Surface Segregation in Blends of Polystyrene and Deuterated Polystyrene

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ABSTRACT: Surface-enhanced Raman scattering (SERS) has been used to investigate surface segregation in blends of high molecular weight polystyrene (PS) and deuterated polystyrene (DPS) following annealing at temperatures above the upper critical solution temperature (UCST). Blends of PS and DPS (both having molecular weight 1 950 000) were spin-coated onto silicon substrates from toluene solutions and annealed at 200 °C for various times. Silver island films were then evaporated onto the blend films and SERS spectra were obtained. The relative intensities of the bands near 1015 and 975 cm^{-1}, which were characteristic of PS and DPS, respectively, were used to determine the relative amounts of PS and DPS at the surface of the blend films. Before annealing, the composition of the surface regions of the blends was similar to that of the bulk. However, after annealing, DPS segregated to the surface and the extent of surface segregation was related to the amount of DPS in the blends.

Introduction

Blend systems containing two polymers which differ only by isotopic substitution such as hydrogen replacement by deuterium have been used to determine polymer–polymer miscibility[1,2] and polymer diffusion in the melt.[3–5] In these studies it is usually assumed that mixtures of protonated and deuterated polymers are thermodynamically ideal. However, Bates et al.[6] showed that mixtures of protonated and deuterated polymers which are otherwise chemically identical are not thermodynamically ideal and are characterized by an upper critical solution temperature (UCST). The segment–segment interaction between protonated and deuterated polymers, which can be represented by the Flory parameter χ, has a very small positive value. As a result, all isotopic mixtures of liquid, high molecular weight polymers are expected to undergo phase separation at temperatures below the UCST.

At temperatures above the UCST, the surface of a blend of protonated and deuterated polymers should become enriched in the component having the lowest surface energy. Polystyrene (PS) has a surface energy that is slightly greater than that of deuterated polystyrene (DPS). The larger surface free energy of PS results from the greater polarizability of a carbon–hydrogen bond compared to that of a carbon–deuterium bond which derives from the more extended electron distribution in the longer carbon–hydrogen bonds.[7] Therefore, the surface of blends of high molecular weight PS and DPS should become enriched in DPS during annealing at temperatures above the UCST.

Several groups have investigated surface enrichment of DPS in blends of PS and DPS. Jones et al.[8] used forward recoil spectrometry (FRES) to study surface segregation in a blend of PS and DPS in which the components had molecular weights of 1.8×10^6 and 1.03×10^6, respectively. Before annealing the samples, the volume fraction of DPS was independent of distance below the surface, indicating a uniform polymer blend. However, the volume fraction of DPS near the surface region increased significantly after the samples were heated at 184 °C for 5 days, indicating that surface enrichment of DPS occurred in the PS/DPS blends.

Neutron reflection has also been used to determine the concentration profile at air/polymer blend interfaces.[9] Polymer films which consisted of 10% DPS and 90% PS were spin-coated onto fused silica from toluene solutions. The neutron reflectivity for the annealed samples was greater than for the unannealed ones, suggesting that DPS segregated to the surface region.

The purpose of this paper is to report results that we have obtained using surface-enhanced Raman scattering (SERS) to characterize surface segregation in blends of PS and DPS following annealing at temperatures above the UCST. SERS is a process in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering. Although many theories of SERS have been reported, two mechanisms are responsible for most of the enhancement. One is associated with the large electric fields that can exist at the surfaces of metal particles with small radii of curvature and is only obtained for metals for which the complex part of the dielectric constant is small. The other mechanism is related to distortions of the polarizability of the adsorbed molecules by formation of charge-transfer complexes with the metal surface. Enhancement due to the charge-transfer mechanism is restricted to molecules immediately adjacent to the substrate but enhancement due to the electromagnetic mechanism may extend a few tens of angstroms from the metal surface.

Venkatachalam et al. investigated SERS from polymer bilayers deposited onto silver island films.[10] As long as the thickness of the first polymer film was more than about 100 Å, Raman scattering was observed from the first film but not from the second film. These results confirmed that SERS was an interfacial effect and that the enhancement extended no more than 100 Å from the silver surface.

SERS was obtained from benzene, pyridine, and cyclohexane adsorbed onto cold-deposited silver island films in ultra-high vacuum.[11] The enhancement dropped by about a factor of 10 when benzene and pyridine were separated by a monolayer of cyclohexane from silver. This result demonstrated a short-range enhancement effect

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which was restricted approximately to the first adsorbed monolayer.

