Molecular Weight Scaling in Critical Polymer Mixtures

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Symmetric binary mixtures of partially deuterated polymers were prepared at the critical composition. The segment-segment interaction energy parameter χ_{eff} was varied by adjusting the difference in deuterium content ΔX_D between species. χ_{eff} was measured as a function of temperature, ΔX_D, and molecular weight by small-angle neutron scattering. The critical point for demixing was determined to scale as $\chi_{\text{eff},c} \sim N^{-\delta}$ with $\delta = 1.01 \pm 0.05$, where N is the degree of polymerization. This result confirms the mean-field prediction of Flory and Huggins.

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Linear polymers are macromolecules composed of long sequences of repeat units (i.e., segments) that are covalently bonded together. In the amorphous state, linear polymers assume random-walk (Gaussian) configurations [1,2], whereby individual chains occupy only a small fraction of the configurational space. Hence, undiluted (bulk) polymers are highly entangled, leading to unique thermodynamic and dynamic effects that involve the cooperative interaction of many molecules [2]. This Letter deals with the mixing of two distinct polymer species in the bulk state. We report experimental results that establish the scaling relationship between the number of chain segments N and the critical point for demixing.

In 1942 Flory [3] and Huggins [4] independently derived similar mean-field theories for incompressible binary polymer mixtures,

$$\frac{\Delta F_m}{kT} = \frac{\phi_1 \ln \phi_1}{N_1} + \frac{1-\phi_1}{N_2} \ln(1-\phi_1) + \phi_1(1-\phi_1)\chi , \tag{1}$$

where ΔF_m represents the mixing free energy per segment, ϕ_1 is the volume fraction of species 1, and k is the Boltzmann constant. χ, generally known as the Flory-Huggins parameter, accounts for the contact energy between dissimilar segments. Application of the Gibbs criterion [1,2], $\partial^2 \Delta F_m / \partial \phi_1^2 = \partial^3 \Delta F / \partial \phi_1^3 = 0$, leads to the critical scaling condition for phase separation $(\chi N)_c = 2$ in symmetric $(N_1 = N_2 = N)$ polymer mixtures.

Even in the ideal limit of structurally identical and incompressible segments, Eq. (1) represents a crude theory that neglects chain self-avoidance, self-contact, and intrachain and interchain segment correlations. Differences in segment structure and finite compressibilities further complicate the application of the Flory-Huggins theory to actual polymer mixtures. These shortcomings are usually addressed empirically by treating χ as a phenomenological parameter, $\chi = \chi_{\text{eff}}(T, \phi, \ldots)$ [5,6] giving $(\chi_{\text{eff}} N)_c = 2$, where χ_{eff} is an effective interaction parameter. Only recently have fundamental improvements to Eq. (1) been reported [7]. In general, these do not affect the Flory-Huggins critical scaling prediction.

Over the past several years, Schweizer and Curro have presented a series of publications describing the reference interaction site model (RISM) integral equation theory for amorphous polymer melts and mixtures [8]. For polymer mixtures based on a mean-spherical approximation (MSA) closure, they contend that local correlations between unlike segments in a polymer mixture are amplified due to the combined effects of large N's and self-avoidance, leading to a renormalization of the segment-segment interaction parameter. In the limit $N \rightarrow \infty$, $\chi_{\text{eff}} = \kappa N^{-1/2} \chi_0$ where κ is an $O(1)$ constant and χ_0 corresponds to the mean-field value of χ. This produces the provocative conclusion that the critical point in symmetric polymer mixtures should scale as $\chi_{0,c} \sim N^{-1/2}$.

Experimentally establishing the molecular weight scaling relationship for critical polymer mixtures is surprisingly tedious, and we are unaware of any prior definitive studies. (However, recent computer simulations by Deutsch and Binder [9] support the Flory-Huggins prediction.) Ideally, both components should have large, equal, and monodisperse molecular weights, as well as structurally equivalent segments. Measurements must be made on a single pair of segment types in order to avoid mixing nonideal effects (e.g., compressibility) that vary from one system to another. Because the experimental temperature window is relatively narrow (above the melt or glass transition, but below the thermal degradation temperature) only a limited range in N can be accessed with a particular pair of polymers. This restriction, along with the experimental uncertainty in N, places severe limitations on the precision in the scaling exponent attainable using chemically distinct polymers. Furthermore, monodisperse, high molecular weight, critical polymer pairs are quite rare.

