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Solubility and Diffusion of Polybutadiene in Polystyrene at Elevated Temperatures

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ABSTRACT: The thermally-induced diffusion of low molecular weight perdeuterated polybutadiene (dPB) in polystyrene (PS) was measured with forward recoil spectroscopy (FRES). Diffusion coefficients were determined for 3000 g/mol dPB penetrating into a 350 000 g/mol PS matrix in the temperature range 97-115 °C. The diffusion coefficients vary from 10^{-15} to 10^{-12} cm^2/s. The apparent activation energy is 99 kcal/mol. Solubility limits for dPB in PS at temperatures ranging from 105 to 160 °C were also determined with FRES. The results were used to construct a portion of the binodal curve for this polymer system. The derived value of the Flory-Huggins interaction parameter, χ, is 0.055 and 0.048 at 105 and 160 °C, respectively.

Introduction

A central and limiting process in a recently reported toughening mechanism in blends of polystyrene (PS) and polybutadiene (PB)[1,2] is the stress-enhanced solubility and subsequent diffusion of the low molecular weight PB rubber into the glassy PS. The diffusion is restricted to regions in the immediate neighborhood of advancing crazes, where the local deformation-induced stress fields are favorable for enhancing the PB solubility. The PB locally plastices the material drawn into crazes, and the crazes advance more rapidly and at lower applied stresses in the blends than in pure PS. Based on results from craze velocity measurements[3] in blends of PS and 3000 g/mol PB and a characteristic length for diffusion equal to the diameter of a craze fibril,[2] the estimated diffusion coefficient for the PB is 3×10^{-12} cm^2/s. Information concerning the rate of polymer-polymer interdiffusion for PB/PS is necessary to probe the limitations of the proposed toughening mechanism.

Blends of polybutadiene and polystyrene exhibit upper critical solution temperatures. The segmental interaction parameter for this system is large enough and positive such that blends of PB and PS phase separate into virtually pure components at temperatures below 200 °C. Hence this polymer pair is generally termed immiscible. Previous polymer-polymer interdiffusion studies have not included this type of system. In our experiments, the molecular weight of the PB is low enough that a miscibility of approximately 3 vol % in PS can be achieved near 120 °C. Conversely, the high molecular weight PS is completely immiscible in the PB. Polymer-polymer interdiffusion across an interface between pure low molecular weight PB and pure high molecular weight PS is essentially penetration of the PB into the PS across a stationary interface. The temperature dependence of this diffusion provides a means to probe the changing properties of the PS matrix.

Forward recoil spectroscopy has been discussed extensively in the recent literature as a means for determining diffusion coefficients for polymer-polymer systems. Some of the research has centered on self-diffusion measurements to probe mechanisms of diffusion in various regimes of molecular weight.[4-8] Other studies have examined mutual diffusion in miscible polymer systems.[9-13] FRES has also been used to measure solubility limits of deuterated polystyrene in brominated polystyrene, a partially miscible polymer system.[14] This technique is capable of measuring atomic concentrations on the order of 0.1% and diffusion coefficients in the range of 10^{-12}-10^{-16} cm^2/s. FRES is expected to be a viable method to measure solubilities and determine diffusion coefficients in our low molecular weight PB/PS system.

Experimental Section

Polymers. The polystyrene used in this study was supplied by Polysar (M_w = 350 000 g/mol, M_n = 170 000 g/mole). Perdeuterated polybutadiene (dPB) was synthesized in our laboratory via homogeneous anionic polymerization in benzene using *n*-butyllithium initiator. The perdeuterated butadiene was obtained from Cambridge Isotope Laboratories and purified as described by Cheng.[15] M_w was determined to be 3000 g/mol and the polydispersity 1.04 based on size exclusion chromatography and an in-line viscometer. Deuterium NMR experiments show that the microstructure of the dPB is 12% 1,2, and 88% 1,4 cis and trans addition. With the exception of the *n*-butyl and proton end groups, the polymer is greater than 97% deuterated based on proton NMR results.

Sample Preparation. All samples were prepared in a similar manner. A piece of silicon wafer was washed in distilled water to remove any dust particles, rinsed with high-purity ethanol, and dried by spinning at 3000 rpm in air. A polystyrene layer was deposited on the wafer in a spin-coating process with solutions of PS in toluene. The samples were annealed in a vacuum oven for at least 8 h at approximately 100 °C to remove any residal solvent. The objective was to create a bilayer sample consisting of dPB on top of the PS. We were unable to form a coherent film with the low molecular weight dPB. Instead heterogeneous films of randomly mixed dPB and PS were made by spin coating solutions of blends of dPB and PS in toluene in which the PS accounted for 30-40% of the total polymer by weight. Thus, the dPB/PS blend layer was spun onto a glass slide, floated onto the surface of a water bath, and picked up with a PS-coated wafer. The glass slides were cleaned in a 50% aqueous solution of hydrofluoric acid, rinsed in distilled water, rinsed with ethanol, and dried by spinning at 3000 rpm in air. Each sample was dried in a vessel with a nitrogen purge at room temperature for at least 12 h. Care was taken in each preparation step to minimize the exposure of the dPB to oxygen, UV light, and heat to reduce the possibility of cross-linking.

