Effect of Annealing Time, Film Thickness, and Molecular Weight on Surface Enrichment in Blends of Polystyrene and Deuterated Polystyrene

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ABSTRACT: Surface-enhanced Raman scattering (SERS) was used to investigate surface segregation in blends of polystyrene (PS) and deuterated polystyrene (DPS) following annealing at temperatures above the upper critical solution temperature (UCST). Blends of PS and DPS were spin-coated onto cleaned silicon wafers from toluene solutions and annealed at temperatures above the UCST. 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. When the blends consisted of PS and DPS with the same molecular weight, DPS segregated to the free surface after annealing. Moreover, the extent of surface segregation increased when the annealing time, the film thickness of the blends, and the molecular weight of the polymers in the blends were increased. When blends contained PS and DPS with different molecular weights, DPS always segregated to the free surface as long as PS had molecular weights that were greater than DPS. However, PS segregated to the surface when PS had a relatively small molecular weight, indicating that the surface free energy of polymers, which caused surface segregation in blends of PS and DPS, was determined by both molecular weight and isotopic effects.

I. Introduction

Mixtures of protonated and deuterated polymers which are otherwise chemically identical are not thermodynamically ideal and are expected to undergo phase separation at temperatures below the upper critical solution temperature (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 in order to minimize the free energy of the whole system. Polystyrene (PS) has a surface energy that is slight greater than that of deuterated polystyrene (DPS).[1] Therefore, the surface of blends of high molecular weight PS and DPS should become enriched in DPS during annealing at temperatures above the UCST.

Numerous techniques have been employed to investigate surface segregation in blends of PS and DPS, including forward recoil spectrometry (FRES),[2,3] dynamic secondary ion mass spectroscopy (SIMS),[4,5] and neutron reflection (NR).[6,7] Jones et al.[2] used FRES to study surface segregation in blends of PS and DPS in which the components had molecular weights of 1.8×10^6 and 1.03×10^6, respectively. It was found that the volume fraction of DPS in the surface region increased significantly after the samples were annealed at 184 °C for 5 days, indicating that surface enrichment of DPS occurred in the PS/DPS blends.

The segregation phenomenon was also observed using dynamic SIMS.[5] Films of PS/DPS ($1.8 \times 10^6/1.03 \times 10^6$) blends around 2–3 μm in thickness were deposited onto silicon wafers and then annealed at 184 °C. Before annealing, the surface concentration of DPS was 33%. However, it was 37.5% and 70% after the samples were annealed for 3 and 29 days, respectively. These results indicated that DPS segregated to the air surface and that the extent of surface segregation increased as the annealing time increased.

Very recently, Hariharan et al.[8] reported the use of NR to determine the effect of film thickness on surface segregation in films of symmetric blends of PS and DPS. It was found that, after annealing at temperatures above the UCST, the extent of surface segregation was constant for film thicknesses of polymer blends that were greater than 4 times R_g (the unperturbed radius of gyration of the polymers). However, when the thickness of the polymer blend films was reduced to less than 4 times R_g, the amount of segregation after annealing decreased with decreasing film thickness.

Most reported experiments involved surface segregation in blends in which PS and DPS had the same molecular weight. In that regard, the larger surface free energy of PS was due to 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.[1] However, for polymer blends in which PS and DPS had different molecular weights, the dependence of surface free energy on the molecular weights should also be considered.

A lattice and off-lattice Monte Carlo simulation of a polymer melt near the surface region was established in order to determine surface segregation in polymer blends.[9] The chain-length dependence of the chemical potential difference suggested that DPS always segregated to the air surface as long as PS had chain lengths that were greater than DPS. However, when PS had a relatively small chain length, PS segregated to the surface. These results showed that the surface free energy was determined by both chain-length and isotopic effects.

Neutron reflection has also been used to determine the concentration profile at air/polymer blend interfaces.[7] Polymer blends in which PS and DPS had molecular

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weights of 720 and 910K, respectively, were spin-coated onto fused silica from toluene solutions. The neutron reflectivity for annealed samples was greater than that of unannealed samples, indicating that DPS segregated to the surface. However, the amount of segregation decreased with increasing annealing temperature or annealing time, suggesting that during annealing DPS evaporated as well as segregated to the surface.

Hariharan, Kumar, and Russell also used NR[10] to determine the dependence of surface segregation on molecular weight in PS/DPS blends. A series of PS/DPS mixtures containing PS and DPS having different molecular weights was studied. The results showed that PS segregated to the surface when the PS had a relatively small molecular weight, indicating the importance of chain-length effects on surface segregation. However, in the NR experiments, more than one model concentration profile can be used to described the observed reflectivity, and hence other independent information is required to quantitatively interpret the data. Therefore, NR is an indirect technique to determine the concentration profiles through the polymer blends.

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 at the roughed surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering. However, the enhancement decreases very quickly as a function of distance, and little enhancement is obtained for molecules that are more than a few monolayers away from the surface of SERS-active metals. As a result, SERS is surface selective and can be used for characterization of the surface property of polymers.

The dependence of the SERS intensity upon the surface-molecule separation was reported by Murray using silver overlayers.[11,12] A layer of poly(methyl methacrylate) (PMMA) having a small 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 PMMA layer, suggesting that SERS could be used to distinguish between a layer directly adjacent to the enhancing substrates and another layer farther away from the substrates.

Few investigations of SERS by polymers have been reported and most of them involved polymer films which were deposited onto substrates which supported SERS (i.e., underlayers).[13-20] It should also be possible to characterize the surface properties of polymers by evaporating thin films of SERS-active metals onto the surfaces of polymers (i.e., overlayers).

Parry and Dendramis studied SERS from PS deposited onto silicon surfaces and then overcoated with silver island films.[21] 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.

Allara, Murray, and Bodoff investigated SERS from poly(*p*-nitrostyrene) (PPNS) using silver "overlayers" and from PS using silver "underlayers".[22] In both cases, the SERS intensity initially increased as a function of polymer film thickness and then became saturated at a certain thickness, which depended on the roughness features of the silver island films. The results suggested that SERS might be useful for depth-profiling the surface regions of polymer films.

