Path-Dependent Morphologies of a Diblock Copolymer of Polystyrene/Hydrogenated Polybutadiene

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ABSTRACT: A crystallizable diblock copolymer of polystyrene/hydrogenated polybutadiene (SEB) was prepared by catalytic hydrogenation of a polystyrene/polybutadiene (SB) precursor. Changes in the morphology of SEB were observed following solution casting at temperatures below and above the melting point of the EB block. Annealing of the bulk copolymer also affected the observed morphology. A qualitative phase diagram is presented to place the observations in perspective.

Introduction

For wholly amorphous block copolymers it is known that variations in processing history (temperature, mechanical stress or strain, solvents) can lead to significant and potentially beneficial alterations[1] in the observed morphology of the bulk material, even though a specific equilibrium morphology is anticipated from thermodynamic arguments.[2] In this paper, we explore this concept for diblock copolymers that contain one block that is crystallizable; the particular crystallizable block considered here is the polyethylene-*co*-butylene product obtained by saturating polybutadiene of microstructure 45% cis 1,4; 45% trans 1,4; and 10% 1,2. The crystallizable diblock, denoted here as SEB, was obtained from a precursor polystyrene/polybutadiene diblock SB for which we have already developed extensive molecular and morphological information.[3,4] In addition to the fact that the SB/SEB pair makes an excellent model system for examining the added effect of crystallinity in block polymers, SEB copolymers have received some attention as potential emulsifying agents[5] in blends of polyethylene and polystyrene.

In this paper, we report on the morphologies we have observed for SEB in bulk following solution casting in two different temperature ranges, below and above the melting point of the EB block. Changes in morphology induced by annealing of the bulk copolymer are also reported. A schematic phase diagram is presented to place the observations in perspective. In addition, we present some information on certain hydrogenation and deuteration reactions on homopolymers to support the assertion that the SEB diblock is the expected analogue of SB, i.e., that there is no degradation of the polybutadiene chain length and no hydrogen substitution on the aromatic rings of the styrene repeat units.[4]

Experimental Section

Hydrogenation Chemistry. The catalyst was a triisobutylaluminum-reduced cobalt caprolactam complex. It was prepared under argon according to Halasa's method.[6] One advantage of this catalyst is that it can be extracted into water leaving the final product free of catalyst. Reagent grade caprolactam (mp 67.5 °C) was recrystallized in dry ether. The melting point after recrystallization was 69.5 °C. Five millimoles of the recrystallized caprolactam was dissolved in about 50 mL of sodium-dried toluene; 5/6 mmol of anhydrous cobalt(II) chloride dispersed in toluene was then added to the caprolactam solution, and the resulting solution was heated to 50 °C. While heating, the solution became deep blue, indicating formation of the cobalt(II) chloride caprolactam coordination complex. The solution was further heated at 80 °C for 15 min, cooled to 5 °C, and then reduced with 5 mmol of triisobutylaluminum; the deep blue solution changed to a deep brown color.

The hydrogenation reactions were carried out in a 300-mL stainless steel Parr bench-top minireactor. A 7 wt % solution of polymer in toluene was added to the reactor. The reactor was evacuated, and then the catalyst solution was injected; one-half millimole of the catalyst was used per gram of polymer sample. The reaction was carried out under 400 psi of hydrogen pressure (Matheson, purity 99.9995%) at 100 °C for about 5 h. After the reactor was opened, the hot toluene solution was transferred to a flask that contained about an equal volume of 1 M HCl. The two-layer liquid medium was stirred with a magnetic stirring bar at about 65 °C. The black organic layer became colorless, and the aqueous solution turned light pink. The organic layer was separated and hot filtered (ca. 65 °C) through a 0.5-μm filter into stirred methanol. The polymer was collected from suspension by filtration and then dried in a vacuum oven. The pure hydrogenated polymers were white. Matheson (99.5%) deuterium was used to deuterate the polybutadiene by using the same procedures.