The samples were heated in a thin-walled copper chamber after it was evacuated and back-filled with pure argon and maintained at a constant pressure of 1.2 atm. In each experiment, the sample and chamber were immersed in an oil bath at a given temperature for a specific period of time. In this way the sample temperature reached 90% of its final steady state value after 20 s and 99% after 40 s. The temperature of the bath itself dropped approximately 0.5 °C immediately after insertion of the sample

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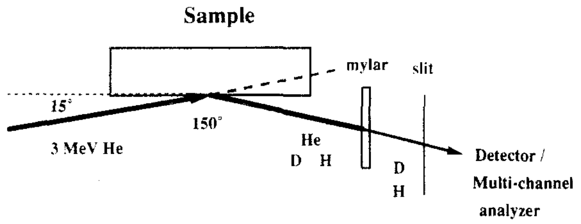

Figure 1. Configuration of the FRES experiment.

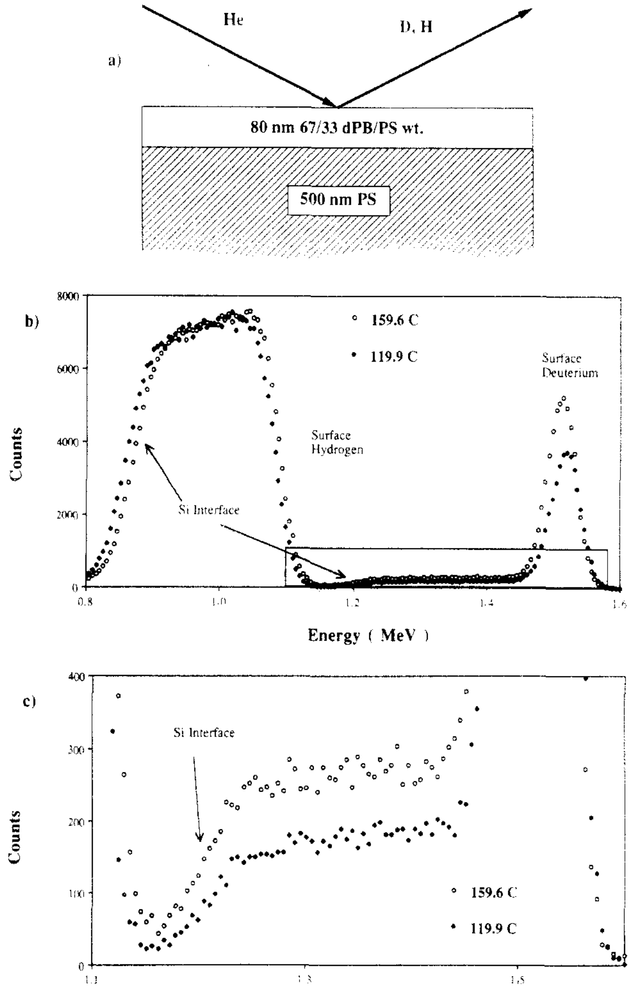

Figure 2. (a) Schematic of a typical sample in the solubility experiments. (b) Overview of FRES data for samples held for 1 h at 159.6 and 119.9 °C. (c) Expanded view of the deuterium profiles.

