Crystallization within Melt Ordered Semicrystalline Block Copolymers: Exploring the Coexistence of Microphase-Separated and Spherulitic Morphologies

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ABSTRACT: The crystalline and microphase-separated morphology of semicrystalline block copolymers are compared in bulk (0.5–1 mm) and thin films (5–0.1 mm), as characterized by transmission electron microscopy (TEM) and polarized light microscopy (PLM). Bulk films of a triblock copolymer of polystyrene, polybutadiene, and polycaprolactone, (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5}, where the subscripts denote the mass fraction, show a lamellar–cylindrical microphase-separated morphology with a lamellar repeat of \( \approx 62 \) nm, as observed by TEM. Bulk films of a diblock copolymer consisting of (PB)_{0.2}(PCL)_{0.8} show an imperfect cylindrical microphase-separated structure by TEM coexisting with crystalline lamellae of PCL. For both bulk specimens, the PLM shows a speckle pattern of birefringence that confirms the PCL is crystallized within the microphase-separated structure, but no large-scale spherulites are observed by PLM. The microstructure in the as-cast thin films (5–10 \( \mu \)m) by TEM is lamellar–cylindrical for the triblock copolymer and cylindrical for the diblock copolymer, as described above for the bulk specimens. Upon thermal treatment of these thin films, large and well-defined PCL spherulites are observed by PLM for both block copolymers. TEM of the thermally treated triblock copolymer thin films shows that, after the formation of spherulites, the microphase structure is no longer lamellar–cylindrical but entirely dominated by PCL lamellar crystals. In contrast, TEM of the thermally treated diblock copolymer thin films shows that the PCL lamellar crystals coexist with the PB microphase-separated cylinders after the formation of PCL spherulites. Bulk specimens could not be induced to form spherulites under similar thermal treatment conditions.

Introduction

The inherent complexity of amorphous block copolymers that self-organize into lamellar, cylindrical, or other microphase-separated structures because of incompatible AB or ABC blocks is greatly increased when one block is no longer amorphous but semicrystalline. The crystallization within a microphase-separated structure can be related to the improvement of mechanical, optical, and other properties for these materials. Because the size scale of “microphase-separated” block copolymers is in the 10–50 nm range, new types of semicrystalline nanocomposite materials are possible that one could not achieve with amorphous block copolymers. Compared to the field of amorphous block copolymers, there has been relatively little work on semicrystalline block copolymers. In general, semicrystalline block copolymers with either polyethylene (PE) or polycaprolactone (PCL) as the semicrystalline component have been most often used for bulk studies. Solution studies of semicrystalline block copolymer micelles and single crystals have also frequently utilized poly(ethylene oxide) (PEO) as the semicrystalline block.

The results on semicrystalline block copolymer morphology often depend on how crystallization proceeds. This is related to the combined effects of microphase separation, glass formation, crystallization temperature, and thermal history (or pathway). Much more is known about semicrystalline homopolymers crystallized from the melt, where the morphology is generally spherulitic (as observed by polarized light microscopy (PLM) or polarized light scattering). Spherulites are comprised of many polymer molecules assembled into chain-folded lamellar crystals that radiate out from a central nucleus to form a spherical supermolecular structure, which is optically birefringent and fairly large in size. In PLM, spherulites of sizes from 2 to 100 \( \mu \)m are easily observed as radially symmetric entities due to their birefringent properties. Smaller crystals (< 2 \( \mu \)m) also appear birefringent under crossed polarizers. We later refer to a speckle pattern resulting from crystallization within a block copolymer microphase where the crystals are restricted in one direction from 10 to 50 nm, and spherulites cannot organize.

Whether spherulites form in semicrystalline block copolymers is a relevant question because spherulitic structure greatly affects the ultimate mechanical properties in semicrystalline polymers, and the boundaries between adjacent spherulites are often the weak point in mechanical performance. In many cases, nucleating agents are added to semicrystalline homopolymers, to enhance nucleation density and reduce the size of spherulites, to improve properties. A more elaborate spherulite boundary strengthening concept was recently given by Lustiger et al., where random ethylene–propylene copolymer or isotactic–atactic polypropylene multiblock polymer was added to a polypropylene matrix. In this case, the polymers are miscible in the melt, but during crystallization the copolymer “fools” the homopolymer into rejection of the copolymer to the...
spherulite boundaries as an impurity. The copolymer subsequently connects adjacent spherulites through recrystallization of the propylene copolymer segments. A similar reinforcement mechanism may be possible in semicrystalline block copolymers, where the attached amorphous component is of sufficiently high molecular weight to be entangled between spherulites.

