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Effect of Gradient Sequencing on Copolymer Order−Disorder Transitions: Phase Behavior of Styrene/*n*-Butyl Acrylate Block and Gradient Copolymers

Michelle M. Mok,[†,∥] Christopher J. Ellison,[‡,⊥] and John M. Torkelson*[,†,§]

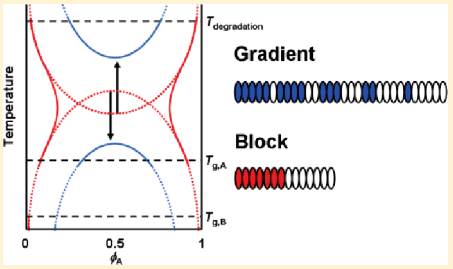
[†]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

[‡]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, United States

[§]Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States

Supporting Information

ABSTRACT: We investigate the effect of gradient sequence distribution in copolymers on order−disorder transitions, using rheometry and small-angle X-ray scattering to compare the phase behavior of styrene/*n*-butyl acrylate (S/nBA) block and gradient copolymers. Relative to block sequencing, gradient sequencing increases the molecular weight necessary to induce phase segregation by over 3-fold, directly consistent with previous predictions from theory. Results also suggest the existence of both upper and lower order−disorder transitions in a higher molecular weight S/nBA gradient copolymer, made accessible by the shift in order−disorder temperatures from gradient sequencing. The combination of transitions is speculated to be inaccessible in S/nBA block copolymer systems due to their overlap at even modest molecular weights and also their location on the phase diagram relative to the polystyrene glass transition temperature. Finally, we discuss the potential impacts of polydispersity and chain-to-chain monomer sequence variation on gradient copolymer phase segregation.



INTRODUCTION

Block copolymers have traditionally been at the forefront of research centered on creating nanostructured polymers.[1−3] Unlike in polymer blends, the junction point between blocks of A- and B-monomers leads to segregation at the nanoscale rather than macroscopic separation.[4] Such phase separation from the disordered state in blends and block copolymers can occur theoretically upon heating or upon cooling.[4−23] In blends, these are called lower and upper critical solution temperatures (LCST and UCST); in copolymers, they are called order/disorder temperatures (LDOT and UODT). The UCST and UODT are predicted through the Flory−Huggins lattice model:[5] the decrease in enthalpic contribution from segmental interactions with increasing temperature allows for an entropically driven mixed state to emerge. The LCST and LDOT are explained by equation-of-state or free volume contributions, which account for differences in component compressibility.[6,7] With increasing temperature, this yields a more densely packed system in the mixed state than the separated state; this loss of configurational entropy leads to phase separation with heating.

In actuality, the driving force behind polymer phase separation is so strong that access to these transitions within experimentally feasible temperatures is rare, and access to both transitions with a single polymeric system is extremely rare. Most systems are limited at lower temperatures by component glass transitions and at higher temperatures by degradation. In the very few blends where both UCST and LCST have been observed, such behavior is often present only for polymers with number-average molecular weight (M_n) < 10 000 g/mol.[11,14] For blends of higher molecular weight, only limited sets of very weakly interacting comonomers exhibit both transitions over an exceedingly narrow range of molecular weights.[8−10,12,13] For block copolymers, the LDOT was seen for the first time in 1994,[15] in a series of styrene/*n*-butyl methacrylate block copolymers, and for only one molecular weight within that series was a combined UODT/LDOT observed. Since that discovery, the family of styrene/*n*-alkyl methacrylate block copolymers has been of great interest.[6,16−23] While further instances of the LDOT were found for some shorter alkyl side chains, no other system was shown to exhibit a miscibility gap over the measured temperature ranges. Interestingly, an immiscibility gap or "closed-loop" behavior has been observed for the styrene/*n*-pentyl methacrylate system[18] and related copolymer systems[19−22] over extremely narrow molecular weight ranges and precisely designed block compositions.

