Phase Behavior of Triblock Copolymers Varying in Molecular Asymmetry

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The transformation from A_1B diblock copolymer to A_1BA_2 triblock copolymers varying in molecular asymmetry is investigated as the A_2 end block is progressively grown via chemical synthesis. Dynamic rheological measurements show that the order-disorder transition (ODT) temperatures of two copolymer series differing in composition and molecular weight decrease when the A_2 block is short relative to the A_1 block, and then increase as the length of the A_2 block is increased further. The resultant ODT minimum, predicted by mean-field theory, is attributed to mixing between long B and short A_2 blocks.

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While immiscible homopolymers commonly undergo phase separation at macroscopic length scales, incorporation of a covalent linkage between two such homopolymers to form a diblock copolymer can have dramatic consequences at significantly reduced length scales. Because of the restriction placed on its constituent blocks, an incompatible diblock copolymer can spontaneously self-organize into a variety of ordered morphologies including spheres arranged on a cubic lattice, cylinders arranged on a hexagonal lattice, bicontinuous channels, and alternating lamellae [1]. Such tunable morphological variation is of keen interest in emerging nanotechnologies [2,3] and reflects entropic differences associated with interfacial chain packing [4], which can be systematically altered by synthesizing block copolymer molecules differing in composition, repeat unit asymmetry [5], or (liquid) crystallinity [6,7]. A second approach by which to regulate the morphology of microphase-ordered diblock copolymers relies on (i) the physical addition of a second (miscible) component, such as a selective solvent [8], a parent homopolymer, or a second copolymer of different composition [9], or (ii) exposure to the vapor of a selective solvent [10]. The morphologies thus generated by chemical or physical modification of self-organized diblock copolymers are accompanied by changes in (micro)phase stability.

Another strategy developed to increase the versatility of diblock copolymers introduces a third block to a diblock copolymer, thereby forming a triblock copolymer. Incorporation of a chemically dissimilar third block results in an *ABC* triblock copolymer, which can substantially extend the assortment of experimentally accessible morphologies by varying relative block lengths and interblock incompatibility [11–14]. If the third block is chemically identical to the first, the result is an *ABA* triblock copolymer, which exhibits the same morphologies as its *AB* diblock counterpart [15,16] but markedly different mechanical and flow properties [17]. The primary reason for these differences is that the third block may locate in either the same microdomain as the first so that the *B* midblock forms a loop or a different microdomain so that the midblock forms a bridge. Several experimental [18,19] and theoretical [16,20,21] studies have examined the consequences of midblock bridging (and network formation) in *ABA* triblock copolymer systems, but nearly all these previous efforts have focused on molecularly (albeit not necessarily compositionally) symmetric copolymers wherein the two *A* end blocks are of identical length. Such limited assessment reflects the commercial relevance of molecularly symmetric triblock copolymers, particularly as thermoplastic elastomers [22].

Although extensive phase studies of *ABC* triblock copolymers varying in block length and composition have been reported, a comparably systematic analysis of molecularly asymmetric A_1BA_2 triblock copolymers, which can elucidate the thermodynamic and property evolution associated with the transformation from diblock to triblock copolymers, is lacking. The pioneering theoretical investigations conducted by Mayes and Olvera de la Cruz [23] and, later, by Dobrynin and Erukhimovich [24] of A_1BA_2 triblock copolymers in the weak-segregation limit have provided evidence that molecular asymmetry can have a profound effect on both order-disorder and order-order transitions. More recently, Matsen [25] has used self-consistent field theory (SCFT) to show that such molecular asymmetry can alter microdomain dimensions and order-order transitions due to the presence of short A_2 blocks that remain mixed upon microphase ordering of the A_1 and B blocks. The objective of the present work is to discern the influence of molecular asymmetry on the order-disorder transition temperature (T_{ODT}) in two series of copolymers in which the A_2 block is progressively grown from parent A_1B diblock copolymers differing in composition and molecular weight.