In semicrystalline block copolymers, precursor melt states ranging from disordered (or “one-phase”) to ordered and either weakly phase segregated or strongly phase segregated have been tailored to investigate the effect of melt structure. One can envision that an “ordered” or preformed microphase-separated melt structure in a semicrystalline block copolymer might dictate the final crystalline morphology, if crystallization is confined within the microphases and spherulite development is arrested. Although it is hard to reconcile the spherulitic model within the confines of a microphase-separated block copolymer morphology, spherulites have been observed in semicrystalline block copolymers by PLM to 18 of thin films (~20 μm) cast from solution or by polarized light scattering to 11 of thicker specimens that were derived from a disordered or weakly phase segregated melt. In most of the studies cited, either wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), or both were used to study the bulk morphology. Few studies of semicrystalline block copolymers have included transmission electron microscopy (TEM) to characterize the morphology. Starting from a one-phase melt, coexistence of a lamellar microphase-separated structure and a lamellar crystalline PE phase has been reported, where spherulites of sizes from 4 to 8 μm are also present. For weakly phase segregated systems containing a rubbery amorphous block, crystallization usually induces simultaneous rearrangement or destruction of an initially lamellar or cylindrical block copolymer microphase morphology. The concept of confining crystallization within the microphase is most often observed for lamellar or cylindrical phases of block copolymers when the system is strongly phase segregated. For example, the amorphous block is glassy, and the amorphous block copolymer was measured by membrane osmetry, and the molecular weight of the diblock copolymer was measured by size exclusion chromatography (SEC); both polydispersity indices or PDI (Mn/Mw) of the amorphous phases, and Tm of the semicrystalline PCL phase, is given in Table 1. The molecular weight of the diblock copolymer was measured by membrane osmometry, and the molecular weight of the diblock copolymer was measured by SEC. Both polymers have order–disorder transition temperatures, Tg, greater than 180 °C, based on previous neutron scattering studies.

Bulk films (0.5–1 mm) were slowly cast from toluene solution at room temperature over a period of ~10 days and studied both as-cast and after thermal treatment. Thermally treated bulk samples were annealed for 1 week at 130 °C (above the Tg of bulk PS 100 °C) to perfect the microphase-separated structure, held at 70 °C for 3 days, and then crystallized at 45 °C for 2 days. Thermal treatments of the bulk samples were done under vacuum to prevent oxidative degradation. The triblock and diblock bulk films were treated in the same fashion. Thin films (5–10 μm) were prepared directly for PLM by rapid solution casting (<5 min) from toluene at room temperature in air or freshly cleaved mica or glass slides. The thin films were studied both as-cast and after a thermal treatment that was similar to the bulk films, except that the long times at high temperature were shortened for the thin films. In the thin films a Mettler FP-2 hot stage was used at a temperature of 130–140 °C for 15 min for the triblock and ~2 min for the diblock copolymer, followed by crystallization at 45 °C for 1–2 days. An intermediate temperature of 70 °C for 3–4 days was also used in some cases for the triblock thin films but did not change the experimental results as discussed below. After heating in air, some disorientation at the surface of the thin film was observed, and

**Table 1. Physical Characteristics of the Semicrystalline Block Copolymers**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mₙ (copolymers) × 10⁻³ (g/mol)</th>
<th>Mₙ (PCL) × 10⁻³ (g/mol)</th>
<th>PDI = Mₙ/Mw</th>
<th>Tg (°C) of PS/PB</th>
<th>Tm (°C) of PCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>triblock copolymer (PS)₀.₃₅(PB)₀.₁₅(PCL)₀.₅</td>
<td>150</td>
<td>75</td>
<td>1.22</td>
<td>97–104</td>
<td>52</td>
</tr>
<tr>
<td>diblock copolymer (PB)₀.₂(PCL)₀.₈</td>
<td>57</td>
<td>46</td>
<td>1.24</td>
<td>82–95</td>
<td>58</td>
</tr>
</tbody>
</table>