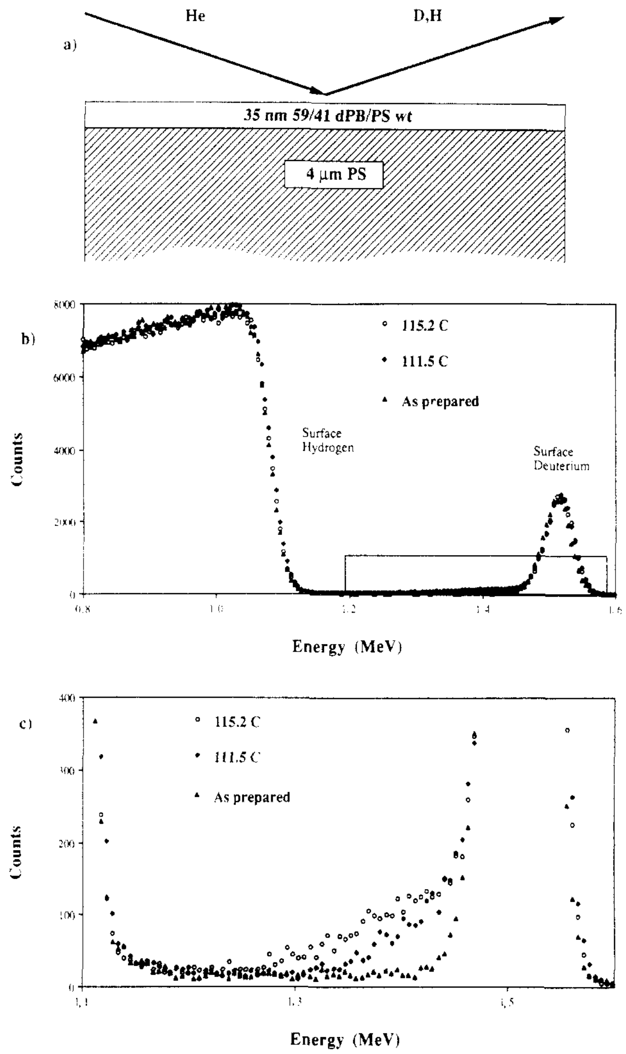

Figure 3. (a) Schematic of typical sample in the diffusion experiments. (b) Overview of FRES data for samples held for 5 min at 115.2 and 115.5 °C and an unheated sample. (c) Expanded view of the deuterium profiles.

chamber and regained a steady-state value (±0.1 °C) after approximately 2 min. The error in reported temperature is greater for those samples which were treated for short time periods. The minimum time period used in these experiments was 5 min.

Forward Recoil Spectroscopy. All of the samples were analyzed with forward recoil spectroscopy (FRES) at the Cambridge Accelerator for Materials Science at Harvard University to determine concentration versus depth profiles of dPB in PS. This technique allows direct measurement of the diffusion profile of the deuterated species in the hydrogenated matrix for penetration depths in the range of 500 nm. Given this depth and a 5-min minimum experimental time period for accurate temperature control, the largest diffusion coefficient that can be measured is approximately 10^{-12} cm^2/s.

The configuration of the FRES experiment is shown in Figure 1. The sample is irradiated with a 1-mm-diameter beam of 3-MeV α particles ($4He^{2+}$) at a glancing angle of 15°. The beam dose for all samples was 15 μC. The slit defines the angle of detection to be 150 ± 0.5° from the incident beam and subtends a solid angle of 6.3×10^{-3} sr. The mylar foil placed in front of the detector is 11.5 μm in thickness. The energy resolution in the experiments was 45 keV. Details of this technique are described elsewhere.[4,8,16]

Results

Some of the samples were held at temperatures ranging from 105 to 160 °C for time periods of 15 to 1 h. The dPB/PS blend layer in these samples was approximately 80 nm thick and was 67% dPB and 33% PS by weight, and the pure PS substrate layer was approximately 490 nm thick. A schematic of a typical sample for the solubility experiments is shown in Figure 2a). The amount of dPB present is more than enough to saturate the PS substrate layer in the present experiment in the temperature range studied, and the thickness of the PS layer allows the determination of the composition at the polymer silicon interface. Figures 2b and 2c show the FRES data for samples held for 1 h at 159.6 and 119.9 °C. The dPB has diffused into the PS layer and the relatively flat concentration profiles indicate that the samples have approached equilibrium. More deuterium is recoiled at energies between about 1.2 and 1.45 MeV in the sample held at the higher temperature. The sample held at 159.6 °C thus has a higher concentration of dPB in the PS layer than the sample held at 119.9 °C. The use of these data to determine the solubility of dPB in PS as a function of temperature is explained in the Discussion section.

Table I
Experimental Diffusion Times

temp (°C)	diff time (min)	temp (°C)	diff time (min)
115.2	5	105.4	20
113.4	5	103.4	75
111.5	5	101.5	240
109.7	8	100.3	420
109.4	10	99.6	511
107.9	10	98.7	767
107.4	15	96.5	2010
105.9	20		

