Gaussian- to Stretched-Coil Transition in Block Copolymer Melts

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Two scaling regimes, $D \sim N^{\delta}$ with $\delta = 0.49 \pm 0.02$ and 0.80 ± 0.04, have been identified in a model set of nearly symmetric diblock copolymer melts, where D and N are the system periodicity and degree of polymerization, respectively. The crossover from $\delta = 0.49$ to 0.80 is identified as the Gaussian- to stretched-coil transition (GST). Contrary to current theory, the GST occurs well below the order-disorder transition (ODT), $N_{\text{GST}} = 0.57 N_{\text{ODT}}$. We associate $\delta = 0.80$ with the crossover from weak-segregation ($\delta = \frac{1}{2}$) to strong-segregation ($\delta = \frac{2}{3}$) behavior.

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Block copolymers are large molecules composed of sequences (i.e., blocks) of chemically distinct repeat units. The simplest molecular architecture is obtained by connecting a block of A repeat units end to end with a block of B repeat units. Such a configuration is known as an A-B diblock copolymer. More complex molecules can be created by linking together two or more diblock copolymers leading to the formation of $(A\text{-}B)_n$ starblock copolymers. The ability to independently specify the molecular architecture, composition, and the overall block sizes, provides unparalleled control over the ultimate phase behavior of these morphologically diverse materials. Accordingly, this class of polymers has commanded both theoretical and experimental attention for over two decades.

The phase behavior of undiluted block copolymers (melts) is determined by three factors:[1,2] the overall degree of polymerization, $N = N_A + N_B$, architectural constraints characterized by n and the composition f (overall volume fraction of the A component), and the A-B segment-segment interaction parameter χ (a segment is usually defined as a repeat unit). The first two factors are regulated through the polymerization stoichiometry and influence translational and configurational entropy, while the magnitude of (the largely enthalpic) χ is determined by the selection of the A-B monomer pairs; e.g., for hydrocarbon polymers $\chi = \alpha T^{-1} + \beta$, where α and β are system-dependent constants.

At equilibrium a block copolymer melt will be arranged such that the overall free energy is minimized. Decreasing temperature (i.e., increasing χ) favors a reduction in A-B segment contacts. If N is sufficiently large, this may be accomplished by local compositional ordering as illustrated in Fig. 1(c) for the symmetric case $f = 0.5$ where a lamellar phase is observed (other ordered-phase geometries are obtained for certain $f \neq 0.5$). Alternatively, if either χ or N is decreased enough, entropic factors will dominate, leading to a compositionally disordered phase as depicted in Fig. 1(a). Since the entropic and enthalpic contributions to the free-energy density scale, respectively, as N^{-1} and χ, it is the product χN that governs the block copolymer phase state.[1] For $f = 0.5$, the order-disorder transition (ODT) occurs when $\chi N / n \sim 10$. Since the $n = 1$ case has received the most comprehensive theoretical treatments and because the above factors qualitatively influence phase behavior independent of n, we have focused our experimental research efforts on model diblock copolymers.

Two limiting regimes have been postulated to characterize the diblock copolymer phase diagram. For $\chi N \ll 10$, a copolymer melt is disordered and the A-B interactions are sufficiently weak that the individual chain statistics are unperturbed (i.e., *Gaussian*). The connectivity of the two blocks and the incompressibility of the melt, however, lead to a correlation hole[1] that is manifested in scattering measurements as a peak corresponding to a fluctuation length $D \sim R_g \sim aN^{1/2}$, where R_g is

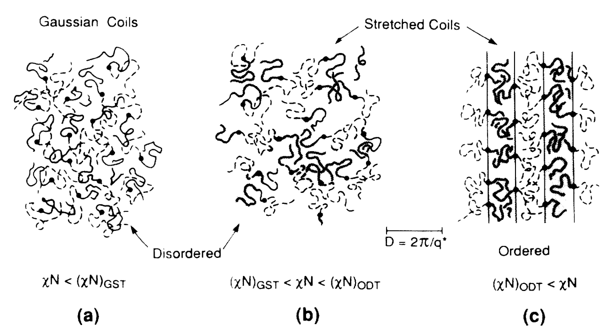

FIG. 1. Schematic illustration of the speculated real-space morphology of a symmetric ($f = \frac{1}{2}$) diblock copolymer melt. GST and ODT refer to the Gaussian- to stretched-coil transition and order-disorder transition, respectively.

