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Near-Surface Composition Profiles in Isotopic Polymer Blends Determined via High-Resolution Nuclear Reaction Analysis

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ABSTRACT: The concentration profiles of high molecular weight, isotopic polystyrene blends in the near-surface region were directly measured using real-space composition−depth profiling based on nuclear reaction analysis. The measured profiles are in good agreement with predictions of the Schmidt−Binder mean field theory. In contrast to previous indications, we find no evidence for a flattening of the concentration profile near the surface.

1. Introduction

In recent years there has been considerable interest in surface enrichment in thin films of polymer mixtures, drawn partly by practical aspects (such as lubrication, wear, and adhesion) related to surface composition. If a mixture of polymers is put in the presence of a wall (or an air surface), often one of the components is preferentially attracted to the surface and will segregate to it. The first theoretical treatments describing the thermodynamics of a binary polymer mixture in contact with a surface were pioneered by Nakanishi and Pincus[1] and later refined by Schmidt and Binder.[2] For bulk concentrations far from the binodal compositions, their theory yields a concentration profile that decays quasi-exponentially from the volume fraction at the surface to the bulk value.

A variety of techniques have been used to measure this concentration profile experimentally in the surface region.[3−8] In general, agreement between the Schmidt−Binder mean field theory and the experiments was found. The techniques with higher resolution,[5−8] however, appeared to indicate some deviations of the profile shape in the near-surface region from theoretical predictions. Indications for flattening of the profile were observed in two experiments: Zhao et al.[6] used SIMS to measure the concentration profile of an isotopic polystyrene blend ($M_{\mathrm{hPS}} = 1.8{\cdot}10^6$, $M_{\mathrm{dPS}} = 1.03{\cdot}10^6$, $\Phi_{\mathrm{dPS},\infty} = 0.33$) annealed at 184 °C. The samples showed agreement with the Schmidt−Binder theory for annealing times up to 33 days, while the sample annealed for 45 days featured a distinctive flattening in the near-surface region. Norton et al.[7] undertook neutron reflectometry measurements of an isotopic poly(ethylene propylene) blend. They could fit their reflectometry data only if a flattening of the profile over a distance of one-third to one-half of the bulk correlation length ξ_{b} was included in their model. Both studies[6, 7] were carried out in the one-phase region of the binodal of the respective polymer mixtures.

In recent years we have used nuclear reaction analysis (NRA)[9,10] to investigate surface segregation and wetting in polymer mixtures under a wide range of conditions, based on α-particle detection in the exothermic reaction $^3\mathrm{He} + {}^2\mathrm{H} \rightarrow {}^4\mathrm{He} + {}^1\mathrm{He} + 18.352$ MeV. The limited resolution of this approach did not in the past permit us to investigate the shape of the near-surface profile in detail. Very recently, we improved the spatial resolution of this method and find that by detecting backscattered protons we can achieve an optimal resolution of some 3 nm at the sample surface. Although neutron reflectometry has in principle a better resolution, it suffers from being an indirect technique and its findings are to some extent model dependent. In contrast, direct methods allow concentration solely on the surface region and are not affected by other effects in the bulk or at the substrate side.[11] With this in mind, we have now examined again the issue of the detailed shape of the profile at a polymer mixture surface. We use an isotopic polystyrene blend with high molecular weights to maximize the extent (if any) of flattening at the surface.

2. Theory

Schmidt and Binder[2] started with a free energy functional in the grand canonical ensemble

$$\frac{\Delta F_{\mathrm{S}}}{k_{\mathrm{B}}T} = \int_0^{\infty}\left\{F_{\mathrm{FH}}[\Phi(z)] - \Delta\mu\Phi(z) + \frac{a^2}{36\Phi(z)[1-\Phi(z)]}[\nabla\Phi(z)]^2\right\}\mathrm{d}z + \frac{f_{\mathrm{S}}^{(\mathrm{b})}(\Phi_1)}{k_{\mathrm{B}}T} \qquad (1)$$

where a is a segment size and F_{FH} is the Flory−Huggins mean field free energy of mixing given by

$$F_{\mathrm{FH}} = \frac{\Phi}{N_{\mathrm{A}}}\ln\Phi + \frac{1-\Phi}{N_{\mathrm{B}}}\ln(1-\Phi) + \chi\Phi(1-\Phi) \qquad (2)$$