Other samples were held at temperatures ranging from 115.2 to 96.5 °C for time periods of 5 to 2010 min. In these experiments the dPB/PS blend layer was approximately 35 nm thick and was 59% dPB and 41% PS by weight. The pure PS substrate layer was approximately 4 μm (4000 nm) thick. A schematic of a typical sample in the diffusion experiments is shown in Figure 3a). Diffusion times were chosen to obtain concentration profiles which would go to zero in penetration depths of order 200 nm. The temperature and time period for each experiment are tabulated in Table I. Figures 3b and 3c show the profiles obtained for samples held for 5 min at 115.2 and 111.5 °C, respectively, compared to an unheated sample. From Figure 3b we can conclude that the sample preparation procedure is very reproducible. The identical deuterium peaks in the FRES data at approximately 1.5 M eV show that all of the samples have an equal amount of dPB in the thin, initially blended surface layer. Figure 3c shows clearly that there is penetration of dPB into the PS in both annealed samples, and that the penetration at 115.2 °C is markedly deeper than at 111.5 °C for the same diffusion time period. All three samples exhibit a consistent nonzero value for the counts of deuterium in the range of energy between the deuterium and hydrogen peaks. These counts are attributed to events when two particles of lower energy reach the detector at the same time and are counted as one single higher energy particle. This background is termed pulse pileup. A model to extract diffusion coefficients from these data is developed in the following section.

Discussion

Solubility limits and diffusion coefficients were determined from the FRES results with the aid of the RUMP software package developed for Rutherford backscattering and FRES data analysis at Corneall University.[17,18] The software was purchased from Computer Graphics Service in Lansing, NY. This program performs complex iterative simulations of FRES data given the specific parameters of the experimental configuration and the physical and chemical characteristics of the species in the sample description. RUMP calculates simulations in terms of counts and energy. These axes are readily transformed to concentration and depth and some of the data are presented in this form.

Figure 4 shows the FRES data and the simulation of the sample held for 1 h at 139.9 °C. A schematic of the sample is shown in Figure 2a. A calibration sample of known composition is used to establish the relative cross sections of deuterium and hydrogen. The height of the hydrogen peak is used to normalize the counts or concentration axis for small errors in measured beam dose from sample to sample. The concentration of dPB in the PS is modeled as constant throughout the layer. We assume that the polymer system has reached an equilibrium, phase-separated state in which one phase consists of a homogeneous mixture of PS saturated with a small volume fraction of dPB, and other other phase is pure dPB. The best fit of this model to the experimental data in Figure 4b is achieved with a solubility of 0.039 volume fraction dPB in PS at 139.9 °C.

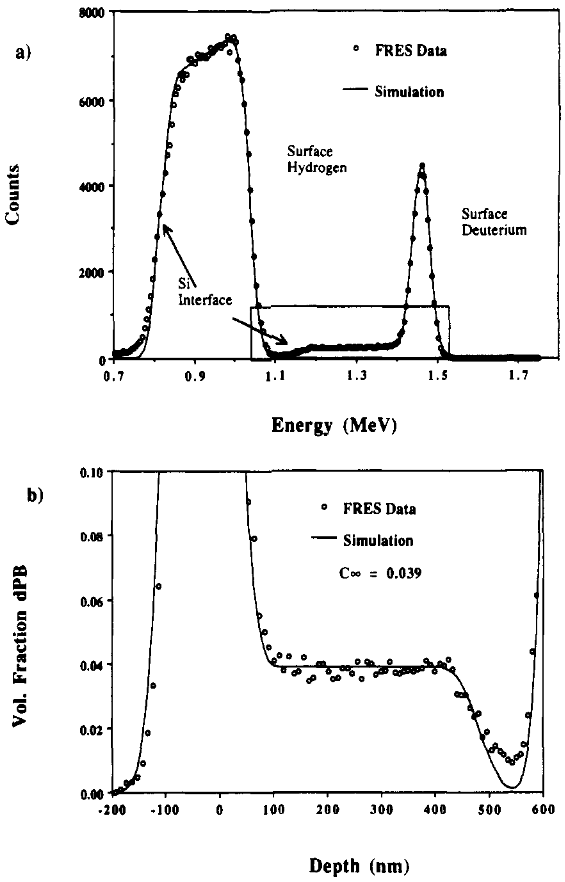

Figure 4. Sample held for 1 h at 139.9 °C. (a) Overview of FRES data and simulation. (b) Expanded view of the deuterium profile and simulation plotted in terms of volume fraction versus depth.

In similar experiments, the solubility limits were found at nine temperatures ranging from 105 to 160 °C. The measured solubilities ranged from 0.027 to 0.043 volume fraction dPB in the PS-rich phase. The data are presented in Figure 5. To construct a portion of the binodal curve from these points for this polymer system, we use an expression for the free energy of mixting per unit volume, ΔG_m, given by[19]

$$\Delta G_m = RT\left[\frac{\phi_{PS}\ln(\phi_{PS})}{V_{PS}} + \frac{\phi_{PB}\ln(\phi_{PB})}{V_{PB}}\right] + \Lambda\phi_{PS}\phi_{PB} \tag{1}$$

where Λ, the segmental interaction parameter, has a constant and temperature-dependent term

$$\Lambda = \lambda_0 + \lambda_t T\ (°C) \tag{2}$$

and where ϕ is the volume fraction, V is the molar volume, and R and T have their usual meaning. Normally Λ also has a concentration-dependent term. The volume fraction of dPB solubilized in the high molecular weight PS does not change enough in the temperature range of our experiments to make the calculation of the concentration dependence meaningful. The Flory–Huggins interaction parameter $\chi = \Lambda V_{PB}/xRT$, where x is the degree of polymerization of the PB.