Quantitative hydrogenation is achieved under the described reaction conditions. IR spectra were obtained[4] on three samples taken at 0.5, 3, and 5 h from a hydrogenation reaction of a polybutadiene homopolymer (M_n = 4800 g/mol). In these IR spectra, the peak at 900 cm^{-1}, which reflects the presence of vinyl unsaturations in the polybutadiene, disappeared completely by 0.5 h of reaction; the peak at 960 cm^{-1}, which indicates the presence of main-chain unsaturations of the 1,4-polybutadiene repeat units, was completely absent in the 5-h sample whose spectrum was essentially indistinguishable from that of low density polyethylene. Proton NMR experiments[4] also verified that the vinyl unsaturation disappeared more rapidly than the double bond of the 1,4 repeat unit.

The products of deuteration reactions on polybutadiene and polystyrene homopolymers were examined to determine the selectivity of the reaction; we wished to know if any unwanted H–D exchange occurs along the polybutadiene chains along with the saturation of the double bonds; also important for the present work is the need to determine whether there is any significant attack of the aromatic rings of the styrene units. The IR spectrum of a 3-h deuteration reaction of the polybutadiene revealed a clear peak at 2150 cm^{-1}, which represents "C–D" stretching, and a small but discernible peak at 960 cm^{-1}, indicating a small amount of double bonds still present in the chain microstructure; at 1300 cm^{-1} a broad –CHD– scissoring band appears while the $-CD_2-$ scissoring band (1046 cm^{-1}) is not present at all in the spectrum. These observations support the contention that there is little or no H/D scrambling with the catalyst system employed here.[4,6,7] The IR spectrum of a 5-h deuteration reaction on PS showed a weak peak at 2300 cm^{-1}, which may represent aromatic carbons attached to deuterium, while the IR spectrum of a deuterated SB diblock showed essentially no sig-

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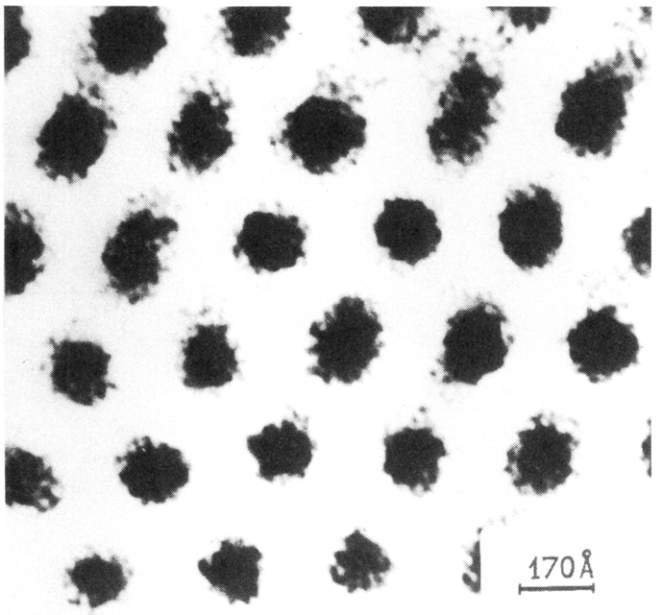

Figure 1. Transmission electron micrograph of osmium tetraoxide stained SB.

nal at 2300 cm^{-1}.[4] From this we conclude that although some small amount of attack of the aromatic carbons may occur for PS homopolymers, the chemistry described here can be applied to SB block copolymers with no significant contamination of the styrene block.

Finally, we note that whenever air was present in the high-pressure reactor, the molecular weight distributions of the products were seriously altered.[4] Careful evacuation of the reactor prior to pressurization with H_2 or D_2 eliminated the oxidative degradation/coupling of the chains. Molecular weights and distributions determined from size-exclusion chromatography experiments remained unchanged during the hydrogenation reactions whenever air was rigorously excluded from the reactor.

Molecular Characterization. The molecular characterization of the SB diblock has been described in detail elsewhere;[3,4] molecular weights are 90 000 and 11 000 g/mol for the polystyrene and polybutadiene moieties, respectively. On the basis of the above-mentioned analysis of the products of control reactions, we arrive at molecular weights of 90 000 and 11 400 g/mol for the blocks of the SEB copolymer.