Table 1. Molecular Weight of Polystyrene (PS) and Deuterated Polystyrene (DPS) and Their Sources

MW of PS	source
1 950 000	Polymer Laboratories
1 950 000[a]	Polymer Laboratories
500 000	Polymer Laboratories
500 000[a]	Polymer Laboratories
70 000	synthesized in our lab
70 000[a]	synthesized in our lab
13 000	synthesized in our lab
13 000[a]	synthesized in our lab
1 000	synthesized in our lab
1 000[a]	synthesized in our lab

[a] Deuterated polystyrene.

Very recently, we reported the first observations of surface segregation in polymer blends using SERS by silver overlayers.[23] Blends of PS and DPS in which both components had molecular weights of 1950K were spin-coated onto cleaned silicon wafers from solutions in toluene and then annealed at a temperature of 200 °C for 1 day. Silver island films were evaporated onto the top of the blend film, and SERS spectra were obtained. 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 segregation was related to the amount of DPS in the blends. This experiment was very simple, and the spectra gave direct information regarding the composition of PS/DPS blends at the air surface.

In this paper, we used SERS to determine the effects of film thickness, annealing time, molecular weight, and disparate chain length on the surface segregation in blends of PS and DPS. When blends consisted of PS and DPS with the same molecular weights, DPS was observed to segregate to the free surface following annealing at temperatures above the UCST. It was also found that the extent of surface segregation increased with increasing the annealing time, the film thickness of the blends, and the molecular weight of the polymers in the blends. When the blends contained PS and DPS with different molecular weights, DPS always segregated to the free surface as long as PS had molecular weights that were greater than DPS. However, PS segregated to the surface when PS had a relatively small molecular weight.

II. Experimental Section

A series of polystyrenes (PS) and deuterated polystyrenes (DPS) having polydispersity indices less than 1.14 were used (see Table 1). 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-bottomed flask filled with nitrogen. Dibutylmagnesium was then slowly added until a pale yellow 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 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. Polymerization was then terminated by adding degassed isopropyl alcohol, resulting in hydrogen end groups. Samples were

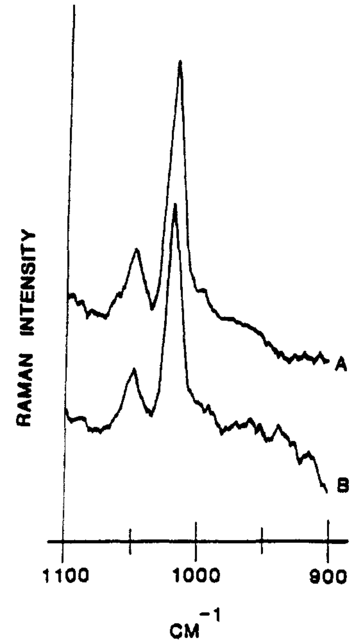

Figure 1. SERS spectra of PS (A) before and (B) after annealing at 200 °C for 24 h.

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, and PS/DPS blends were deposited onto cleaned silicon wafers by spin-coating from solutions in toluene with different concentrations 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 under argon at a temperature above the upper critical solution temperature (UCST) of blends for various times and then cooled rapidly to room temperature. After annealing, silver was evaporated onto the films 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.

SERS spectra were obtained using a Raman 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. The slits of the monochromator were set for a 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 and was polarized perpendicular to the plane of incidence. Scattered light was collected by an *f*/0.95 lens and focused onto the entrance slit of the monochromator. Spectra were obtained using the 5145-Å line of the laser, a scan rate of 25 cm^{-1}/min, and a time constant of 10 s. Laser power was always less than about 25 W for the SERS experiments.

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.

III. Results and Discussion

SERS spectra of PS and DPS are shown in Figures 1A and 2A, respectively. Most of the observed bands were assigned to vibrations of the benzene rings using Wilson's numbering system and have been discussed elsewhere.[20] 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 $\nu(12)$, a symmetric ring deformation mode, shifted to near 975 cm^{-1} in the SERS spectra of DPS. The band related to the ring stretching mode $\nu(18a)$ was observed near 1045 cm^{-1} in the SERS spectrum of PS but shifted to near 1018 cm^{-1} in the spectrum of DPS. Due to the differences in band positions, particularly for the band assigned to $\nu(12)$, SERS spectra of PS and DPS could easily be distinguished. No changes were observed in the SERS spectra of PS and DPS after annealing at 200 °C for 24 h (see Figures 1B and 2B, respectively).

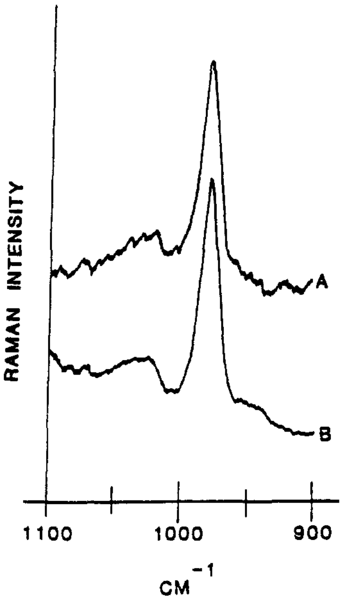

Figure 2. SERS spectra of DPS (A) before and (B) after annealing at 200 °C for 24 h.

Effect of Annealing Time. SERS spectra obtained as a function of annealing time from thin films of PS/DPS blends having a molecular weight of 1 950 000 and a weight fraction of 50% DPS are shown in Figure 3. 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 3A). Considering that SERS is a surface-selective effect and assuming that the Raman scattering cross sections for $\nu(12)$ were the same in PS and in DPS,[23,24] the SERS intensities of the bands near 1015 and 975 cm^{-1} should 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.

