Surface Enrichment in an Isotopic Polymer Blend

Richard A. L. Jones and Edward J. Kramer
Department of Materials Science and Engineering and the Materials Science Center,
Cornell University, Ithaca, New York 14853

Miriam H. Rafailovich
Department of Physics, Queens College, 65-30 Kissena Blvd., Flushing, New York 11367

Jonathon Sokolov
Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973

Steven A. Schwarz
Bellcore, Red Bank, New Jersey 07701-7040
(Received 26 September 1988)

Forward-recoil spectrometry reveals that the surface of a blend of deuterated polystyrene (*d*-PS) and protonated polystyrene (PS) is enriched with *d*-PS relative to the bulk; the surface excess of *d*-PS increases almost linearly with the bulk volume fraction ϕ of *d*-PS at 184 °C. The results may be interpreted quantitatively with mean-field theory, and yield a form of the bare surface energy of the blend consistent with the surface enrichment being driven by a surface-energy difference between *d*-PS and hydrogenated polystyrene (*h*-PS) of isotopic origin.

PACS numbers: 68.10.−m, 61.16.Fk, 61.25.Hq

It has long been recognized that the surface composition of a mixed condensed phase is usually different from the bulk; any surface-energy difference between the pure components allows the system to lower its total free energy by increasing the surface concentration of the lower-energy component. Such effects have been observed in binary alloys[1] and in liquid mixtures of small molecules.[2] Recently, additional interest has been generated in this class of phenomena by the discovery of surface phase transitions in which quantities such as the surface coverage change discontinuously or diverge as a result of some vanishingly small change of a system parameter.[3,4] The theory of these effects in binary mixtures is also very closely related to theories of adsorption onto a solid substrate from a vapor and of surface magnetic phase transitions.[5] It has been suggested that melts of polymer-polymer mixtures (blends) might be a fruitful area for the study of such effects[6,7]; not only does one have an extra experimental variable, the chain length, but also the natural length scales of such systems can be rather long, potentially making experiments less demanding.

One expects surface enrichment in polymer blends to be both technically important, controlling such properties as contact angle, friction, and weatherability, and ubiquitous, on account of the small combinatorial entropy gained by mixing high polymers. Previous experimental studies[8,9] have been restricted to demonstrating that such enrichment occurs and to measuring its rough extent away from the surface. Quantitative comparisons with theory have not been made, probably because of the complexity of most real polymer blends.[10]

In this Letter we demonstrate that the surface of a relatively dilute mixture of deuterated polystyrene (*d*-PS) in protonated polystyrene (PS) is enriched in *d*-PS and that the amount of such enrichment increases strongly with the *d*-PS volume fraction in the bulk. It has recently been shown[11] that such isotopic blends are attractive model systems, in that the segment-segment interaction, as approximated by the Flory parameter χ, is weakly unfavorable (positive). The interaction is thought to be almost entirely of dispersive origin[12] because of the difference in polarizability between C—H and C—D bonds. In the case of polystyrene χ has been determined both from small-angle neutron scattering[12,13] and measurements of mutual diffusion.[14] Using this χ and the simple Flory-Huggins model of the blend thermodynamics, we show that the experimental surface enrichment is in good agreement with that predicted by theory.

The PS (from Pressure Chemical Co.) and *d*-PS (from Polymer Laboratories) had weight-averaged molecular weights of 1.8×10^6 and 1.03×10^6 with narrow molecular-weight distributions (polydispersity index <1.3 and 1.15, respectively). Thin films of the blends were prepared by spin-coating polished silicon substrates with solutions of the polymers in toluene; film thicknesses were around 3 μm. Samples were sealed in glass tubes under vacuum and annealed for periods up to a week at 184 °C. For these molecular weights the Flory-Huggins model predicts an upper critical temperature of 176 °C and a critical *d*-PS volume fraction of 0.57; thus at 184 °C all samples are in the one-phase region of the phase diagram. The samples were cooled rapidly enough that there was no chance for significant changes in the depth profile to take place by diffusion before the glass