ΔG_m is plotted as a function ϕ_{PS} at a particular temperature and the points of double tangency determine

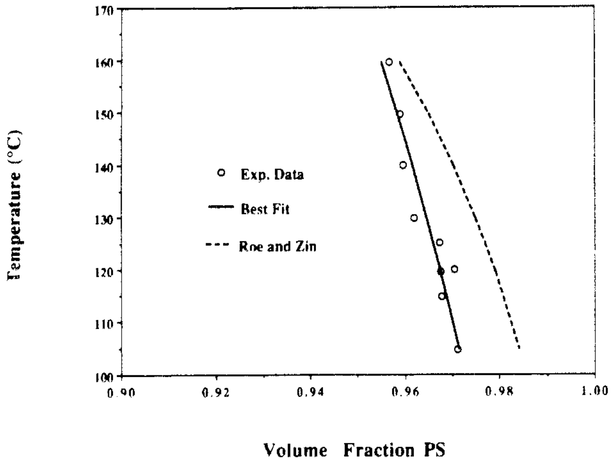

Figure 5. Plot of temperature versus the solubity of dPB in PS. (●) denotes solubilites determined from FRES data. The solid line is the best fit of a binodal curve to the data with Λ = 0.71 − 0.00020(T °C). The dashed line is the binodal curve calculated for Λ = 1.05 − 0.0022(T °C) which is based on the results of Roe and Zin.

the binodal composition of the two phases in equilibrium. The calculated concentration of PS in the PB-rich phase is so small that it is effectively zero. The set of points of tangency on the PS-rich side of the curves for various temperatures defines the binodal curve. The solid line in Figure 5 represents the best nonlinear least squares fit[20] to the data and corresponds to values of λ_0 = 0.71 and λ_t = −0.00020. The value of χ is thus 0.055 and 0.048 at 105 and 160 °C, respectively.

We have specifically chosen the expression of the interaction parameter in eq 2 to compare our results to those of Roe and Zin.[19] They determined binodal curves based on light scattering experiments for polymer systems of PB (94% 1,4 addition, 6% 1,2 addition, M_n = 2350 g/mol) and three polystyrenes with M_w = 2400, 3500, and 5480 g/mol. If the ϕ-dependent term in their expression for Λ (ϕ is always close to 1 in our system) is added to the constant term in their expression, we calculate average values of λ_0 and λ_t in their experiments to be 1.05 and −0.0022, respectively. The binodal curve for our polymers predicted with these values is plotted in Figure 5 as the dashed line.

The major difference in the interaction parameter determined from the present FRES results and that of Roe and Zin is in the temperature dependence. This difference is responsible for the larger curvature in the dashed line in Figure 5. The molecular weights of the polybutadienes in both studies are similar. The use of perdeuterated polybutadiene instead of its protonated analog is not expected to have a significant effect on λ_t. However, the 1,2 content of the PB in the Roe and Zin study was 6% compared to a 1,2 content of 12% in the dPB used in this study. In addition, the polystyrene molecular weights in the Roe and Zin experiments were 60–150 times smaller than the molecular weight of the PS in the present study, suggesting that λ_t is a function of molecular weight. In fact, the temperature dependence of Λ in the Roe and Zin experiments decreases with increasing PS molecular weight (λ_t = −0.0026, −0.0023, and −0.0016 for M_{wPS} = 2400, 3500, and 5480). Our results produced λ_t = −0.00020 at M_{wPS} = 350 000 g/mol.

We extract diffusion coefficients from the samples in which the concentration of dPB decays with depth in the PS layer. Figure 6 shows the FRES data and the simulations for a sample held 15 min at 107.4 °C. A schematic of the sample is shown in Figure 3a). We assume that the blended dPB/PS surface layer (whose detailed morphology is unknown) rapidly transforms to a layer of pure dPB on top of a layer of PS saturated with dPB when heated to the temperature of a diffusion experiment. Evidence to support this assumption was obtained from secondary ion mass spectroscopy analysis of annealed samples which revealed a significant concentration enhancement of dPB on the surface compared to the unannealed samples.[21] The PS saturated with dPB is simulated as a layer 13.5 nm thick based on mass balance considerations.