$f_{\mathrm{S}}^{(\mathrm{b})}(\Phi_1)$ is the “bare” surface energy at a surface volume fraction Φ_1. Φ and $1 - \Phi$ designate the volume fraction of the polymer species A and B of the incompressible polymer blend, respectively, and N_{A} and N_{B} their degrees of polymerization. χ is the Flory−Huggins interaction parameter describing the interactions between the different kinds of monomers. The chemical potential difference between the two components is given by

$$\Delta\mu = \left.\frac{\mathrm{d}F_{\mathrm{FH}}}{\mathrm{d}\Phi}\right|_{\Phi_\infty} \qquad (3)$$

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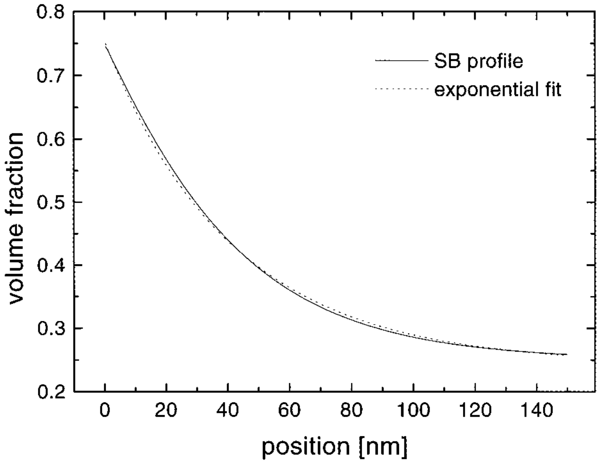

Figure 1. Comparison of a Schmidt–Binder profile with an exponential decay function. The Schmidt–Binder profile was calculated for a hPS/dPS blend of molecular weight $1.95 \cdot 10^6$ each and an annealing temperature of 245 °C.

where Φ_∞ is the bulk concentration far from an interface. The restriction to the square gradient term makes sense only in the long wavelength limit, where the concentration variation on the scale of the gyration radius, R_{gyr}, is small:[12]

$$a^2(\nabla\Phi)^2 \ll N^{-1} \tag{4}$$

Here

$$\mathrm{a} = \sqrt{(1-\Phi){\sigma_{\mathrm{A}}}^2 + \Phi{\sigma_{\mathrm{B}}}^2} \tag{5}$$

is a weighted statistical segment length (with statistical segment lengths of the single components defined via the radius of gyration, ${R_{\mathrm{gyr}}}^2 = N\sigma^2/6$), and N, the degree of polymerization.

Schmidt and Binder assumed that the bare surface energy $f_{\mathrm{S}}^{(\mathrm{b})}$ depends on the local volume fraction $\Phi_1 = \Phi(z = 0)$ at the surface only. This allows an analytical solution for the composition profile $\Phi(z)$ that minimizes the free energy. Variational calculus yields

$$\mathrm{z} = \frac{a}{6}\int_{\Phi_1}^{\Phi(z)} \frac{\mathrm{d}\Phi}{\sqrt{\Phi(1-\Phi)[F_{\mathrm{FH}}(\Phi) - F_{\mathrm{FH}}(\Phi_\infty) - \Delta\mu(\Phi - \Phi_\infty)]}} \tag{6}$$

As the boundary condition at the surface enters only through the lower integration limit for the short range forces assumed here, the profile is exclusively determined by the bulk properties of the mixture. For a bulk concentration Φ_∞ far from the binodal compositions $\Phi_{\mathrm{coex},1}$ and $\Phi_{\mathrm{coex},2}$, this mean field theory predicts a decay from the surface concentration Φ_1 to the bulk concentration Φ_∞, which is very close to exponential (Figure 1).

Chen et al.[13] and Jones[14] tried to explain the observed flattening of the profile in the direct vicinity of the surface by inclusion of long-range forces into the Schmidt–Binder theory. Although these long-range interactions led to a flattening over a distance of a few angstroms, their effect does not suffice to explain the observed deviations quantitatively.