After annealing the blend samples at a temperature of 200 °C for several hours, the intensity of the band near 975 cm^{-1} increased relative to that near 1015 cm^{-1} (see Figure 3B–E). The intensity ratios of the band near 975 cm^{-1} characteristic of DPS and that near 1015 cm^{-1} characteristic of PS became 1.2, 1.4, and 4.0 as the annealing time was increased from 2 h, to 4 h, and then to 16 h.

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.[2] 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.

The volume fraction of DPS near the surface region was calculated from the intensities of the bands near 975 and

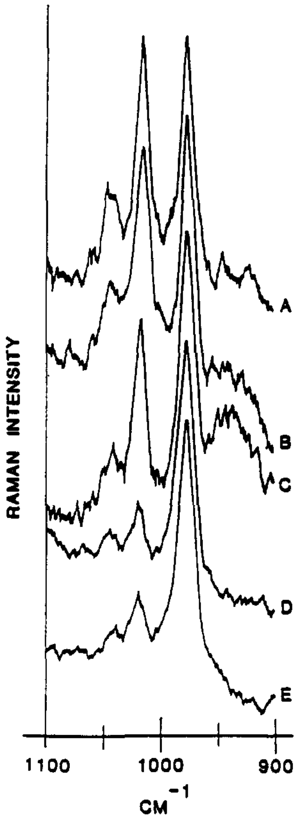

Figure 3. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS after annealing at 200 °C for (A) 0, (B) 2, (C) 4, (D) 16, and (E) 24 h. The molecular weight of both polymers was 1.95×10^6, and the film thickness of the polymer blends was around 2400 Å.

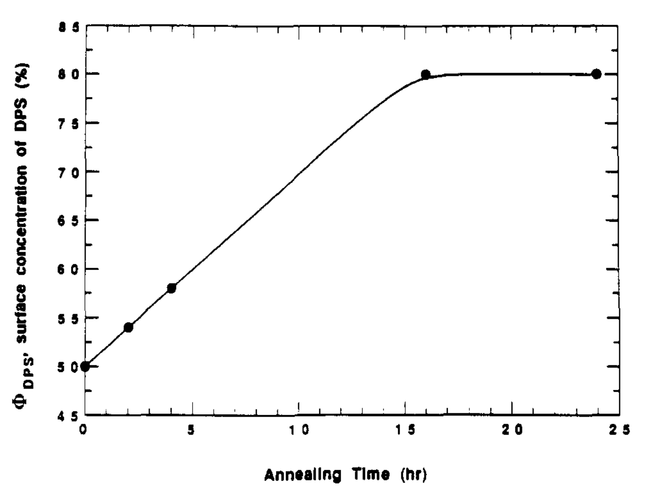

Figure 4. Plot of the surface concentration of DPS vs annealing time. The annealing temperature was 200 °C.

1015 cm^{-1} using the expression:

$$\Phi_D = I_{975}/(I_{975} + I_{1015}) \quad (1)$$

where I_{975} and I_{1015} were the heights of the peaks near 975 and 1015 cm^{-1}, respectively. The surface composition of DPS was 50%, 54%, 58%, and 80% after the samples were annealed at 200 °C for times of 0, 2, 4, and 16 h, respectively. These results showed that the enrichment of DPS at the air surface increased as annealing time increased (see Figure 4). No further changes in the relative intensities of the bands near 975 and 1015 cm^{-1} were observed as the annealing time was increased to 24 h (see Figure 3E), indicating that the system had reached equilibrium.

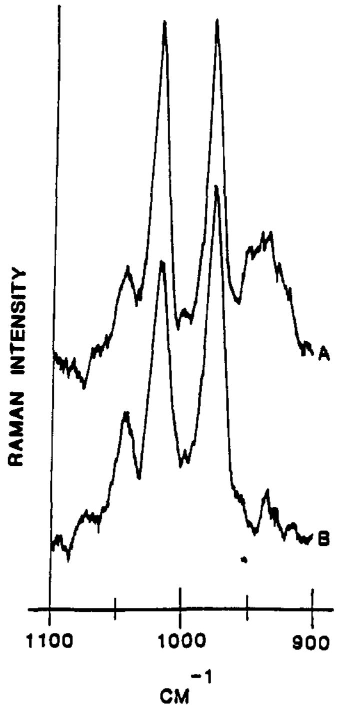

Figure 5. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h. The molecular weight of both polymers was 1.95×10^6, and the film thickness of the polymer blends was around 600 Å.

In our SERS experiments, a significant increase in the amount of DPS at the surface was observed after the blend samples were annealed for 16 h. However, significant surface segregation of DPS was not observed until the annealing time was increased to 29 days in the SIMS experiments reported by Zhao et al.[5] These differences were probably due to a higher annealing temperature (about 17 °C larger) and a reduced film thickness (about 10 times less) in the experiments reported here compared with those reported by Zhao et al.

Effect of Film Thickness. The effect of film thickness on the surface segregation of DPS in PS/DPS blends having a weight fraction of 50% DPS was studied. SERS spectra obtained from PS/DPS blends having film thicknesses of 600, 1200, and 2400 Å are shown in Figures 5–7, respectively. Before annealing, the intensity of the band near 975 cm^{-1} was approximately the same as that of the band near 1015 cm^{-1} (see Figures 5A, 6A, and 7A). However, after the samples were annealed at 200 °C for 24 h, the band near 975 cm^{-1} increased in relative intensity in all cases (see Figures 5B, 6B, and 7B). The intensity ratio of the band near 975 cm^{-1} relative to that near 1015 cm^{-1} increased from 1.4 to 4.0 as the film thickness of the polymer blends increased from 600 to 2400 Å, indicating that DPS segregated to the air surface following annealing of the samples at 200 °C and that the amount of DPS on the surface increased as the film thickness of the polymer blends increased. The concentration of DPS near the surface region after annealing was calculated using 1 and was 58%, 65%, and 80% for samples having thicknesses of 600, 1200, and 2400 Å, respectively. A plot of the surface concentration for DPS vs film thickness for polymer blends after annealing is shown in Figure 8.