Morphological Characterization. Film specimens of SB and SEB were prepared by solution spin casting from toluene or xylenes according to procedures described elsewhere.[4,8] These films were subjected to various thermal histories in vacuo at 85, 105, and 140 °C. Characterization of the morphologies of these films included differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-IV, transmission electron microscopy (TEM) of suitably stained ultramicrotomed (LKB Cryogenic ultratome) sections using a Phillips 300 TEM, and small-angle X-ray scattering (Rigaku Cu rotating anode point source, Charles Supper double mirror focusing optics, Nicolet two-dimensional detector).

Results

Selected results of morphology characterization experiments are given in Figures 1–10. For the SB diblock, a spherical microphase-separated morphology is clearly observed in the TEM of osmium tetraoxide stained sections (Figure 1). SAXS spectra showed a large peak at $Q = 0.018$ $Å^{-1}$, indicating a sphere spacing of 350 Å. SANS spectra[4] not shown here could be reasonably well fit with a combination[9] of an intraparticle form factor (sphere radius = 95 Å) and a Percus–Yevick interparticle interference function (hard-sphere radius = 150 Å). Thermal analysis of SB revealed a polystyrene T_g of near 104 °C.

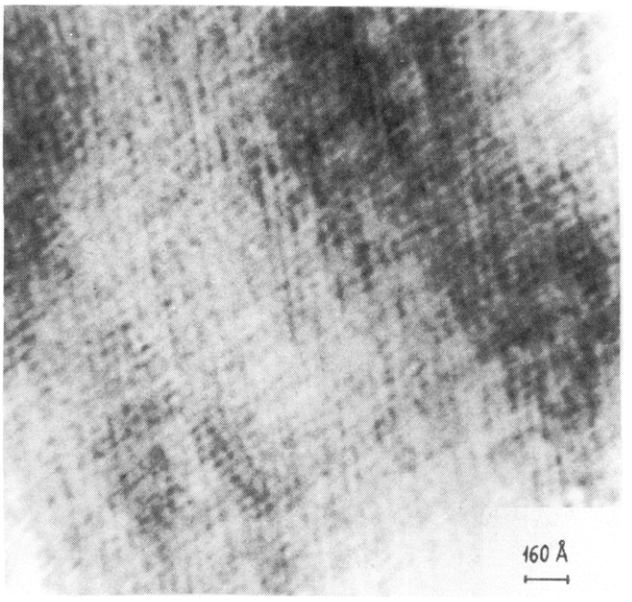

Figure 2. Transmission electron micrograph of ruthenium tetraoxide stained SEB cast from toluene at 65 °C. Essentially identical micrographs are seen for specimens as-cast, annealed at 85 °C, and annealed at 105 °C.

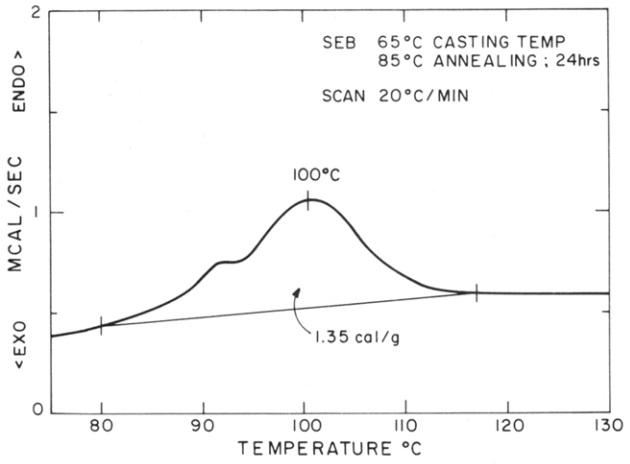

Figure 3. Differential scanning calorimetry of SEB cast at 65 °C and annealed at 85 °C.