We have developed a strategy that circumvents these complications. Deuterated and protonated polymers, otherwise of identical chemical structure, are known to be characterized by a small positive $\chi_{\rm eff}$ owing to the slight differences in the length and polarizability of C-H and C-D bonds [10,11]. We expect $\chi_0 \sim [\Delta X_{\rm D}/(X_{\rm H}+X_{\rm D})]^2$, where $X_{\rm H}+X_{\rm D}$ is the total number of protons and deuterons per segment, and $\Delta X_{\rm D}$ is the difference in segment deuterium content between two polymer isotopes [11]. Thus, the magnitude of χ_0 can be systematically varied while maintaining nearly perfect segment symmetry (i.e., without perturbing the chemical structure).

Poly(ethylene-propylene) (PEP) was selected as a model compound for this study. Partially deuterium labeled PEP's ($[C_5D_XH_{10-X}]_N$) were prepared by hydrogenating and/or deuterating anionically polymerized 1,4-polyisoprenes ($[C_5H_8]_N$ or $[C_5D_8]_N$) [12]. This procedure yielded a variety of narrow molar mass distribution PEP's, $N_W/N_N < 1.05$, where N_W and N_N are the weight and number average degrees of polymerization. N_W was determined (±5%) by light scattering and calibrated size exclusion chromatography (Table I). Hereafter N always refers to the weight average quantity. Deuterium content was established by using the density gradient column technique. Fluctuations in deuterium (hydrogen) content along a chain are localized to approximately a segment length [13] as a consequence of each polyisoprene repeat unit participating in the catalytic saturation reaction.

Three sets of $\phi=0.5$ mixtures were prepared as indicated in Table I. The critical composition is given by $\phi_c = N_1^{1/2}/(N_1^{1/2}+N_2^{1/2})$ [1,2]. Thus these specimens were either strictly critical (i.e., those obtained by combining isotopes that were derived from a common polyisoprene) or nearly so, $\phi_c = 0.49$ [14]. Mixing was accomplished by codissolution in pentane followed by drying and annealing above the critical temperature (see below). Neutron scattering measurements were conducted on the 30-m small-angle neutron scattering (SANS) instrument at the W. C. Koehler small-angle scattering facility located at Oak Ridge National Laboratory. $\lambda = 4.75$ Å wavelength neutrons ($\Delta\lambda/\lambda = 0.06$) and a pinhole collimation geometry were employed. Sample temperature was controlled within ±1 °C. 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. The reduced intensities were converted to units of absolute differential scattering cross section per unit solid angle (cm^{-1}, $\pm < 5\%$) using a secondary standard that was previously calibrated against a host of other primary standards [15]. Three sets of representative SANS results are presented in Fig. 1.

The intensity of scattered neutrons from a single-phase polymer mixture is given by [2,10]

$$V^{-1}(b_1-b_2)^2 I^{-1}(q) = [N_1\phi_1 g_d(x_1)]^{-1} + [N_2(1-\phi_1)g_d(x_2)]^{-1} - 2\chi_{\rm eff}, \tag{2}$$

where V is the segment volume, b_1 and b_2 are the seg-

TABLE I. Binary isotopic mixtures ($\phi=0.5$). In the first column, values in parentheses represent $\Delta X_{\rm D} = |X_{\rm D,1} - X_{\rm D,2}|$.

Mixture	10^3N_1	10^3N_2	$X_{\rm D,1}$	$X_{\rm D,2}$
PEP-A(9.90)	2.14	2.36	9.90	0
PEP-A(7.04)	2.14	2.36	9.90	2.86
PEP-A(4.87)	2.14	2.36	9.90	5.03
PEP-A(5.03)	2.36	2.36	0	5.03
PEP-A(2.86)	2.36	2.36	0	2.86
PEP-B(5.32)	7.91	7.91	0	5.32
PEP-C(5.32)	10.1	10.1	0	5.32