**Experimental Section**

**Sample Preparation.** A triblock copolymer of (PS)₀.₃₅(PB)₀.₁₅(PCL)₀.₅ and a diblock copolymer of (PB)₀.₂(PCL)₀.₈, where the subscripts denote the mass fraction of each block, were prepared by anionic polymerization. To simplify the nomenclature, these will be referred to simply as “triblock” and “diblock” throughout the text. A summary of physical characteristics, including average molecular masses, Mn, polydispersity indices or PDI (Mn/Mw), Tg of the amorphous phases, and Tm of the semicrystalline PCL phase, is given in Table 1. The molecular weight of the diblock copolymer was measured by membrane osmometry, and the molecular weight of the diblock copolymer was measured by SEC. Both polymers have order–disorder transition temperatures, Tg, greater than 180 °C, based on previous neutron scattering studies. Bulk films (0.5–1 mm) were slowly cast from toluene solution at room temperature over a period of ~10 days and studied both as-cast and after thermal treatment. Thermally treated bulk samples were annealed for 1 week at 130 °C (above the Tg of bulk PS 100 °C) to perfect the microphase-separated structure, held at 70 °C for 3 days, and then crystallized at 45 °C for 2 days. Thermal treatments of the bulk samples were done under vacuum to prevent oxidative degradation. The triblock and diblock bulk films were treated in the same fashion. Thin films (5–10 μm) were prepared directly for PLM by rapid solution casting (<5 min) from toluene at room temperature in air or freshly cleaved mica or glass slides. The thin films were studied both as-cast and after a thermal treatment that was similar to the bulk films, except that the long times at high temperature were shortened for the thin films. In the thin films a Mettler FP-2 hot stage was used at a temperature of 130–140 °C for 15 min for the triblock and ~2 min for the diblock copolymer, followed by crystallization at 45 °C for 1–2 days. An intermediate temperature of 70 °C for 3–4 days was also used in some cases for the triblock thin films but did not change the experimental results as discussed below. After heating in air, some disorientation at the surface of the thin film was observed, and
experiments were repeated under vacuum to prevent oxidative degradation. No obvious differences were observed between these two samples.

**Polarized Light Microscopy (PLM) and Transmission Electron Microscopy (TEM).** Cross sections of bulk films were prepared for PLM by microtomy using a Leica Ultracut UCT with a cryo attachment at −90 °C. The sections were cut with a freshly made glass knife and collected on glass microscope slides. The thin films (5–10 μm) were examined by PLM as-cast, and the formation of PCL spherulites could be directly observed on the substrates.

The bulk films were prepared for TEM by cryomicrotomy at −90 °C using a diamond knife, and sections were transferred dry to carbon-coated 200 mesh Cu grids. The nominal thickness of the ultrathin electron transparent sections is 50–80 nm. The grids were exposed to OsO4 vapor for 2 h to stain the amorphous blocks. Bright-field TEM images were obtained on a Philips 400T at 120 kV. The thin films (as prepared above for PLM) were cross-sectioned for TEM after first staining with OsO4 vapor for 2 h and then embedding in Epofix resin. Ultrathin films were cryo sectioned from the epoxy blocks at −100 °C, normal to the thin film plane, mounted on grids, and stained as described above. The TEM view is thus orthogonal to the view in PLM. The nominal thicknesses of the thin films cast for optical microscopy were easily determined from the TEM cross sections to be in the range 5–10 μm.

**Results and Discussion**

**Morphology of (PS)_{0.35}(PB)_{0.15}(PCL)_{0.5}**. A microphase-separated, lamellar—cylindrical structure is formed in the as-cast and thermally treated triblock copolymer bulk films, as shown in Figure 1a,b. In the TEM images, the PB cylinders appear darkest, the gray contrast (lamellar layers) corresponds to partially stained PS, and the PCL is unstained as shown by the lightest contrast regions, as schematically depicted in Figure 2. The lamellar—cylindrical morphology has been observed to be the equilibrium morphology of ABC amorphous block copolymers having a similar block composition.6,7

In Figure 2, we have shown the cylinders to be directly opposed, but as pointed out by Stadler et al.,6 a staggered configuration is also possible under some circumstances. The quality of microphase ordering in our triblock copolymer, even after annealing, is insufficient to distinguish whether the structure is directly opposed or staggered from the TEM images.