The DPS that segregated to the free surface came from the bulk, and hence the maximum segregation of DPS should be obtained in the thickest films of PS/DPS blends and that was observed. Another explanation for thinner films of polymer blends resulting in a smaller amount of

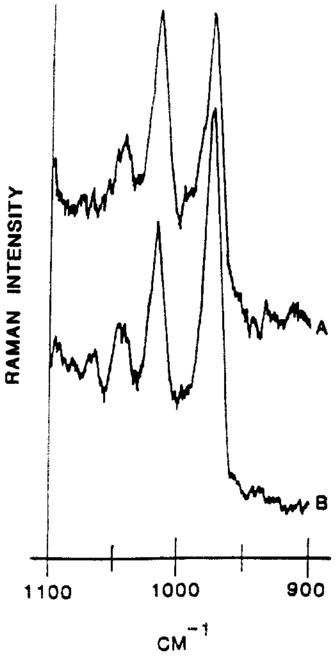

Figure 6. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h. The molecular weight of both polymers was 1.95 × 10^6, and the film thickness of the polymer blends was around 1200 Å.

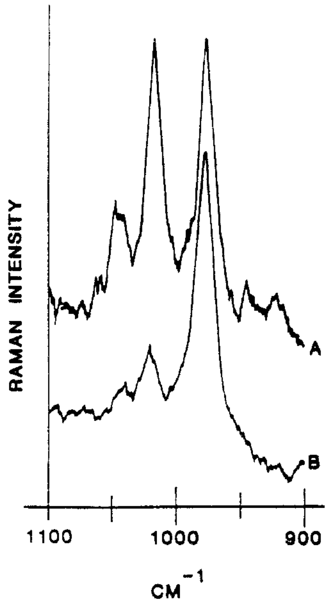

Figure 7. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h. The molecular weight of both was 1.95 × 10^6, and the film thickness of the polymer blends was around 2400 Å.

DPS segregated to the surface was considered. It had been reported that DPS segregated to both air and silicon surfaces and that the amount of DPS which segregated to the silicon surface was larger than that at the air surface.[8] Thus, when the film thickness of a blend was reduced, the amount of DPS enriched at the air surface would be greatly limited by the segregation of DPS to the silicon surface.

Effect of Molecular Weight. Experiments were also carried out to determine the effect of molecular weight on surface segregation in PS/DPS blends. The polymers used in these experiments had molecular weights of 1 950 000, 500 000, and 70 000. The thickness of the blend films was around 2400 Å in all cases. All the spectra showed that the band near 975 cm^{-1} increased in relative intensity after the samples were annealed at a temperature of 200 °C for 1 day. However, the extent of enrichment of DPS at the surface was a function of the molecular weight of the polymers in the blends.

SERS spectra obtained from thin films of PS/DPS blends in which the polymer molecules had a molecular weight of 1 950 000 and the weight fraction of DPS was around 50% are shown in Figure 7. Using eq 1, the surface concentration of DPS was 50% before annealing but 80% after annealing. For the case in which both PS and DPS had molecular weights of 500 000, the surface concentration of DPS was about 50% before annealing but increased to 70% after annealing (see Figure 9). When the polymers in the blends had molecular weights of only 70 000, the surface concentration of DPS was 50% before annealing but 60% after annealing (see Figure 10). These results suggested that higher molecular weight polymers showed the greatest enrichment of DPS at the surface (see Figure 11).

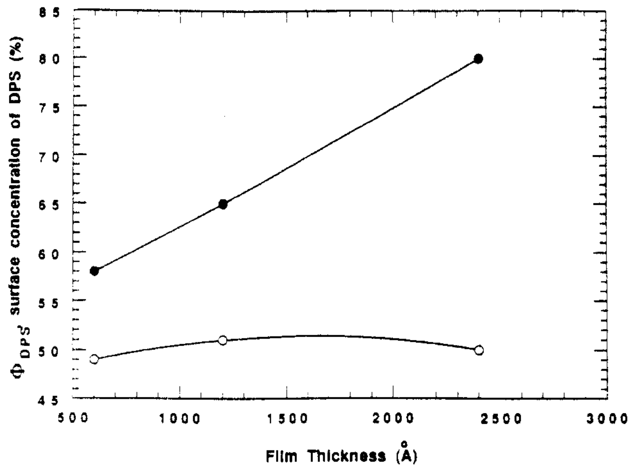

Figure 8. Plot of the surface concentration of DPS vs thickness of the polymer blends. The open and solid symbols represent the surface concentration of DPS before and after annealing, respectively.

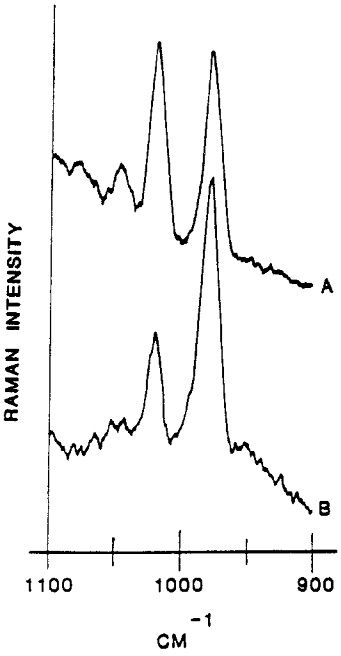

Figure 9. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h. The molecular weight of both polymers was 5 × 10^5, and the film thickness of the polymer blends was around 2400 Å.

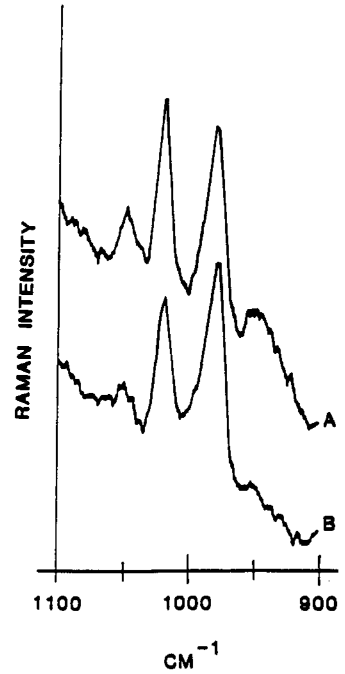

Figure 10. SERS spectra obtained from thin films of PS/DPS blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h. The molecular weight of both polymers was 7 × 10^4, and the film thickness of the polymer blends was around 2400 Å.

