Order–Disorder Transition: Diblock versus Triblock Copolymers

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ABSTRACT: A nearly symmetric *cis*-1,4-polyisoprene-1,2-polybutadiene (1,4-PI–1,2-PB) diblock copolymer was anionically polymerized and partially coupled to form a mixture of diblock and 1,4-PI–1,2-PB–1,4-PI triblock copolymers. This mixture was subsequently hydrogenated and fractionated, yielding a homologous pair of poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock and PEP–PEE–PEP triblock copolymers, along with three intermediate mixtures containing both molecular architectures. The order–disorder transition temperature, T_{ODT}, which was determined for each mixture by dynamic mechanical spectroscopy, was found to vary significantly with molecular architecture. For the triblock material T_{ODT} was 72 °C higher than that for the homologous diblock specimen, which compares favorably with the 61 °C difference anticipated by mean-field theory. Above T_{ODT} the dynamic mechanical properties are insensitive to variations in molecular architecture, while below the order–disorder transition subtle variations in the low-frequency viscoelastic response are apparent.

Introduction

Varying molecular architecture can dramatically influence the physical properties of bulk block copolymers.[1–3] Perhaps the most familiar examples are the thermoplastic elastomers, which derive rubbery-like behavior from polystyrene–polyisoprene–polystyrene (SIS), or related triblock copolymer architectures, that form spherical microdomains of the polystyrene component. Analogous SI diblock copolymers exhibiting a spherical microstructure are virtually useless as elastomers since only one end of the rubbery block is anchored to a glassy domain making these systems merely viscous fluids. Figure 1 illustrates these architectural differences where A and B would correspond to S and I blocks, respectively. Whereas the viscoelastic properties are profoundly affected by molecular architecture in the strong segregation limit (SSL), $\chi N \gg 10$ (χ and N are the Flory–Huggins parameter and degree of polymerization, respectively), the thermodynamic properties are almost indistinguishable; here energetic effects dominate over minor conformational differences between diblock and triblock copolymers. According to Helfand,[4] triblock copolymers obtained by coupling two identical diblocks should exhibit microdomain types and dimensions that are equivalent to the diblock precursor. With the exception of an apparent arm number dependence to the occurrence of the ordered bicontinuous double-diamond phase,[5] this prediction is supported by experiments.[6]

Near the order–disorder transition (ODT) we expect a different scenario. Here the local composition profile is more sinusoidal-like making it easier to transport blocks between microdomains provided the temperature is well above the glass transition of either component. Accordingly, we expect weakly ordered triblock and diblock copolymers to be rheologically more similar than the strongly segregated counterparts. In contrast, certain thermodynamic differences should become evident as the ODT is approached. This is easily rationalized based on the delicate balance between energetic and entropic factors at the ODT. Triblock copolymers should be characterized by a slightly different conformational entropy for a given ordered microstructure that will be manifested through the ODT temperature. We are unaware of any prior quantitative evaluations of this difference.

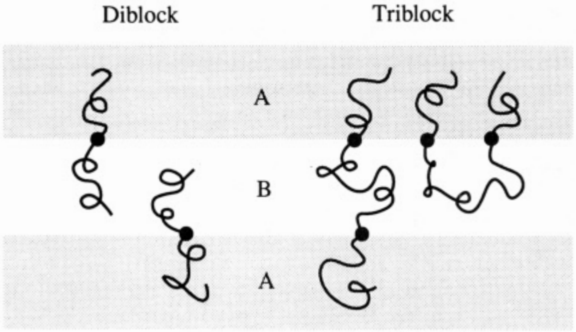

Figure 1. Schematic illustration of a symmetric (f = 0.55) diblock (A–B) and triblock (A–B–A) copolymer melt, where A and B represent two distinct monomers.

Mean-field treatments of the ODT are now available for both diblock and triblock copolymer melts. Leibler[7] pioneered the development of weak segregation theory predicting that a symmetric ($f = 0.5$ where f refers to the volume fraction of one component) diblock copolymer would order when $\chi N = 10.5$. Mayes and Olvera de la Cruz[8] recently extended this treatment to triblock copolymers, concluding that coupling a symmetric diblock modifies the ODT to $\chi N = 18$. After a doubling of N is accounted for, the required difference in χ for ordering is approximately 15% so that the ODT temperature is predicted to be only modestly different. For example, if χ is inversely proportional to temperature and $T_{ODT} = 100$ °C, the triblock copolymer would be predicted to order roughly 60 °C higher than the diblock. This difference may be somewhat dependent on fluctuation corrections that have been shown to be important near the ODT.[9–11] However, because the fluctuation effects are expected to influence both architectures similarly, the magnitude of the difference in ODT temperatures, ΔT_{ODT}, is likely to be closely approximated by the mean-field theories.

