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Polydispersity-Induced Stabilization of a Disordered Bicontinuous Morphology in ABA Triblock Copolymers

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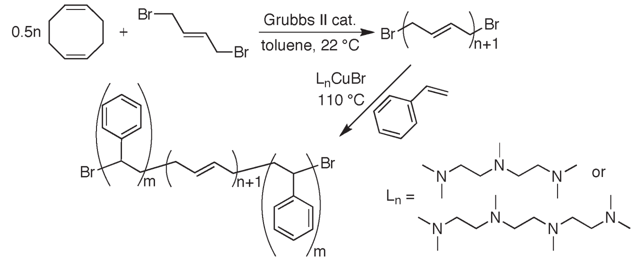
Tandem and controlled polymerization methodologies have enabled the synthesis of a wide variety of block copolymers with variable compositions, molecular weights, and molecular weight distributions.[1,2] These syntheses often yield copolymers with unimodal molecular weight distributions and continuous and broad polydispersities ($M_w/M_n > 1.1$). A subset of these synthetic protocols also enables selective incorporation of tunably polydisperse homopolymer segments into block copolymers.[3−5] The resulting materials are expected to exhibit desirable processabilities by virtue of their broad polydispersities.[6]

Whereas the microphase separation behavior of monodisperse AB diblock and A/B multiblock copolymers ($M_w/M_n \leq 1.1$) is well understood both theoretically and experimentally,[1,7−9] the effects of polydispersity on block copolymer phase behavior have only recently been studied. Lynd et al. have comprehensively reviewed both theoretical and experimental studies of these polydispersity effects.[2] In brief, self-consistent mean-field theory (SCMFT) for polydisperse AB diblock copolymer melts agrees qualitatively with experimental observations that block polydispersity shifts the composition windows associated with the typically observed spherical, cylindrical, lamellar, and gyroid phases. A general experimental observation is that the polydisperse segment behaves as if it occupies a smaller volume than that indicated by the bulk polymer composition, thereby favoring interfacial curvature toward the polydisperse domain. Experimental and theoretical studies also show that order−disorder transition temperature (T_{ODT}) increases with concomitant domain spacing dilation upon increasing block polydispersity, especially when the polydisperse segment is the minority component. Reports by the groups of Matsushita,[10,11] Bendejacq,[12] Leibler,[13] Hillmyer,[5,14−16] Register,[17] and the group at Dow Chemical[18,19] on block copolymers with both discrete and continuous polydispersities resulting from controlled/tandem polymerizations also indicate that these materials may adopt the typically observed morphologies with relatively small perturbations in the composition-dependent phase boundaries.

Relatively few experimental phase behavior studies have interrogated the effects of segmental polydispersity in A/B multiblock copolymers in which both ends of the polydisperse segment are constrained at block junctions. Noro et al. observed larger domain dilations in blends of monodisperse poly(2-vinyl pyridine-*b*-styrene-*b*-2-vinyl pyridine) copolymers with variable PS chain lengths as compared with diblock blends at identical compositions.[11] Pitet and Hillmyer observed well-ordered morphologies in mixtures of high molecular weight polydisperse diblock and triblock copolymers having a polydisperse poly(1,4-butadiene) segment flanked by monodisperse poly(lactide) blocks.[16] They have also observed the formation of a disordered bicontinuous phase in related compositionally asymmetric poly(lactide-*b*-ethylene-*b*-lactide) triblock copolymers containing a polydisperse center block ($M_w/M_n = 2.5$), from which they produced nanoporous membranes.[20] Related bicontinuous structures have also been observed by Wagner et al. in multiblock polycarbonate/polycyclooctenamer copolymers.[19] This communication describes the formation of a disordered bicontinuous phase in weakly segregated, compositionally symmetric poly(styrene-*b*-1,4-butadiene-*b*-styrene) (SBS) triblock copolymers with a polydisperse poly(1,4-butadiene) center segment and relatively monodisperse polystyrene end blocks. We further demonstrate that this unusual morphology persists at low segregation strengths as a consequence of center block polydispersity.