For the case of the SEB diblock cast at 65 °C there were no discernible spherical domains in the TEM of ruthenium tetraoxide stained sections of as-cast films and for films annealed at 85 and 105 °C for 24 h. Figure 2 shows the type of morphology seen in the TEM for these films. The two-dimensional SAXS patterns for all of these films showed only featureless backgrounds. These disordered morphologies did show evidence of crystallinity, however; DSC traces revealed an endothermic process indicative of crystal melting superimposed on the polystyrene T_g (Figure 3). Wide-angle X-ray scattering patterns[4] not shown here revealed 110 and 200 polyethylene reflections.

When the film of SEB cast at 65 °C is annealed at 140 °C, a striking change in morphology is observed. Ruthenium tetraoxide stained sections now reveal (Figure 4) a microspherical morphology with contrast which is inverted from that of Figure 1. A fit of SANS data[4] on microphase-separated SEB gave the following parameters: sphere radius = 145 Å and hard-sphere radius 215 Å. A SAXS pattern (Figure 5) of the high-temperature (140 °C) annealed, 65 °C cast sample showed a peak corresponding to a value of $Q = 0.012$ $Å^{-1}$ or a sphere spacing of 480

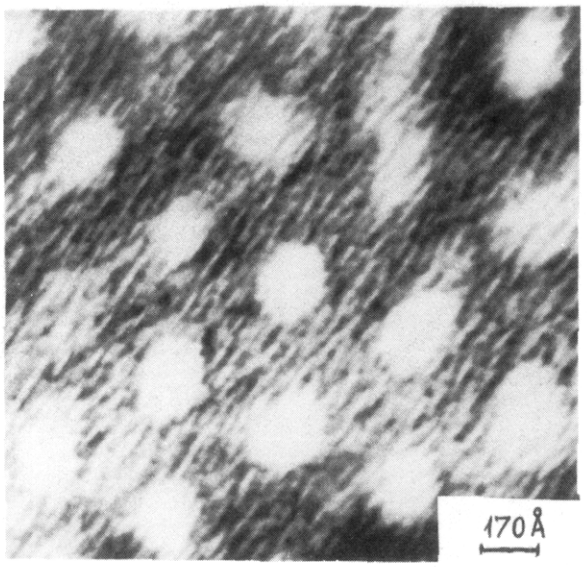

Figure 4. Transmission electron micrograph of ruthenium tetraoxide stained SEB cast at 65 °C and annealed at 140 °C for 3 h.

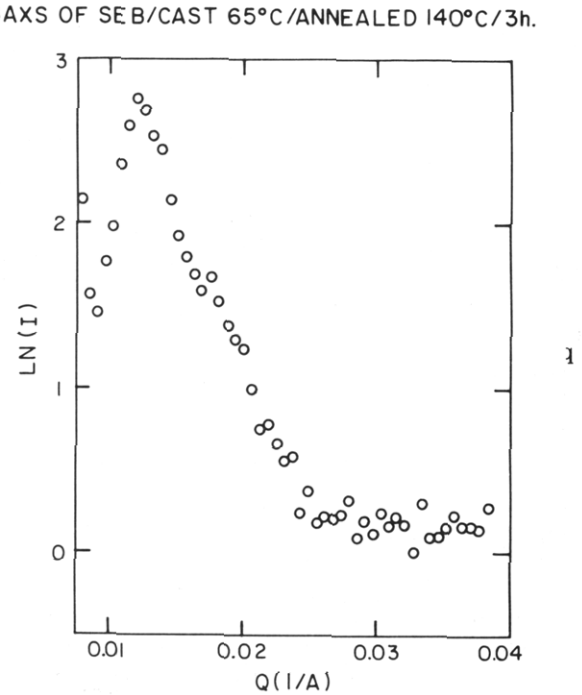

Figure 5. SAXS intensity vs scattering vector for SEB cast at 65 °C and annealed at 140 °C. Morphology is shown in Figure 4.

Å. The two-dimensional pattern from which this average plot was taken was symmetric, indicating no preferred orientation or alignment of the spherical domains. DSC traces had the same form as those of the unannealed sample and the 85 °C/105 °C annealed samples but with the important addition of a new peak at 110 ± 2 °C (Figure 6); the relative magnitude of this latter peak (compared to the magnitude of the features appearing near 100 °C) increased with annealing time when 140 °C was employed as the annealing temperature.

