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The interface between immiscible polymers studied by low-energy forward recoil spectrometry and neutron reflectivity

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Abstract

The superb depth resolution of low-energy forward recoil spectrometry, (LE-FRES), is demonstrated by measuring the interfacial profile between 1,4-polybutadiene (PB), and deuterated polystyrene (dPS), at 175°C. To enhance depth resolution, the top dPS layer is 'thinned' by ion sputtering, prior to LE-FRES analysis, to achieve a resolution of 13 nm at the interface. An interfacial width of 6.0 ± 3.5 nm is measured. To compliment this study, neutron reflectivity (NR) is used to determine the interfacial volume fraction profile between PB and an isotopic mixture of polystyrene (dPS:PS) having a dPS volume fraction of 0.30. After annealing at 175°C, the interface broadens to 3.3 nm. However, no interfacial segregation of dPS or PS is observed suggesting that the difference between the PB–dPS and PB–PS interaction parameters (χ) is insufficient to drive interfacial segregation. Using a self-consistent field model (SCF) and known values of χ, the width is calculated to be 2.2 nm. By adding capillary wave broadening, this width increases to 2.8 nm, in better agreement with the NR value. In agreement with the NR measurement, the SCF model predicts no segregation of dPS or PS. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polystyrene; polybutadiene; Immiscible polymers; Interface

1. Introduction

Studies of polymer blends are currently of widespread commercial and fundamental interest. Because many plastics contain a mixture of incompatible polymers, the mechanical properties of such a multiphase polymer blend, are directly related to the strength of the interface between phases. On a molecular level, the interfacial strength depends on chain interpenetration and entanglement, and is thus, directly related to the width of the interface [1]. This width, in turn, is controlled by thermodynamics, in particular the segment–segment interaction parameter.

The technological importance of optimizing interfacial strength, has motivated the development of theoretical tools for predicting the concentration profiles near an interface. In the 1970s, Helfand and Tagami developed the first rigorous description of the interface between two incompatible polymers [2,3]. Using a self-consistent field (SCF) theory they derived analytical expressions for the interfacial width, w_∞, and interfacial tension, χ_∞, for polymer pairs with the same segment length in the infinite molecular weight limit. They found that w_∞ and γ_∞ vary as $\chi^{-1/2}$ and $\chi^{1/2}$, respectively, where χ is the Flory–Huggins interaction parameter. Thus, the interfacial width is predicted to range from about 2 to 6 nm for incompatible polymer blends (i.e. $10^{-1} > \chi > 10^{-2}$). Recently, Broseta et al. [4] and Tang and Freed [5] derived corrections to w_∞ and γ_∞ due to finite molecular weight. Because these corrections were relatively small (1%–5 %), the main trends predicted by the Helfand–Tagami theory remain valid.

From the discussion above, it is apparent that the χ parameter plays an important role in both interfacial structure and blend thermodynamics. In principle, χ can be determined, from measurements of the interfacial tension, or interfacial width, between two incompatible polymers. The first approach was adopted by Anastasiadis and coworkers [6,7], who used the pendant drop technique and digital image processing to determine the interfacial tension. Recently neutron reflectivity (NR) has proven to be a very reliable technique for measuring interfacial widths, and therefore χ [8–16]. Ion beam profiling techniques, such as forward recoil spectrometry (FRES), have also become valuable tools for studying polymer interface problems such as, surface enrichment in polymer blends [17]. However, conventional FRES lacks the depth

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Table 1
Polymer characteristics. Molecular parameters of polymers; $\overline{M}_w$, $\overline{M}_w/\overline{M}_n$, and N denote the weight-average molecular weight, the polydispersity index (both as reported by vendor) and the number of segments, respectively

Polymer	$\overline{M}_w$ (g/mol)	$\overline{M}_w/\overline{M}_n$	N	Source
PB[a]	270 000	1.32	5029	Scientific Polymer Products
PS	575 000	1.06	5521	Pressure Chemical
DPS	550 000	1.05	4901	Polymer Laboratories

[a] The microstructure of PB (as reported by vendor) is: *cis* 49.8%, *trans* 43.5% and vinyl 6.7%.

resolution to quantify narrow (about 10 nm) interfacial widths. Recently, we have shown that the depth resolution of conventional FRES can be greatly improved from about 80 to 13 nm at the sample surface by combining a low energy, ion beam with a glancing geometry. We call this technique low-energy forward recoil spectrometry (LE-FRES) [18]. One goal of this paper is to demonstrate the superb depth resolution of LE-FRES by measuring the interfacial profiles between 1,4-poly(butadiene) (PB) and deuterated polystyrene (dPS).