Two poly(styrene-*b*-isoprene) A_1B diblock copolymers were independently synthesized via living anionic polymerization in cyclohexane at 60 °C with *sec*-butyllithium as the initiator. The molecular characteristics of these diblock copolymers, as well as the molecularly asymmetric triblock copolymers grown from each by subsequent living anionic polymerization, were measured by ^{1}H NMR and gel permeation chromatography (GPC). The first copolymer series, designated 9–46-A_2, was generated from a diblock copolymer with block masses of 9400 (styrene, A_1) and 46 000 (isoprene, B), whereas the second series, denoted 9–17-A_2, employed a parent diblock copolymer with block masses of 8800 (A_1) and 17 000 (B). The maximum polydispersity index measured in both triblock copolymer series was determined from GPC to be 1.04. Specimens for rheometry were prepared by compression molding a platen approximately 1.2 mm thick of each copolymer. Disks measuring 30 mm in diameter were punched from each platen and heated to 170 °C under vacuum for 2 h, after which time the materials were cooled to ambient temperature under vacuum.

Dynamic shear measurements were conducted on an ARES strain-controlled rheometer equipped with 25 mm parallel plates separated by a 1 mm gap. Strain sweeps were performed to discern the linear viscoelastic limit and revealed that the onset of nonlinear behavior occurred at 2%–5% strain amplitude at 160 °C. All subsequent measurements used lower strain levels to ensure that linear viscoelasticity was maintained. The T_{ODT} of each copolymer under investigation was established from precipitous reductions in the dynamic elastic (G') and viscous (G'') moduli during isochronal temperature sweeps performed at heating rates of 1 and 5 °C/ min at a frequency of 1 rad/s. Frequency sweeps were also conducted from 10^{-1} to 10^2 rad/s at 2% strain at selected temperatures for additional validation through the use of G' vs G'' cross plots.

Values of T_{ODT} are presented as a function of the growing A_2 block mass (M_{A_2}) for both copolymer series in Fig. 1. While T_{ODT} is anticipated to increase with increasing copolymer molecular weight due to greater interblock incompatibility (expressed in terms of χN, where χ is the temperature-dependent Flory-Huggins interaction parameter and N is the number of statistical units along the copolymer backbone), this expected trend does not become evident in Fig. 1 until the A_2 block is of comparable size to or larger than the A_1 block. At shorter A_2 block lengths, however, T_{ODT} is depressed, exhibiting a clearly discernible minimum in both copolymer series. The measured reduction in T_{ODT} relative to the parent diblock copolymer is nontrivial: 35 °C in the 9–46-A_2 series and 43 °C in the 9–17-A_2 series. This signature feature in both copolymer series must also be considered in light of the A_2-induced change in copolymer composition. That is, an increase in the composition of the minority block in an ordered block copolymer (f_A) is generally accompanied by a net decrease in χN and, consequently, an increase in T_{ODT}. Thus, the concurrent increases in M_{A_2} and f_A in the two copolymer series displayed in Fig. 1 would naively favor monotonic increases in T_{ODT}. To explain the observed minimum in T_{ODT}, we turn our attention to the mean-field theory proposed by Mayes and Olvera de la Cruz [23].