the copolymer radius of gyration and a is a characteristic segment length. As χN is increased to ~ 10, a delicate balance between energetic and entropic factors produces a disorder-to-order transition. Current ODT theories[1,3] make the *assumption* that in the vicinity of this transition the A-B interactions are sufficiently weak that the individual copolymers remain essentially Gaussian, the microdomain period scales as $N^{1/2}$, and the ordered-phase composition profile is approximately sinusoidal. This is referred to as the weak-segregation-limit (WSL) assumption. The second limiting regime of phase behavior is referred to as the strong segregation limit (SSL) and corresponds to $\chi N \gg 10$. In the SSL narrow interfaces of width[4] $a\chi^{-1/2}$ separate well-developed, nearly pure A and B microdomains. The interaction energy associated with A-B contacts is localized in these interfacial regions. Equilibrium is established by minimizing the total interfacial area under the entropic penalty of extended chain configurations, necessitated by the constraint of incompressibility. These opposing forces lead to *stretched* coil configurations and ordered-phase periods that scale as[4,5] $D \sim aN^{2/3}\chi^{1/6}$. The crossover behavior of D between these extreme limits of WSL and SSL can evidently be described by an expression of the form $D \sim aN^{1/2}\Psi(\chi N)$, where the crossover scaling function $\Psi(x)$ has the limiting behaviors $\Psi(x) \sim 1$ for $x \to 0$, and $\Psi(x) \sim x^{1/6}$ for $x \to \infty$.

Although there exists an extensive literature dealing with block copolymer melts, we are unaware of any experimental evidence of a Gaussian- to stretched-coil transition which would signal a departure from strictly weak-segregation behavior. Neither have we found direct experimental support for the WSL assumption in the vicinity of the ODT. In the ordered regime several experimental studies report[6-8] $D \sim N^{2/3}$ (with one noteable exception[9] where $D \sim N^{0.79}$) and the SSL predictions are widely accepted as factual. In this Letter we report, to our knowledge, the first experimental evidence of a Gaussian- to stretched-coil transition in block copolymer melts. We also identify a previously unrecognized crossover scaling regime that separates the weak and strong segregation limits.

A series of nearly monodisperse poly(ethylene-propylene)-poly(ethylethylene) (PEP-PEE) diblock copolymers containing 55% by volume PEP was synthesized and characterized as described in a previous publication;[10] based on a repeat unit mass of 56 g/mol the samples range in size from $N = 125$ to 1890. Neutron-scattering contrast was obtained by preferentially substituting deuterium for hydrogen on one of the blocks. The molecular structure of the PEP-PEE molecule is shown in Fig. 2. These nearly symmetric block copolymers are characterized by a lamellar morphology for $\chi N > (\chi N)_{\mathrm{ODT}}$ as demonstrated in a recent publication.[11]

Small-angle neutron-scattering (SANS) data were obtained at 23 °C using the 30-m instrument at the W. C. Koehler small-angle-scattering facility located at Oak

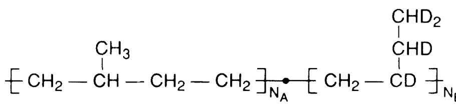

FIG. 2. Molecular structure of the poly(ethylene-propylene)-poly(ethylethylene) diblock copolymer. This depiction shows one type of deuterium (D) labeling used to obtain neutron-scattering contrast.

Ridge National Laboratory. Experiments were conducted with $\lambda = 4.75$ Å ($\Delta\lambda/\lambda = 0.06$) wavelength neutrons and a pinhole collimation geometry. The azimuthally symmetric two-dimensional scattering patterns were reduced to one-dimensional form [intensity versus scattering wave vector $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle] following established procedures. Four representative SANS patterns are presented in Fig. 3. As shown elsewhere[12] smearing effects for this type of SANS pattern are not significant for the measurements reported here.

The characteristic lamellae period D for symmetric block copolymers is inversely proportional to the small-angle-scattering-peak position q^*,

$$D = 2\pi/q^*$$

so that

$$q^* \sim N^{-\delta},$$

where $\delta = \frac{1}{2}$ and $\frac{2}{3}$ for the WSL and SSL theories, respectively. The results of our SANS experiments on

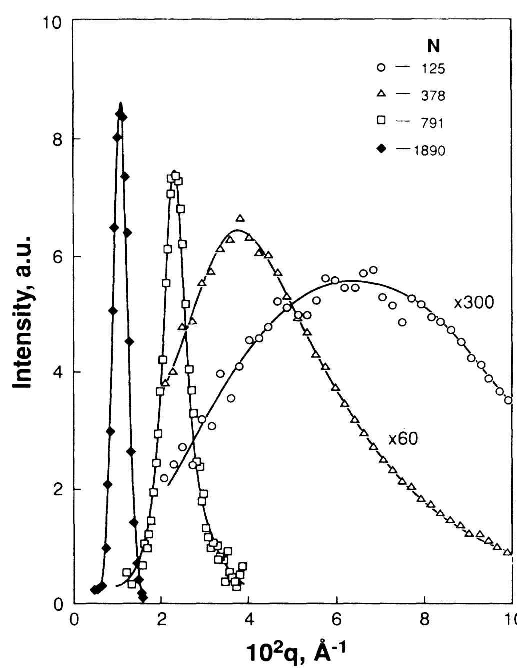

FIG. 3. Representative SANS patterns for the PEP-PEE diblock copolymers. Curves are a guide to the eye.