In the inset of Figure 1a, a speckle pattern of birefringence in PLM confirms the crystallization of PCL within the microphase-separated structure, but if spherulites or precursors are present, they must be <2 μm in diameter. Evidence of morphological deformation from the local crystallization of PCL within the lamellar microphase-separated morphology is not observed for the as-cast film, except as a slight waviness of the lamellae (Figure 1a). Upon thermally treating the bulk film, regions with somewhat better long-range lamellar—cylindrical order can be identified, as shown in Figure 1b. The lamellar repeat distance was estimated from TEM of such regions to be 62 nm, and the cylinder diameters are approximately 10 nm. The cylinders sometimes appear elliptical rather than circular in cross section; this is caused by a variation in the microphase orientation with respect to the angle of cutting as described by Stadler et al.,6 for an amorphous lamellar—cylindrical block copolymer. A speckle pattern of birefringence in the PLM (inset of Figure 1b) was also observed for the thermally treated specimen, indicating local crystallization of PCL within the microphase-separated structure. Presumably, reorganization into spherulites cannot occur because the PS lamellar phase is glassy at 70 °C, well above the crystallization temperature of PCL. Upon heating the films above the melting point of PCL, the speckle patterns disappeared, indicating the birefringence is not due to the microphase-separated structure but to the PCL crystals within the microphase-separated structure.

The thermally treated bulk films of the triblock copolymer shown above (Figure 1b) were analyzed by SAXS and WAXS as well, to better characterize the microphase-separated morphology and correlate with the TEM results. We present in a companion paper28 a detailed model to interpret the SAXS data in terms of the relative order of the PB cylinders, where the coherence length is half of the full lamellar repeat. The simultaneous WAXS data obtained show peaks due to the crystallization of PCL in the block copolymer that were well matched with those of pure PCL crystals having an orthorhombic structure at room temperature.23
lamellar–cylindrical morphology as described above for the bulk films. The speckle pattern in the PLM again indicates the local crystallization of PCL in the block copolymer thin film (inset of Figure 3a). The formation of a fairly well-defined lamellar–cylindrical morphology in the thin film under relatively rapid solvent evaporation conditions suggests that the imperfect bulk morphologies seen in Figure 1a are not due to kinetic constraints. In addition, the morphology of the as-cast thin film reveals that fast solvent evaporation interferes more with the formation of crystallized PCL spherulites than with the microphase separation. Upon thermally treating the triblock copolymer thin film at 140 °C, well above the $T_g$ of PS, prior to crystallization at 45 °C, the microphase morphology is no longer lamellar–cylindrical but is instead replaced by PCL lamellar crystals, which appear in TEM as white lines of $\approx 10$ nm width (Figure 3b). Large spherulites of PCL ($\approx 100 \mu m$ in diameter) are formed as shown by PLM in the inset of Figure 3b, with a concentric banded ring pattern often seen in spherulites of homopolymers and previously reported in thin films of PS–PB–PCL and PB–PCL block copolymers.17,18 We note that the regions having weak contrast of PCL crystal lamellae in the TEM micrograph are because the PCL lamellar crystals are twisted and thus not aligned parallel to the electron beam in every region, as confirmed by tilting studies in TEM.

The relatively high mass fraction (0.35) of PS in the triblock copolymer in our experiments would be expected to seriously restrict the overall movement of the crystallizable block chains. The formation of a long-range, ordered lamellar–cylindrical structure, as shown in Figure 1b, suggests that the glassy PS lamellae prevent the formation of PCL spherulites in bulk films. Presumably, the PS lamellar phase “frames” the microphase-separated structure, precluding the formation of PCL spherulites either by providing multiple nucleation sites for PCL crystals or by preventing massive reorganization into spherulites. This result agrees well with some previous studies of semicrystalline block copolymers based on PS, PB, and PCL. For example, Balsamo et al.17 and Heuschen et al.18 used differential scanning calorimetry (DSC) and PLM directly on thin films to show that the crystallization of PCL is dependent on the block composition and the rigidity of PS amorphous blocks. In the PS–PCL (over 0.4 mass fraction PS) and

Figure 2. Schematic of lamellar–cylindrical morphology for the (PS)$_{0.35}$(PB)$_{0.15}$(PCL)$_{0.5}$ triblock copolymer in cross section, where the white areas are PCL-rich lamella, the gray regions are PS-rich lamella, and the black areas represent PB-rich cylinders.