Another important assumption inherent to the Schmidt–Binder approach is the square gradient approximation: the theory is only valid for rather shallow concentration gradients. Approaching the surface from the bulk, this gradient increases, and the theory might not predict the correct concentration profile in the vicinity of the surface. Genzer et al.[15] constructed a self-consistent field (SCF) theory that removes the square gradient approximation but retains the mean field approximation. The differences in the Schmidt–Binder and self-consistent field profiles turned out to be largest near the surface, where the long wavelength assumption is not justified anymore. The SCF theory does not, however, lead to a flattening of the profile as indicated in the earlier experiments.[6, 7]

3. Experimental Section

3.1. Materials. In our experiments we used two blends of polystyrene (hPS) and its deuterated counterpart (dPS). The first blend consisted of deuterated and protonated polystyrene of molecular weight $1.95 \cdot 10^6$ each (abbreviated dPS 1.95M/hPS 1.95M), with a polydispersity of 1.04 and 1.14, respectively. The average volume fraction (Φ_{dPS}) of deuterated polystyrene was 30%. The constituents of the second blend had molecular weights of $1.3 \cdot 10^6$ (dPS) and $1.15 \cdot 10^6$ (hPS) (abbreviated dPS 1.3M/hPS 1.15 M), with a polydispersity of 1.1 and 1.09, respectively. In this blend Φ_{dPS} was 33%. All of the polymers were obtained from Polymer Labs (Church Stretton, U.K.). Polished silicon wafers (P-type, ⟨100⟩ oriented, 6–13 Ω/cm) were obtained from the Institute of Electronic Materials Technology Warsaw. The toluene used was analytical grade (Frutarom Ltd.).

3.2. Sample Preparation. The polymers were dissolved in toluene and spin cast on thin silicon wafers (about 1 by 1 cm). The resulting film thickness was about 300 nm. After allowing the residual toluene to evaporate at room temperature for 1–2 days, the samples were sealed in glass ampules in a vacuum of $p < 10^{-4}$ Torr and subsequently annealed. The dPS 1.95M/hPS 1.95M samples were annealed at 245 °C for 8 days, the dPS 1.3M/hPS 1.15M samples at 180 °C for 23 days.

The thermodynamic properties of dPS/hPS blends have been examined using small angle neutron scattering (SANS) measurements[16] via the random phase approximation and in a different approach using NRA via determination of the binodal.[17] The values of the interaction parameter χ using the two approaches are similar, though the SANS-deduced value, $\chi_{\mathrm{SANS}}(T) = 0.204/T - (3.04 \pm 0.05) \cdot 10^{-4}$, is somewhat lower than the interaction parameter deduced from the coexistence curve.[18] In what follows we use the SANS value, which provides a lower limit on the bulk correlation length.

Figure 2 shows the phase diagrams of the two blends. The annealing coordinates were chosen to be close to the critical temperature (T_{c}) to get a sufficiently long correlation length. Yet, they had to be clearly in the one-phase region of the phase diagram to rule out the possibility of complete wetting.

3.3. Controls for Polymer Degradation. To ensure that no degradation had occurred in our samples, control measurements were performed. Figure 3 shows the concentration profiles of two samples of dPS 1.95M/hPS 1.95M annealed at 245 °C for 8 and 25 days, respectively. The differences between the profiles are within the experimental scatter and show, moreover, that the chosen annealing time of 8 days for the experiments above was sufficiently long to reach equilibrium. Additionally, GPC measurements of pure dPS 1.95M and hPS 1.95M, annealed at a pressure of $p < 10^{-4}$ Torr at 245 °C for 0, 8, and 13 days, were kindly undertaken by Dr. L. J. Fetters. Within the experimental scatter for these high molecular weight polymers, the method revealed no indication of thermal degradation.

3.4. Measurements. The measurements of the resulting depth profiles were done with nuclear reaction analysis (NRA).[9,10] NRA is a technique to obtain concentration versus depth profiles of labeled polymer chains in films up to several microns thick with a spatial resolution of down to a few nanometers: A monoenergetic ^{3}He beam, incident on the sample under a well-defined angle, loses energy while pen-

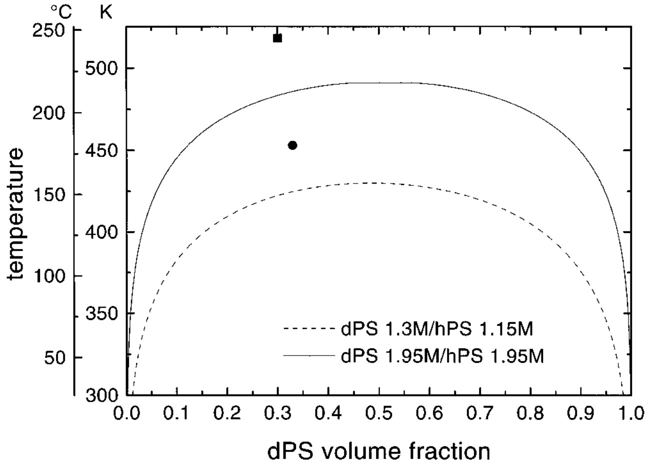

Figure 2. Coexistence curves for the dPS 1.95M/hPS 1.95M and the dPS 1.3M/hPS 1.15M blend. The coexistence values were calculated with a common tangent construction to the Flory-Huggins free energy of mixing, using an interaction parameter as described in the text. The filled square and circle mark the annealing coordinates for the dPS 1.95M/hPS 1.95M and the dPS 1.3M/hPS 1.15M blend, respectively.