Experimentally determining ΔT_{ODT} is not trivial. The synthesis of individual diblock and triblock samples[12] would lead to uncertainties of several percent in composition and approximately 10% in N, which represents the entire effect being investigated. In order to eliminate this source of error, we have prepared specimens from a single living diblock copolymer precursor, followed by fractionation. In this case uncertainties in the absolute molecular weight and composition are much less significant and ΔT_{ODT} can be quantitatively compared with theory. We

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have selected $f = 0.55$ poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) (f represents the volume fraction of PEP) for these experiments since previous studies by us have established a lamellar morphology, $\chi(T)$, and the methodology for determining T_{ODT} in these materials.[10,11,13-15] In this report we describe our determination of ΔT_{ODT} and compare the dynamic mechanical properties of a homologous pair of diblock and triblock copolymers.

Experimental Section

A *cis*-1,4-polyisoprene–1,2-polybutadiene (PI–PB) diblock copolymer was synthesized in cyclohexane using a lithium counterion following the methods described in a previous publication.[13] Upon completion of the second block (1,2-polybutadiene) a 1 to 2 molar ratio of freshly distilled dichlorodimethylsilane (Aldrich, 99%) was added to the "living" polymer. Subsequently, the product was recovered by precipation in methanol (quantitative yield) and vacuum dried. Saturation of the PI–PB material was accomplished using a calcium carbonate supported palladium catalyst suspended in cyclohexane at 70 °C and at 500 psi of hydrogen.[16] ^{1}H NMR analysis confirmed >99% saturation efficiency. The product of this reaction scheme was a poly(ethylenepropylene)–poly(ethylethylene) diblock (PEP–PEE)/triblock (PEP–PEE–PEP) mixture as described below.

The 2% cyclohexane solution recovered from the hydrogenation reaction was diluted with toluene (E.M. Science, 99.99%) to produce a 1% polymer–cyclohexane–toluene solution. Fractionation of the PEP–PEE/PEP–PEE–PEP mixture was accomplished by the nonsolvent addition method.[17] Methanol (E.M. Science, 99.8%) was slowly added to the vigorously stirred polymer solution at ambient temperature until the solution became cloudy. The solution was allowed to equilibrate overnight, and additional methanol was added as necessary. The solution was heated to 40 °C, placed in an insulated separatory funnel, and allowed to slowly cool to ambient temperature. Within 12 h two distinct liquid phases developed, with complete separation after 24–36 h. Ten fractionations were completed using this procedure, leading to nearly pure diblock and triblock, and two diblock/triblock mixtures, in addition to the starting mixture.

Gel permeation chromatography (GPC) traces of the PEP–PEE/PEP–PEE–PEP mixtures were obtained from a Waters 150C instrument fitted with three Phenogel columns operated at 25 °C with tetrahydrofuran (Fisher, 99.9%) as the mobile phase at a flow rate of 1 mL/min. Elution times were monitored by a differential refractometer following the injection of 0.25 mL of 0.1% (w/v) solution. Calibration was accomplished using a set of previously characterized PEP–PEE diblock copolymer.[13] For the diblock $M_{\mathrm{N}} \cong 5 \times 10^4$ with a polydispersity of $M_{\mathrm{W}}/M_{\mathrm{N}} = 1.08$. The triblock copolymer polydispersity is $M_{\mathrm{W}}/M_{\mathrm{N}} = 1.05$.