In both LE-FRES and NR, contrast between polymers is achieved by labelling one polymer with deuterium. Thus, the influence of isotopic labelling on blend thermodynamics must be considered. The first evidence that deuterium labelling may affect the phase behavior, was reported for poly(-vinyl methyl ether) and polystyrene [19,20]. Here, replacing PS by dPS of the same chain length produces a 40°C increase in the lower critical solution temperature. Similar dramatic isotope effects have been reported for other systems. Bates and co-workers found that deuterium labelling, causes phase separation in high molecular weight, dPS:PS blends [21]. For strongly incompatible polymers, the interaction parameters have also been found to depend on isotopic labelling as reported by Russell [22] for poly(methyl methacrylate) (PMMA) and PS. In regard to this paper, the influence of isotopic labelling on PB/PS miscibility is still unclear. Atkin et al. [23] reported a dPB:PS critical temperature, which was about 13°C greater than the analogous PB:PS pair. Tomlins and Higgins [24] found that the interaction parameter depends on the isotopic labelling of PS in PB/PS blends. On the other hand, Lin and co-workers [25] found that isotope substitution of PS does not change the PB/PS thermodynamics. As a second goal of this paper we will investigate interfacial segregation in PB/dPS:PS blends, in order to determine whether the isotope labelling of PS has an influence on the PS/PB interaction parameter.

In our system, an isotopic mixture of polystyrene is placed in contact with polybutadiene. This bilayer geometry results in an interface between homopolymer (A) and a binary polymer mixture (B:C). A comprehensive theory of the A/B:C interface for the infinite molecular weight case was developed by Helfand [26] and later refined by Yoon and Pak [27]. For long polymer chains, the entropic terms in the total free energy density are negligible, and the free energy is determined mainly by the enthalpy. Thus the free energy density of a high-molecular weight A/B:C system is:

$$\frac{f}{\rho_0 k_B T} = \chi_{AB}\phi_A\phi_B + \chi_{AC}\phi_A\phi_C + \chi_{BC}\phi_B\phi_C \qquad (1)$$

where ρ_0 is the lattice density, k_B is the Boltzmann constant, T is the absolute temperature, ϕ_k is the volume fraction of polymer *k*, and χ_{jk} is the Flory–Huggins interaction parameter between *j* and *k* segments. In general, B and C are miscible with each other, but have different repulsive interactions with A. If the repulsion between A and B is weaker than that between A and C, B will segregate to the A/B:C interface. This interfacial segregation will be energetically favored, because it lowers the total free energy of the system, and also decreases the interfacial tension. As a result of the segregation, the interfacial region in the A/B:C system broadens, leading to an increase of interfacial width. On the other hand, no segregation of B or C takes place if the interactions of B and C with A are the same. Although segregation depends in part on χ_{BC}, the primary parameter that controls the interfacial properties is the difference $\chi_{AC} - \chi_{AB}$. The above conclusions are generally valid as long as the numbers of segments of B and C are the same and/or very large. For B:C mixtures with very different segment numbers, the contribution of the entropy of mixing becomes appreciable. Recently we have presented a self-consistent mean field (SCF) model of A/B:C interfaces which accounts for the effect of finite polymer molecular weights (numbers of segments) [28]. We have also carried out the first experimental study of polymer segregation at the A/B:C interface, and found good agreement between these measurements and the SCF predictions [29,30].