Casting at 125 °C from xylenes resulted in the direct appearance of the spherical morphology in the as-cast samples (Figure 7). Annealing of these samples at 140 °C led to the emergence of the melting transition near 110 °C; annealing also has the effect of randomizing the morphology, eliminating the slight tendency for preferred packing arrangements of spheres exhibited by the as-cast films obtained at 125 °C from xylenes (Figures 8 and 9).

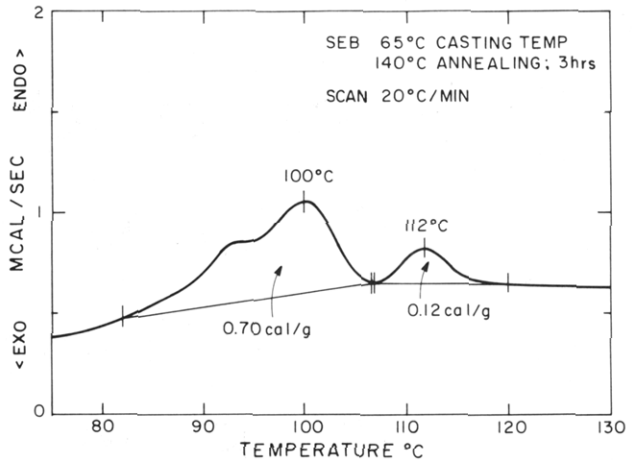

Figure 6. DSC trace for the SEB specimen cast at 65 °C and annealed at 140 °C.

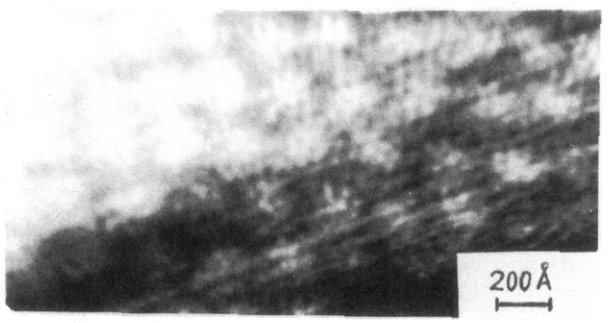

Figure 7. Transmission electron microscopy of the unannealed SEB specimen as-cast from xylenes at 125 °C, stained with ruthenium tetraoxide.

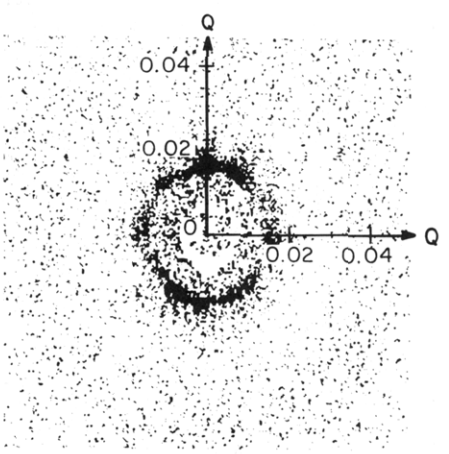

Figure 8. Two-dimensional SAXS pattern for SEB as-cast from xylenes at 125 °C; variation of intensity around the circular pattern suggests some preferred spatial arrangements of the spheres in this unannealed specimen.

Discussion

The series of results presented above can be explained in a unified, internally consistent manner by postulating a plausible qualitative form for the temperature–composition phase diagram for the SEB diblock in solvent. In Figure 10 the isothermal solvent casting process is represented by a horizontal arrow that starts at the left of the diagram (our starting concentrations were about 10 wt % copolymer) and proceeds to the right

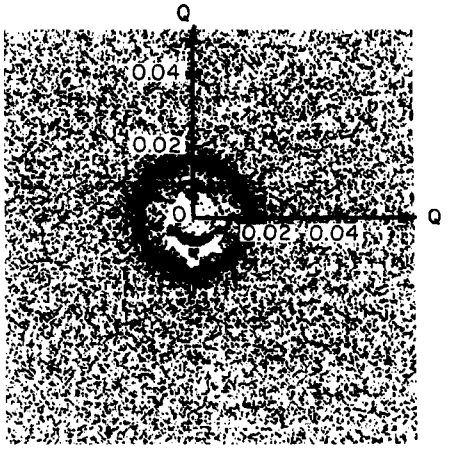

Figure 9. Two-dimensional SAXS pattern for SEB cast at 125 °C and annealed at 140 °C.