The dependence of the SERS intensity upon the surface–molecule separation was also reported by Murray.[12,13] A layer of poly(methyl methacrylate) (PMMA) having a weak Raman cross section was placed as a spacer between a strongly Raman-active layer of *p*-nitrobenzoic acid (PNBA) and a silver island film. The Raman intensity of PNBA dropped off rapidly by a factor of 10 for each 35–50 Å of PMMA layers, suggesting that SERS could be used to distinguish between a layer directly adjacent to the enhancing substrates and another layer away from the substrates.

Boerio and Hong[14] applied SERS to investigate the interface region between silver island films and a multicomponent acrylic adhesive. They found that the SERS spectra of the adhesive were similar to SERS spectra of saccharin and the normal Raman spectra of the sodium salt of saccharin, indicating that saccharin, a relatively minor component of the adhesive, segregated to the silver surface and formed a salt. These results suggested that SERS had great potential to monitor the surface segregation in a polymer blend.

Most of the SERS experiments that have been reported involved polymer films which were deposited onto substrates which support SERS (i.e., underlayers). It should also be possible to characterize the surface properties of polymers by evaporating thin films of SERS-active metals onto the surfaces of the polymers (i.e., overlayers). However, aside from the work of Allara et al.[15] and Parry and Dendramis[16] describing the SERS spectra of poly(*p*-nitrostyrene) and polystyrene films onto which silver had been evaporated, few such experiments have been reported.

Allara, Murray, and Bodoff investigated SERS from poly(*p*-nitrostyrene) (PPNS) using silver "overlayers" and PS using silver "underlayers".[15] In both cases, when the silver films were nearly continuous, enhanced scattering was observed from several hundred angstroms into the polymer films. However, enhanced Raman scattering was observed from only the first few tens of angstroms of polymer at the silver surface when the silver surface had sharp features. It was suggested that SERS might be useful for depth profiling the surface regions of polymer films.

Parry and Dendramis studied SERS from PS deposited onto silicon surfaces and then overcoated with silver films.[16] When SERS spectra of PS were obtained from samples exposed to the atmosphere, bands between 1200 and 1600 cm^{-1} which were attributed to graphitic species were observed. However, when SERS experiments were carried out on samples held under vacuum, these bands were not observed and the SERS spectra were similar to the normal Raman spectra of PS.

We report here the first observations of surface segregation in polymer blends using SERS. In particular, we observe that DPS segregates to the surface of blends of high molecular weight PS and DPS following annealing at temperatures above the UCST. We also find that the extent of segregation is related to the amount of DPS in the blends.

Experimental Section

Polystyrene (PS) and deuterated polystyrene (DPS) having molecular weights of 1.95×10^6 and polydispersities less than 1.14 were purchased from Polymer Laboratories. A PS/DPS diblock copolymer with a molecular weight of 100K in each block was synthesized in our laboratories using the technique described below.

Styrene and deuterium-labeled styrene were purchased from Aldrich and Cambridge Isotope Laboratories, respectively, and were purified before using. The monomers were first added to a clean, dry round-bottom flask filled with nitrogen. Dibutylmagnesium was then slowly added until a pale yellow color appeared, indicating titration of the impurities and a complex of dibutylmagnesium and styrene monomer. The purified monomers were selectively distilled since the impurities were in the form of magnesium salts which were nonvolatile.

Cyclohexane, which was purchased from Phillips Petroleum, and the desired amount of purified styrene were added in a clean reactor. The reactor was heated to 60 °C and titrated by dropwise addition of *sec*-butyllithium. Once a persistent yellow color was achieved, the amount of *sec*-butyllithium was charged to give the desired molecular weight. A period of time around 45 min was required to convert the styrene monomer completely, and then the deuterated styrene was added. Another 45 min was allowed for complete conversion of the deuterated styrene monomer. Samples were characterized by gel permeation chromatography (GPC) to determine the molecular weight and polydispersity.

Silicon wafers were cleaned in toluene and then blown dry using nitrogen. Thin films of PS/DPS blends were deposited onto cleaned silicon wafers by spin-coating from 3% solutions in toluene and then dried for 1 day in vacuum at room temperature to assure that there was no residual solvent in the samples. Samples were annealed at a temperature of 200 °C in argon for 1 day and then cooled rapidly to room temperature. After annealing, silver was evaporated onto the films at room temperature in a vacuum chamber equipped with sorption, sublimation, and ion pumps at a rate of approximately 1 Å/s to a final thickness of approximately 46 Å, as determined by a quartz crystal oscillator thickness monitor.