Scheme 1. Tandem ROMP−ATRP Synthesis of Polydisperse SBS Triblocks



Polydisperse SBS triblock copolymers were prepared using an optimized variant of the tandem chain transfer ring-opening metathesis polymerization (ROMP-CT) and atom transfer radical polymerization (ATRP) synthesis initially reported by Bielawski et al.(Scheme 1).[21] ROMP-CT of scrupulously purified 1,5-cyclooctadiene[22] in the presence of the chain transfer agent 1,4-dibromo-2-butene using Grubbs' second generation catalyst at 22 °C yielded polydisperse α,ω-dibromo-poly(1,4-butadiene) having $M_w/M_n = 1.73−1.90$ and 85% trans content, as determined by size-exclusion chromatography (SEC) at 40 °C in a tetrahydrofuran (THF) using Mark−Houwink corrected poly(1,4-butadiene) calibration curve based on monodisperse polystyrene standards and ^{1}H NMR, respectively. (See the Supporting Information for details.) The agreement within 10% between the $M_{n,B}$ obtained from SEC and from polymer end group analyses by ^{1}H NMR indicates a high degree of chain end functionality ($F_n = 2.0$).[23] Subsequent ATRP of styrene at 110 °C using L_nCuBr (L_n = PMDETA or HMTETA)[24] yielded unimodal SBS triblock copolymers with $M_w/M_n = 1.40−1.63$. By using metathesis degradation of the polydiene segment with 1-hexene to isolate the PS end blocks,[25] the molecular weights and polydispersities of the end blocks were independently measured by SEC to be in the range $M_w/M_n = 1.09−1.20$. The fact that the $M_{n,S}$ values from SEC are in good agreement with those obtained by quantitative ^{1}H NMR analyses indicates the absence of any substantial S or B homopolymer contamination. From ^{1}H NMR composition analyses of the resulting block copolymers and the melt homopolymer densities at 140 °C for each block,[26] polymer compositions were determined to be $f_B = 0.48−0.53$. Literature values of T_{ODT} as a function of N at symmetric compositions for a series of anionically synthesized monodisperse poly(styrene-*b*-1,4-butadiene) diblock copolymers[27−30] were used to determine the Flory−Huggins interaction parameter $\chi_{SB}(T) = (30.137/T) − 0.03813$ from the mean-field theory result[7] $(\chi N)_{ODT} = 10.495$, where N is the volume degree of polymerization relative to the 118 Å^3 reference volume. The molecular parameters of five SBS

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Table 1. Molecular Characterization of Polydisperse SBS Triblock Copolymers

sample	$M_{n,total}$ (kg/mol)	PDI[a]	w_B	f_B[b]	N[c]	$M_{n,B}$ (kg/mol)[a]	PDI_B[a]	$M_{n,S}$ (kg/mol)[e]	PDI_S[a]	q^* (Å^{-1})[f]	d (nm)
SBS-1	12.3	1.60	0.49	0.53	194	6.1	1.90	3.2	1.09	0.0160	39.3
SBS-2[g]	28.2	1.57	0.47	0.51	442	13.2	1.73	7.5	n.d.	0.0180	34.9
SBS-3	32.9	1.63	0.47	0.51	517	15.3	1.79	8.8	n.d.	0.0159	39.5
SBS-4[h]	35.5	1.57	0.45	0.49	555	16.0	1.90	9.8	1.20	0.0158	39.8
SBS-5[h]	36.1	1.40	0.44	0.48	564	16.0	1.90	10.1	n.d.	0.0158	39.8
SBS-6[d]	30.6	1.05	0.48	0.52	481	14.6	n.d.	8.0	1.09	0.0330	18.9

[a] Measured by SEC in THF at 40 °C against PS standards; $M_{n,B}$ values were measured using Mark−Houwink correction; n.d. = not determined. [b] Calculated using the homopolymer melt densities at 140 °C from ref 26. [c] Calculated using the 118 Å^3 reference volume. [d] Sample synthesized by sequential anionic polymerization at 40 °C initiated with *s*-butyllithium. [e] $M_{n,S}$ determined by quantitative ^{1}H NMR spectroscopy based on $M_{n,B}$. [f] Measured by lab source SAXS at 150 °C. [g] 1,5,9-cyclododecatriene was used in the ROMP-CT reaction. [h] 1,1,4,7,10,10-Hexamethyltriethylene tetramine (HMTETA) was used instead of 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) in the ATRP reaction.