This paper has two objectives. First, we demonstrate the superb depth resolution of LE-FRES by measuring the volume fraction profiles of dPS in the PB/dPS system. Second we apply NR to measure the polymer volume fraction profiles at the interface between PB and a dPS:PS mixture. From the latter measurement we attempt to determine the difference between the interaction parameters for PB/PS and PB/dPS. We compare the experimental results from NR with concentration profiles calculated using SCF and show that experiment and theory are in good agreement.

2. Experimental

The polymers of interest were 1,4-polybutadiene (PB), polystyrene-d_8 (dPS) and polystyrene (PS). To simplify nomenclature they are denoted as A (PB), B (dPS) and C (PS). The polymer characteristics are listed in Table 1. Two sets of samples were prepared. A/B and A/B:C bilayers were prepared for LE-FRES and NR studies, respectively. Substrates for NR were silicon wafers 2 in. in diameter

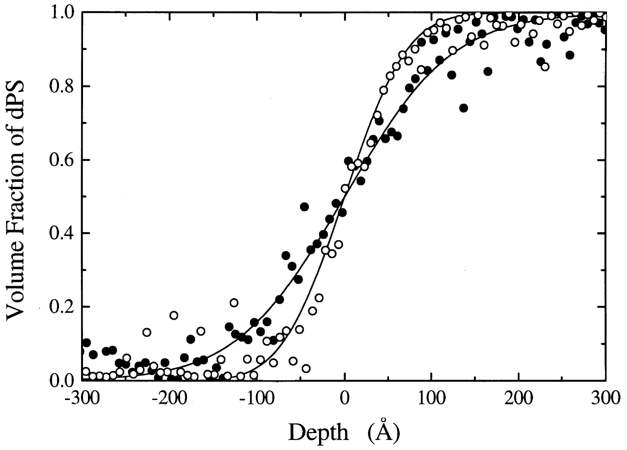

Fig. 1. Volume fraction profiles of dPS across the PB/dPS interface as determined using LE-FRES for the as-cast sample (open circles) and a sample annealed at 175°C for 7 days (solid circles). The solid lines are the best fits to the hyperbolic tangent function convoluted with the instrumental resolution of FWHM = 13 nm.

and 4.5 mm thick. For LE-FRES, the silicon wafers were about 1.5 × 1.5 cm and 10 mm thick. Substrates were first rinsed in a water–hydrofluoric acid solution to remove native oxide, washed in deionized water, and dried. The first polymer layer, PB, was spin-coated from toluene solution, and then dried under vacuum (1.4×10^{-2} Pa) at 60°C overnight. The ellipsometric thickness, 396 nm, was chosen to reduce reflectivity from the silicon/PB interface. For LE-FRES, the top layer, dPS, was spin-coated onto a microscope glass slide, floated off onto a bath of de-ionized water, and picked up with a silicon wafer covered by the PB layer. For the NR samples, the second layer contained a mixture of dPS and PS, having a dPS volume fraction $\phi_{\mathrm{dPS},\infty} = 0.30$. For the NR and LE-FRES samples, the top layers were 55 nm or 60 nm, respectively. Samples were allowed to dry overnight, under vacuum, at 50°C, to remove residual solvent and water, and subsequently annealed at 175°C.

The LE-FRES measurements were carried out on a model 5SDH Pelletron tandem accelerator (National Electrostatic Corporation, WI), interfaced with a custom-designed scattering chamber at the ion beam facility, of the Laboratory for Research on the Structure of Matter, at the University of Pennsylvania. The technique has been described elsewhere [18]. Briefly, in LE-FRES, 1.3 MeV $^4\mathrm{He}^+$ ions impinge on a target at an angle θ with respect to the sample normal. As a result of collisions between He and the target atoms, light nuclei (i.e. H and D) recoil from the sample and travel towards a detector placed at the angle of 150° with respect to the incident beam. Helium nuclei are also forward scattered after colliding with heavy target and substrate nuclei (i.e. C and Si). To prevent the flux of forward scattered He from masking the H and D signals, a 4.5 μm thick Mylar™ stopper foil is placed in front of the detector. The resultant LE-FRES spectrum of recoiled yield versus detected energy is then converted to a depth profile for both D and H nuclei.