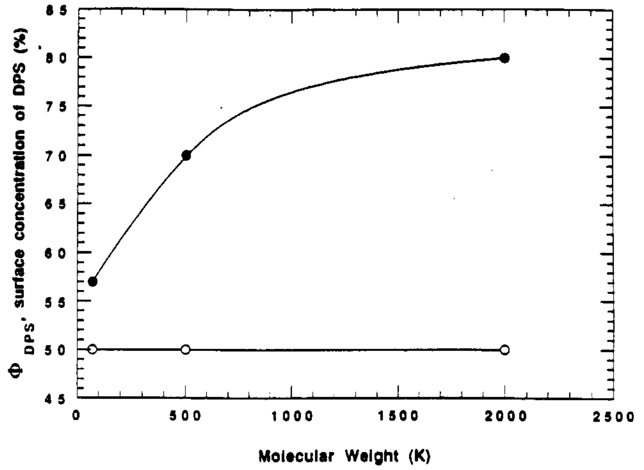

Figure 11. Plot of the surface concentration of DPS vs the molecular weight of the polymers. The open and solid symbols represent the surface concentration of DPS before and after annealing, respectively.

DPS, which has the lower surface energy when the molecular weights are equal, would segregate to the surface to minimize the free energy of the whole system. However, this specific arrangement of making one component segregate to the surface from the bulk would destroy the random order of the mixtures of PS and DPS (the random order would show the greatest entropy). Hence, the segregation resulted in a loss of entropy, which is unfavorable. Consequently, the relative magnitude of these two competitive effects would determine the final surface composition of DPS.

For the case in which the polymers in the blends had large molecular weights, the amount of entropy loss associated with segregation of DPS to the surface was small compared to the free energy saving. As a result, enrichment of DPS at the surface was expected to be significant. In fact, that was observed (see Figure 7). For the case in which the blends had small molecular weights, the entropy loss associated with the segregation of DPS to the surface was large and could not be offset by the reduced free energy. Therefore, the extent of surface segregation of DPS was expected to be small, and that was observed (see Figure 10).

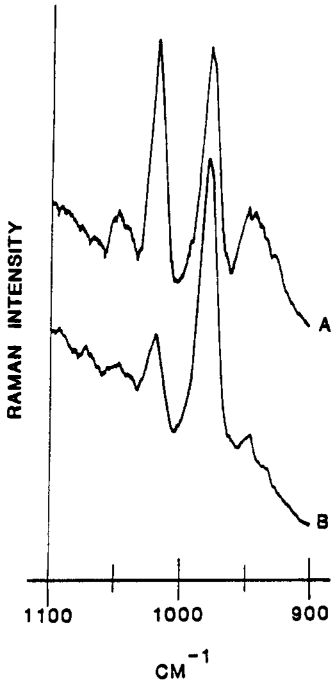

Figure 12. SERS spectra obtained from thin films of PS/PDS (500K/1950K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h.

Effect of Disparate Chain Length. All of the experiments discussed above were carried out using blends in which PS and DPS had the same molecular weights. It was also of interest to determine surface segregation in PS/DPS mixtures containing PS and DPS having different chain lengths. SERS spectra obtained from a series of polymer blends in which DPS had a molecular weight of about 1950K and PS had a molecular weight varying from 1950K to 1K are shown in Figures 12–15.

SERS spectra obtained from thin films of PS and DPS blends in which the polymer molecules had molecular weights of 500K and 1950K, respectively, and the weight fraction of DPS was 50% are shown in Figure 12. Before annealing, the intensities of the bands near 975 and 1015 cm^{-1}, which were characteristic of DPS and PS, respectively, were about the same, but the relative intensity of the band near 975 cm^{-1} increased significantly after the sample was annealed at 200 °C for 1 day, indicating again that DPS segregated to the surface.

Figure 13 shows the SERS spectra obtained before and after annealing thin films of PS/DPS blends in which the polymer molecules had molecular weights of 70K/1950K and the weight fraction of DPS was 50%. No changes were observed in the spectra after annealing at 200 °C for 1 day, indicating no segregation of DPS or PS to the surface.

SERS spectra of blends in which the molecular weight of PS was only 13K and the molecular weight of DPS was 1950K are shown in Figure 14. Since the weight fraction of DPS was also 50% in this blend, the intensities of the bands due to PS and DPS were expected to be similar before annealing. However, the intensity of the band near 1015 cm^{-1} was slightly stronger than that of the band near 975 cm^{-1}, indicating that PS had already segregated to the free surface before annealing. After annealing, the relative intensity of the band near 1015 cm^{-1} increased, indicating that segregation of PS to the free surface during annealing increased.

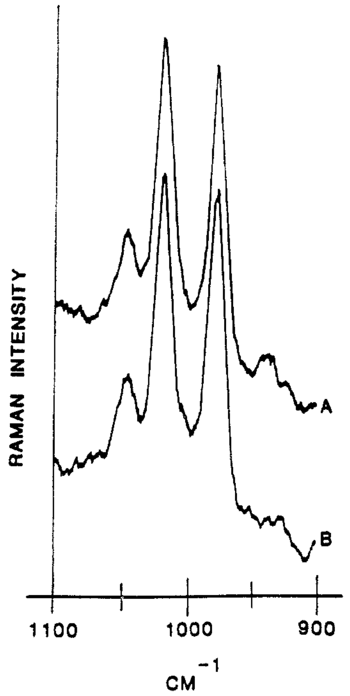

Figure 13. SERS spectra obtained from thin films of PS/DPS (70K/1950K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h.