Raman spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, ITT FW-130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. In the SERS experiments, the slits of the monochromator were set for spectral resolution of 10 cm^{-1}. The laser beam was incident on the SERS samples at an angle of 65° relative to the normal to the sample surface. Scattered light was collected by an *f*/0.95 lens and focused onto the entrance slit of the monochromator. Spectra were obtained with the 5145-Å line of the laser, a scan rate of 50 cm^{-1}/min for survey spectra (from 400 to 1800 cm^{-1}) or 25 cm^{-1}/min for high-resolution spectra (from 900 to 1100 cm^{-1}), and a time constant of 10 s. The thickness of the polymer films was determined by using a Rudolph Research Model 436 ellipsometer to examine the silicon substrates before and after the polymer films were deposited.

Results and Discussion

SERS spectra of PS and DPS are shown in Figure 1. Most of the observed bands were assigned to vibrations of the benzene rings using Wilson's numbering system[17] and have been discussed elsewhere.[18] Differences in frequency between bands in the SERS spectra of PS and DPS were due to the replacement of hydrogen in PS by deuterium in DPS. For example, the very strong band near 1015 cm^{-1} in the spectra of PS, which was attributed to $\nu(1)$, the totally symmetric ring breathing mode, shifted to near 975 cm^{-1} in the SERS spectra of DPS. Therefore, SERS spectra of PS and DPS could easily be distinguished. A band apparently related to sulfite contaminant adsorbed onto the silver island films was observed near 940 cm^{-1} in SERS spectra of PS and DPS.[19]

The broad bands near 1375 and 1600 cm^{-1} were related to graphitic species that resulted from silver-catalyzed oxidative degradation of PS during intense laser irradiation.[20,21] Similar results were reported by Parry and Dendramis.[16]

SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS are shown in Figure 2. The film thickness of the polymer blends was

Figure 1. SERS spectra of (A) polystyrene and (B) deuterated polystyrene.

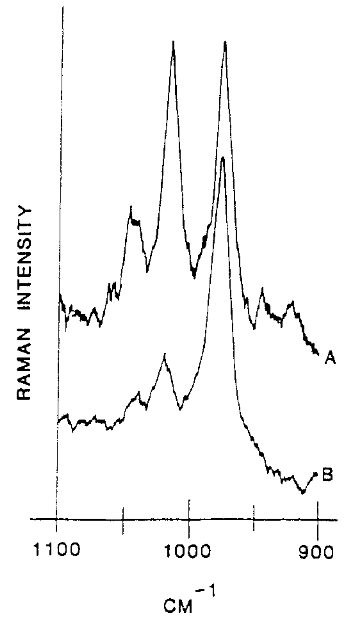

Figure 2. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C in argon for 1 day. The molecular weight of both polymers was 1 950 000, and the film thickness was around 2400 Å.

around 2400 Å. Before annealing, strong bands near 975 and 1015 cm^{-1}, which were characteristic of DPS and PS, respectively, were observed to have the same intensity (see Figure 2A).

Experiment and ab initio simulation have showed that the Raman intensity of the ring breathing mode $\nu(1)$ was similar in benzene and deuterated benzene.[22] Thus, it was reasonable to assume that the Raman scattering cross section for $\nu(1)$ was the same in PS and DPS. This was confirmed by obtaining the normal Raman spectra of a diblock copolymer consisting of PS and DPS with molecular weights of 100K in each block (see Figure 3). The intensity of the band near 1012 cm^{-1} due to PS was similar to that of the band near 973 cm^{-1} due to DPS, suggesting that the Raman scattering cross section for the $\nu(1)$ vibration was the same in PS and DPS.

Considering that SERS is a surface-selective effect and that the Raman scattering cross section for the $\nu(1)$ mode is the same in PS and DPS, the SERS intensities of the bands near 1015 and 975 cm^{-1} were expected to be proportional to the amounts of PS and DPS located in the near-surface region. Since the ratio of the weight fractions of PS and DPS for this blend was 1.0, the ratio of the band intensities was expected to be similar and that was observed.