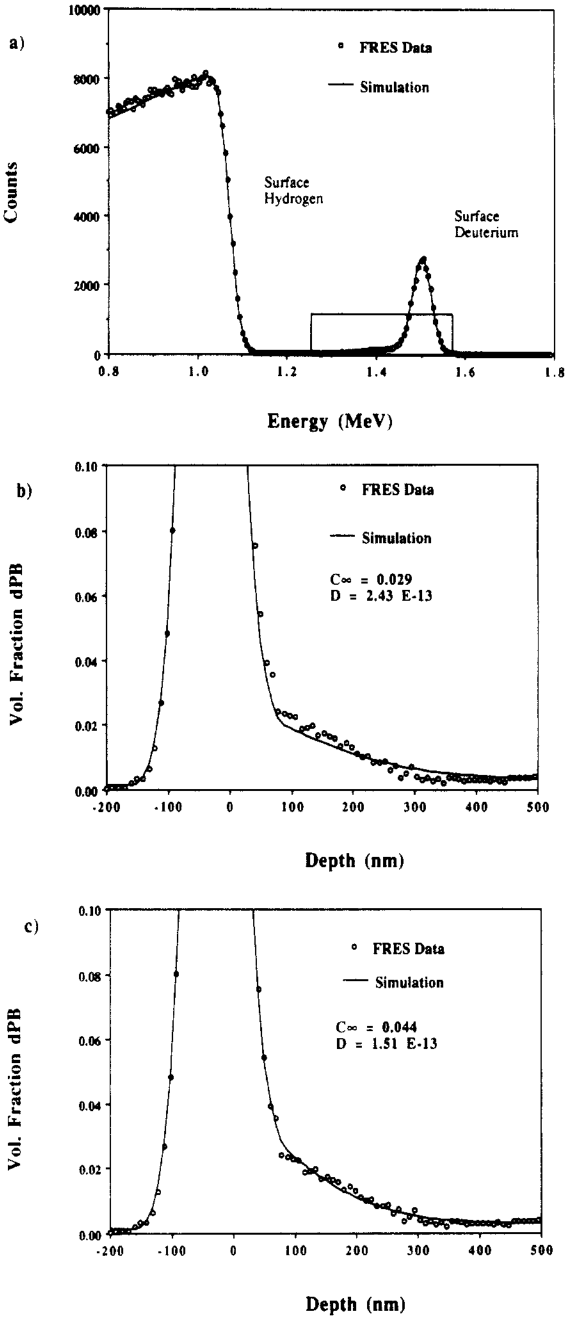

Figure 6. Sample held 15 min at 107.4 °C. (a) Overview of FRES data and simulation. Expanded views of the deuterium profile and simulations in terms of volume fraction versus depth are presented for (b) a simulation where C_∞ was determined from the binodal curve fit to the experimental solubility data and (c) a simulation with the best two-parameter fit for C_∞ and D.

The concentration profile of dPB in the PS layer is modeled as Fickian diffusion of a species at constant concentration at the interface diffusing into a half space. The constant concentration in this case is the equilibrium solubility limit, C_∞, of the dPB in PS at the temperature

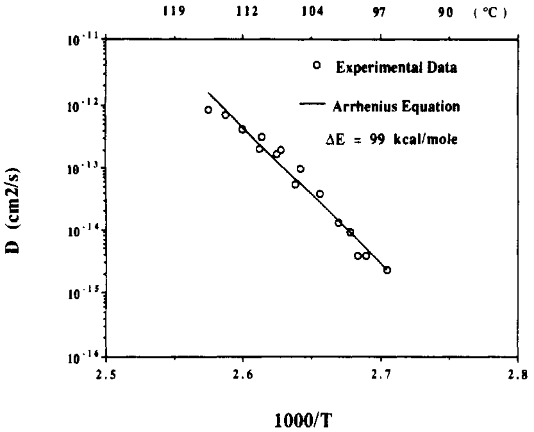

Figure 7. Semilogarithmic plot of D versus $1000/T$. The solid line represents the best fit of an Arrhenius equation to the data with ΔE_{act} = 99 kcal/mol.

of the experiment. The concentration profile is given by[22]

$$C(x,t) = C_\infty \operatorname{erfc}\left[\frac{x}{(4Dt)^{1/2}}\right] \tag{3}$$

where x is the depth of penetration, D is the diffusion coefficient, and t is time. The baseline of nonzero values for the concentration of dPB at depths greater than the penetration depth of dPB is simulated as pulse pileup described above.