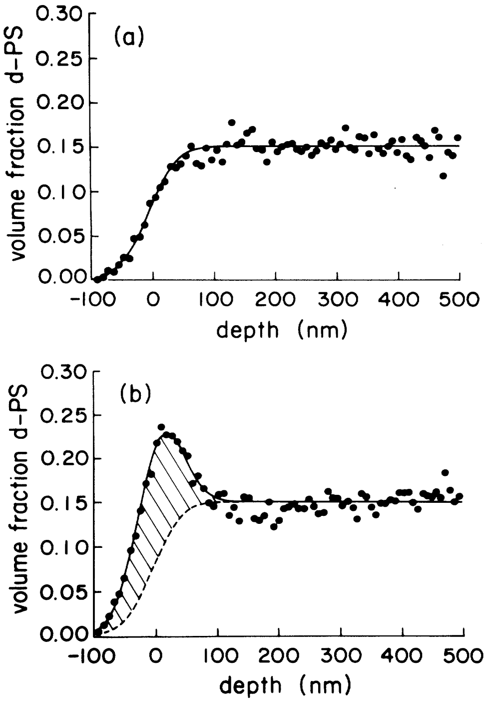

FIG. 1. Depth profiles of *d*-PS in a blend with PS with an initial volume fraction *d*-PS of 0.15, (a) before and (b) after annealing at 184 °C for 5 days, as revealed by forward-recoil spectrometry (FRES). The solid lines are the fits to the experimental data produced by the simulation program (Ref. 15); in (a) the sample simulated is a uniform 0.15 blend; in (b) the surface layer is represented by a uniform layer of pure *d*-PS, whose thickness is varied to produce the best fit. (The uniform layer simulation cannot be distinguished from that of a exponentially decreasing profile with a decay length of ≈ 250 Å and the same surface excess due to the relatively poor depth resolution of FRES.) The surface excess is the shaded area in (b).

transition temperature of 100 °C was reached.

The volume fraction ϕ versus depth profiles of deuterated polystyrene were measured after annealing with use of forward recoil spectrometry (FRES)[15,16] with an incident beam of 2.8-MeV He^{++} ions. Figure 1 shows depth profiles from specimens before and after annealing; these clearly show the appearance of an enriched layer of *d*-PS at the surface. The instrumental depth resolution, at 80 nm, is too poor to resolve the detailed structure of the enriched layer; we measure the (integrated) surface excess of *d*-PS, represented in Fig. 1(b) by the shaded area, by means of a simulation program.[17] In systems of such high molecular weight, diffusion is slow and care has to be taken to make sure the system has reached equilibrium; this point was checked by annealing for a number of increasing times until there was no further increase in the measured surface excess. Figure 2 shows the equilibrium surface excess as a function of the volume fraction of *d*-PS in the bulk, ϕ_∞.

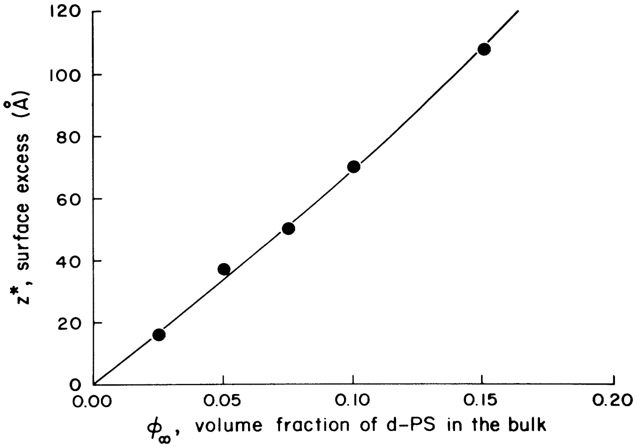

FIG. 2. FRES measurements of the surface excess z^* of *d*-PS as a function of the initial volume fraction of *d*-PS. The solid line is the predicted z^* from Eqs. (3) and (4) and the bare surface-energy parameters $\mu_1 = 0.024$ Å and $g = -0.0046$ Å determined from the best-fit line shown in Fig. 3.