In block copolymers, these order/disorder transition temperatures are controlled through overall chain length (N), comonomer incompatibility (defined through χ, the Flory−Huggins interaction parameter), and A−B volume fraction. More recent

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developments in polymer chemistry have provided greater control over comonomer sequencing along polymer chains;[24−28] this yields greater tunability of the strength and localization of molecular interactions governing self-assembly, introducing a powerful new factor for controlling phase segregation.[29,30] It is now simple to synthesize copolymers from a wide variety of comonomers in which the composition changes monotonically along the entire chain length, i.e., gradient copolymers.[25−28,31−36] Theory predicts that gradient structures can also control the location of order/disorder transitions, such that greater comonomer incompatibility or higher molecular weights are required to provide the driving force for ordering transitions[37,38] and micellization.[39] Specifically, the critical χN value at which phase segregation takes place is increased from 10.5 for a symmetric block copolymer to ∼29−30 for a symmetric, linear gradient copolymer.[37,38] Gradient sequencing also introduces much greater control over levels of phase segregation. For example, theory predicts that gradient copolymers can form nanostructures possessing sinusoidal composition profiles intermediate between steplike profiles and fully disordered systems over exceptionally large ranges of χN compared to block copolymers.[37,38,40]

Experimental research on gradient copolymers has supported these predictions from theory. When added to selective solvents or to homopolymer blends,[41−47] gradient copolymers demonstrate a lower driving force for phase segregation and hence have better solubility[36,41,42] and higher critical micelle concentrations[43,44] than block copolymers. Studies of viscoelasticity in neat gradient copolymers indicate that gradual rheological changes are observed over broad temperature ranges.[32] Indirect evidence of sinusoidal composition structures comes from glass transition-related studies,[29,48−61] where gradient copolymers exhibit extremely broad glass transition regions associated with a wide composition range.[51−56] However, few studies have explicitly found order/disorder transitions.[31]

Outside of copolymers with entirely gradient structures, researchers have also studied the incorporation of tapered regions intermediate to pure A and B end blocks ("tapered" or "graded" block copolymers) to reduce the segregation force from that of normal block copolymers. Such structures have been found to be an effective means of shifting UODTs.[30,62−65] (For a more detailed review of previous studies of both gradient and tapered block copolymers, please see ref 32.) With a completely gradient structure, where pure A and B end blocks are not present to drive the phase segregation, even more significant shifts to the block copolymer phase diagram can potentially be realized.

Here, we demonstrate gradient sequencing as a tool for shifting copolymer order/disorder transitions to experimentally feasible temperatures at higher ranges of molecular weights, as predicted by theory. A high molecular weight styrene/*n*-butyl acrylate (S/nBA) gradient copolymer was designed which appears to exhibit both UODT and LDOT. In comparison, block copolymers of the same comonomers exhibit only one transition over a small window of lower molecular weights. Thus, not only does the gradient structure allow for access to ordering transitions at industrially relevant temperatures and molecular weights (yielding useful mechanical properties), but it can also potentially access dual order/disorder transitions.

EXPERIMENTAL SECTION

Materials. Block and gradient copolymers of styrene and *n*-butyl acrylate were prepared using nitroxide-mediated controlled radical polymerization using the initiator 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (A29). The block copolymer (S-*block*-nBA) was made by chain extension from a polystyrene (PS) macroinitiator (M_n = 39K, PDI = 1.28). The PS was dissolved into nBA monomer at 2.14 × 10^{-3} mol/L, purged with N_2 for 30 min, and then heated for 2.5 h at 90 °C. The reaction mixture was then precipitated into methanol and cleaned by repeated cycles of dissolution and precipitation into tetrahydrofuran and methanol. The M_n value of 60 kg/mol was calculated from the M_n of the macroinitiator, as measured by gel permeation chromatography (GPC) using universal calibration with PS standards and its final comonomer composition (cumulative styrene fraction or F_S = 0.70) as measured by ^{1}H NMR. (The M_n values in the remainder of the article will be abbreviated as follows: 60 kg/mol = 60K.)

Table 1. Molecular Characterization of S/nBA Copolymer Materials

sample	M_n (g/mol)	F_S	PDI[b]
S-*block*-nBA	60 000[a]	0.70	1.39
PS macroinitiator	39 000	1	1.28
S-*grad1*-nBA	152 000[b]	0.61	1.60
S-*grad2*-nBA	95 000[b]	0.60	1.37

[a] M_n value was determined from the M_n of PS macroinitiator and the F_S value. [b] Characterized relative to PS standards by GPC with THF as eluent.