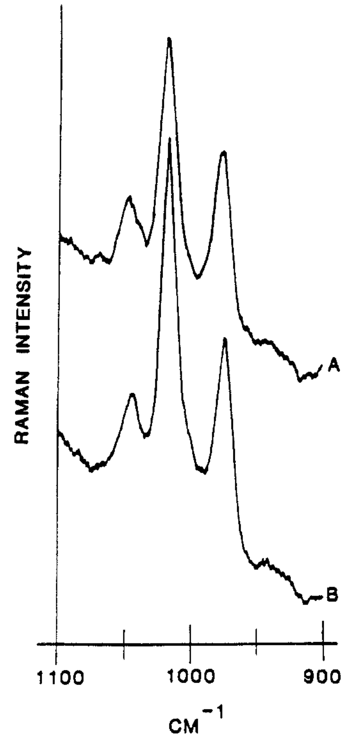

Figure 14. SERS spectra obtained from thin films of PS/DPS (13K/1950K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h.

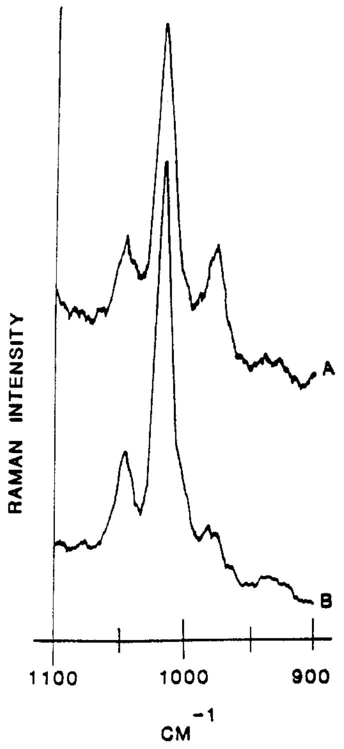

Figure 15. SERS spectra obtained from thin films of PS/DPS (1K/1950K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 150 °C for 24 h.

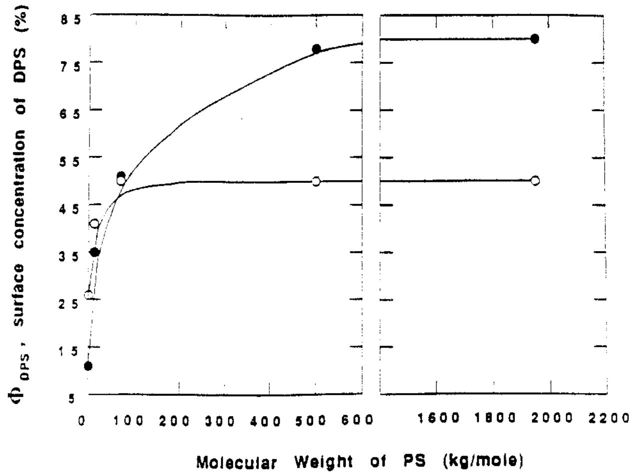

Figure 16. Plot of the surface concentration of DPS vs the molecular weight of PS. The molecular weight of DPS was kept constant at 1950K. The open and solid symbols represent the surface concentration of DPS before and after annealing, respectively.

The SERS spectra of PS/DPS (1K/1950K) blends with a weight fraction of 50% DPS are shown in Figure 15. Before annealing, the intensity of the band near 975 cm^{-1} was very strong compared to that of the band near 1015 cm^{-1}, indicating strong segregation of PS to the free surface. The glass transition temperature (T_g) of this blend system was only 60 °C and was much lower than those of the blend systems discussed previously (around 100 °C). Therefore, the annealing temperature chosen here was 150 °C in order to keep the value of $T - T_g$ approximately the same. After annealing the sample at a temperature of 150 °C for 1 day, the spectrum was almost dominated by the band near 1015 cm^{-1} due to PS and only a very weak band near 975 cm^{-1} due to DPS was observed. A plot of the surface concentration of DPS vs the molecular weight of PS is shown in Figure 16 (the molecular weight of DPS in all blends was kept constant at 1950K).

Results shown in Figure 16 clearly show that the surface composition of PS/DPS blends depends strongly on the length of the PS chains if the length of the DPS chains is large and fixed and that both energetic and entropic effects contribute to the surface segregation. Considering just the entropic effect, PS, which had a shorter chain length than DPS in the experiments summarized in Figures 12–16, should segregate to the surface. However, considering the energetic effect which results from the polarizability difference between C–D and C–H bonds, DPS should segregate to the surface. Therefore, the energetic and entropic factors compete with each other, and their relative magnitudes determine the final segregation behavior and surface composition of the blends.

When blends consisted of PS and DPS with the same molecular weight of 1950K, only the isotopic effect was considered to cause the surface free energy difference between PS and DPS. Therefore, strong segregation of DPS at the surface was expected and was observed (see Figure 7). As the molecular weight of PS decreased from 1950K to 500K (Figure 11), isotopic as well as chain-length effects should be considered. However, because the chain length of PS was not short enough compared to that of DPS, the surface energy difference between PS and DPS was mostly dependent on the isotopic effect. Hence, a strong enrichment of DPS at the surface was also observed in Figure 12.

As the molecular weight of PS became less and less, the chain-length effect became more and more important. At the point where the chain-length effect equalled the isotopic effect, the surface free energy difference between PS and DPS became zero and no segregation of DPS or PS was observed. This phenomenon was confirmed by the spectra shown in Figure 13, which were obtained from PS/DPS blends in which the molecules had molecular weights of 70K and 1950K, respectively.

As the molecular weight of PS was reduced further, the chain-length effect dominated over the isotopic effect. In this case, segregation of PS at the surface was observed in the SERS spectra which were obtained from blends consisting of very short chain lengths of PS and very long chain lengths of DPS (see Figures 14 and 15). It should be noted that PS which has a molecular weight of 13K or 1K was enriched at the air surface before annealing. This occurred because, as the films were spin-coated onto the silicon wafers from solutions, toluene would carry out more PS to the surface due to the lower glass transition temperature of PS compared to that of DPS. (The glass transition temperature increased as the molecular weight of PS or DPS increased and reached a constant value of around 100 °C when the molecular weight was larger than 23K.)