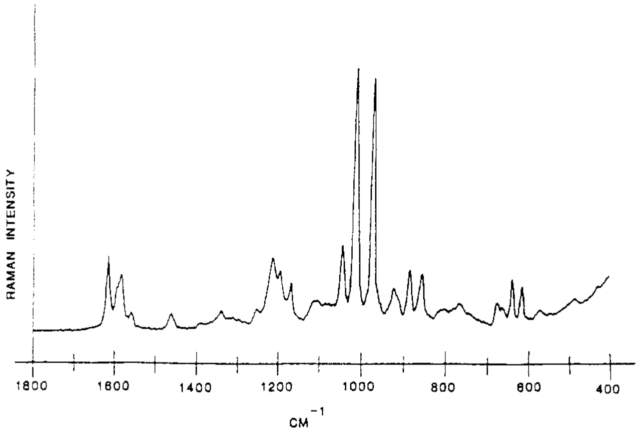

Figure 3. Normal Raman spectrum of a diblock copolymer having polystyrene and deuterated polystyrene with molecular weights of 100K in each block.

The SERS spectra obtained after annealing the PS/DPS blend at a temperature of 200 °C are shown in Figure 2B. After annealing for 1 day, the intensity of the band near 976 cm^{-1} increased significantly relative to that of the band near 1015 cm^{-1}. The Flory–Huggins model predicts an upper critical solution temperature of 176 °C and a critical volume fraction of DPS around 0.5 for the molecular weights used here.[8] Therefore, at a temperature of 200 °C, PS and DPS are completely miscible and DPS, which has a lower surface energy than PS, segregates to the surface through diffusion in order to decrease the total surface energy of the system. Since SERS is an interfacial effect and the intensities of the bands near 1015 and 975 cm^{-1} were proportional to the amounts of PS and DPS located at the surface region, an increase in the intensity of the band near 975 cm^{-1} relative to that near 1015 cm^{-1} indicates segregation of DPS to the surface and that was observed.

Similar experiments were carried out to investigate the effect of composition on the surface segregation of PS/DPS blends. The blends investigated had 20 and 10 weight % DPS. The results (see Figures 4 and 5) obtained showed that the intensity of the band near 975 cm^{-1} increased relative to that of the band near 1015 cm^{-1} after the samples were annealed at a temperature of 200 °C for 1 day, indicating that the air/polymer interface was enriched in DPS.

The extent of enrichment of DPS was observed to be different for polymer blends having different compositions. This phenomenon was investigated by measuring the change in relative intensity of the bands near 975 and 1015 cm^{-1} before and after annealing. A "tangent-line" technique was used to determine the intensity ratio of the bands near 975 and 1015 cm^{-1}. A line was drawn which was tangent to the base line at about 925 and 1065 cm^{-1}. The peak heights above the tangent line were then measured. When the polymer blend contained 50% DPS, the intensities of the band characteristic of PS near 1015 cm^{-1} and of the band characteristic of DPS near 975 cm^{-1} were approximately the same before annealing. However, after annealing, the band near 975 cm^{-1} increased in intensity and the ratio of its intensity to that of the band near 1015 cm^{-1} was 4.0. The increase in the intensity ratio of the bands near 975 and 1015 cm^{-1} from 1.0 before to 4.0

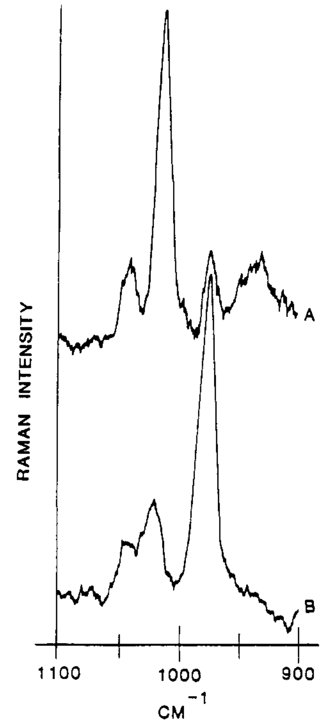

Figure 4. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 20% DPS (A) before and (B) after annealing at 200 °C in argon for 1 day. The molecular weight of both polymers was 1 950 000, and the film thickness was around 2400 Å.

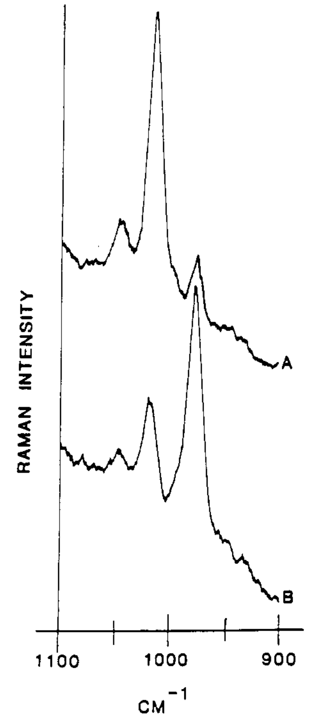

Figure 5. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 10% DPS (A) before and (B) after annealing at 200 °C in argon for 1 day. The molecular weight of both polymers was 1 950 000, and the film thickness was around 2400 Å.

after annealing corresponded to an increase in the concentration of DPS in the surface region from 50% to 80%.