Viscoelastic properties were determined for the PEP–PEE/PEP–PEE–PEP mixtures using a Rheometrics Solids Analyzer (RSA II) operated in the dynamic mode ($0.01 \leq \omega \leq 100$ rad/s) with a 0.5-mm shear sandwich as the test fixture. The sample temperature was controlled (±1 °C) between 25 and 160 °C using a thermally regulated air (<100 °C) or nitrogen (>100 °C) purge. All dynamic shear modulus measurements were conducted using a 2% strain amplitude. The order–disorder transition temperature, T_{ODT}, was determined by measuring G' at a fixed frequency ($\omega = 0.1$ rad/s) while slowly heating (<1 °C/min) the specimens. Selected isothermal frequency scans were also acquired for the pure diblock and triblock samples. Here we note that ordered (isotropic) block copolymers are inherently nonlinear viscoelastic materials due to a susceptibility to shear-induced orientation. Nonlinearity is manifested below a critical reduced frequency ω_{c}, which is defined in the following sections. For modest strain amplitudes (ca. 20%) the determination of T_{ODT} (a thermodynamic parameter) is not influenced by these effects as shown elsewhere.[14] Our selection of a 2% strain amplitude balances the necessity of generating sufficient stresses for the adequate determination of G' and G'' over the entire range of temperatures and frequencies studied while minimizing these nonlinear effects. Under these conditions neither the terminal relaxation time τ nor ω_{c} are detectably effected.

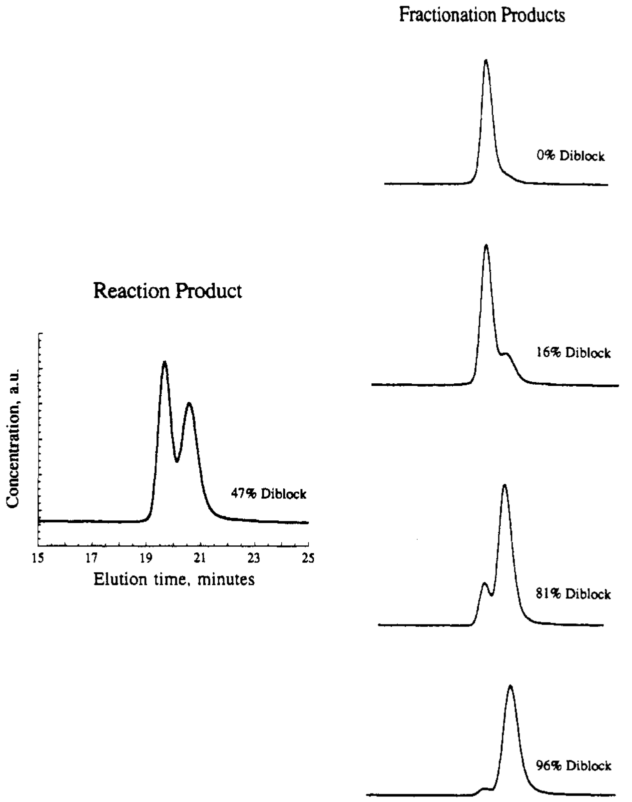

Figure 2. Gel permeation chromatographs of the PEP–PEE/PEP–PEE–PEP reaction mixture (47% diblock) and the four fractionation products containing varying amounts of diblock copolymer as indicated.

Table I
Order–Disorder Transition Temperatures for Diblock Copolymer–Triblock Copolymer Mixtures

diblock copolymer (±2%), %	T_{ODT} (±2 °C), °C
0	144
16	140
47	117
81	94
96	75

Results and Discussion

Addition of dichlorodimethylsilane to the living PI–PB produced partial coupling of the diblock copolymer as indicated by the GPC trace of the hydrogenation reaction product shown in Figure 2.[18] Subsequent fractions provided a total of five diblock/triblock mixtures (see Table I) with diblock copolymer contents of 0% (essentially pure triblock), 16%, 47% (reaction product), 81%, and 96% (nearly pure diblock). These compositions were established (±2%) by modeling the GPC traces shown in Figure 2 with weighted fractions of the diblock and triblock peaks obtained from the nearly pure fractions.

Order–disorder transiton (ODT) temperatures were determined following the procedure established in earlier studies.[10,11,14] Low-frequency isochronal ($\omega < \omega_{\mathrm{c}}'$, see below) dynamic elastic shear moduli were obtained while slowly heating a specimen. At the weakly first-order ODT the elasticity drops discontinuously, signaling the "melting" of the ordered structure to a disordered, viscous fluid state. The results of such measurements for the five PEP–PEE/PEP–PEE–PEP specimens are shown in Figure 3. In each case a distinct drop in G' is observed over a 2 °C temperature increment (corresponding to the instrument temperature resolution) that provides for the precise determination of T_{ODT}. These values are listed in Table I and plotted in Figure 4 as a function of diblock content.