SERS spectra were also obtained from another series of polymer blends in which the molecular weight of PS was kept constant at 1950K, while that of DPS was varied from 1950K to 1K. Considering both isotopic and chain-length effects, DPS was expected to always segregate to the surface. However, the extent of segregation of DPS was different for different polymer blends.

Figures 7 and 17–19 are the SERS spectra obtained from a series of polymer blends consisting of PS having a molecular weight of 1950K and DPS having a molecular weight of 1950K, 500K, 70K or 13K. Before annealing, the intensity of the band near 975 cm^{-1} was the same as that of the band around 1015 cm^{-1}. However, the band near 975 cm^{-1} increased in relative intensity when the samples were annealed at 200 °C for 1 day. The surface concentration of DPS calculated from eq 1 became 79%, 78%, 67%, and 76% for PS/DPS blends in which the molecular weights were 1950K/1950K, 1950K/500K, 1950K/70K, and 1950K/13K, respectively. In the case of blends of PS and DPS in which both polymers had a molecular weight of 1950K, the driving force for DPS to segregate to the surface came from the isotopic effect only. For blends in which PS and DPS had molecular weights of 1950K/500K, 1950K/70K, and 1950K/13K, respectively, the driving force came from both isotopic and chain-length effects and would be enhanced. However, the amount of DPS segregated at the surface in the case of PS/DPS (1950K/70K) (see Figure 18) was smaller than that in the case of PS/DPS (1950K/1950K) (see Figure 7). This was probably because the energy cost to make the blends demix was larger in the case of blends of PS/DPS (1950K/70K) than in the case of blends of PS/DPS (1950K/1950K). A plot of the surface concentration of DPS as a function of the molecular weight of DPS is shown in Figure 20 for blends in which the molecular weight of PS was kept constant at 1 950 000 but the molecular weight of DPS was varied.

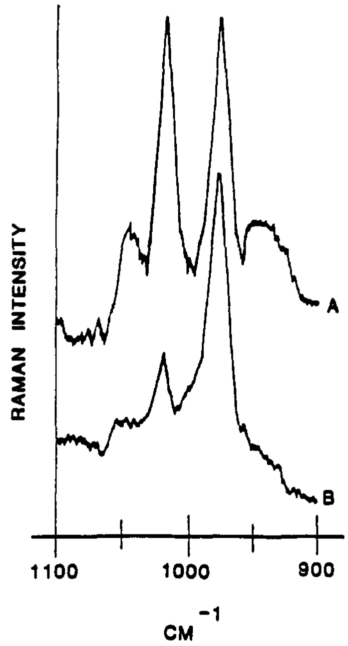

Figure 17. SERS spectra obtained from thin films of PS/DPS (1950K/500K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h.

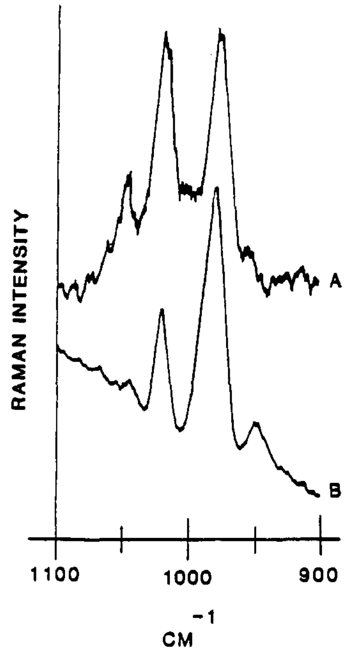

Figure 18. SERS spectra obtained from thin films of PS/DPS (1950K/70K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h.

It is interesting to compare the SERS spectra of PS/DPS (1950K/1K) with that of PS/DPS (1K/1950K) (see Figures 21 and 15). According to the energetic and entropic effects, the surface enrichment of DPS in the case of PS/DPS (1950K/1K) was expected to be larger than that of

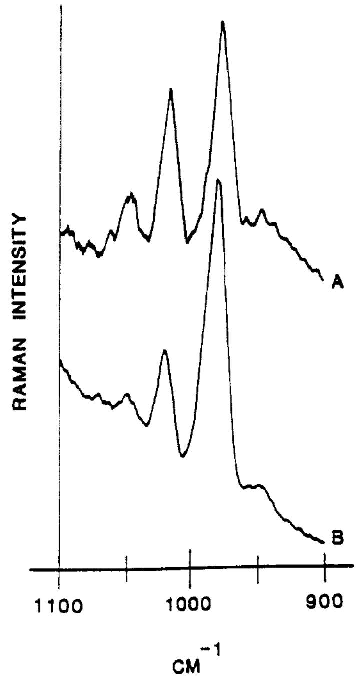

Figure 19. SERS spectra obtained from thin films of PS/DPS (1950K/13K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 200 °C for 24 h.

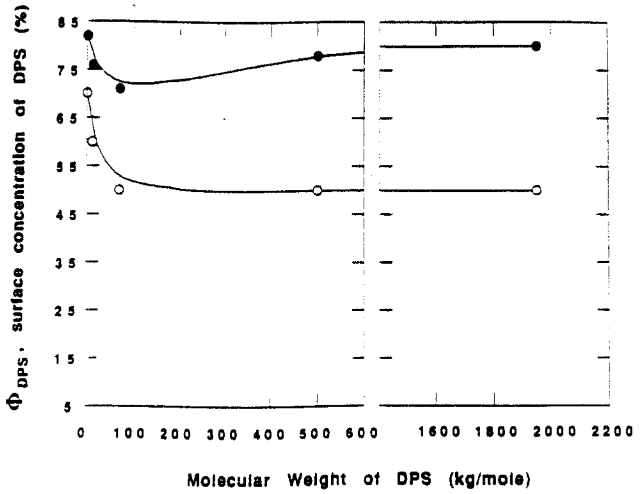

Figure 20. Plot of the surface concentration of DPS vs the molecular weight of DPS. The molecular weight of PS was kept constant at 1950K. The open and solid symbols represent the surface concentration of DPS before and after annealing, respectively.