Figure 3. Microphase morphology of (PS)$_{0.35}$(PB)$_{0.15}$(PCL)$_{0.5}$ triblock copolymer thin films by TEM with insets of PLM. (a) As-cast film shows a lamellar–cylindrical morphology by TEM and local crystallization of the PCL as a speckle pattern in PLM. (b) After thermal treatment, TEM reveals thin PCL lamellar crystals (white lines) and no remaining evidence of the lamellar–cylindrical microphase-separated morphology; PLM confirms the reorganization of the morphology into large spherulites.

the PS–PB–PCL block copolymers (0.5 mass fraction PCL), Balsamo et al.17 observed that the reduction of growth rate of spherulites is significant relative to PCL homopolymer, because of the glassy PS block. No TEM of the thin films studied by PLM or DSC, however, was included in either of these reports, so the microphase structure was not identified.

We observe that in the thin films of triblock copolymer the formation of spherulites and propagation of PCL crystal lamellae by chain folding (Figure 3b) can change the microphase-separated PS and PB domains into a “microphase-separated structure” consisting of PCL lamellar crystals and an amorphous phase between lamellar crystals at equilibrium, as predicted theoretically. A number of other preparation and thermal treatment conditions were investigated to better understand the factors that allow the formation of spherulites in the thin films compared to the bulk films. We found that if an as-cast thin film is thermally treated at 70 °C, below the $T_g$ of PS but at a temperature well above the melting point of PCL, and then crystallized at 45 °C, large PCL spherulites are not observed by PLM (Figure 4a). This suggests a confined geometry effect...
for the crystalline PCL phase structure in the thin-film morphology, where the rigid framework of the glassy PS lamellae preserves the previous PCL crystal nuclei arrangement. However, once the thin film is “thermally activated” by heating briefly to 140 °C (for 15 min), the glassy PS lamellar framework (even after stabilizing for 4 days at 70 °C, well below the $T_g$ of PS) does not appear to function in the same way. In this case, the formation of PCL crystal nuclei during subsequent crystallization at 45 °C results in spherulitic growth, as shown in Figure 4b. Last, a bulk film that did not produce well-defined spherulites even after thermal treatment (such as that shown in Figure 1b) was cross-sectioned to a thickness of 5–10 μm and treated to the identical thermal history as the solution cast thin film, with the resultant formation of large spherulites. From this experiment, it is clear that the spherulitic morphology is a result of the thin-film geometry rather than differences in the formation or history of the bulk precursor films, such as different rates of solvent casting or longer annealing times at high temperature (130 °C for 1 week).

We considered that one explanation for the different crystallization behavior between thin and bulk films may be that the $T_g$ of PS is shifted to lower temperature due to an incomplete phase separation (microphase impurity) in the thin films, perhaps because of a faster cooling rate and concomitant partial miscibility of one of the other blocks. Although PCL homopolymer is widely studied in polymer blends due to miscibility with many polymers, it has been shown to have very limited miscibility with oligomers of PS. We also note that the $T_g$ in this triblock copolymer was measured by DSC to be 97 °C, after similar thermal history and cooling rate. Because the thermal data were obtained without crystallizing the PCL (due to a difficulty encountered in separating the PCL melting endotherm and detecting the PS peak adequately), this is good evidence that the PS was indeed microphase separated at 70 °C and relatively pure. More specific experimental studies will be necessary to explain why the thin films and bulk films of this polymer behaved so differently.