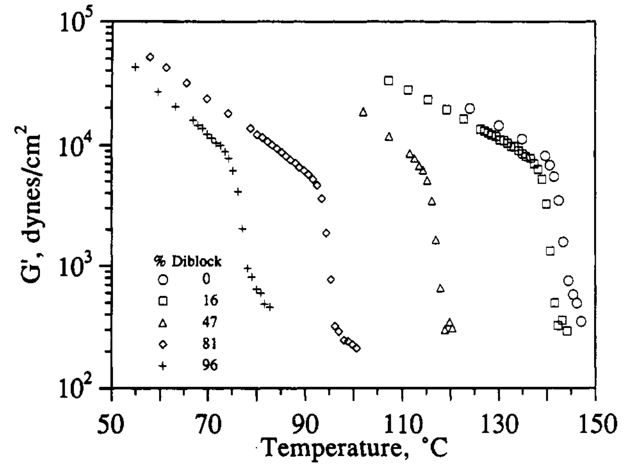

Figure 3. Temperature dependence of G' obtained at 2% strain amplitude and $\omega = 0.1$ rad/s for the PEP–PEE/PEP–PEE–PEP mixtures. The discontinuity in G' at 144, 140, 117, 94, and 75 °C represents the order–disorder transition temperature, T_{ODT}.

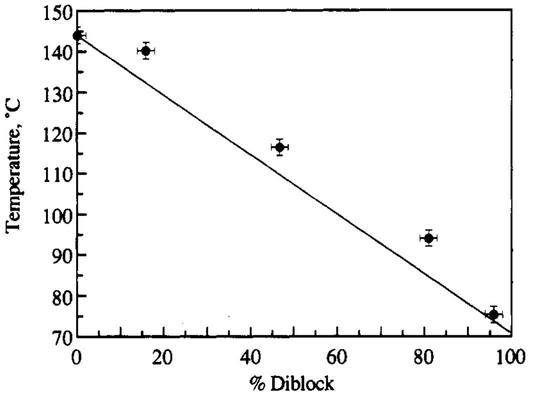

Figure 4. Dependence of the order–disorder transition temperature, T_{ODT}, on diblock copolymer content. T_{ODT} is shown to be dependent on molecular architecture. The triblock copolymer has T_{ODT} = 144 °C, while the estimated T_{ODT} for the diblock copolymer is 72 °C. The solid line indicates a linear combination of these limiting values.

Clearly, T_{ODT} is significantly dependent on the molecular architecture. For the PEP–PEE–PEP triblock copolymer T_{ODT} = 144 ± 2 °C while we estimate T_{ODT} = 72 ± 2 °C for pure PEP–PEE diblock copolymer, leading to ΔT_{ODT} = 72 ± 3 °C.

Mean-field theories have been developed for diblock and triblock copolymer melts near the ODT. Leibler[7] pioneered such calculations in his seminal treatment of diblock copolymers. For $f = 0.55$ the mean-field ODT is given by

$$(\chi N)_{ODT} = 10.7 \text{ (diblock)} \qquad (1)$$

Mayes and Olvera de la Cruz[8] extended Leibler's treatment to triblock copolymers, arriving at a condition of

$$(\chi N)_{ODT} = 17.9 \text{ (triblock)} \qquad (2)$$

for $f = 0.55$ symmetric triblock copolymer melts; here symmetric refers to an ABA architecture where each A block is equal in length. Since fluctuation effects have not been incorporated into the triblock theory, we must restrict our analysis to mean-field theory. Following this evaluation, we comment on the anticipated effects of fluctuations.

In a previous set of publications[10,11,14] ODT temperatures have been associated with three different $f = 0.55$ PEP–PEE diblock copolymers: T_{ODT} = 96, 125, and 291 °C for N_N = 895, 977, and 1450, respectively, where N_N corresponds to the number-average degree of polymerization based on a 56 (i.e., PEE) repeat unit. On the basis of these values and assuming eq 1, we arrive at

$$\chi = 4.89/T - 0.00125 \qquad (3)$$

This relationship is somewhat different from that reported previously[11] since it is based on N_N rather than N_W[19] and does not include fluctuation effects. Equations 1 and 3 with T_{ODT} = 75 °C leads to N_N = 840, which lies within the experimental error of the molecular characterization result. The triblock copolymer has twice this degree of polymerization, which, with eqs 2 and 3, produces a predicted order–disorder transition of T_{ODT} = 136 °C. Thus, mean-field theory predicts ΔT_{ODT} = 61 °C, which is reasonably close to the experimentally determined value.