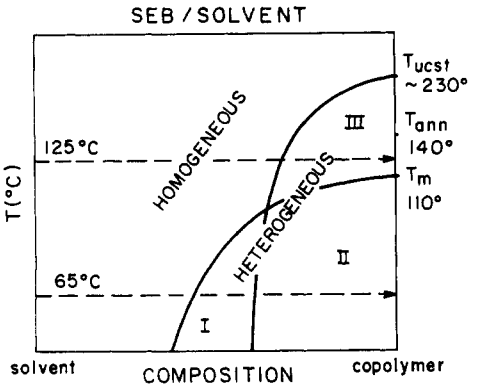

Figure 10. Qualitative temperature–composition phase diagram for the SEB/solvent system.

(toward the bulk copolymer) as solvent evaporates. To explain our observations it is necessary that, when the casting temperature is below the melting point of the EB block, crystallization precedes microphase separation; thus at lower temperatures the boundary between the homogeneous solution on the left and the heterogeneous medium on the right represents the point at which the EB crystallizes from solution, carrying the attached S block with it. At still lower amounts of solvent, further to the right in the phase diagram, a second thermodynamic boundary is shown; in region II the diblock molecules would like to self-assemble into the lower free energy state of a microphase-separated morphology. Once crystallized, however, the diblock material is kinetically locked into the morphology formed in region I and it is this morphology that is eventually seen (Figure 2) in the as-cast specimens when 65 °C is the temperature of the casting process.

Above the melting point of the EB block, regions I and II merge into a single region III. Crystallization cannot occur and microphase separation occurs directly from solution and persists into the bulk state, as observed in the 125 °C casting process.

The results of annealing are also explained by the schematic phase diagram. In the bulk state, the kinetically locked nonequilibrium morphology of Figure 2 will not be released until $T_{anneal} > T_m$, thereby explaining why the 85 and 105 °C anneals produced no hint of the microspherical morphology. Annealing in the region above T_m releases the constrained molecules and allows them to reorganize into the preferred microspherical morphology. In the region between T_m and T_{ucst} the microspheres are amorphous EB domains; when cooled below T_m these microspheres crystallize giving the microphase-separated semicrystalline morphology shown in Figure 4.

At T_{ucst} the SEB melt changes from heterogeneous to homogeneous, and in principle this homogeneous amorphous state could be kinetically locked into the bulk material by very rapid cooling to room temperature. On the basis of qualitative considerations of solubility parameters, we conclude that T_{ucst} for our SEB diblock must be greater than the value of about 142 °C found by Gouinlock and Porter[10] for an SBS triblock of lower molecular weight. Thus the position of T_{ucst} is qualitatively correct in Figure 10, lending support to the overall explanation presented here. We have seen a small but reproducible DSC transition near 230 °C in experiments on the SEB diblock; we are currently attempting to conduct high-temperature small-angle X-ray scattering experiments of the type reported by Fishkis and Roe[11] to determine whether this represents T_{ucst} for the SEB diblock.

Summary

Variations in solvent-casting pathways and in bulk annealing conditions led to a variety of morphologies for a single SEB diblock copolymer; some of these are kinetically trapped structures while others are consistent with expectations of equilibrium thermodynamics. Independent control of the morphological scale (microphase-separated vs disordered) and degree/perfection of crystallinity was demonstrated. These degrees of freedom offer both opportunities and problems for those attempting to develop meaningful structure/processing/properties relationships for semicrystalline block copolymers and for blends in which they are meant to act as emulsifiers.

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References and Notes

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