The gradient copolymers were made by semibatch polymerization starting from styrene, with nBA being added at increasing rates through the polymerization (S-*grad1*-nBA, M_n = 152K, F_S = 0.61 and S-*grad2*-nBA, M_n = 95K, F_S = 0.60). These are apparent molecular weights measured relative to PS standards rather than absolute values. The S-*grad1*-nBA case was synthesized by combining A29 (2.62 × 10^{-3} mol/L) and styrene (10 mL) in a test tube. This was purged with N_2 for 30 min and then placed under continuous N_2 purging inside an oil bath set at 100 °C, where nBA was added at rates of 1 mL/h for 3 h, 4 mL/h for 3 h, and finally 6 mL/h for 2 h. The S-*grad2*-nBA case was synthesized by combining A29 (3.14 × 10^{-3} mol/L) and styrene (10 mL) in a test tube. This was purged with N_2 for 30 min and then placed under continuous N_2 purging inside an oil bath set at 100 °C, where nBA was added at rates of 2 mL/h for 3 h, 4 mL/h for 3 h, and finally 6 mL/h for 3 h. In order to verify the formation of a composition gradient, aliquots (∼1 mL) of the reaction mixture were collected throughout the polymerization process and analyzed using GPC and ^{1}H NMR. All aliquots and final products were recovered following the procedure described above.

Rheology and Small-Angle X-ray Scattering (SAXS). Samples for rheology and SAXS were prepared by hot-pressing at 160 °C for 2 h. Rheological characterization was carried out using a Rheometrics Scientific ARES controlled-strain rheometer with 2.5 and 5.0 cm parallel-plate geometries. Copolymers were subjected to strain sweeps to verify their linear region of strain response followed by frequency sweeps at increasing temperatures using a shear strain (γ) of 10%. Synchrotron-based SAXS was performed at the Advanced Photon Source at Argonne National Laboratory, using 10 keV radiation and an 8.0 m sample−detector distance. The temperature of the SAXS samples were controlled using a Linkam DSC hot stage with an inert purge gas.

RESULTS AND DISCUSSION

Gradient Copolymer Structures. The molecular characterizations for the block copolymer and two gradient copolymer materials are summarized in Table 1. The polydispersity indices (PDIs) for the samples are high relative to that of block copolymers produced by anionic polymerization. The potential

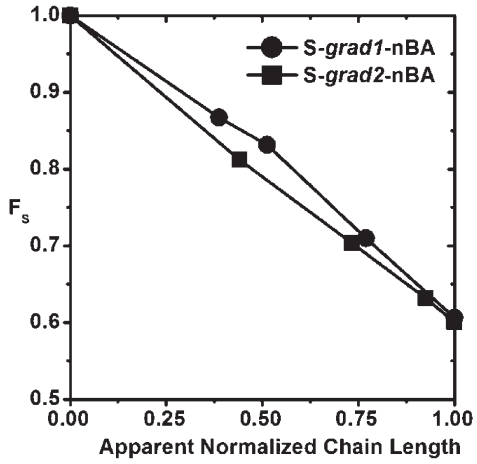

Figure 1. Cumulative styrene mole fraction (F_S) as a function of apparent normalized chain length for S-*grad1*-nBA (circles) and S-*grad2*-nBA (squares).

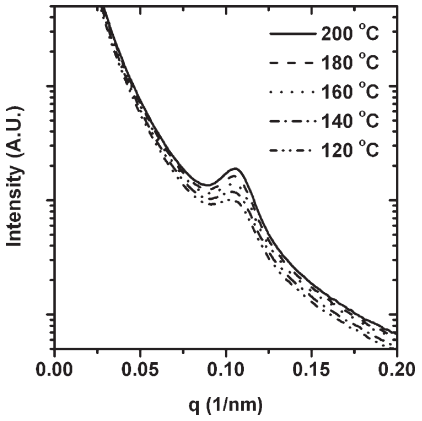

Figure 2. Small-angle X-ray scattering intensity curves for M_n = 60K S-*block*-nBA as a function of scattering wavevector (q). Note that the curves have not been shifted to emphasize the decrease in intensity with decreasing temperature.

implications of this for the order/disorder transitions are discussed later in the text.

Figure 1 demonstrates the formation of composition gradients in the gradient copolymer samples through the evolution of the cumulative styrene mole fraction (F_S, as determined from ^{1}H NMR) with increasing apparent normalized chain length. The apparent normalized chain length was determined via the ratio of the M_n value for an aliquot copolymer sample recovered at a given time during the polymerization relative to that obtained for the copolymer at the end of the polymerization. (Given that the aliquot sample and copolymer M_n values were determined by GPC relative to PS standards, the normalized chain length is only apparent and not absolute.) Both gradient copolymers exhibit a gradient structure over the entire chain and show comparable evolution in terms of gradient strength as a function of chain length, so their dominant difference lies in their molecular weights and not gradient structure.

