphologies has not been established.

The semi-crystalline block copolymer in this work consists of polycaprolactone (PCL) in combination with polybutadiene (PB) and polystyrene (PS) (3-4, 12). Previously, diblock and triblock copolymers of this series have been studied by thermal analysis to measure the melting and glass transition temperatures and detect any miscibility between the two blocks, and optical microscopy to examine the formation of spherulites and measure the kinetics of crystallization (4). In this work, the formation of PCL lamellar crystals in a semicrystalline block copolymer comprised of (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5} is discussed. Both bulk (1mm) and thin film (5-10 μm) morphologies of this triblock copolymer were studied as a function of annealing and crystallization conditions. The microphase separated morphologies were investigated using transmission electron microscopy (TEM) and the formation and growth of crystallized PCL spherulites in the block copolymer thin films were investigated using polarized light microscopy (PLM). The twisting of the crystallized PCL lamellae during the formation of PCL spherulites was investigated with tilting studies in the TEM.

Experimental Procedure

(PS)_{0.35}(PB)_{0.15}(PCL)_{0.5} block copolymer (3) with $M_n = 150,000$ g/mol (13) and $M_w/M_n = 1.22$ were studied, where the subscripts denote the mass fraction of each block. The order-disorder transition temperature (T_{ODT}) was found to be above 180 °C from small angle neutron

scattering studies in the melt. Bulk films of thickness 0.5-1 mm were slowly cast (10 d) from 5 % (mass fraction) toluene solution. These as-cast samples were annealed at 130 °C for 7 d, 70 °C for 3 d and then crystallized at 45 °C for 2 d under vacuum. For optical microscopy, approximately 10 µm thick sections of the bulk films were cryo-microtomed on a Leica Ultracut UCT (14) with cryo attachment at -90 °C using a diamond knife. The sections were collected on glass slides. For TEM, electron transparent films of nominal thickness 50 to 80 nm were cryo-microtomed at -90 °C using a diamond knife and transferred to Cu grids. Both the as-cast and the annealed specimens were exposed to OsO₄ vapor for 2 h to stain the amorphous blocks. The morphology was studied on a Philips EM400T at 120 kV by bright-field TEM.

Films of 5-10 µm thickness of (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5} were cast (< 5 min) from 5% (mass fraction) toluene solution on freshly cleaved mica in air. One of the as-cast PS-b-PB-b-PCL films was annealed at 140 °C for 15 min and crystallized at 45 °C using a Mettler FP-2 hot stage in air. PLM was used to study the formation of PCL spherulites in the block copolymer thin films directly on the substrates. After PLM, both sides of the as-cast and the annealed films on mica were exposed to osmium vapor for 2 h. The stained thin films were floated from the substrate on water, collected, embedded in epoxy resin (Epofix) and cured at room temperature. The electron transparent thin sections were cross-sectioned at -100 °C, transferred to Cu grids and the morphologies were studied by TEM.

Results and Discussion

A spherulitic morphology was not observed in either the as-cast or annealed bulk film specimens of (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5} as seen in Figure 1, but both are clearly microphase separated on a local scale. The as-cast, bulk film shown in Figure 1a has a coarse, microphase-separated morphology consisting of a lamellar structure with undulations at the interphase boundaries as PB cylinders try to organize. After osmium staining, the PB cylinders appear dark, the gray regions are the partially stained PS and the lightest regions correspond to the unstained PCL. In the as-cast film, the propagation of PCL lamellae causes a waviness of the microphase separated lamellar morphology, indicative of the formation of small PCL dendrites during slow solvent evaporation. The dendrites are too small (< 2 µm) to be observed by PLM, as shown in the insert in Figure 1a, but local crystallization is revealed by the observed birefringence (speckle pattern). Vacuum annealing reveals a more perfect and somewhat longer range order of the lamellar-cylindrical structure with PB cylinders at the interphase boundaries (Fig. 1b). This is the expected morphology based on the mass fraction of block

components in amorphous ABC type block copolymers with similar minor composition, as determined by the interfacial tension of each polymer and the block composition (15, 16). Again, PLM on the annealed specimen (insert of Figure 1b) shows no visible spherulites. A weak birefringence (speckle pattern) indicates that the PCL phase is probably crystallized within the microphase separated structure at the local level, but no supermolecular crystallization occurs in the bulk, annealed film.