Molecular asymmetry in an A_1BA_2 triblock copolymer can be taken into account by introducing an asymmetry parameter (τ), defined as the fraction of A units comprising the A_1 block, in which case the number of A units in the A_1 block (N_{A_1}) is written as $\tau f_A N$. Conversely, the number of A units in the A_2 block (N_{A_2}) is given by $(1 - \tau)f_A N$ so that τ can be alternatively expressed as f_{A_1}/f_A, where f_{A_1} is the number fraction of A units in the A_1 block. When $\tau = 1$, the triblock copolymer reduces to a diblock copolymer. When, on the other hand, $\tau = \frac{1}{2}$, the triblock copolymer possesses end blocks of equal mass and becomes molecularly (albeit not necessarily compositionally) symmetric. These limits are displayed in Fig. 2(a), in which $(\chi N)_{ODT}$ is presented as a function of τ for copolymers differing in molecular composition (f_A). The values of $(\chi N)_{ODT}$ provided in Fig. 2(a) correspond to the lowest order-disorder transition condition identified for the lamellar, hexagonal cylindrical, and body-centered-cubic spherical morphologies. In all the cases examined, $(\chi N)_{ODT}$ is observed to decrease with increasing τ from $\tau = \frac{1}{2}$ to 1. This predicted behavior is symmetric around $\tau = \frac{1}{2}$, and the extent of reduction in $(\chi N)_{ODT}$ with increasing τ is more pronounced for compositionally asymmetric copolymers. It is important to recognize that, for f_A to remain constant with varying τ, N_{A_1} must decrease commensurate with an increase in N_{A_2}. Although this scenario differs from the present experimental study, the predictions shown in Fig. 2(a) can be compared with the SCFT predictions of Matsen [25] and demonstrate that the order-disorder transition (ODT) in molecularly asymmetric triblock copolymers is sensitive to both τ and f_A.

Predictions of $(\chi N)_{ODT}(\tau)$ for the two copolymer series investigated here are displayed in Fig. 2(b) and reveal a more complex dependence on τ since f_A increases with decreasing τ. In both cases, however, a maximum in $(\chi N)_{ODT}$ is apparent, which indicates that T_{ODT} is predicted to exhibit a minimum, in accord with the experimental findings provided in Fig. 1. Direct comparison of the experimental measurements in Fig. 1 with the theoreti-

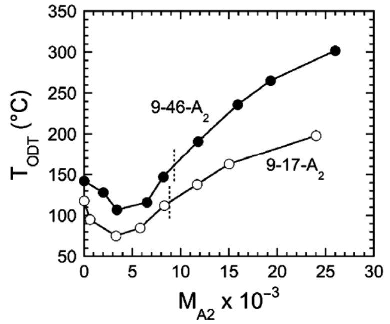

FIG. 1. Dependence of the order-disorder transition temperature (T_{ODT}) measured by dynamic rheology on the mass of the growing A_2 end block (M_{A_2}) in the 9–46-A_2 (●) and 9–17-A_2 (○) triblock copolymer series (see the text for details). The solid lines connect the data, and the dotted vertical lines identify the conditions corresponding to molecularly symmetric triblock copolymers wherein $M_{A_1} = M_{A_2}$.

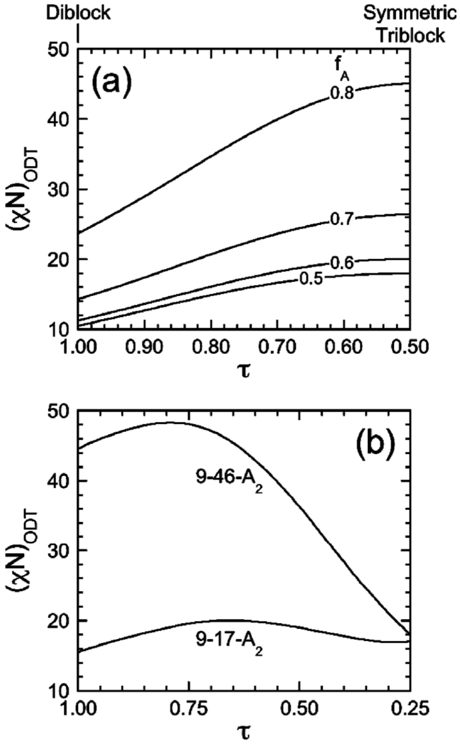

FIG. 2. Values of $(\chi N)_{\mathrm{ODT}}$ presented as a function of molecular asymmetry (τ) as predicted from the mean-field theory of Mayes and Olvera de la Cruz [23] for two asymmetric triblock copolymer designs: (a) fixed molecular composition (f_A) and (b) variable molecular composition. Corresponding values of f_A are listed in (a), and the two copolymer systems under investigation (see the text for details) are labeled in (b).