In our LE-FRES set-up, the depth resolution is greatly improved by using a glancing exit geometry ($\theta < 75°$) to increase the H/D path length in the target. For $\theta = 62.5°$, the geometry in this paper, the depth resolution (FWHM) is ca. 13 nm near the sample surface [18]. This resolution degrades as one probes deeper beneath the surface, because of multiple scattering events between the incident/recoiled ions and target nuclei.[2] To maximize the depth resolution, the dPS/PB samples were ‘thinned’ prior to LE-FRES analysis by sputtering the top dPS film. After tilting by 45° with respect to the sample normal, a 3 keV Ar beam was rastered across an area of about 8 × 8 mm. The vacuum was 5.3×10^{-3} Pa. To maintain a uniform dPS thickness, a very low sputtering rate of about 0.7 nm/min was used. After sputtering, the ellipsometric thickness was about 25 ± 1.5 nm.

The NR measurements were performed at the POSY II reflectometer of the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory in Argonne, IL [31]. This technique has been described extensively elsewhere [8]. Briefly, a neutron beam with a broad wavelength distribution (0.5–1.2 nm) impinges on the sample at a well-defined glancing angle (usually 0.5°–3.0°). Because the scattering length, b, of deuterium is much higher than that of hydrogen, labelling one of the components with deuterium provides contrast for NR. The intensity of the specularly reflected neutrons contains information about the scattering length density (b/V) profile as a function of the perpendicular component of neutron momentum. From this (b/V) profile the polymer volume fraction profile can be determined. NR has superb depth resolution (better than 1 nm) and is most sensitive to abrupt changes in (b/V). This makes NR very suitable for studying narrow polymer interfaces. However, because phase information is lost during the NR measurement, the experimental data cannot be directly converted from reciprocal space into real space. Instead, the experimental reflectivity curves are compared with simulations based on an assumed (b/V) profile. Iterative comparison leads to a best-fit profile.

3. Results and discussion

To demonstrate its superb depth resolution, LE-FRES was used to determine the polymer volume fraction profiles and interfacial width in the PB/dPS system [32]. The interfacial width, w, is defined by the slope at midpoint of the volume fraction profile [2,3]:

$$w = \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^{-1}_{\phi=0.5} \tag{2}$$

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[2] For example, the depth resolution of LE-FRES at a depth of 100 nm below the surface of PS was about 25 nm. For details see Ref. [18].

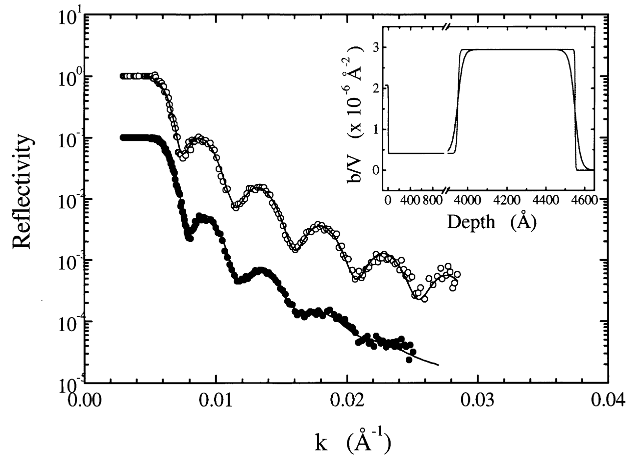

Fig. 2. Neutron reflectivity data from the silicon/A/B:C sample as-cast (open circles) and after 4 days at 175 °C (solid circles). The solid lines represent the fits to experimental data that were calculated using the scattering length density profiles shown in the inset of the figure.

The value of w can be determined from the experimental measurements by subtracting the roughness between the two polymer films in the as-cast sample, a_0, from the interfacial width measured after the interdiffusion, a_1, so:

$$w = \sqrt{a_1^2 - a_0^2} \qquad (3)$$

Fig. 1 shows the volume fraction profiles of dPS in the as-cast sample (open circles) and a sample that was annealed at 175°C for 7 days (solid circles). The solid lines were obtained by convoluting a profile described by $\tanh(2x/a_i)$ with a Gaussian resolution function of FWHM = 13 nm. The values of a_0 and a_1 extracted from the best fits were $a_0 = 3.0 \pm 1.5$ nm and $a_1 = 6.7 \pm 2.5$ nm, respectively, which using Eq. (3) gives $w = 6.0 \pm 3.5$ nm. In addition to demonstrating the excellent depth resolution of LE-FRES, this measurement shows that ion beam techniques can be used to detect features that are comparable to, or smaller than, a single polymer chain.