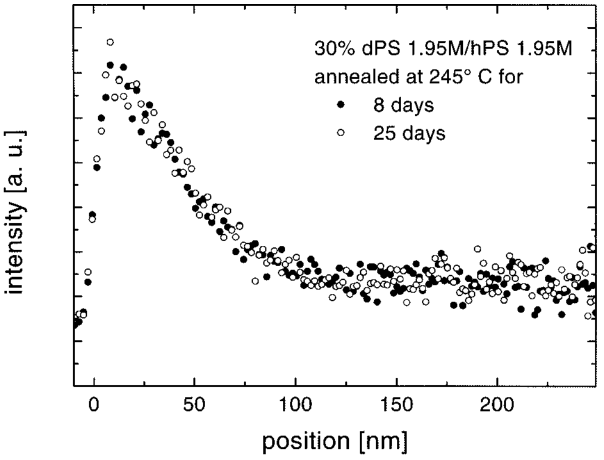

Figure 3. Concentration profiles of two dPS 1.95M/hPS 1.95M samples annealed at 245 °C for 8 and 25 days, respectively.

etrating the polymer film. When a ^{3}He particle hits a deuterium atom on one of the labeled polymer chains, the nuclear reaction $^3\mathrm{He} + {}^2\mathrm{H} \rightarrow {}^4\mathrm{He} + {}^1\mathrm{H} + 18.352$ MeV occurs with a certain probability. The energy of the detected reaction products after leaving the sample can be related to the depth at which the reaction took place through the known energy loss rate of the incoming and outgoing particles as they traverse the sample. The concentration of labels at a certain depth can then be deduced from the number of counts in the respective energy interval.

Our measurements were performed with the van de Graaff accelerator at the Weizmann Institute with a 700 keV ^{3}He beam impinging the sample at a grazing angle of 8°. The protons generated by the nuclear reaction were detected in backscattering geometry at an angle of 176° to the incoming beam. The resulting resolution σ (Gaussian half-width) at the sample surface is 5.5 nm.

4. Results and Discussion

In the first step of our experimental analysis, Schmidt–Binder profiles, calculated according to eq 6, were convoluted with the depth-dependent system resolution, $\sigma(x) = 5.5$ nm $\exp(x/116$ nm$)$, and fitted to the converted spectra. A statistical segment length of $a = 6.7$ Å was used in the calculations. The resulting fits are shown in Figure 4. Within the scatter the Schmidt–Binder model describes the experimental data rather well.

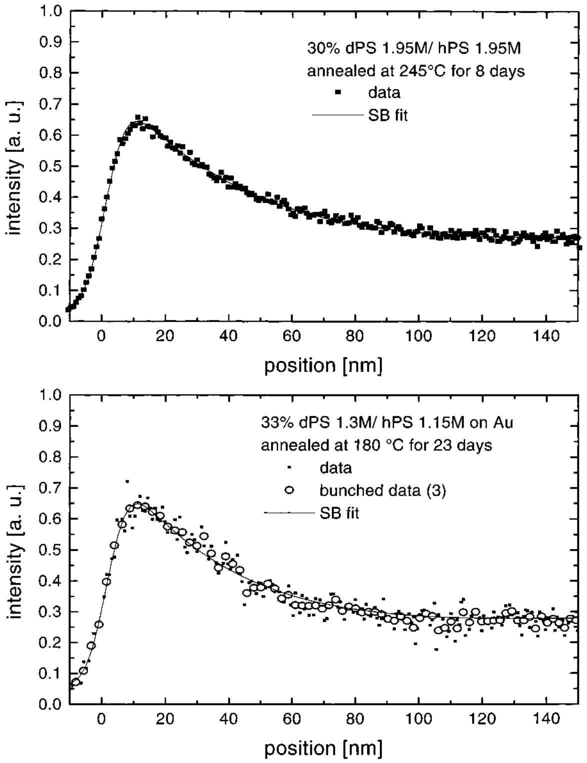

Figure 4. NRA profiles of the dPS 1.95M/hPS 1.95M and dPS 1.3M/hPS 1.15M blend (filled squares). To reduce the scatter of the latter sample, three of the original data points were bunched to one new data point (open circles). The drawn lines are fits of the Schmidt–Binder profile (6), convoluted with the depth-dependent system resolution.