SAXS and Rheology. Figure 2 shows SAXS results for S-*block*-nBA, with intensity plotted as a function of scattering wavevector (q). A noticeable peak is seen at $q \sim 0.11$ nm^{-1} (d-spacing ~57 nm). The peak intensity shrinks monotonically as

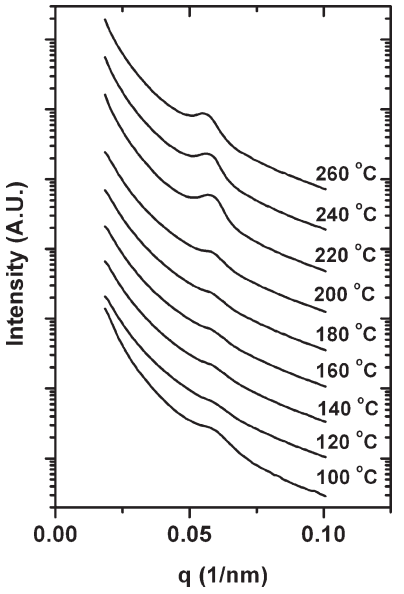

Figure 3. Small-angle X-ray scattering intensity curves for M_n = 152K S-*grad1*-nBA as a function of scattering wavevector (q). Note that the curves have been shifted vertically for clear visibility of the disappearance and reappearance of the scattering peak.

temperature decreases from 200 to 120 °C, suggesting an initially ordered material which approaches a disordered regime at lower temperatures. These results are qualitatively similar to those by Russell et al.[15] for a M_n = 68K styrene/*n*-butyl methacrylate (S/nBMA) block copolymer, for which copolymer LDOTs were first reported. The S/nBMA system has a lower comonomer incompatibility than the S/nBA system used here;[32] thus, there is a greater driving force for phase segregation in our system.

Rheological data for the S/nBA block copolymer have previously been reported[32] and are included in the Supporting Information (Figure S1). They reveal the non-Newtonian behavior characteristic of phase-segregated block copolymers, which changed minimally with temperature.

Scattering plots for S-*grad1*-nBA are shown in Figure 3. At 260 °C, a strong peak is seen at $q \sim 0.055$ nm^{-1} (d-spacing ~114 nm). (The SAXS data in Figure 3 show no evidence of a second-order peak which, as discussed in ref 32, is typically the case for nanostructured gradient copolymers.) The intensity is dramatically reduced between 220 and 200 °C and then gradually vanishes as temperature is lowered to 120 °C. As temperature is further decreased to 100 °C, the peak re-emerges at a very slightly higher scattering wave-vector ($q \sim 0.057$ nm^{-1} and d-spacing ~110 nm). These results suggest that this material undergoes both ordering and disordering phase transitions over this temperature range. The slightly higher q and lower d-spacing at lower temperatures could be explained through the high-temperature ordered state being entropically favored due to increased free volume. A similar disappearance and reappearance of peaks was reported by Russell et al. for their only block copolymer (M_n = 99K, S/nBMA) that showed both UODT and LDOT transitions.[15] A small increase in q from the higher temperature ordered state (~0.18 nm^{-1}) to the lower temperature ordered state (~0.185 nm^{-1}) was also observed.

Rheological data for S-*grad1*-nBA were taken to verify the trends seen by SAXS. In Figure 4a,b, loss and storage moduli (G' and G'') measured as a function of oscillation frequency (ω) are