cal predictions in Fig. 2(b) requires two additional relationships. The first, needed to account for the difference between A and B mass density in describing the molecular characteristics of each copolymer (i.e., N, f_A, and τ), puts the number of A and B repeat units on a common density basis. It immediately follows that N_i ($i = A_1$, B, or A_2) is given by $(M_i/m_i)(\rho_i/\rho_0)$, where m_i is the molecular mass of repeat unit i, ρ_i is the mass density of i (taken as 1.04 and 0.913 g/cm^3 for polystyrene and polyisoprene, respectively), and ρ_0 is the geometric-mean reference density. The second requisite relationship is an expression for $\chi(T)$. For this purpose, we use the result reported by Lodge *et al.* [26] for poly(styrene-*b*-isoprene) diblock copolymers in which $\chi = 33.0/T$–0.0228.

Since values of T_{ODT} determined from the predicted $(\chi N)_{\mathrm{ODT}}$ in Fig. 2(b) are sensitive to the coefficients used to describe $\chi(T)$ and since we are primarily interested in determining whether mean-field theory accurately predicts the minimum observed in $T_{\mathrm{ODT}}(\tau)$, we have elected to normalize $T_{\mathrm{ODT}}(\tau)$ with respect to $T_{\mathrm{ODT}}(\tau = 1)$. Reduced T_{ODT} (denoted $T_{\mathrm{ODT},r}$) values obtained in this fashion are presented as functions of τ and f_A in Figs. 3(a) and 3(b), respectively. In Fig. 3(a), the normalized ODT measurements from both copolymer series are surprisingly consistent, and mean-field theory predictions for the 9–17-A_2 series are observed to be in generally favorable agreement with the experimental data. Similar agreement between theory and experiment is evident in Fig. 3(b). Predictions for the more compositionally asymmetric 9–46-A_2 series tend to overpredict $T_{\mathrm{ODT},r}$ (due to the normalization scheme adopted here), but nonetheless exhibit a discernible minimum in $T_{\mathrm{ODT},r}$. Regressions of the mean-field $(\chi N)_{\mathrm{ODT}}$ predictions displayed in Fig. 2(b) to the non-normalized $T_{\mathrm{ODT}}(\tau)$ values measured from both copolymer series are included for comparison in Fig. 4. The fitted curves accurately describe the two data sets and yield the following expressions for $\chi(T)$: 52.6/T–0.0739 for the 9–46-A_2 series and 35.0/T–0.0445 for the 9–17-A_2 series. While previous studies [27] find that χ can be composition dependent and we implicitly neglect fluctuation corrections, it is comforting that the $\chi(T)$ coefficients determined from Fig. 4 are comparable to those reported [26].

The unequivocal agreement between mean-field theory and experimental data evident in Figs. 3 and 4 provides confidence that T_{ODT} initially decreases as the A_2 block is grown onto a diblock copolymer. This reduction can be explained in terms of block segregation and stretching, following the arguments of Matsen [25] and schematically depicted in the inset of Fig. 4. Upon microphase ordering,