The value of C_∞ in the model of the concentration profile is an important parameter in the determination of D. Figure 6b shows the fit obtained when C_∞ is equal to 0.029, the value determined from the point at 107.4 °C along the binodal curve that was fitted to the solubility data given above. The best value for D using this value for C_∞ in a least squares fit between the simulation and the FRES data is 2.43×10^{-13} cm^2/s. However, the simulated concentration profile using this C_∞ and D underestimates the experimental data at the front of the diffusion profile and overestimates the concentration of dPB at greater depths (Figure 6b). We therefore consider the diffusion coefficients found with values of C_∞ from the experimentally determined binodal curve to be upper bounds at each temperature.

A second approach of find D was to perform a two-parameter fit in which C_∞ and D are both varied to find the combination that yields the best possible fit between the simulation and the FRES data. The best combination for the sample held 15 min at 107.4 °C is shown in Figure 6c) where C_∞ = 0.044 and $D = 1.51 \times 10^{-13}$ cm^2/s. In all of the samples studied, the C_∞ values employed in the two-parameter fits were higher than those obtained from the binodal curve developed in the solubility experiments; at times, the difference was as much as a factor of 2. Possible explanations for the inconsistency include the difficulty in precisely determining the location of the dPB/PS interface, the steepness of the concentration profile in this region, a concentration-dependent diffusion coefficient, and the error associated with describing the baseline as pileup. We consider the diffusion coefficients found with two-parameter fits to be lower bounds at each temperature. The values of D presented in the discussion below are an average of the upper and lower bounds, and the average D differs from the bounds by ±5–30%. The value of D at 107.4 °C is thus 1.97×10^{-13} cm^2/s ± 23%.

Diffusion coefficients were determined for 3000 g/mol dPB diffusing into a high molecular weight PS matrix in the temperature range of 97 to 115 °C. The diffusion coefficients range from 10^{-15} to 10^{-12} cm^2/s. The data are presented in Figure 7 in a semilog plot of D versus $1000/T$. We were unable to measure diffusion coefficients at temperatures higher than 115 °C because of the uncertainty of the sample temperature at short times in the oil bath. Longer times at higher temperatures result in penetration depths which extend out of the deuterium window of the FRES experiment and/or place the boundary conditions of the diffusion model in question. Conversely, measurements of diffusion coefficients at temperatures below 97 °C are possible but require very long time periods.

The solid line in Figure 7 represents the best fit of an Arrhenius expression, $D = D_0 \exp(\Delta E_{\text{act}}/RT)$, to the data. The apparent activation energy, ΔE_{act}, is 99 kcal/mol. The temperature dependence of polymer–polymer interdiffusion at temperatures less than 100 °C above T_g is not usually well described by an Arrhenius equation, particularly when a wide range of temperature is considered. The data usually exhibit curvature not accounted for by the temperature-independent activation energy of the Arrhenius equation and so a more appropriate expression such as the WLF equation is generally employed. Our data do not span a large enough range to merit a fit beyond the Arrhenius equation. The value of ΔE_{act} in this polymer system can be compared with data from other researchers by finding the local slope of their data

$$\frac{\mathrm{d}(\ln D)}{\mathrm{d}(1/T)} = \frac{\Delta E_{\text{act}}}{R} \tag{4}$$

evaluated in the temperature range of our experiments.

Green and Kramer have studied the temperature dependence of PS (55 000 < M (g/mol) < 43 000) diffusing into a PS matrix (2×10^7 g/mol) with FRES.[23] They determined tracer diffusion coefficients in the range of 10^{-12}–10^{-16} cm^2/s for temperatures between 220 and 130 °C. The temperature dependence was modeled with the WLF type equation

$$\log\left(\frac{D}{T}\right) = A' - \frac{B}{T - T_\infty} \tag{5}$$

where A' is a constant, B = 710, and T_∞ = 49 °C. The local slope at $T = T_1$ is equal to

$$\left.\frac{\mathrm{d}(\ln(D))}{\mathrm{d}(1/T)}\right|_{T=T_1} = \left.\frac{\Delta E_{\text{act}}}{R}\right|_{T=T_1} = -\left.\frac{2.303BT^2}{(T - T_\infty)^2} - T\right|_{T=T_1} \tag{6}$$

If we extrapolate the fitted equation beyond the temperature range of the experiments by Green and Kramer to the average temperature in this study, 107 °C, we calculate an apparent activation energy for the PS/PS tracer diffusion at 107 °C to be 140 kcal/mol.