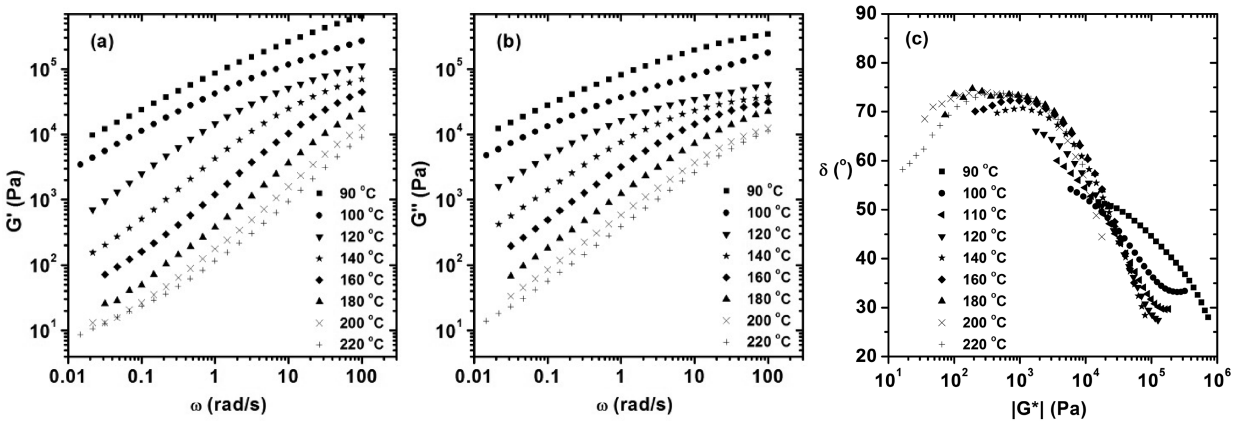

Figure 4. Frequency dependence of M_n = 152K S-*grad1*-nBA storage (a) and loss (b) moduli (G' and G'') at various temperatures and a strain amplitude of 10%. (c) Corresponding Van Gurp−Palmen plot of phase angle versus complex modulus.

compiled for temperatures from 90 to 220 °C. Data were not taken above 220 °C due to possible sample degradation at time scales needed for data collection. On heating from 100 to 120 °C, the slopes of G' and G'' at low frequencies increase in steepness from elastic-like, low frequency dependence to more liquid-like, higher frequency dependence; this is consistent with a transition to a more disordered material. At 140−180 °C, an inflection point emerges at low frequencies for G'. This anticipates the appearance of a secondary elastic-like regime, as G' frequency dependence is diminished at frequencies below the inflection point. This trend is more apparent at 200 and 220 °C, as the material has not relaxed into the Newtonian behavior characteristic of disordered, homogeneous materials ($G' \sim \omega^2$, $G'' \sim \omega$). Russell and co-workers observed a similar reappearance of a secondary elastic regime of their S/nBMA block copolymer which showed both UODT and LDOT transitions.[16]

These changes become more apparent when the data are compiled as master curves of phase angle (δ) vs complex modulus ($|G^*| = (G'^2 + G''^2)^{1/2}$) in van Gurp-Palmen plots[32] (Figure 4c). This form of graphing eliminates uncertainty associated with shifting data along the frequency axis. A plot of liquid-like, disordered behavior would show δ increasing as $|G^*|$ decreases, reaching a plateau of $\delta = 90°$ at the lowest $|G^*|$ values. Ordered, solid-like behavior would exhibit much lower values of δ at low $|G^*|$. The plot for S-*grad1*-nBA shows a transition in behavior between 100 to 160 °C as the phase angle at low $|G^*|$ increases from ∼55° to ∼70°, or from solid-like behavior to more liquid-like behavior. This is indicative of a UODT. Above 160 °C, the data collapse onto a single curve rather than continuing toward fully disordered behavior. This discontinuation of phase angle increases at higher temperatures is suggestive of a LDOT. Thus, the presence of both UODT and LDOT for S-*grad1*-nBA is suggested by both scattering and rheological studies.

The S-*grad2*-nBA SAXS data revealed no scattering peak, and rheology from this sample showed near-Newtonian behavior, consistent with a disordered material.[32] When graphed on a van Gurp-Palmen plot, data at increasing temperatures collapsed onto a single curve, with δ at low $|G^*|$ approaching 85° (see Figure S2). This is indicative of a material much closer to the disordered state than S-*grad1*-nBA.

Discussion. To summarize our observations, we have observed an S/nBA block copolymer with M_n = 60K exhibiting only ordered behavior, an S/nBA gradient copolymer with M_n = 90K exhibiting only disordered behavior, and an S/nBA gradient copolymer with M_n = 152K exhibiting what appears to be both LDOT (∼100 °C) and UODT (∼200 °C) transitions. The changes in molecular weight producing these shifts in behavior are remarkable compared to the very small changes in molecular weight typically observed for shifts in block copolymer systems.