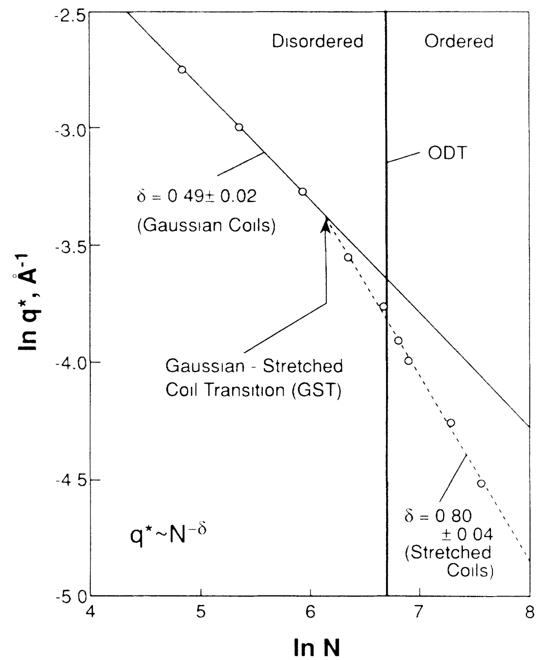

FIG. 4. Dependence of the SANS peak position q^* on the degree of polymerization N. Location of the ODT has been independently determined (Refs. 11 and 13).

nine PEP-PEE diblock copolymers are summarized in Fig. 4. Two scaling regions are clearly evident in this plot of $\ln(q^*)$ vs $\ln(N)$ (here N refers to the number average degree of polymerization). For the three lowest-molecular-weight samples $\delta=0.49\pm0.02$, essentially in exact agreement with *Gaussian*-coil statistics ($\delta=0.5$). Furthermore, the WLS prediction[1,3] for $q^*(N)$, based on independently determined values of a for PEP and PEE,[11] is within 10% of that obtained experimentally.

The six highest-molecular-weight samples follow a distinctly different scaling behavior, with $\delta=0.80\pm0.04$. Here the polymer coils are clearly in a *stretched* configuration; for our largest specimen, $N=1890$, the measured D is nearly 1.6 times that obtained by extrapolation from the Gaussian-coil (WSL) regime. We identify the Gaussian- to stretched-coil transition, denoted GST, as the intersection of these two scaling regimes: $N_{\mathrm{GST}}=460$ at 23 °C for the $f=0.55$ PEP-PEE system.

In several recent publications we have shown that the block copolymer order-disorder transition can be precisely located using either rheological[13] or small-angle-scattering techniques.[11] We have exploited these methods in identifying T_{ODT} for four of the samples included in Fig. 4, from which we determine $N_{\mathrm{ODT}}=803$ at 23 °C as indicated by the vertical line in Fig. 4. Thus, the stretched-coil behavior extends well into the *disordered state*, $N_{\mathrm{GST}}=0.57N_{\mathrm{ODT}}$, contrary to the Gaussian-coil assumption which characterizes the current ODT theories.[1,3] It should be noted, however, that Semenov[5] has recently proposed a pretransitional micellar phase for strongly asymmetric ($f\rightarrow0$ or 1) copolymers in which chains within spherical micelles are characterized by stretched configurations. At the ODT the block copolymer coils are stretched 13% relative to the unperturbed dimension. This is in striking agreement with a recent Monte Carlo simulation by Minchau, Dünweg, and Binder,[14] where a 15% increase in R_g was recorded as the ODT was approached. [Conversely, Chakrabarti, Toral, and Gunton[15] find agreement with WSL behavior ($\delta=0.5$) in a two-dimensional Monte Carlo simulation of diblock copolymers.]

As indicated in Fig. 4 we find $\delta=0.80\pm0.04$ for $N>N_{\mathrm{GST}}$. This confirms the generally overlooked result of Hadziioannou and Skoulios,[9] $\delta=0.79\pm0.02$, for ordered polystyrene-polyisoprene diblock copolymers. However, this confirmation conflicts with the SSL prediction, and other experimental studies[6-8] that report $\delta=\frac{2}{3}$.