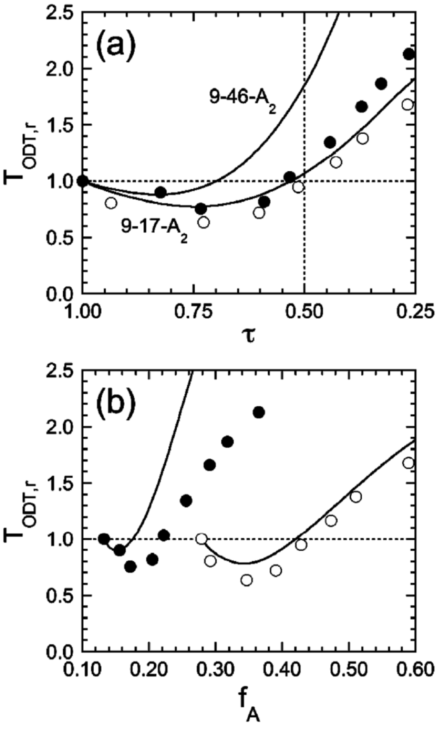

FIG. 3. Values of T_{ODT} for the 9–46-A_2 (●) and 9–17-A_2 (○) triblock copolymer series normalized with respect to T_{ODT} for the parent diblock copolymer ($\tau = 1$) in each series and presented as functions of (a) molecular asymmetry (τ) and (b) molecular composition (f_A). The solid lines are mean-field theory predictions used in conjunction with $\chi(T)$ reported by Lodge *et al.* [26]. The dotted lines identify the conditions corresponding to $\tau = 0.5$ (a) and $T_{\mathrm{ODT},r} = 1$ [(a) and (b)].

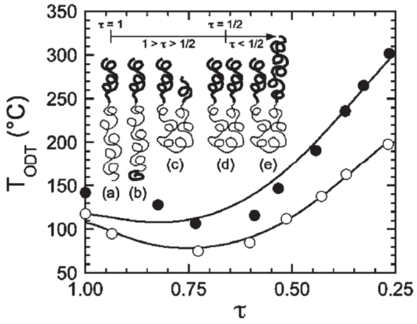

FIG. 4. Dependence of T_{ODT} on τ for the 9–46-A_2 (●) and 9–17-A_2 (○) triblock copolymer series. The solid lines represent fits of the mean-field predictions displayed in Fig. 2(b) to both data sets. Expressions for $\chi(T)$ generated by this nonlinear regression are provided in the text. The inset is a schematic illustration depicting the chain conformations associated with the transformation of an A_1B diblock copolymer (a) to an A_1BA_2 triblock copolymer (b)–(e). A relatively short A_2 block initially remains mixed with the B midblock (b). As the length of the A_2 block is further increased, it microphase separates to form a bidisperse brush with the A_1 block (c). When $\tau = \frac{1}{2}$, the triblock copolymer becomes molecularly symmetric: the lengths of the A_1 and A_2 blocks are identical (d). A further increase in the length of the A_2 block ($\tau < \frac{1}{2}$) is accompanied by a bidisperse brush and an ODT governed by the A_2 block (e).

the constituent blocks of a diblock copolymer (at $\tau = 1$) become stretched to relieve unfavorable interactions and promote chain packing along the A/B interface [Fig. 4(a)]. Incorporation of a short A_2 block results in mixing between the A_2 and B blocks, which permits the stretched B midblock to relax [Fig. 4(b)], thereby lowering T_{ODT}. As the length of the A_2 block is increased further, it eventually reaches a point where it also microphase separates from the B block and joins the A_1 block to form a bidisperse brush composed of long A_1 blocks and short A_2 blocks [Fig. 4(c)]. Milner and Witten [28] have shown that the stretching energy of a bidisperse brush is less than that of its monodisperse analog, and so T_{ODT} of a molecularly asymmetric A_1BA_2 triblock copolymer with $\tau > \frac{1}{2}$ remains less than that of the parent A_1B diblock copolymer. This effect diminishes as the length of the A_2 block approaches that of the A_1 block at $\tau = \frac{1}{2}$ [Fig. 4(d)]. Once the A_2 block is longer than the A_1 block (and $\tau > \frac{1}{2}$), T_{ODT} is dictated by the longer A_2 block comprising the bidisperse $A_1 + A_2$ brush so that $T_{\mathrm{ODT},r} > 1$ in Fig. 3. The ability of molecularly asymmetric A_1BA_2 triblock copolymers to modify phase stability (e.g., T_{ODT}) and generate bidisperse polymer brushes in tunable fashion through synthetic means provides a single-molecule alternative to investigating the benefit of constrained chain mixing in confined nanoscale environments [29], as well as an improved molecular-level understanding of the difference between microphase-ordered diblock and triblock copolymers [30].

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