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# Electric-Field-Induced Morphologies in Polystyrene/Poly(styrene-*b*-ethylene oxide) Blends

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**Introduction.** Recent work in these laboratories has demonstrated that solvent casting of incompatible polymer blends in electric fields can lead to the development of unusual morphologies.[1-4] Particular attention has been given to the system poly(ethylene oxide) (PEO) and polystyrene (PS) where it has been established that solution casting in applied fields up to ca. 10 kV/cm affords pearl-chained spheres or long, columnlike structures depending upon component molecular weights. Experiments by others with melts have demonstrated elongation and bursting in blends[5] and alignment of lamellae in block copolymers.[6] We recently reported[2] that casting of binary blends of PEO and PS containing a few percent of poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) stabilizes elongated phases toward breakup and proposed that this is the result of interfacial tension lowering by the diblock. In this paper, we present results of experiments on binary blends of PS-*b*-PEO in PS. In this system, PS-*b*-PEO is dispersed in spherical micelles whose sizes are roughly 2 orders of magnitude smaller than those which can be obtained in blends of immiscible homopolymers. Accordingly, it was of interest to determine whether the conditions employed in our earlier work on homopolymer blends would be sufficient to modulate the morphology of the micellar PEO domains formed in the PS-*b*-PEO/PS system. Indeed, we have observed orientation and an apparent sphere-to-cylinder transition in samples cast under applied fields similar to those employed in the previous work. More unexpected was the observation that phase separation of a micellar block copolymer was induced in films cast in an electric field of 2 kV/cm. This paper discusses these observations and offers explanations of the molecular processes involved in the phase separation, orientation, and sphere-to-cylinder transitions.

**Experimental Section.** The block copolymer, PS-*b*-PEO, was prepared by anionic polymerization, and details of the polymerization and characterization are described elsewhere.[2] The number-average molecular weight of the PS block was found by GPC to be about $8.8 \times 10^4$ with a polydispersity of 1.3. The overall composition of the block copolymer was 60/40 molar PS/PEO, respectively, as determined by $^1$H NMR. The molecular weight of the PEO block was calculated to be about $2.7 \times 10^4$. PS homopolymer was obtained from Aldrich and had a molecular weight of about $1 \times 10^5$ and a polydispersity of about 2.0. All solvents used were reagent grade and were used as received.

A 10–12 wt % solution was prepared by dissolution of polymer in a ternary solvent containing 85% toluene, 10% THF, and 5% methanol. This solvent system was selected in order to minimize crystallization of the PEO domains and allow for incorporation of inorganic salts in future experiments. The binary blend consisted of 80% PS and 20% PS-*b*-PEO. The overall percentage of PEO in the blends was about 5% by weight.

Film casting in an electric field was accomplished as follows. A few drops of solution was cast between evaporated aluminum fingers on a glass substrate and covered with a Petri dish. The aluminum fingers were prepared photolithographically to improve electrode smoothness. An electric field was applied until all the solvent evaporated. Electric field strengths of 2, 4, or 8 kV/cm were applied using a Model 6516A Hewlett-Packard dc power supply. The resulting films were then cut from the glass surface between the electrodes and subsequently embedded in a room-temperature-curing epoxy resin in silicone molds (E.F. Fullam). The epoxy component was Araldite GY6020 (Ciba-Geigy), and the amine component was Ancamide 503 (Pacific Anchor Chemical; division of Union Carbide). These were mixed in a ratio of 65/35 by weight. The films were typically about 25 μm in thickness. The resulting molded blocks were sectioned using a Reichert–Jung ultramicrotome at cutting speeds of 0.2–0.6 mm/s. Ultrathin sections (60–90 nm) were immediately collected from a water surface, stained with a filtered 1% w/v aqueous phosphotungstic acid solution (pH 1.0), and dried on medium filter paper. Transmission electron micrographs were taken with a Phillips CM 12 instrument at 80-kV accelerating voltage.

**Results and Discussion.** Blend films of PS-*b*-PEO in PS cast in the absence of the field, when viewed by TEM, reveal dark regions which are the stained PEO block micellar core. These are approximately spherical (ca. average 0.03 μm in diameter) and homogeneously distributed in the PS matrix as shown in Figure 1A. TEM photographs of films of similar composition cast in a 2 kV/cm applied electric field reveal large clusters containing a high density of block copolymer micelles (Figure 1B). This electric-field-induced phase separation of an otherwise thermodynamically stable dispersion of a micellar block copolymer phase has, to our knowledge, never been observed before. The diblock copolymer micellar core, composed of PEO chains, should have a dielectric constant higher than that of the PS matrix (as well as the PS corona), allowing for polarization within the micelles and the formation of nonuniform local fields which can be greater than the applied field. It is postulated that clustering occurs due to the electrostatic attractions among the polarized micelles. This phenomenon is known as mutual dielectrophoresis and is frequently seen in dispersions of higher dielectric constant particles in a lower dielectric constant fluid.[7]

Films cast in the presence of a 4 kV/cm applied field reveal narrow islands beginning to form within the clusters which are aligned in the field direction (Figure 1C).[8] Within these islands wormlike phases are observed and presumed to be cylindrical. Casting in still higher fields (8 kV/cm) leads to the formation of cylindrical phases which are aligned in the field direction. It should be noted that regions between these groupings of cylinders appear to be depleted in micellar block copolymer. Also, examination of many areas in TEM photographs of the sectioned films cast in the 4 kV/cm applied field (Figure 1C) reveals a few regions similar to those in parts B and D of Figure 1. The coexistence of different morphologies suggests that clustering of block copolymer micelles and orientation of the block copolymer islands precedes the formation of cylinders. We now offer an explanation for these observations.