In another series of experiments, Green and Kramer measured the diffusion of low molecular weight polystyrenes in a PS matrix ($M = 2 \times 10^7$ g/mol).[6] These experiments were conducted at 112, 118, and 120 °C. We chose a PS oligomer of molecular weight 11 200 g/mol to compare to the dPB diffusant on the basis of approximately equal chain length. At 112 °C, the diffusion coefficient for the PS/PS system is approximately 2×10^{-15} cm^2/s, 2 orders to magnitude smaller than the diffusion coefficient we measured in the dPB/PS system at 111.5 °C. Diffusion rates in the PS/PS experiments may have been influenced by the presence of approximately 10 vol % diffusant species, which could have altered the properties of the matrix. The apparent activation energy for the PS/PS diffusion between 112 and 120 °C is 60 kcal/mol, 40% less than the value obtained for the dPB/PS diffusion between 97 and 115 °C. We expect the activation energy to be significantly lower in the higher temperature range. The

WLF equation used to describe the overall temperature dependence of the diffusion coefficients exhibits a high degree of curvature in this region.

Comparison of the activation energies for PS/PS diffusion and dPB/PS diffusion is not ideal in this temperature range. In the PS/PS system, both the diffusant and the matrix polymers are approaching their glass transition temperatures. The activation energy reflects drastically decreasing mobility for both species. This is evident especially in the case of high molecular weight PS diffusing into a high molecular weight PS matrix. In our dPB/PS experiments, the dPB is approximately 200 °C above its glass transition temperature. The activation energy at 107 °C reflects primarily the changing properties of the PS matrix. The change in mobility of the dPB molecule with temperature in this range is in contrast insignificant.

Tracer diffusion in high molecular weight PS near the glass transition temperature has been measured for photoreactive dye molecules. Ehlich and Sillescu[24] measured the diffusion of tetrahydrothiophene–indigo (TTI, 256 g/mol) in PS (270 000 g/mol) between 78 and 160 °C. Kim et al.[25] determined diffusion coefficients for tetramethyl [3.3](1,4)naphthaleno-(9,10)anthracenophane-2,2,-15,15-tetracarboxylate (cyclophane, 674 g/mol) in PS (422 000 g/mol). The tracer diffusion coefficients were determined by forced Rayleigh scattering in samples containing less than 0.5% TTI and in samples containing less than 0.04% cyclophane. The values obtained for TTI at 97, 105, and 112 °C were 3×10^{-15}, 1×10^{-13}, and 1×10^{-12} cm^2/s, respectively. The value for cycophane at 107 °C is approximately 1×10^{-14} cm^2/s. The diffusion coefficients determined for dPB in PS at 96.5, 105.4, and 111.5 °C were 2×10^{-15}, 7×10^{-14}, and 3×10^{-13} cm^2/s and were within the same order of magnitude. The apparent activation energy for the TTI diffusion at 107 °C is calculated to be 92 kcal/mol from the local slope of the WLF equation used to describe[24] the temperature dependence of the diffusion coefficient above T_g. In a similar way, the apparent activation energy for cyclophane[25] at 107 °C is calculated to be 109 kcal/mol. These values compare favorably with the 99 kcal/mol apparent activation energy found for the diffusion of dPB in PS. The fact that the rigid dye molecules and the low molecular weight dPB are diffusing at similar rates and with similar apparent activation energies implies that both types of experiments are probing the changing properties of the PS matrices near the glass transition temperature.

The largest diffusion coefficient we measured was 8.4 $\times 10^{-13}$ cm^2/s at 115.2 °C. The estimated minimum D required in the crazing mechanism at room temperature is 3×10^{-12} cm^2/s. At room temperature, the dPB is still well above its glass transition temperature. Evidence from the thermally-induced diffusion measurements above suggests that the diffusion in the crazing mechanism is controlled by the PS matrix properties. The local concentration of negative pressure and tuft drawing processes of craze growth must alter the properties of the PS in these regions to such a degree that the PB becomes significantly more soluble in the PS and the diffusion rate is quite substantially increased. Research in progress attempts to quantify these effects.

Summary

FRES is a viable technique to measure both solubilities and diffusion coefficients in the dPB/PS polymer system. The solubility of the 3000 g/mol dPB is only 2–4 vol % in 350 000 g/mol PS in the temperature range from 100 to 160 °C. A binodal curve was determined with the segmental interaction parameter $\Lambda = 0.71$ ($\Lambda = \chi x RT/V_{PB}$) with little temperature dependence. We conclude that Λ is a function of molecular weight to explain the difference between our results and the Roe and Zin values found for a system with similar molecular weight polybutadiene but with low molecular weight PS. Tracer diffusion coefficients were measured for dPB in PS which ranged from 10^{-15} to 10^{-12} cm^2/s in the temperature range from 97 to 115 °C. The apparent activation energy is 99 kcal/mol. The values of the diffusion coefficients and the apparent activation energy are in good agreement with those found for the diffusion of photoreactive dye diffusion in PS in the same temperature range. This implies that dPB molecule, like the dye molecules, is acting as a probe of the changing properties of the PS matrix.

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