**Morphology of (PB)$_{0.2}$(PCL)$_{0.8}$.** Both the as-cast and thermally treated bulk films of diblock copolymer show an imperfect cylindrical microstructure consisting of PB cylinders in a PCL matrix, as shown in Figure 5, where the PB cylinders are stained dark with OsO$_4$. A hexagonally ordered cylindrical microstructure would be
expected as the equilibrium morphology based on the mass fraction of PB in reference to an AB type amorphous block copolymer system. Here, however, the cylinders are not well ordered in either the as-cast or thermally treated films, perhaps because the soft PB cylindrical phase structure does not effectively withstand the crystallization of PCL, resulting in distortion of any melt ordered arrangement of domains. In addition, the cylinders in the as-cast bulk morphology (Figure 5a) have diffuse or jagged surfaces, due to the coexistence of PCL lamellar crystals, which appear as white lines extending through the PCL matrix. This makes measurement of the cylinder diameters difficult. After thermal treatment above the $T_m$ of PCL, a locally improved microphase-separated cylindrical structure is observed, with smoother interfaces between the cylinders and matrix (Figure 5b). Some cylinders are also seen in cross section in this case, and the diameters of the cylinders are more regular (about 30 nm). The smoother interfaces may be due to slower, more controlled crystallization at 45 °C. Formation of large spherulites is not observed by PLM in either the as-cast or the thermally treated bulk films (insets of Figure 5). The speckle pattern of birefringence in the PLM images and the observation of crystal lamellae in the electron micrographs indicate local crystallization of PCL has occurred.

The thermally treated bulk films of the diblock copolymer with morphology similar to Figure 5b were analyzed by SAXS and WAXS at room temperature and at 90 °C, above the melting point of PCL. The scattering data confirm that a well-ordered or hexagonally arranged cylindrical microstructure is not formed; a model along with the data is presented elsewhere.28 As was observed for the triblock copolymer, the simultaneous SAXS for a PE- polyethylethylene (PEE) block copolymer having a similar block composition (0.75 mass fraction PE) with the diblock copolymer in this study. The SAXS data demonstrated that the hexagonally ordered cylindrical PEE domains in PE matrix formed below the ODT were completely destroyed upon PE crystallization below $T_m$ of PE (108 °C). This was because the soft PEE could not preserve the microphase-separated structure during cooling because of its low $T_g$ (−20 °C). However, the SAXS pattern after cooling did not clarify the type of the solid morphology as a crystal lamellar morphology but revealed a broad peak. This might be due to a similar preservation of the PEE cylindrical domains after PE crystallization, but without long-range order, as was the seen here for the diblock copolymer.
Summary

In semicrystalline block copolymers, under conditions where crystallization of the crystalline block chains is restricted within the microphase-separated morphology, behavior is observed very much like amorphous block copolymers as predicted in ABC and AB type amorphous block copolymers. Below the Tm of the semicrystalline block, crystallization occurs and is strongly affected by the presence of rigid amorphous blocks (below the Tg of amorphous block component). The rigid amorphous blocks can prevent the formation of supermolecular spherulites and preserve the well-ordered microphase-separated structure formed in bulk films during the crystallization. In a thin film of the same copolymer, however, the microphase-separated structure formed below the ODT is completely ruined by the formation of supermolecular spherulites. The lamellar crystals dominate the overall morphology, and the mixed amorphous phases are situated between lamellar crystal regions.

The formation of spherulites in the semicrystalline block copolymers studied here is strongly affected by the thickness of the specimen. We observed that thin films crystallize into spherulites more easily than bulk films. Since common measurement techniques utilized for semicrystalline polymers (PLM, DSC, X-ray scattering, TEM) often require samples of different thicknesses by their very nature, the experimental results presented here are a reminder that the importance of the effect of film thickness may need to be modified to accurately characterize the structure and properties of these complex materials.

Acknowledgment. We dedicate this paper to our friend and colleague, Professor Reimund Stadler, who passed away in May of 1998 shortly after this work was initiated. The polymers studied here were synthesized in his research group at the University of Bayreuth, Bayreuth, Germany. We gratefully acknowledge Professor V. Balsamo, Universidade Simon Bolivar, Caracas, Venezuela, for the synthesis of the PS–PB–PCL block copolymer and Dr. F. von Gyldenfeldt for the synthesis of the PB–PCL block copolymer. We also acknowledge Professor Volker Abetz of the University of Bayreuth and Dr. Freddy Khoury of NIST for helpful comments during the course of this work.

References and Notes

(29) 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.
(30) According to ISO 31-8, the term “molecular weight (Mw)” has been replaced with “relative molecular mass”, symbol M_r. The conventional notation, rather than the ISO notation, has been employed for this article.
(31) In ref 17, a value of M_w = 146 000 g/mol is given for the diblock by SEC using a PS calibration. A more accurate subsequent determination was made by membrane osmometry to obtain the quoted value of M_w = 57 000 g/mol.
(41) McLaren, J. V. Polymer 1963, 4, 175.
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