Mean-field theory accounts for 85% of the change in T_{ODT} associated with the triblock versus the diblock copolymer architecture. Yet we have shown earlier that fluctuation effects are responsible for inducing a weakly first-order order–disorder transition in block copolymers.[11] At first glance these two results may seem contradictory. However, for N = 840, f, = 0.55 PEP–PEE diblock copolymer fluctuation effects represent only a 17% correction to the mean-field $(\chi N)_{ODT}$. Although we cannot quantitatively assess the magnitude of the fluctuation correction for the corresponding triblock copolymer, it seems unlikely that it will change dramatically since this correction scales as $N^{-1/3}$.[9] The disordered state rheological properties of the triblock copolymer support this hypothesis as described below.

Since the interaction energy (E) between PEP and PEE segments is unaffected by molecular architecture, we can attribute the increase in T_{ODT} for triblocks to a decrease in the configurational entropy (S) in the ordered state. This is intuitively obvious since the center block coils are forced to assume configurations that localize both ends at the microdomain boundary; diblock copolymers are constrained at only one end (see Figure 1). Thus, balancing E and TS requires a higher temperature to offset the reduced system entropy in triblock versus diblock copolymers. This thermodynamic difference will be most apparent near the ODT. When $\chi N \gg 10$, the ordered state free energy becomes dominated by energetic effects as shown by Helfand.[4]

Subtle but distinct differences in the rheological properties of the homologous diblock and triblock copolymers can also be identified. In Figures 5 and 6 we present representative dynamic elastic (G') and loss (G'') data for the two molecular architectures. These data have been temperature and density corrected[20] and time–temperature superpositioned using the high-frequency ($\omega > \omega_c$) branches of the spectra based on a common reference temperature (T_0 = 35 °C). The crossover frequencies ω_c' and ω_c'' identified in Figures 5 and 6, respectively, separate the low- and high-frequency viscoelastic regimes. At high frequencies ($\omega > \omega_c$) the response is dominated by intramolecular (i.e., entanglement) dynamics that are largely unaffected by the presence of a microdomain structure. Accordingly, both ordered and disordered data can be superimposed onto a single master curve in this frequency regime. At low frequencies ($\omega < \omega_c$) the rheological response is strongly influenced by microstructure that can thwart the long-range motion of block copolymer coils. We have located ω_c' and ω_c'' based on the point of intersection of the low- and high-frequency branches. The reduced crossover frequencies do not depend on molec-

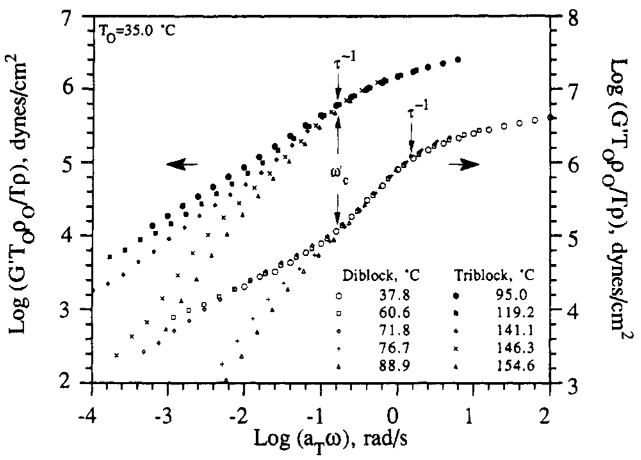

Figure 5. Reduced-frequency plot for dynamic elastic data obtained from the diblock and triblock copolymers. The G' data are temperature and density corrected and time–temperature superpositioned to 35 °C using the high-frequency ($\omega > \omega_c'$) branches of the spectra. The reduced crossover frequency and dynamic behavior of the disordered state does not depend on molecular architecture within the resolution of our measurements. However, the dynamic behavior in the ordered states at $\omega < \tau^{-1}$ shows subtle differences between the diblock and triblock copolymers.