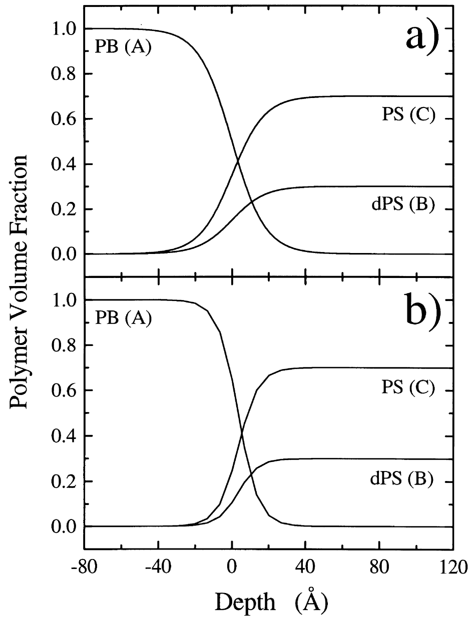

Fig. 3. The volume fraction profiles of polymers across the A/B:C interface (a) as determined from the NR data for the sample annealed at 175 °C for 4 days and (b) calculated using the SCF model with the parameters listed in the text.

A numerical SCF model [28] was used to calculate the polymer volume fraction profiles and interfacial width at the A/B interface. The input parameters include the numbers of segments from Table 1 and the experimental value of $\chi_{\mathrm{PB/PS}}$. It has to be noted that the actual value of $\chi_{\mathrm{PB/PS}}$ depends on the microstructure of PB. We use the $\chi_{\mathrm{PB/PS}}$ reported by Rigby et al. [33] because their PB has a similar microstructure. For the value of $\chi_{\mathrm{PB/PS}} = 5.80 \pm 0.06 \times 10^{-2}$ at 175°C, the calculated interfacial width is $w = 2.2$ nm.[3] Because of the large uncertainty in the LE-FRES measurement, the difference between the measured and predicted w, is difficult to address. For such narrow interfaces, higher resolution techniques like NR are needed to provide a rigorous test of the SCF model.

Let us now address the second objective of this work, namely the question of how the interactions between PB and PS are affected by the isotopic labelling of PS. For an A/B:C sample, Fig. 2 shows the reflectivities from an as-cast sample (open circles), and one annealed at 175°C for 4 days (solid circles). The (b/V) profiles used to simulate the reflectivity data are shown in the inset to Fig. 2. Relative to the as-cast sample, the reflectivity fringes broaden after annealing because the A/B:C interface becomes more diffuse. For the annealed sample, the reflectivity is damped, in part, because of surface roughness. We will return to this point later.

The best fits to the reflectivity curves, were obtained by minimizing the χ^2_{fit} fit. The values of χ^2_{fit} were 1.9 and 2.8 for the fits to the reflectivities from the as-cast and annealed samples, respectively. In the inset of Fig. 2, the silicon/PB, A/B:C, and air/mixture interfaces are located at 0, 396 and 455 nm, respectively. For the as-cast sample, the surface roughness and interface roughness are 1.0 and 1.5 nm, respectively. After annealing the interface broadens to $a_1 = 3.6$ nm. Using Eq. (3), the interfacial width is $w = 3.3$ nm. This value is in fair agreement with measurements by Geoghegan and co-workers [16] who report dPB/PS widths of 2.0–3.0 nm. The (b/V) profile across the A/B:C interface is symmetrical and changes smoothly from 0.415×10^{-6} Å^{-2} for pure A to 2.946×10^{-6} Å^{-2} for B:C with $\chi_{\mathrm{B},\infty} = 0.30$. Considering that the $(b/V)_{\mathrm{dPS}}$ ($= 6.515 \times 10^{-6}$ Å^{2}) is much larger than $(b/V)_{\mathrm{PB}}$ ($= 0.415 \times 10^{-6}$ Å^{-2}) and $(b/V)_{\mathrm{PS}}$ ($= 1.4177 \times 10^{-6}$ Å^{-2}), the (b/V) profile is determined mainly by $(b/V)_{\mathrm{dPS}}$. In Fig. 2, note that the (b/V) profile shows no excess or depletion of the