A spherulitic morphology was found after annealing thin films (5-10 µm) prepared directly for PLM and subsequently cross-sectioned for TEM; the morphology is not lamellar-cylindrical but dominated by the PCL lamellar crystals. Initially, the as-cast thin film has a lamellar-cylinder morphology without the formation of visible PCL spherulites, as shown in Figure 2a. The birefringence in the optical micrograph, however, indicates the local crystallization of PCL in the block copolymer on a size scale < 2 µm. After annealing the thin film at 140 °C for 15 min and crystallizing at 45 °C, however, well-defined spherulites (>100 µm in diameter) are formed and the microstructure is no longer similar to amorphous block copolymers, as shown in Figure 2b. The crystallized PCL lamellae are seen as thin white lines of thickness <12 nm surrounded by intermixed amorphous blocks in the TEM; no regions of lamellar-cylinder structure are found after the formation of the large PCL spherulites. The supermolecular spherulitic structure seen in the PLM insert of Figure 2b shows a banded ring-pattern attributed to an irregular twist of lamellae about their long axes as they grow (17). This result indicates that the microphase separated morphology is ruined by the local rearrangement of PCL chains to PCL lamellar crystals and the overall morphology is changed into a “microphase separated” structure consisting of PCL lamellar crystals intermixed with amorphous PS and PB. In comparing Figure 2a and 2b, it is apparent that a relatively well-defined lamellar-cylindrical morphology is formed in the thin film even under fast solvent evaporation conditions, suggesting that the imperfect morphologies seen in Figure 1 are not a result of kinetic constraints. In addition, the morphology shown in Figure 2 for the as-cast and annealed thin film reveals that fast solvent evaporation interferes more with the formation of crystallized PCL spherulites than with microphase separation.

The weak contrast regions in the electron micrograph after spherulitic crystallization (Fig. 2b) are not large regions of amorphous phase, as might appear at first glance; these regions exist because some of the PCL lamellar crystals are not aligned parallel to the electron beam. This is expected because of the stresses generated at the lamellae surface between the PCL and PB block junctions as the crystalline lamellae twist within the

growing spherulite (17). By tilting in TEM, however, the presence of twisted PCL lamellar crystals can be confirmed, as shown in Figure 3. The dark spots at the top right in the electron micrographs are the reference points to demonstrate that the tilting was done in the same area of the specimen. Before tilting, the central area of the film shows no contrast of PCL lamellae. After tilting the sample -15° , the image of PCL lamellae becomes clear. When the sample is tilted -25° , the propagation of crystallized PCL lamellae is even clearer in the TEM image. When the sample is tilted to $+10^\circ$, the contrast, however, becomes worse. The contrast enhancement in TEM by tilting also confirms that PCL crystals are formed as lamellar layers, not cylinders.

Factors controlling the reorganization of this semi-crystalline block copolymer from a microphase separated lamellar-cylinder morphology into PCL spherulites are multiple and complex. We will consider T_g of the amorphous phase, film thickness and cooling rate, although there may be other factors. In $(PS)_{0.35}(PB)_{0.15}(PCL)_{0.5}$, the PS blocks are not directly linked with PCL blocks, but the high mass fraction (0.35) of PS and lamellar morphology would be expected to restrict the overall movement of the block copolymer chains below the T_g of PS ($\approx 90^\circ\text{C}$). In the annealed bulk specimen (Figure 1b), the temperature was held at 70°C for 3 days to lock-in the microphase separated morphology, and the glassy PS appears to interfere with the propagation of PCL lamellar crystals and the formation of PCL spherulites. This has been observed previously in other semi-crystalline block copolymer systems (4, 7, 9, 18). Heuschen et al. (7) and Balsamo et al. (4) studied PS-b-PCL diblock copolymer thin films and found that spherulitic crystallization did not occur in the case of high PS content and sufficiently high molecular weight polymers. Hamley et al. (9) compared two block copolymers of polyethylene, one with a rubbery and one with a glassy amorphous block component and found that the crystallization rate and extent was retarded when the amorphous block was glassy. Nojima et al. (18) found that the crystallizability of PCL in PS-b-PCL diblock copolymer is dependent on the T_g of PS, which was varied by adding a plasticizer or oligomer to the PS block. When the T_g of PS was higher than the T_c of PCL in PS-b-PCL diblock copolymer, the PCL blocks did not crystallize in the PS-b-PCL thin film.

The film thickness and cooling rate also play a role in the ultimate morphology. We observed that in the thin films (5-10 μm), spherulites formed more easily under thermal history conditions that did not produce spherulites in the bulk. This may be a result of surface nucleation (transcrystallization) or cooling rate effects, although we tried to achieve exactly identical conditions for the bulk and thin film experiments. Previous workers have compared thin film specimens cast from solution directly

for PLM to be equivalent to the morphology seen in bulk (1 mm thick) specimens used for TEM, but our work suggests this is not necessarily the case. Theoretical (19-21) and experimental studies (22-23) have shown that the rate of crystallization is reduced as the film thickness decreases, but these results assume that volume nucleation occurs. In the case of bulk versus thin film specimens studied here, the thin films were found to crystallize into spherulites more readily, suggesting that surface nucleation may be important.