PS in the case of PS/DPS (1K/1950K). However, the surface concentration of DPS shown in Figure 21 was 82%, which was slightly smaller than the surface concentration of PS shown in Figure 15 (89%). The discrepancy was probably due to the evaporation of oligomers at the surface. The glass transition temperature of DPS having a molecular weight of 1K was about 20 °C, while that of PS with the same molecular weight was around 40 °C, which implied that segregation as well as evaporation of oligomers should be observed as the blends of PS/DPS (1950K/1K) and PS/DPS (1K/1950K) were annealed at a temperature of 150 °C for 24 h. For the same annealing temperature, the evaporation of DPS (1K) from the blend of PS/DPS (1950K/1K) should be faster than that of PS (1K) from the blend of PS/DPS (1K/1950K). Consequently, the surface concentration of DPS shown in Figure 21 would be smaller than that of PS shown in Figure 15.

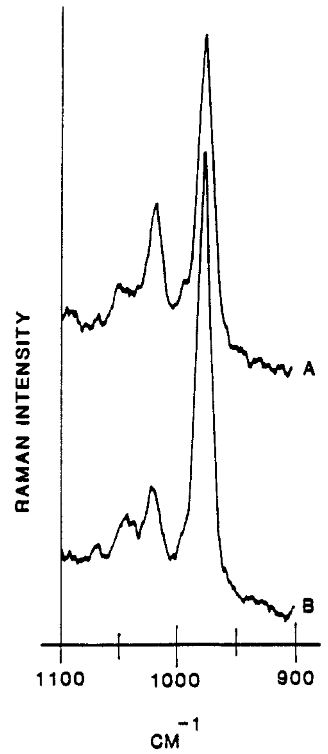

Figure 21. SERS spectra obtained from thin films of PS/DPS (1950K/1K) blends having a weight fraction of 50% DPS (A) before and (B) after annealing at 150 °C for 24 h.

IV. Conclusions

Surface-enhanced Raman scattering was used to investigate surface segregation in blends of PS and DPS by evaporating silver island films onto blend films before and after annealing at a temperature 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. When blends consisted of PS and DPS with the same molecular weights, DPS segregated to the free surface during annealing at a temperature above the UCST. Moreover, the extent of surface segregation increased with increasing the annealing time, the film thickness of the blends, and the molecular weight of polymers in the blends. When the blends contained PS and DPS having different molecular weights, DPS always segregated to the free surface as long as PS had a molecular weight that was greater than that of DPS. However, PS segregated to the surface when PS had a relatively small molecular weight, indicating that the surface free energy, which caused the surface segregation, was determined by both molecular weight and isotopic effects.

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References and Notes

(1) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.

(2) Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. H.; Skolov, J.; Schwarz, S. A. *Phys. Rev. Lett.* **1989**, *62*, 280.

(3) Sokolov, J.; Rafailovich, M. H.; Jones, R. A. L.; Kramer, E. J. *Appl. Phys. Lett.* **1989**, *54*, 590.

(4) Goldblatt, R. D.; Scilla, G. J.; Park, J. M.; Johnson, J. F.; Huang, S. J. *J. Appl. Polymn.* Sci. **1988**, *35*, 2075.

(5) Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkens, B. J.; Jones, R. A. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 5991.

(6) Composto, R. J.; Stein, R. S.; Kramer, E. J.; Jones, R. A. L.; Mansour, A.; Karim, A.; Fletcher, G. P. *Physica* **1989**, *156B*, 343.

(7) Composto, R. J.; Stein, R. S.; Felcher, G. P.; Mansour, A.; Karim, A. *Mater. Res. Soc. Symp. Proc.* **1990**, *166*, 485.

(8) Hariharan, A.; Kumar, S. K.; Russell, T. P., submitted to *J. Chem. Phys.*

(9) Kumar, S. K.; Russell, T. P. *Macromolecules* **1991**, *24*, 3816.

(10) Hariharan, A.; Kumar, S. K.; Russell, T. P., submitted to *J. Chem. Phys.*

(11) Murray, C. A. In *Surface-Enhanced Raman Scattering*; Chang, R. K., Furtak, T. E., Eds.; Plenum Press: New York, 1982; p 203.

(12) Murray, C. A. In *Advances in Laser Spectroscopy*; Garetz, B. A., Lombardi, J. R., Eds.; John Wiley & Sons: New York, 1986; Vol. 3, p 49.

(13) Boerio, F. J.; Hong, P. P.; Clark, P. J.; Okamoto, Y. *Langmuir* **1990**, *6*, 721.

(14) Lippert, J. L.; Brandt, E. S. *Langmuir* **1988**, *4*, 127.

(15) Suh, J. S.; Michanelian, K. H. *J. Phys. Chem.* **1987**, *91*, 598.

(16) Boerio, F. J.; Tsai, W. H.; Montaudo, G. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1017.

(17) Venkatachalam, R. S.; Boerio, F. J.; Roth, P. G.; Tsai, W. H. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 2477.

(18) Xue, G.; Dong, J.; Zhang, J. *Macromolecules* **1991**, *24*, 4195.

(19) Garrell, R.; Beer, K. D. *Langmuir* **1989**, *5*, 452.

(20) Hong, P. P.; Boerio, F. J.; Clarson, S. J.; Smith, S. D. *Macromolecules* **1991**, *24*, 4770.

(21) Parry, D. B.; Dendramis, A. L. *Appl. Spectrosc.* **1986**, *40*, 656.

(22) Allara, D. L.; Murray, C. A.; Bodoff, S. In *Physicochemical Aspects of Polymer Surfaces*; Mittal, K. L., Ed.; Plenum Press: New York, 1983; Vol. 1, p 33.

(23) Hong, P. P.; Boerio, F. J.; Smith, S. D., submitted to *Macromolecules.*

(24) Ozkabak, A. G.; Thakur, S. N.; Goodman, L. *Int. J. Quant. Chem.* **1991**, *39*, 411.