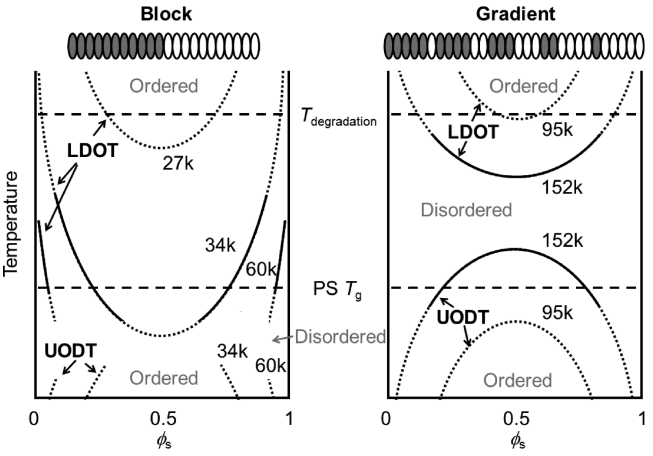

Figure 5. Hypothetical phase diagrams depicting the molecular weight dependence of LDOT and UODT for S/nBA block and gradient copolymers relative to temperature as a function of styrene fraction (ϕ_s). Data include results from ref 67. The solid lines indicate where phase-separated behavior was observed, whereas the dotted line behavior is inferred from the data. Horizontal dashed lines are included as points of temperature reference, corresponding to the approximate degradation temperature of the material ($T_{degradation}$) and the bulk glass transition temperature of polystyrene (PS T_g).

That S/nBA systems should show LDOT-type behavior is not without precedence, but this is the first time it has been recognized as such. In 2003, Mayes and co-workers[23] explored using S/nBA block copolymers as baroplastic materials, demonstrating pressure-induced miscibility. They had previously found that baroplastic behavior in S/nBMA has similar entropic origins as the LDOT.[66] While these results indicate the potential for S/nBA to demonstrate LDOT behavior, such studies have not been reported. In 2005, Shimada and co-workers[67] used SAXS to evaluate the temperature-dependent behavior for two

S/nBA block copolymers. They noted that the higher molecular weight case (M_n = 34.3K) exhibited sharp scattering peaks indicative of an ordered system, while the lower molecular weight case (M_n = 26.8K) showed weak, broad peaks consistent with concentration fluctuations and disorder. (Again, we emphasize the relatively small shift in molecular weight that produces these very different behaviors in a block copolymer system.) What had not been noted was the increase in peak intensity for both cases with increasing temperature, as we had seen in our S/nBA block copolymer SAXS results, indicating LDOT-type behavior. These results indicate that S/nBA gradient copolymers have the potential as materials for pressure-assisted processing, given the common entropic origins of LDOTs/LCSTs and baroplastic characteristics. Scientifically, the experimental and theoretical exploration of gradient copolymer phase behavior as a function of pressure would be of great interest.

In Figure 5, hypothetical phase diagrams of S/nBA block and gradient copolymers are depicted, including results extrapolated from the work of Shimada and co-workers.[67] A degradation temperature ($T_{degradation}$) and the bulk glass transition temperature of polystyrene (PS T_g) are included to indicate approximate temperature boundaries within which observable phase changes are expected. No S/nBA block copolymer has yet been designed yielding access to the LDOT point; only phase-mixed (M_n = 26.8K, ref 67) or phase-segregated (M_n = 34.3K, ref 67, and our M_n = 60K S-*block*-nBA) systems have been observed. Based on ref 67, only a block copolymer with M_n between 27K and 34K could demonstrate a LDOT over experimentally feasible temperatures. Access to the UODT for these specimens is prevented by the PS T_g. Even if a higher molecular weight specimen were used to push the UODT to higher temperatures, the transition would not be seen, as the concurrent lowering of the LDOT would cause the two transitions to overlap, giving an hourglass-type phase diagram.