Previous experimental investigations of length scaling in block copolymers have been conducted exclusively with polystyrene-polydiene diblock and triblock copolymers.[6-9] In all cases, small-angle-scattering specimens were prepared by solvent casting, a procedure notorious for producing nonequilibrium states. For example, two separate groups[7,16] found $\delta\cong0.4$ for solvent-cast polystyrene-polydiene block copolymers characterized by a spherical microstructure. The reason for this seemingly anomalous ($\delta<0.5$) result is that the ODT occurs in a solution state;[16] subsequent solvent removal produces a trapped, nonequilibrium bulk state. In fact, solvent casting is commonly used to induce nonequilibrium phase formation. Such nonequilibrium phases can remain stable for long times owing to sizable free-energy barriers to microstructural rearrangement. Because polystyrene is a glass below 100 °C, these nonequilibrium effects are fixed indefinitely at room temperature, where small-angle-scattering measurements are typically conducted. What distinguishes the work of Hadziioannou and Skoulios[9] is that these authors employed a novel shearing device, operated above 100 °C, in order to overcome barriers to achieving equilibrium, prior to cooling their scattering specimens to room temperature.

Achieving an equilibrium state in our experiments is facilitated by two factors. First, the glass transition for the PEP-PEE materials lies more than 50 °C below room temperature, which means our samples are continuously annealed. Second, our ordered-state experiments were conducted considerably closer to the ODT, $N/N_{\mathrm{ODT}}<2.4$, than most of the polystyrene-polydiene experiments. Free-energy barriers for structural rearrangement are lowest near the ODT. Thus, we conclude that $\delta=0.80$ represents the equilibrium scaling behavior that emerges from the WSL regime.

The results of this study lead us to conclude that block copolymer melts are characterized by four distinct states. When $\chi N<(\chi N)_{\mathrm{GST}}$, the system exists as a spatially homogeneous melt of unperturbed Gaussian coils, as depicted in Fig. 1(a), corresponding to the conventional WSL ($\delta = \frac{1}{2}$). For $(\chi N)_{\rm GST} < \chi N < (\chi N)_{\rm ODT}$, the system remains disordered but is characterized by large-amplitude compositional fluctuations accompanied by chain stretching, leading to $\delta = 0.80$. Our interpretation of the (instantaneous) morphology in this regime is illustrated in Fig. 1(b). Compelling evidence of composition fluctuations in disordered PEP-PEE block copolymers near the ODT can be found in rheological and SANS data as detailed in separate publications.[11,13,17] Increasing χN above $(\chi N)_{\rm ODT}$ leads to a weak first-order transition to an ordered phase as illustrated in Fig. 1(c). Although ordering has a profound effect on the system dynamics,[13] $q^*(N)$ appears to be unaffected by the ODT; i.e., $\delta = 0.80$ above and below this transition. [In a recent report[11] we have shown that $q^*(T)$ is also unaffected by the ODT.] Based on the results obtained by Hadziioannou and Skoulios[9] this scaling regime appears to persist well into the ordered phase, i.e., for $N/N_{\rm ODT} \gtrsim 10$. Compelling theoretical arguments[4,5] lead us to believe that there is likely to be a final transition into the SSL, where $\delta = \frac{2}{3}$. Thus, we conclude that the $\delta = 0.80$ scaling behavior represents a crossover regime that separates the WSL and SSL. Current theories,[4] however, suggest the existence of a crossover regime with an exponent intermediate between the two limits, i.e., $\delta \cong 0.64$.

In summary, we have identified the Gaussian- to stretched-coil transition in a model set of block copolymer melts. Departure from Gaussian-coil statistics preceeds the order-disorder transition and extends well into the ordered state. We find $D \sim N^{0.80 \pm 0.04}$ in the stretched-coil regime, where D and N represent the system periodicity and degree of polymerization, respectively. These results are not accounted for by current theory.

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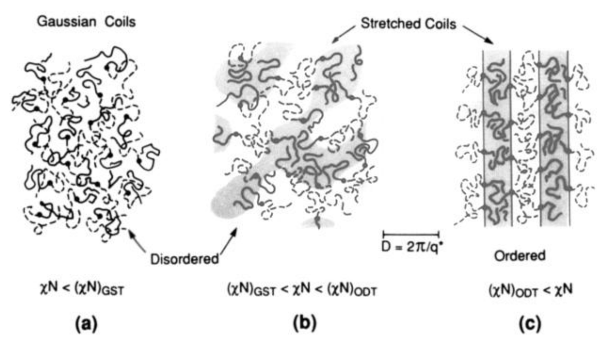

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