Conclusions

A semi-crystalline block copolymer of $(PS)_{0.35}(PB)_{0.15}(PCL)_{0.5}$ forms either a lamellar-cylindrical microphase separated structure where the PCL is locally crystallized, or a spherulitic supermolecular structure where the PCL crystallization essentially destroys the microphase separated morphology. The structure which forms depends on the thermal history and film thickness. It is somewhat surprising that the spherulitic reorganization of PCL can occur with such a high glassy PS content, but this type of morphology may yield a very tough material since the spherulites are reinforced by the attached and entangled amorphous polymer segments.

References

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13. The conventional notations, M_n and M_w have been used for molecular weight in place of the ISO notation for molecular masses in this publication.

14. Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

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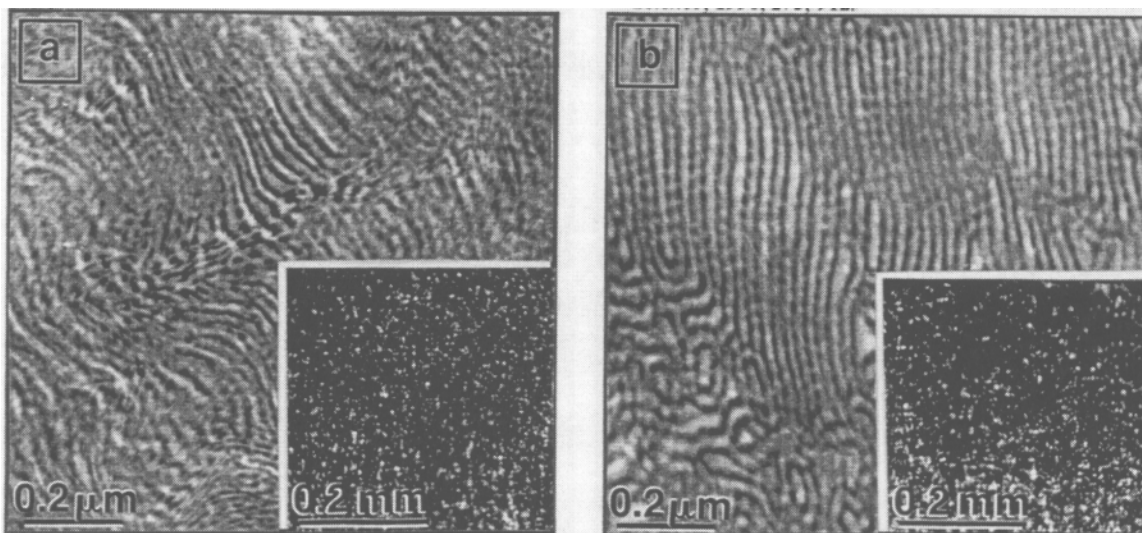


Figure 1-Osmium stained TEM images with polarized PLM images of the $(PS)_{0.35}(PB)_{0.15}(PCL)_{0.5}$ bulk films; (a) as-cast; (b) annealed at 130 °C for 1 wk, at 70 °C for 3d and 45 °C for 2d.

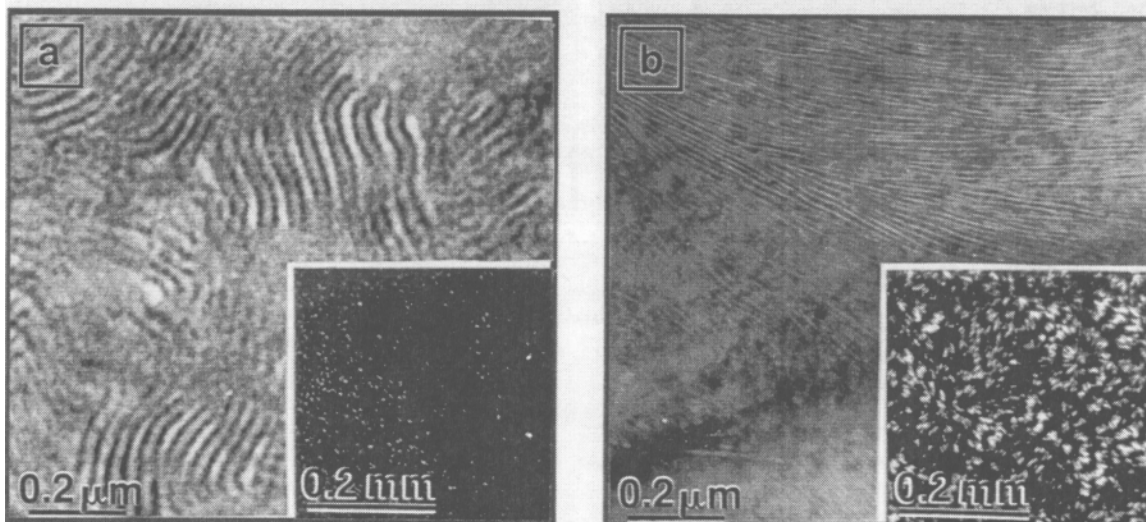


Figure 2-Osmium stained TEM images with polarized PLM images of the $(PS)_{0.35}(PB)_{0.15}(PCL)_{0.5}$ thick films; (a) as-cast; (b) annealed at 140 °C for 15 min and crystallized at 45 °C.