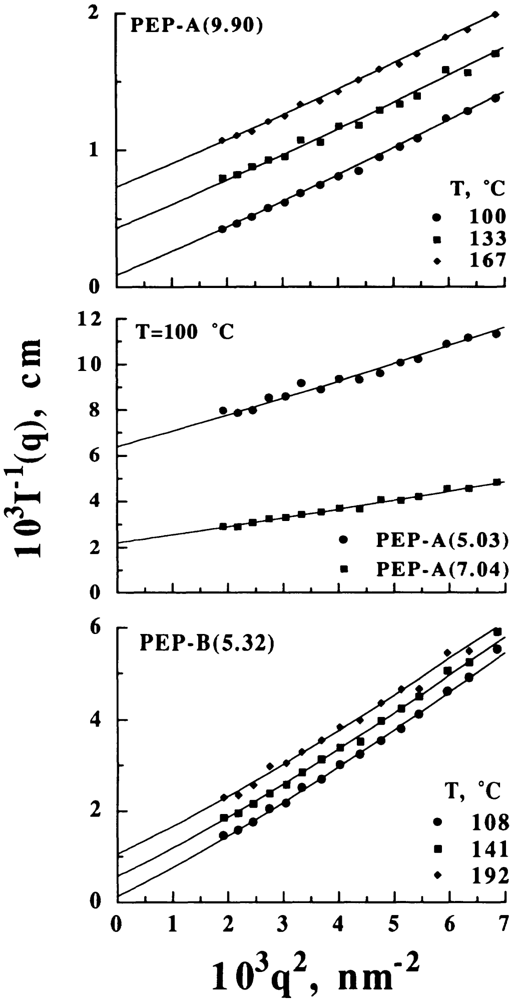

FIG. 1. Representative small-angle neutron scattering results. The curves were fitted to the data using Eq. (2) with $\chi_{\rm eff}$ as the only adjustable parameter.

ment coherent scattering lengths, and $g_d(x)$ is the Debye function with $x=q^2R_g^2=q^2\mathbf{a}^2N/6$. We have fixed the statistical segment length $\mathbf{a}(T)$ according to the results of Zirkel *et al.* [12] and have assumed a typical thermal expansivity for amorphous polyolefins, $\partial \ln V/\partial T = 7.5\times10^{-4}\ \mathrm{K}^{-1}$ [16]; based on our density measurements $V=1.36\times10^{-22}\ \mathrm{cm}^3$ at 23 °C. Excellent agreement with Eq. (2) was obtained for all the SANS data using $\chi_{\rm eff}$ as the sole adjustable parameter as illustrated by the solid curves in Fig. 1.

The dependence of $\chi_{\rm eff}$ on temperature and $\Delta X_{\rm D}$ is presented in Fig. 2. As anticipated [17] $\chi_{\rm eff}\sim(\Delta X_{\rm D})^2$ as demonstrated by the SANS results obtained from the PEP-A mixtures [Fig. 2(a)] [18]. The PEP-A(9.90) mixture yielded the familiar [5,10,11] temperature dependence, $\chi_{\rm eff}=AT^{-1}+B$ [Fig. 2(b)], where A and B are constants that may depend on composition. Combining these results we obtain

$$\chi_{\rm eff}=\left(\frac{\Delta X_{\rm D}}{10}\right)^2\left[\frac{0.571\pm0.007}{T}-(6.56\pm0.18)\times10^{-4}\right]\pm2\times10^{-5} \qquad (3)$$

for $\phi=0.5$ isotopic PEP mixtures. Systematic errors in N and $I(q)$ that do not influence the critical scaling exponent (see below) are not included in Eq. (3); these add approximately 6% more uncertainty to the absolute value of $\chi_{\rm eff}$. Within experimental error this relationship also accounts for the SANS results obtained from the PEP-B(5.32) and PEP-C(5.32) mixtures [Fig. 2(b)] demonstrating that $\chi_{\rm eff}$ does not depend on N, consistent with previous measurements [19].

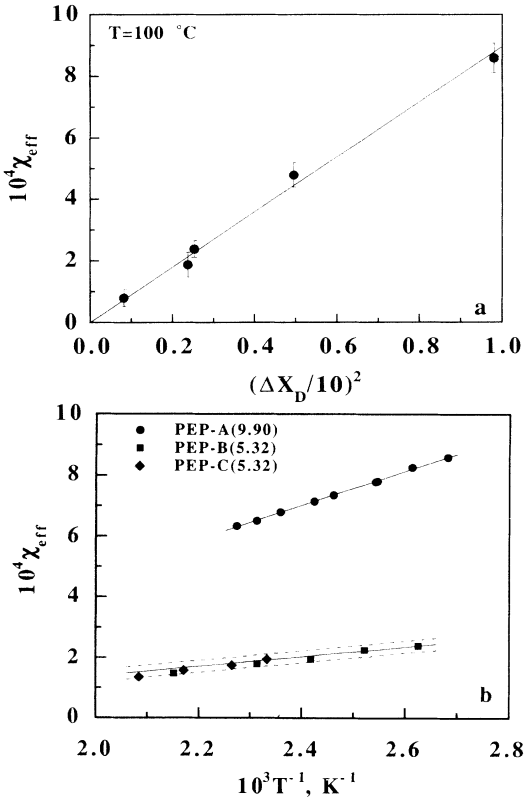

FIG. 2. (a) Dependence of $\chi_{\rm eff}$ on $\Delta X_{\rm D}$. These data were obtained with the PEP-A mixtures (see Table I). (b) Temperature dependence of $\chi_{\rm eff}$. The solid lines correspond to Eq. (3) which was obtained using the PEP-A SANS results. The dashed lines indicate the envelope of the experimental error.