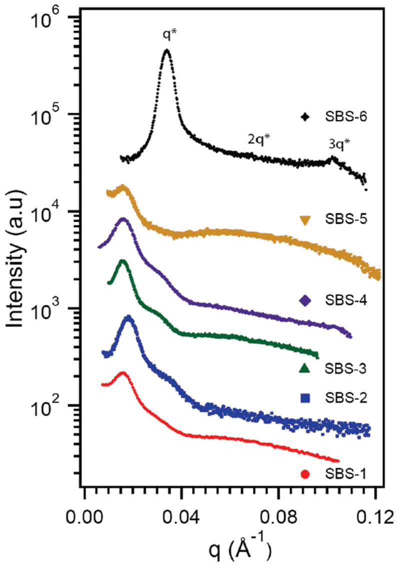

Figure 1. Log intensity versus q (Å^{-1}) plots derived from azimuthal integration of 2D lab source SAXS patterns acquired at 140 °C for symmetric polydisperse SBS triblock copolymers and monodisperse SBS-**6** (indexed to a lamellar morphology), demonstrating that polydispersity disrupts long-range ordering. (Data has been vertically shifted for clarity.)

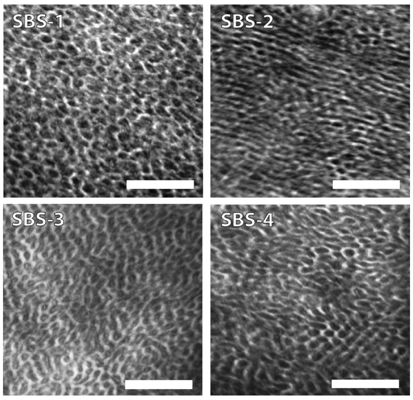

Figure 2. TEM micrographs of a disordered bicontinuous morphology for SBS-**1** melt-pressed at 150 °C, SBS-**2** sheared in a rheometer at 140 °C (ω = 2.0 Hz for 10 min), channel die-aligned SBS-**3** at 160 °C, and toluene solvent cast and vacuum annealed (24 h at 130 °C) SBS-**4**; dark regions correspond to polybutadiene selectively stained with OsO_4. Scale bars in all micrographs are 200 nm.

triblocks having $M_{n,total}$ = 12.3−36.1 kg/mol (containing 0.5 to 1 wt % Irganox antioxidant) with calculated segregation strengths χN = 6.42−18.7 at T = 150 °C are enumerated in Table 1.