Subsequently we fitted profiles which featured a flattened region, i.e., a constant volume fraction of deuterated polymer in the near-surface region, to the data of the dPS 1.95M/hPS 1.95M samples. An average of three measurements of identical samples was used for the further analysis to reduce the scatter of our experimental data. To keep the time required for this multi-parameter fit within reasonable limits, we restricted ourselves to an exponentially decaying profile of the form

$$\Phi(z) = \begin{cases} \Phi_1 & 0 < z \le z_0 \\ \Phi_\infty + (\Phi_1 - \Phi_\infty)e^{-(z_0 - z)/\xi_b} & z > z_0 \end{cases} \qquad (7)$$

The form of this profile prior to convolution is shown as the inset to Figure 5. The deviations of the exponentially decaying profile from the Schmidt–Binder profile calculated according to eq 6 are of minor importance, as had been shown in Figure 1. In the fits the width z_0 of the flat region was kept at fixed values and only the other parameters were allowed to vary. For each value z_0 the deviation of the profile (7) from the experimental data was calculated as

$$\mathrm{dev} = \sum_i (y_i^{\mathrm{fit}} - y_i^{\mathrm{data}})^2 \qquad (8)$$

where only the data points within the range from −10 to 150 nm are taken into account in the summation. y_i^{fit} and y_i^{data} are the values of the fitting function and the experimental data at the depth, x_i, respectively. The deviation as a function of the width z_0 of the flat is

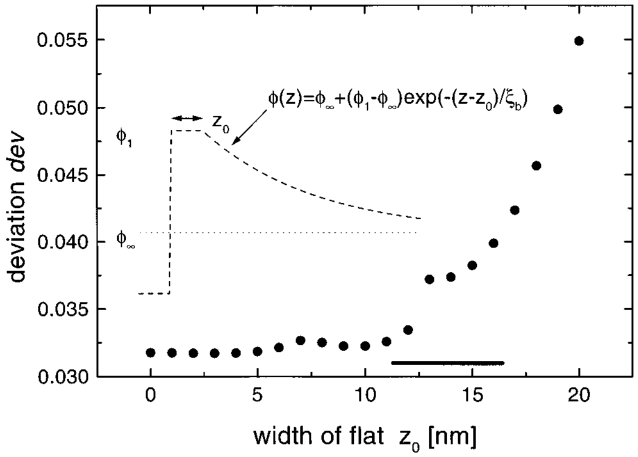

Figure 5. Deviation of the fits of (7) to the data of a dPS 1.95M/hPS 1.95M sample as function of the width z_0 of the flat region. The bar indicates a flattening of one-third to one-half of the bulk correlation length. The inset shows the form of the unconvoluted profile (eq 7) used (after convolution with the system resolution) to fit the data.

displayed in Figure 5. The quality of the fits, as indicated by the magnitude of the deviation, remains approximately constant for a width z_0 of the flat region that is smaller than the FWHM of our system's resolution at the surface (13 nm). Deviations of the experimental data from the model profile are not resolvable within that range. As soon as the width of the plateau exceeds this value, however, the quality of the fits decreases sharply and monotonically. This reveals an increasing disagreement between the experimental and theoretical profiles for increasing plateau width. The bar at the z_0-axis marks a flattening of one-third to one-half of the bulk correlation length ξ_b, as suggested by Norton et al.[7] based on their neutron reflectometry experiments with poly(ethylene propylene). The bulk correlation length in our system is given as[19]

$$\xi_b = \frac{a}{6}\Big/\sqrt{\frac{1-\Phi}{2N_{\mathrm{dPS}}} + \frac{\Phi}{2N_{\mathrm{hPS}}} - \chi\Phi(1-\Phi)} \qquad (9)$$

where a = 6.7 Å is the statistical segment length of polystyrene. This yields a value of 32.4 nm for the higher molecular weight blend. As Figure 5 clearly shows, a flattening of this magnitude is quite inconsistent with our data.