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[3] Using the expression of w from Ref. [2] for the case of two immiscible polymers with infinite molecular weights, we obtain $w = 2.3$ nm, which is almost identical to the value calculated from the numerical SCF model.

B component at the A/B:C interface. From this observation one may deduce that the interaction parameters between the PB/dPS and PB/PS pairs are not different enough to produce interfacial segregation at the A/B:C interface.

For comparison, a numerical SCF model of the A/B:C interface [28] was used to determine the interfacial profile for each species. In these calculations χ_{AC} ($= \chi_{PB/PS}$), and χ_{BC} ($= \chi_{dPS/PS}$)[4] were held constant, whereas χ_{AB} ($= \chi_{PB/dPS}$) was varied from 5.51×10^{-2} ($0.95\chi_{AC}$) to 6.09×10^{-2} ($1.05\chi_{AC}$). From the SCF volume fraction profiles, the (b/V) profiles and, consequently, the reflectivities were calculated and compared with the experimental data. Good agreement was found for $\chi_{AB} = (5.80 \pm 0.05) \times 10^{-2}$, which is exactly the value reported in Ref. [33]. Thus within experimental error, the PB–dPS and PB–PS interaction parameters are approximately the same, suggesting that the deuteration effect (being about two orders of magnitude weaker) plays a minor role in this interface problem. It is interesting to note that segregation at the air/dPS:PS surface is readily observed under similar conditions [13].

The experimental and calculated volume fraction profiles across the A/B:C interface are shown in Fig. 3a and b, respectively. Their comparison reveals that the interfacial region in the latter case is narrower. Indeed the value of w extracted from the SCF is 2.2 nm, about 30% less than the experimental value, 3.3 nm. It must be noted that similar discrepancies between the predicted and observed interfacial widths were reported for the dPS/PMMA interface [9,10]. As pointed out by several authors [34], the polymer/polymer interface can also be broadened by thermally induced capillary waves, which force the interface to fluctuate around its average position. Recently Shull et al. [35] showed that the measured interfacial width, contains contributions from the ‘static’ interfacial width and capillary wave broadening. We have adapted their approach to explain the difference between the predicted, and observed, interfacial widths. The mean-squared deviation of the position of the interface from its average value can be described as [35,36]:

$$\langle \sigma^2 \rangle = \frac{k_B T}{4\pi\gamma} ln\left[\frac{1 + 2(\pi l/\lambda_{min})^2}{1 + 2(\pi l/\lambda_{max})^2} \right] \qquad (4)$$

where γ is the interfacial tension, l is a capillary constant, and λ_{min} and λ_{max} are the minimum and maximum values of the capillary fluctuations, respectively. For many cases, l dominates and Eq. (4) becomes:

$$\langle \sigma^2 \rangle = \frac{k_B T}{2\pi\gamma} ln\left[\frac{\lambda_{max}}{\lambda_{min}} \right] \qquad (5)$$

Following Shull et al. [35] we approximate the maximal wavelength cut-off by the lateral coherence length, which is on the order of 10^{-6} m for the neutron beam [8]. In addition, the λ_{min} value is taken as the calculated interfacial width. Using $\gamma = 2.46\ \mathrm{mJ/m^2}$ from SCF, $\lambda_{min} = 2.2$ nm, and $\lambda_{max} = 10^3$ nm, the root mean-square displacement, $\langle \sigma^{1/2} \rangle$, is 1.6 nm. Finally, convolution of the ‘static’ interfacial profile from SCF with a Gaussian function of FWHM equal to $\langle \sigma^2 \rangle^{1/2}$ yields an interfacial width of 2.8nm. Thus, the addition of capillary broadening, brings the calculated width into better agreement with the NR value, $w = 3.3$ nm. Capillary broadening has also been invoked, to explain recent measurements of the interfacial width between coexisting phases [37], and strongly incompatible polymer pairs [38].