When the polymer blend contained only 20% DPS, the intensity ratio of the bands near 975 and 1015 cm^{-1} was about 0.25 before annealing the samples but increased to about 3.6 after annealing. This corresponded to an increase in the amount of DPS near the surface from 20% to 78%.

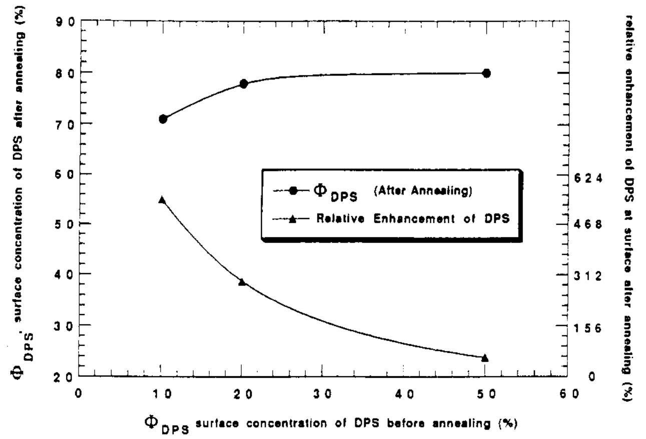

Figure 6. (Circle) plot of surface concentration of DPS after vs before annealing. (Triangle) plot of relative surface enhancement of DPS after annealing vs the surface concentration of DPS before annealing.

However, when a blend contained only 10% DPS, the intensity ratio of the bands near 975 and 1015 cm^{-1} was 0.13 before annealing but 2.5 after annealing, corresponding to an increase in the amount of DPS at the surface from 12% to 71%. Thus, blends which had bulk concentrations of DPS equal to 50%, 20%, and 10% before annealing had relative increases of 58%, 290%, and 545% in the amount of DPS at the surface after annealing (see Figure 6). The sample which had the smallest bulk concentration of DPS before annealing had the greatest relative increase in the amount of DPS at the surface after annealing.

Similar results were reported by Sokolov et al.[23] They used forward recoil spectrometry to determine surface enrichment of PS/DPS blends. Two different blends having bulk concentrations of 14% and 30% DPS were considered. After lengthy annealing of the samples at 184 °C, the amount of DPS at the air surface increased from 14% to 52% and from 30% to 76%, respectively. The relative increase in the amount of DPS at the surface was 271% and 153%, respectively. Thus, the sample having the smallest bulk concentration of DPS showed the greatest relative surface enrichment of DPS.

Hariharan et al. developed a model based on the polymer–surface and polymer–polymer energetic interaction to predict the effect of the bulk volume fraction of the components in the melt on the degree of segregation.[24] A relative enhancement R_2 of component 2 at the surface was defined as

$$R_2 = A_2/\Phi_{2,b}$$

where $\Phi_{2,b}$ is the volume fraction component 2 in the bulk and A_2 was the excess volume fraction of component 2 at the surface relative to the bulk. From the profile of R_2 vs $\Phi_{2,b}$, it was easily found that the relative enhancement was very large in the limit of $\Phi_{2,b} \rightarrow 0$. The experimental results obtained using SERS were consistent with the theoretical results obtained by Hariharan et al.

The results obtained here demonstrate that SERS can be used to determine the properties of polymer surfaces as well as those of polymer interfaces with SERS-active substrates. In the specific case investigated here, SERS was used to show that deuterated polystyrene segregated to the surface of blends with polystyrene during annealing at temperatures well above the upper critical solution temperature and that the extent of segregation depended on the amount of DPS in the blend. Using SERS for such purposes is considerably easier than using other techniques such as neutron reflectivity.

Conclusions

Surface-enhanced Raman scattering (SERS) was used to investigate surface segregation in blends of high molecular weight (about 1 950 000) polystyrene (PS) and deuterated polystyrene (DPS) by evaporating silver island films onto the blend films after annealing at temperatures above the UCST. The relative intensities of the bands near 1015 and 975 cm^{-1}, which were characteristic of PS and DPS, respectively, were used to determine the relative amounts of PS and DPS at the surface of the blend films. Before annealing, the composition of the surface regions of the blends was similar to that of the bulk. However, after annealing DPS segregated to the surface and the extent of surface segregation was related to the amount of DPS in the blends.

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