Azimuthally integrated lab source small-angle X-ray scattering (SAXS) data collected at 140 °C for polydisperse SBS triblocks are shown in Figure 1, along with data associated with monodisperse SBS-**6** with f_B = 0.52 for comparison. These scattering patterns demonstrate that these polydisperse triblocks exhibit low levels of long-range order, evidenced by the small number of broad scattering peaks that cannot be clearly indexed to any known morphology. Temperature-dependent SAXS analyses indicate that these polymers remain microphase-separated up to 220 °C with no signs of peak broadening indicative of proximity to ODT. Because of the inaccessibility of ODT, we attempted to induce better ordering and to mitigate nonequilibrium effects in these polymer samples by toluene solvent casting and subsequent vacuum annealing at 130−180 °C for up to 96 h, by channel die alignment at 160 °C, or by shearing in an ARES-LS2 rheometer at 140 °C (ω = 2.0 Hz for 10 min). These variously prepared samples did not display appreciably higher degrees of order by SAXS over the temperature range 22−220 °C. The characteristic domain spacing for these polymers, $d = 2\pi/q^* \approx$ 39 nm, depends only weakly on the overall polymer molecular weight (Table 1). This behavior sharply contrasts the high degree of order observed in monodisperse SBS-**6**, which exhibits expected SAXS reflections at q^* and $3q^*$ with the expected structure factor extinction at $2q^*$ for a symmetric ABA copolymer and an accessible order−disorder transition at $T_{ODT} \approx 171$ °C. All SAXS samples were subsequently redissolved in THF and subjected to SEC analyses to verify that cross-linking had not occurred during characterization. The terminal low-frequency rheological response of SBS-**1** in the linear viscoelastic regime corroborates a microphase-separated melt over the range 120−200 °C (see the Supporting Information), with similarities to that of bicontinuous microemulsions.[31−33] These results are quite striking given that polydisperse SBS-**1** has $T_{ODT} > 220$ °C with χN = 6.54, indicative of substantial microphase-separated melt-stabilization, because SCMFT for monodisperse ABA triblock copolymers predicts that the minimum segregation strength required for microphase separation is $(\chi N)_{ODT} = 17.9$.[34,35] Theoretical treatments of polydisperse diblock copolymers are conflicted in predicting the effects of polydispersity on the value of $(\chi N)_{ODT}$: SCMFT that neglects fluctuation effects[36] predicts a 28% reduction in $(\chi N)_{ODT}$ (microphase separated melt-stabilization) at symmetric compositions,[37] whereas Monte Carlo simulations predict a smaller effect.[38] Analogous predictions for polydisperse triblock copolymers are absent from the literature. Because the ODT for these polydisperse SBS triblocks is inaccessible, it is unclear whether the disordered bicontinuous morphology is an equilibrium or metastable phase.[3,39]

Transmission electron microscopy (TEM) studies provided further insight into the morphology adopted by these variously processed polydisperse SBS triblock copolymers. Polymer samples were cryomicrotomed between −120 and −150 °C, and the poly(1,4-butadiene) block was selectively stained with OsO_4 for imaging. Representative TEM micrographs shown in Figure 2 demonstrate that polydisperse SBS-**1**, SBS-**3**, and SBS-**4** adopt a disordered bicontinuous morphology, in which domain interfaces typically curve toward the polydisperse block. TEM analysis of rheometer-sheared SBS-**2** shows a low level of domain alignment with a texture reminiscent of polymeric bicontinuous microemulsions;[40] the slight domain spacing compression is ascribed to the lower polybutadiene segment polydispersity.

We hypothesize that the substantial microphase-separated melt stabilization and disordered bicontinuous morphology adopted by SBS triblock copolymers with polydisperse center B blocks arise from a confluence of factors. The tendency to form a morphology in which interfaces preferentially curve toward the polydisperse segment likely arises from relaxed chain stretching and reduced packing frustration associated with these configurations.[2] This entropic stabilization of the ordered melt results in a polydispersity-induced increase in T_{ODT} that is significantly larger than those in previously studied systems, wherein the polydisperse segment has only one constrained chain end.[14] We speculate that the coupling of block polydispersity, the consequent composition polydispersity, and ABA triblock chain topology frustrate long-range ordering to yield a disordered bicontinuous structure that remains microphase-separated at very low values of χN as compared with corresponding monodisperse ABA triblocks. The weak dependence of domain size on N may result from the ability of a segregation strength-dependent population of SBS triblocks with small B segments to act like S homopolymers that swell the domains;[17,41] therefore, the principal spacing mainly depends on a small number of high-molecular-weight chains in the sample. We are currently studying the detailed properties of this bicontinuous morphology and the full phase portrait of polydisperse SBS triblock copolymers with a polydisperse center segment.

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Supporting Information Available: Detailed synthesis and characterization procedures and rheology data for SBS-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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