Even though the SCF model is in relatively good agreement with NR experiments, Monte Carlo simulations show that SCF predictions slightly underestimate the interfacial width between two incompatible polymers [39]. This may be the reason why the SCF PB/dPS:PS width, corrected by capillary broadening, is still smaller than the experimental value. Müller and co-workers [40] have addressed the use of capillary wave broadening to explain the discrepancies between the experimental and calculated interfacial widths. Although they show that capillary waves contribute to broadening, these Monte Carlo simulations reveal that this contribution to the total interfacial width is much smaller than expected. The authors suggest an alternative mechanism to explain the broader than expected interfacial widths. By measuring the chain orientation across the interface, Müller and co-workers show, that the total polymer density of the chains located at the interface center is reduced, and that the chain end concentration is enhanced at the interface. Further, chains are slightly deformed, resulting in more self-contacts and fewer hetero-contacts at the interface. This last effect leads to a decrease in the enthalpic cost of interface formation, and a somewhat smaller effective interaction parameter than found in a bulk blend. Hence it is the effective reduction of the interaction parameter at the immiscible interface, that produces the additional broadening of the interfacial region. This issue is still far from being resolved, and additional experiments are needed to confirm Müller et al.’s explanation.

As mentioned earlier, the reflectivity from the annealed sample displays damping at high values of k (cf. Fig. 2). Because layer A is very thick, the contribution to the reflectivity from the roughness at the silicon/A interface is quite small. Thus, damping of the reflectivity in this case indicates a rough surface. Indeed, a significant increase in off-specular reflection was detected, another indication of surface roughness. A good fit to the reflectivity data is found using a surface roughness of 6 nm. Although not directly observable, we speculate that this large surface roughness indicates, that the PS layer dewets from the underlying PB. Polymer/polymer dewetting has been observed previously by Faldi et al. [41], Pan et al. [42] and others [43–45]. Sample roughening was also observed on silicon/PS/dPMMA and silicon/PS/PBrS samples by Fernandez et al. [11] and Hüttenbach et al., respectively [14]. As stressed in the latter study, a large surface roughness (about 37 nm), does not interfere with

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[4] From Ref. 16, the value of $\chi_{dPS/PS}$ is $(1.564 \pm 0.624) \times 10^{-4}$ at 175°C.

extracting the interfacial profile. Also the features of the reflectivity curve that characterized interfacial broadening, namely the sharpness of the interference fringes, were not affected at small *k*. We take a similar approach in our data analysis.

4. Conclusion

We demonstrate the superb depth resolution of LE-FRES, by measuring the volume fraction profiles of dPS in the PB/dPS system at 175°C. Because depth resolution degrades below the surface, the top dPS layer was 'thinned' by ion sputtering prior to LE-FRES analysis. A depth resolution of 13 nm at the interface was achieved. An interfacial width of 6.0 ± 3.5 nm was measured. In addition, neutron reflectivity was used to determine the volume fraction profiles, at the interface between 1,4-polybutadiene and an isotopic mixture of two high-molecular weight, polystyrenes, with a dPS bulk volume fraction of 0.30. At 175°C, the interfacial width was 2.2 nm. Because no interfacial segregation of dPS or PS was observed, we conclude that the interaction parameters in PB/dPS and PB/PS are approximately the same or that their difference is smaller than the error associated with measuring $\chi_{PB/PS}$. By using a self-consistent field model (SCF) and known values of χ the width was calculated to be 2.2 nm. By adding capillary wave broadening, the predicted width increased to 2.8 nm, in good agreement with the NR value. Similar to the NR measurement, the SCF model shows no segregation of dPS or PS. Thus, the isotope effect plays only a minor role in dictating the interfacial properties in the PB/dPS:PS system.

Acknowledgements

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