Figure 6 gives a direct comparison of convoluted fits of the profiles of eq 7 to our experimental data with plateau widths z_0 of 0, 10, and 17 nm. The plot illustrates that plateau widths z_0 smaller than the 13 nm FWHM of the system's resolution are hardly resolvable. Any flattening (were it present) exceeding the FWHM of the surface resolution, on the other hand, could be clearly distinguished within the scatter.

We have no clear explanation for the discrepancy between our directly measured composition profiles showing that there is no flattening (or that, if there is a flattening, it is less than one-third of the correlation length ξ_b) and those of Norton et al.[7], which suggests a flattening on the order of ξ_b/3 to ξ_b/2, and of Zhao et al.[6] The Norton et al.[7] results are based on a fit to neutron reflectometry data, which, while having higher intrinsic spatial resolution than NRA, is indirect and can be influenced by the nature of the profile in thin films in ways that may be difficult to detect. For example, a small enrichment at the solid−polymer interface could affect the fit to the data significantly.[11] The Zhao et al.[6] data were obtained using a direct profiling approach (dynamic SIMS). One possible reason for the flattening they report, as suggested in their paper, is that it may be a sign of incipient wetting at the longest times by the surface-preferred phase. Some support for this comes from a recent study suggesting that dynamics of wetting from polymer mixtures is an extremely slow process.[20]

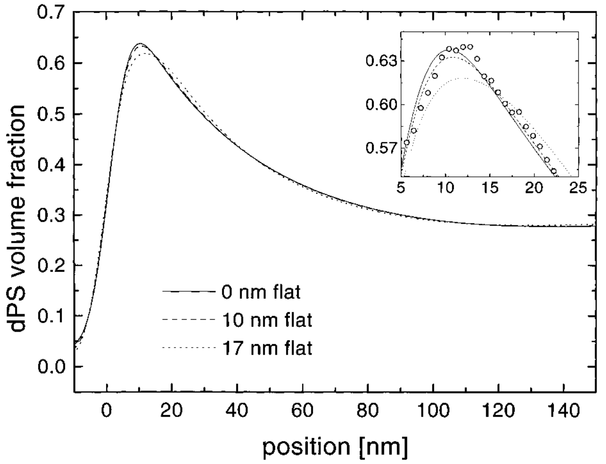

Figure 6. Direct comparison of three convoluted fits of (7) to our experimental data. The plateau width z_0 is 0, 10, and 17 nm, respectively. While the two profiles with a width of the flat region smaller than the FWHM of the system's resolution at the surface (13 nm) differ only slightly from each other, the difference in profile shape of the 17 nm flat fit is well-resolvable within our resolution. The inset shows a magnification of the profiles in the near-surface region together with the experimental data (averaged over five adjacent data points).

5. Conclusions

Within our experimental resolution our measured surface enrichment profiles from an isotopic hPS/dPS blend agree rather well with the predictions of the Schmidt−Binder mean field theory. While we cannot draw any conclusions about a flattening of the profile over a width less than our spatial resolution at the surface (13 nm FWHM), our data show that, if any flattening exists, it has an upper bound of ξ_b/3, where ξ_b is the bulk correlation length of the polymer mixture. This conclusion appears to be at variance with the recent suggestion by Norton et al.,[7] based on a neutron reflectometry study indicating a flattening of the enrichment profile at the surface on the order of ξ_b/3 to ξ_b/2.

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(12) In the present study this condition is approximately correct, justifying analysis in terms of the Schmidt−Binder approach. Thus from Figure 4 (top), for example, or from the corresponding unconvoluted profiles (e.g. Figure 1), we see a $\delta\phi \approx 0.3$ over a $\delta(\text{depth}) \approx 40$ nm for the enrichment profile decaying from the surface. This yields $\nabla\phi \approx 6 \cdot 10^{-3}$ nm^{-1}, compared with $(1/R_{\text{gyr}}) \approx (2-2.5) \cdot 10^{-2}$ nm^{-1} for the polymers used, which is $\approx(3-4)\nabla\phi$. That is, the long wavelength limit of eq 4 is reasonably well-obeyed.

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(18) The authors[15] themselves give a value of $\chi_{\text{SANS}} = (0.20 \pm 0.01)/T - (2.9 \pm 0.4) \cdot 10^{-4}$, which results in an uncertainty in T_c of more than 100 K. Our own fit yields $\chi_{\text{SANS}}(T) = 0.204/T - (3.04 \pm 0.05) \cdot 10^{-4}$ and better fits their reported experimental data. The deviations of the reported values may be due to rounding errors in the fit. The resulting differences in χ and ξ_b are in any case small.

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