Through the gradient copolymer phase diagram, we show how copolymer sequence distribution can lead to shifting of critical points, allowing for observation of a UODT. Represented are the two gradient copolymers: the M_n = 152K S-*grad1*-nBA, yielding both UODT and LDOT, and the M_n = 95K S-*grad2*-nBA, which demonstrated only phase-mixed behavior. As predicted by theory,[37,38] the arrangement of comonomers in gradient copolymers leads to lower inherent segmental incompatibility, such that higher molecular weights and more extreme temperatures are needed to create sufficient driving force for segregation. Most notably, whereas in a S/nBA block copolymer system the molecular weight necessary to induce phase segregation is ~30K, in the gradient copolymer it is ~100K−150K, a 3−5-fold increase. This is directly comparable to the increase in $(\chi N)_c$ predicted by Lefebvre et al.[37] and Jiang et al.[38] from 10.5 in a symmetric block copolymer to ~29−30 in symmetric linear gradient copolymer.

Let us examine the behavior of these systems near the PS T_g (100 °C). The M_n = 34K and 60K block copolymers are ordered at 100 °C and demonstrate LDOT-type behavior. The M_n = 95K gradient copolymer is disordered at 100 °C, presumably in the phase-mixed region between its UODT and LDOT. Meanwhile, the LDOT of the M_n = 152K gradient copolymer is well above this temperature, with the material exhibiting UODT-type behavior at 100 °C. This demonstrates the power of sequence distribution in shifting the UODT and LDOT to lower and higher temperatures, respectively, for higher molecular weight systems. Phase transitions can then be observed in higher molecular weight materials, instead of hourglass-shaped phase diagrams, and UODTs inaccessible in block copolymers can be accessed.

Finally, we consider the impact of variation in terms of average chain length (PDIs)[68] and in terms of chain-to-chain monomer distribution that is inherent to gradient copolymers synthesized by controlled radical polymerization. Many theoretical studies of block copolymer phase behavior have predicted a significant stabilization of the ordered state relative to the disordered state,[69−74] such that $(\chi N)_c$ is reduced by more than half for the symmetric case as $PDI_A = PDI_B$ increases from 1.0 to 2.0.[70] Increasing polydispersity systematically within one block in diblock systems has been shown to yield decreases in $(\chi N)_c$ where the polydisperse block formed the majority component.[75,76] Finally, diblock copolymers synthesized by controlled radical polymerization techniques yield polydispersity in both blocks; these can still lead to microphase segregation and ordered structures.[77,78]

In our studies, the S-*block*-nBA case was also synthesized using controlled radical polymerization and has a relatively high PDI compared to anionically synthesized cases.[67] However, its PDI is comparable to those of our two gradient cases, and we believe that this should end up mitigating any significant effect of polydispersity in our gradient copolymers relative to the impact of overall molecular weight and gradient sequencing in interpreting the results. More significantly, having monodisperse gradient copolymers would in fact increase $(\chi N)_c$ relative to our polydisperse cases, requiring even greater increases in molecular weights to induce phase segregation than the substantial increases we already observe.

Gradient copolymers have the added complexity of variation in their chain-to-chain monomer sequence distribution, as recently investigated through computational analysis by Wang and Broadbelt.[79,80] We are unaware of any investigations into the impact of this inherent variation on order−disorder transitions. We speculate that the impact of this variation enhances the changes already introduced by using gradient rather than block sequencing in terms of the phase segregation being driven by gradual changes in composition along the chain rather than a single sharp change,[37,38,40] thus increasing $(\chi N)_c$.

CONCLUSION

Order/disorder transition shifting through gradient sequence distributions in copolymers is a powerful means of phase transition design. In a S/nBA copolymer system, we are able to increase the molecular weight necessary to induce phase segregation by over 3-fold through a shift from block to gradient sequencing. This is consistent with predictions from theory of an increase from $(\chi N)_c$ = 10.5 for block copolymers to 29−30 in gradient copolymers.[37,38] Results also suggest the existence of both LDOT and UODT in our higher molecular weight gradient copolymer, made accessible by the shift in order/disorder temperatures by gradient sequencing. The combination of transitions is speculated to be inaccessible in S/nBA block copolymer systems due to their overlap at even modest molecular weights and also their location on the phase diagram relative to the polystyrene glass transition temperature. Thus, order/disorder transitions in gradient copolymers are not only found at molecular weights that are higher and potentially more industrially relevant for mechanical strength than those of block copolymers, but these transitions can also be designed to occur

at temperatures which are lower and industrially feasible for processing.

■ ASSOCIATED CONTENT

Supporting Information. Figures related to rheological measurements of S-*block*-nBA and S-*grad2*-nBA. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j-torkelson@northwestern.edu.

Present Addresses

[||]Currently at Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

[⊥]Currently at Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712.

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