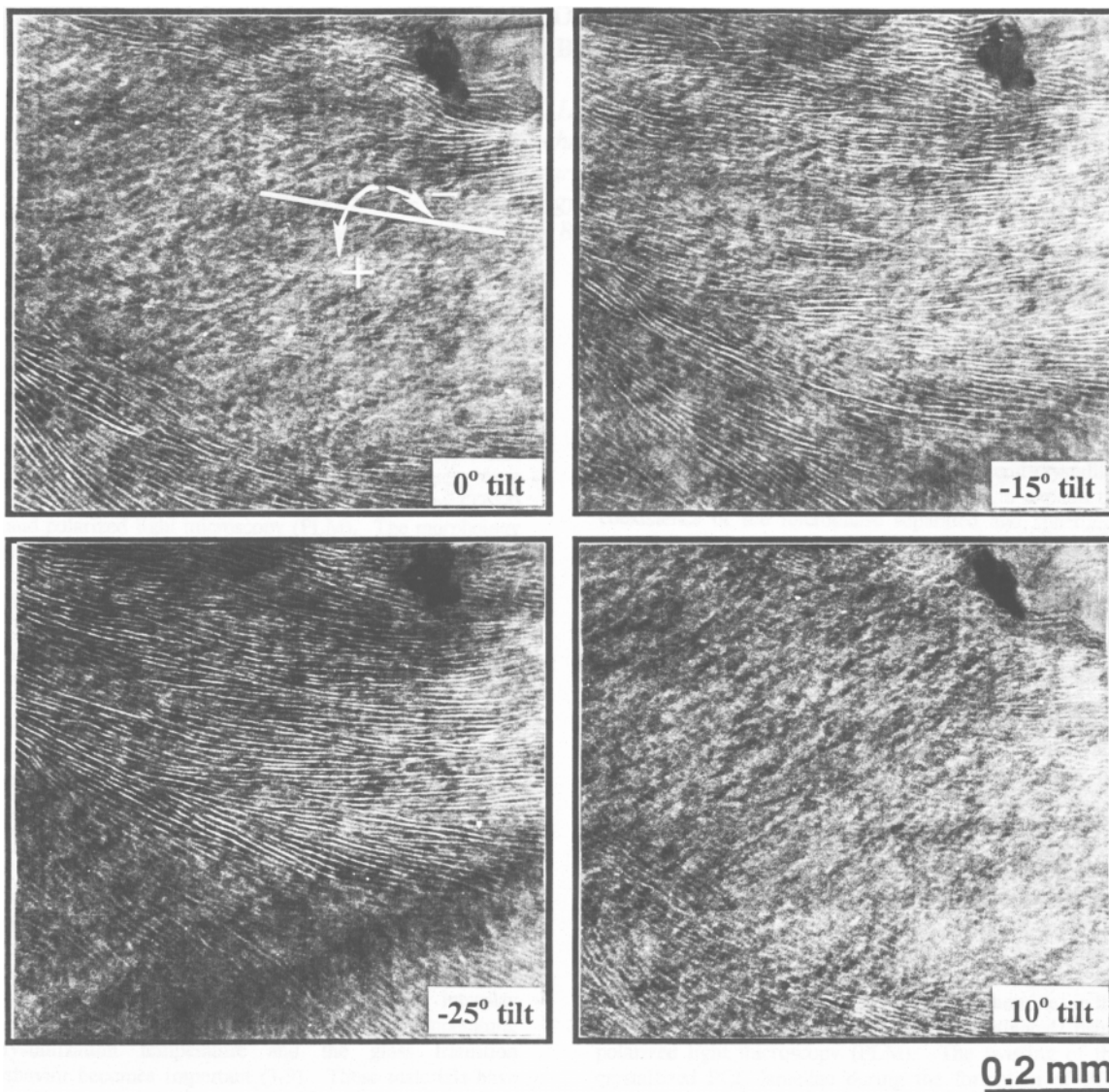


Figure 3-Tilted TEM images of (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5} thick films indicating the twisting of PCL lamellar crystals