The mean-field theory due to van der Waals for a liquid-vapor interface was adapted to liquid mixtures by Cahn[3] and to polymer blends by Nakanishi and Pincus,[7] and Schmidt and Binder[6]; we use the Schmidt and Binder notation in what follows. The effect of a surface is represented by a bare surface energy which depends on the surface volume fraction ϕ_1 as

$$f_s(\phi_1) = -\mu_1\phi_1 - \tfrac{1}{2}g\phi_1^2\,, \qquad (1)$$

where μ_1 is a chemical potential favoring one component at the surface, and g expresses the way interactions between the components are modified by the presence of the surface. In the theory f_s is expressed in terms of a site on a Flory-Huggins lattice and has dimensions of length; it may be converted to familiar surface-energy units by multiplying by the factor kT/b^3, where b is the unit-cell dimension of the Flory-Huggins lattice. The surface-free-energy difference between the pure components is given by $(\mu_1 + g/2)kT/b^3$.

The grand thermodynamic potential of the system per unit area is

$$F/kT = \int_0^\infty dz \left[G(\phi) - (\Delta\mu)\phi + \frac{a^2}{36\phi(1-\phi)} \left(\frac{d\phi}{dz} \right)^2 \right] - \mu_1\phi_1 - \tfrac{1}{2}g\phi_1^2\,, \qquad (2)$$

where G is the Gibbs free energy of mixing per lattice site, $\Delta\mu$ is the exchange chemical potential $(\partial G/\partial\phi)$, and a is the statistical segment length. The variation of ϕ from its surface value ϕ_1 to its bulk value ϕ_∞ is described by $\phi(z)$. One finds the $\phi(z)$ which minimizes the functional of Eq. (2)[3,5,6] using Euler's equation and hence determines ϕ_1 to be given by

$$-\frac{df_s}{d\phi_1}=\mu_1+g\phi_1=\pm\frac{a}{3}\left[\frac{G(\phi_1)-G(\phi_\infty)-\Delta\mu(\phi_1-\phi_\infty)}{\phi_1(1-\phi_1)}\right]^{0.5} \tag{3}$$

and the surface excess z^* (Ref. 4)

$$z^*=\int_0^\infty[\phi(z)-\phi(\infty)]dz=\frac{a}{6}\int_{\phi_1}^{\phi_\infty}\frac{d\phi(\phi-\phi_\infty)}{\{\phi(1-\phi)[G(\phi)-G(\phi_\infty)-\Delta\mu(\phi-\phi_\infty)]\}^{0.5}}\,. \tag{4}$$

If we use the Flory-Huggins form of the free energy $G(\phi)$,[18]

$$G(\phi)=\frac{\phi}{N_A}\ln(\phi)+\frac{1-\phi}{N_B}\ln(1-\phi)+\chi\phi(1-\phi)\,, \tag{5}$$

where N_A and N_B are the degrees of polymerization of each component, the experimentally determined[13,14] values of the interaction parameter χ and the statistical segment length a, we can use Eq. (3) to calculate values of ϕ_1 from our experimental surface excess values, and then use Eq. (4) to extract values of $-(\partial f_s/\partial\phi_1)=\mu_1+g\phi_1$. This quantity is plotted in Fig. 3 against ϕ_1, the calculated surface volume fraction.

The surface-energy difference [7.8×10^{-5} J m^{-2} $=-(kT/b^3)\partial f_s/\partial\phi_1$ at $\phi_1=0.5$] we deduce between *d*-PS and hydrogenated polystyrene (*h*-PS) is far too small to measure directly with available techniques. However, any surface-energy difference due to an isotope effect will be, to a first approximation, a function only of the density of C—D or C—H bonds. Thus we compare in Fig. 3 values of the surface-energy difference between analogous small-molecule liquids, benzene and toluene and their deuterated counterparts,[19] at a temperature at which the density of C—H bonds is similar to their density in polystyrene at 184 °C. These are in good agreement with the value we find for *d*-PS-PS.[20]