Outside a narrow window near the critical point polymer mixtures exhibit mean-field behavior ($T-T_c\gtrsim2$ °C for the PEP mixtures) [20,21]. Therefore, the critical temperature can be closely estimated from the intercept of a plot of $I^{-1}(0)$ vs T^{-1} as shown in the inset of Fig. 3. Critical temperatures of 93, 99, and 152 °C were obtained for the PEP-A(9.90), PEP-B(5.32), and PEP-C(5.32) mixtures, respectively. When cooled below T_c these mixtures scatter light, due to spinodal decomposition, which is easily observed with the unaided eye. Using T_c in Eq. (3) we have plotted $\chi_{{\rm eff},c}$ vs N in double-logarithmic form in Fig. 3. Assuming the scaling relationship $\chi_{{\rm eff},c}\sim N^{-\delta}$, we find $\delta=1.01\pm0.05$.

These experiments confirm the Flory-Huggins scaling prediction and corroborate the computer simulations of Deutsch and Binder [9]; the RISM-MSA theory scaling prediction for symmetric polymer mixtures [8] is inconsistent with these results.

A potential complication in interpreting our results with respect to the RISM-MSA theory is the random placement of deuterons on each segment that results from isotope exchange events during the saturation of polyisoprene. Random copolymerization of two distinct monomers is predicted [8] to destroy the $O(N^{-1/2})$ renormalization of χ_0 leading to Flory-Huggins behavior. However, our results appear to rule out this possibility since both the partially labeled ($0<\Delta X_{\rm D}<10$) and fully

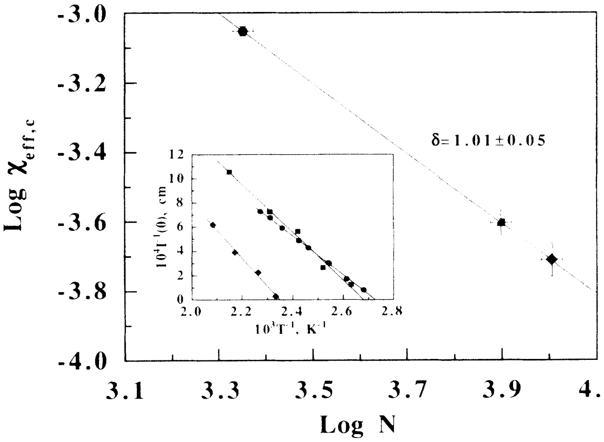

FIG. 3. Scaling of the critical segment-segment interaction parameter with the degree of polymerization; symbol notation is the same as in Fig. 2. The critical temperature was obtained by extrapolation of $I^{-1}(0)$ as shown in the inset, and used with Eq. (3) to determine $\chi_{{\rm eff},c}$.

labeled ($\Delta X_D = 10$) mixtures adhere to the $\chi_{\text{eff}} \sim (\Delta X_D)^2$ and $\chi_{\text{eff},c} \sim N^{-1}$ scaling behaviors. An enormous decrease in χ_{eff} for PEP-A(9.90) (which cannot be affected by randomness), relative to the other mixtures, would be predicted by the RISM-MSA theory if fluctuation effects were significant in the latter.

In conclusion, we have experimentally determined the scaling relationship between the segment-segment interaction parameter χ_{eff} and molecular weight in critical polymer mixtures, $\chi_{\text{eff},c} \sim N^{-\delta}$ where $\delta = 1.01 \pm 0.05$. This confirms the mean-field prediction proposed by Flory [3] and Huggins [4] fifty years ago.

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[13] Small-angle neutron scattering from partially deuterium labeled PEP homopolymers produces a q-independent incoherent scattering intensity for $0.005 \lesssim q \lesssim 0.3$ Å^{-1}, confirming a homogeneous distribution of deuterons over length scales greater than approximately a segment length along the polymer chain. Fluctuations in the deuterium content over several or more segment lengths would lead to a q-dependent coherent scattering signal.

[14] Based on Eqs. (1) and (3) with $\chi_{\text{eff}} = \chi$ this slightly off-critical composition will produce a stability temperature less than 0.1 °C below the critical temperature.

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[18] $\chi_{\text{eff}}(\Delta X_D)$ is constrained by the requirement that $\chi_{\text{eff}}(0) \equiv 0$. This significantly reduces the uncertainty in χ_{eff} due to systematic errors in $I(q)$ and N for the PEP-B(5.32) and PEP-C(5.32) mixtures.

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