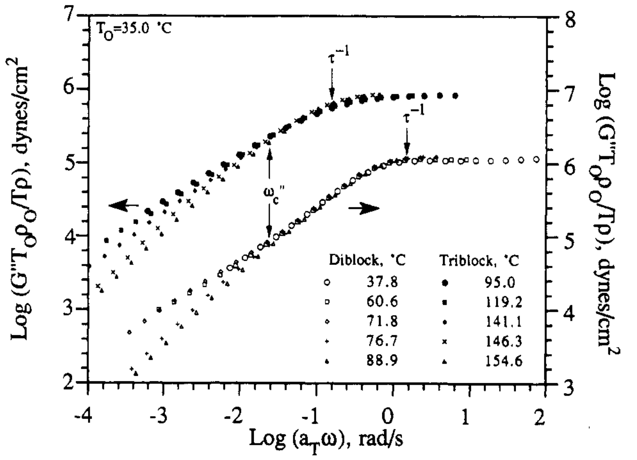

Figure 6. Reduced-frequency plot for dynamic loss data obtained from the diblock and triblock copolymers. The G'' data have been temperature and density corrected and superpositioned to 35 °C using the same shift factors employed in Figure 5.

ular architecture within the resolution of our measurements.

The high-frequency G' and G'' regimes resemble the viscoelastic response of entangled homopolymer melts. Accordingly, we have identified a characteristic relaxation time τ in Figures 5 and 6 based on the frequency where G' and G'' cross. In the case of simple homopolymers τ is essentially the longest relaxation (i.e., reptation) time for individual coils. Coupling the diblock copolymer increases τ by approximately an order of magnitude, in agreement with the predicted behavior for entangled homopolymer melts where $\tau \sim N^{3.4}$.

Two low-frequency ($\omega < \omega_c$) branches are apparent in both samples. Above T_{ODT} the results are almost indistinguishable. Aside from the effects of fluctuations (evidenced by a failure of time–termperature superposition), the lowest frequency data become essentially terminal (i.e., $G' \sim \omega^2$ and $G'' \sim \omega$). At comparable distances from T_{ODT} the zero shear viscosity, $\eta_0 = G''(\omega\rightarrow 0)/\omega$, for the triblock material is roughly 5 times greater than that for the diblock copolymer, in qualitative agreement with the trend in τ; the 2-fold difference between these relaxation processes may reflect a variation in fluctuations between architectures although the uncertainties in the time–temperature superpositioning of the data preclude drawning any firm conclusions in this regard. The ordered-state low-frequency branches exhibit some differences. Most obvious is the failure of time–temperature superpositioning in G' at all temperatures and frequencies below ω_c' for the triblock specimen.

We believe the most significant dynamic result associated with the architectural difference relates to the crossover frequencies ω_c' and ω_c''. These frequencies represent the point at which the molecular relaxation process couples to the microdomain structure. For diblock copolymers $\omega_c' \ll \tau^{-1}$,[14] which suggests that a collective (i.e., multimolecular) dynamical response is associated with the ordered branches below ω_c, although a convincing theoretical description of this behavior is lacking. In the triblock material the crossover occurs at approximately τ^{-1}, at which point G' is 5 times greater than at the crossover point in the diblock copolymer. We attribute this difference to the localization of both ends of the PEE block at the lamellar domain boundaries as sketched in Figure 1. Two configurations of the triblock molecules are possible: one that produces bridging between domains and a second that localizes both block joints at a common interface. To the best of our knowledge, the preferred orientation has not been determined experimentally although theoretical arguments factor the later.[21] In either case, cooperativity in domain relaxation is greatly enhanced by the introduction of a triblock architecture since the PEP end blocks become coupled through the PEE center block. This coupling will naturally be manifested at a time (i.e., frequency) when block entanglement effects are dissipated, i.e., at $\omega \approx \tau^{-1}$. These effects should be further exacerbated by increasing the block arm functionality as occurs in star-block copolymers.

Summary

A homologous pair of PEP–PEE/PEP–PEE–PEP diblock and triblock copolymers has been prepared near the order–disorder transition (ODT). Molecular architectural differences were shown to be manifested in the thermodynamic and dynamic properties. The triblock copolymer exhibits an ODT temperature that is 72 ± 3 °C higher than the corresponding diblock material. This result is in reasonable agreement with mean-field theories which anticipate a 61 °C difference. Coupling the diblock copolymer led to predictable increases in the single-chain terminal relaxation time τ and zero shear viscosity in the disordered state; i.e., neither property is significantly affected by substituting triblock for diblock copolymer. In the ordered (lamellar) state the low-frequency properties were influenced by changing the molecular architecture. In particular, the effects of block localization on G' are manifested in triblock copolymer for $\omega \lesssim \tau^{-1}$ in contrast with the homologous diblock specimen where such behavior becomes apparent when $\omega \lesssim 0.1\ \tau^{-1}$.

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