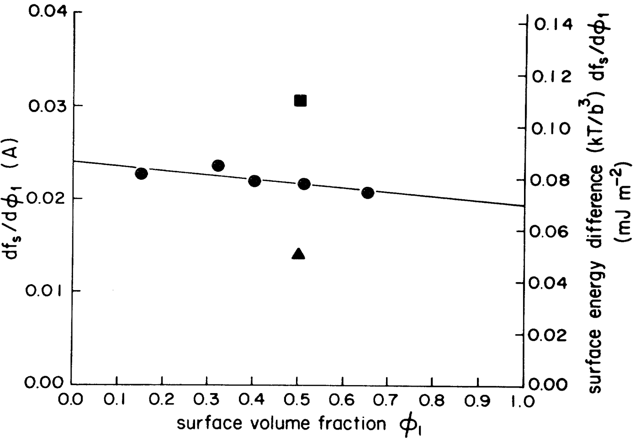

FIG. 3. Derivative of bare surface energy with respect to surface volume fraction *d*-PS, as derived from the measured z^* data in Fig. 2. In the approximation discussed in the text, these are expected to be linearly related, with the slope and intercept giving the bare surface-energy parameters μ_1 and g, respectively. The difference in surface energy between the pure components is given by the value of this function for $\phi_1=0.5$; the triangle and the square are the values of the surface-energy difference between benzene and toluene and their respective deuterated counterparts, at 30 °C, taken from Ref. 19.

In the absence of a full microscopic theory of the surface of a polymer blend, we have no reliable prediction of g. However, simple bond-counting arguments consistent with the nearest-neighbor interaction assumed in the Flory-Huggins model suggest that g should be negative and of the same order of magnitude as $4b\chi$ (=0.0033 Å), which is consistent with what we find, $g=-0.0046\pm0.0020$ Å.

Using the theory of Ref. 6, the previously measured value of χ,[13] and the values of μ_1 ($=0.0240\pm0.0009$ Å) and g that we have extracted,[21] we can make some predictions about the wetting phase diagram in this system. The small ratio of $-g/\mu_1=0.19$ implies that the wetting transition along the coexistence curve must be first order; we can calculate that the transition occurs for rather small *d*-PS volume fractions, less than 0.02, and that the prewetting line follows the coexistence curve very closely. Unfortunately, the very slow diffusion of these very-high-molecular-weight polymers makes it impossible to investigate the wetting or prewetting behavior experimentally with the present system.

We can also predict the full shape of the profiles we expect. These are given by the solution of[3,6,7]

$$z=\frac{a}{6}\int_{\phi_1}^{\phi(z)}\frac{d\phi}{\{\phi(1-\phi)[G(\phi)-G(\phi_\infty)-\Delta\mu(\phi-\phi_\infty)]\}^{0.5}}\,. \tag{6}$$

For small ϕ this predicts profiles that are close to exponential, with a decay length close to the bulk correlation length for concentration fluctuations. Using our values for μ_1 and g we find for $\phi_\infty=0.14$ blends, for example, that the decay length found by direct numerical solutions of Eq. (6) is 210 Å, compared to a bulk correlation length of 204 Å. This length is too small to be resolved with use of conventional FRES. However, we have recently used a new higher-resolution FRES technique to analyze the surface of a blend with $\phi_\infty=0.14$ annealed at 184 °C (Ref. 22); we find a decay length of 250 ± 30 Å, in reasonable agreement with the 210-Å prediction.[23] A systematic study of enrichment in this system, with use of high-resolution FRES, dynamic secondary ion mass spectrometry, and neutron reflectivity in addition to conventional FRES, is now under way.

In conclusion, we have measured surface enrichment in blends of high-molecular-weight polystyrene and deuterated polystyrene. Our results are consistent with mean-field theory, and yield a form for the bare surface energy of the blend consistent with the interpretation that the surface enrichment is driven by a surface-energy difference of isotopic origin.

This work was supported by the NSF-DMR Polymer Program Grant No. DMR-8719123 (R.A.L.J. and E.J.K.) and by U.S. Department of Energy Contract No. DE-AC02-76CH00016 (M.H.R. and J.S.). We also used the central facilities of the Cornell Materials Science Center which is supported by the NSF-DMR-MRL program. E.J.K. especially appreciates stimulating discussions with Professor K. Binder which were made possible by the financial support of the Alexander von Humboldt Stiftung.

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