In pure block copolymer systems the micellar state or state of aggregation (e.g., spheres, cylinders, lamellae) of

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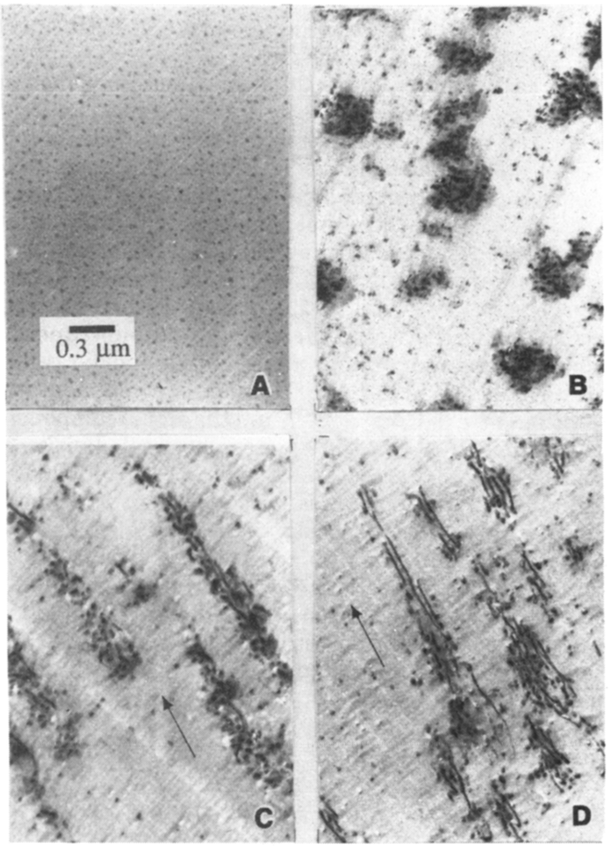

**Figure 1.** Transmission electron micrographs of 80/20 wt % PS/PS-*b*-PEO cast from 85%/10%/5% toluene/THF/methanol (A) in the absence of an electric field and in the presence of applied dc electric fields of (B) 2, (C) 4, and (D) 8 kV/cm. The scale is the same in all of the micrographs. Arrows indicate the applied field direction. The applied field direction in B is uncertain.

the block copolymer molecules is determined by the relative volume fraction of each segment and their degree of polymerization. In dilute, binary composites of block copolymer in a homopolymer host, the morphology tends toward that of spherical micelles of block copolymer molecules homogeneously dispersed in the host. The accepted picture of a spherical micelle of a diblock copolymer (A–B) in a matrix of a homopolymer of B is that of a core region of the aggregating block (A) surrounded by a corona region comprised of B blocks and some B homopolymer. It has been shown experimentally that an increase in the volume fraction of the core with respect to that of the corona favors the formation of cylindrical micelles.[9–11] There are at least three ways to change the core volume fraction relative to that of the corona region and thereby trigger a transition from spherical to cylindrical morphologies: (1) by increasing the molecular weight of the homopolymer continuous phase which can increase the core volume fraction by depleting the corona region of homopolymer, (2) by increasing the molecular weight of the A block segment, and (3) by simply increasing the concentration of the diblock copolymer, provided that the diblock has a composition which tends to form cylindrical or lamellar phases in the absence of homopolymer. This last point is particularly applicable to our study.

In the PS/PS-*b*-PEO system which we have investigated, the composition of the block copolymer, roughly 80/20% by weight, is near the predicted composition for a sphere-to-cylinder transition in noncrystallizable block copolymers.[12] In fact, we find that films of the *pure* PS-*b*-PEO block copolymer cast from the ternary solvent system (near 50 °C) yield a cylindrical morphology. We therefore suggest that, in the samples cast in electric fields (Figure 1B–D), mutual dielectrophoresis, an attraction between cores due to higher fields generated at the core/corona interface of the micelle, causes localized clustering of the micellar phases. As a consequence of this electric-field-induced phase separation, the local concentration of block copolymer is substantially increased, ultimately leading to the formation of cylinders, as is the case in films of the pure diblock copolymer. The cylinders are aligned in the field direction as expected, since this orientation should represent a minimum in potential energy when compared with other possible orientations.[13]

Our studies of these novel electric-field-induced morphology transformations in binary block copolymer/homopolymer systems are continuing and are being extended to pure block copolymer systems of differing composition.

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