An Investigation of the Interdiffusion of Polystyrene and Deuterated Polystyrene Using Surface-Enhanced Raman Scattering

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ABSTRACT: Interdiffusion of layers of polystyrene and deuterated polystyrene was investigated by surface-enhanced Raman scattering (SERS). Silver island films having a thickness of about 45 Å were evaporated onto glass slides. Polystyrene films were then deposited on the silver films by spin-coating from solutions in toluene. Films of deuterated polystyrene were deposited on clean glass slides by spin-coating from solution. The slides were then immersed in water, resulting in delamination of the deuterated polystyrene films. These films were then picked up on the polystyrene-coated silver island films to form bilayers. When SERS spectra were obtained from the as-prepared bilayers, a band characteristic of the polystyrene films adjacent to the surface was observed near 1014 cm^{-1} but no bands related to deuterated polystyrene were observed, indicating the relatively short-range nature of SERS. However, after the specimens were heated at 170 °C for a few minutes, a band characteristic of deuterated polystyrene began to appear near 976 cm^{-1}. After heating for several additional minutes, equilibrium was reached and the relative intensities of the bands near 1014 and 976 cm^{-1} did not change with heating time. The time required for equilibrium to be reached and the thickness of the polystyrene films were used to calculate the diffusion coefficient using equations given in the literature. The calculated diffusion constants were in good agreement with reported values. As expected, the most reasonable values of the diffusion constant were obtained with relatively thick polystyrene films. In those cases, the calculated values were within a factor of 2 of the reported values.

I. Introduction

Diffusion of entangled polymer molecules in the melt is important in areas such as the adhesion of polymers and the kinetics of phase separation of polymer blends. For several years, the diffusion theory of polymers in entangled systems has been dominated by the idea of reptation.[1,2] In the reptation model, a single polymer molecule is considered to be trapped inside a virtual tube defined by the other molecules. A single polymer may diffuse by crawling along its tube via wormlike motion. The diffusion coefficient D of a linear polymer with a degree of polymerization N was described by the reptation relation:

$$D = (N_e B_0 k_B T)/N^2 \qquad (1)$$

where N_e is the entanglement degree of polymerization for the polymer ($N \gg N_e$), B_0 is a monomer mobility, and k_B and T are Boltzmann's constant and temperature, respectively.

Due to the slow motion of polymers in entangled systems, the study of diffusion in polymers usually requires long times and measurement techniques having high sensitivity. Therefore, it is necessary to decrease the diffusion distance to reduce the diffusion time and to use diffusant molecules that are deuterated or radio-labeled to distinguish them from the similar matrix molecules. Numerous techniques are now employed to measure polymer diffusion in entangled systems, such as radioactive tracer techniques,[3-5] pulsed field gradient nuclear magnetic resonance,[6-8] infrared microdensitometry,[9-11] forward recoil spectroscopy,[12-14] and secondary ion mass spectroscopy.[16]

The self-diffusion coefficient in an entangled polymer fluid was first measured by Bueche et al.[3] using a radioactive tracer technique. They concluded that the product of the diffusion coefficient and the bulk viscosity was equal to a constant. Radioactive polystyrene was laid down on a flat base block of similar but nonradioactive polystyrene. As the radioactive polystyrene diffused into the base polystyrene, the intensity of radiation emitted from the surface of the system decreased due to the absorption of the radiation by the bulk polymer. Therefore, the diffusion coefficient D could be calculated from the decrease in the radioactive count rate I with time t according to the equation

$$\begin{aligned} I/I_0 = {} & \{\exp(u^2Dt)/2[1 - \exp(-ua)]\}\{\exp(ua) - \\ & \exp(-ua) - \exp(ua)\,\mathrm{erf}\,[(a + 2uDt)/2(Dt)^{0.5}] + \\ & \exp(-ua)\,\mathrm{erf}\,[(-a + 2uDt)/2(Dt)^{0.5}]\} + \\ & \mathrm{erf}\,[a/2(Dt)^{0.5}]/[1 - \exp(-ua)] \qquad (2) \end{aligned}$$

where u is the absorption coefficient of the block materials.[5] Bueche also showed that it was possible to obtain the diffusion coefficient directly from viscosity data according to the relationship between diffusion coefficient and viscosity.[3,4] Although the radioactive tracer technique was a simple way to measure the diffusion coefficient of a polymer, no significant diffusion was observed if the diffusion rate was slow. Thus, only polymers with relatively large diffusion coefficients could be detected by this technique.

Klein and co-workers[9] used infrared microdensitometry (IRM) to measure the diffusion coefficient of polyethylene. A high molecular weight polyethylene (PE) diffusion matrix was contacted with a mixture of 2% deuterated polyethylene (DPE) and 98% PE as a diffusant. The band around 2170 cm^{-1} due to the C–D stretching mode was observed from the IR spectra of DPE, which was not observed from that of PE. Therefore, the concentration profile of DPE within the PE matrix could

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be carried out by IRM. At the beginning of the experiment, the concentration/distance profile showed a very sharp interface region between these two layers. However, the interface region between the layers became broadened after heating the sample at 176 °C for several days, indicating that the DPE had diffused into the PE matrix. Thus the diffusion coefficient of PE could be calculated from the diffusion-broadened step function.

The mutual diffusion of high and low molecular weight polystyrene in polymer blends was also investigated by IRM.[11] A distinct asymmetry in the concentration profiles was observed. Such asymmetry was not observed when these two polymers had the same molecular weight. The results suggested that the mutual diffusion is controlled by the mobility of the faster moving polymer. Due to the limited spatial resolution of IRM (50 μm), a large diffusion distance and a long diffusion time are required.

Pulsed field gradient nuclear magnetic resonance (PFG NMR) was also used to measure the diffusion coefficients of polyethylene (PE), polystyrene (PS), and poly(dimethylsiloxane) (PDMS).[6,8] Garrido and co-workers measured the diffusion coefficient of PDMS by PFG NMR.[8] In addition to the transverse relaxation, the diffusion behavior caused the spin echo to be damped. The echo attenuation was given by

$$A(g)/A(0) = \exp[-D\gamma^2 g^2 \delta^2(\Delta - \delta/3)] \quad (3)$$

where $A(g)$ and $A(0)$ are the echo amplitudes with and without the field gradient pulses, respectively, γ is the gyromagnetic ratio of the nuclei, and g is the magnitude of the gradient. D is the diffusion coefficient, and Δ and δ are the lengths of the pulses and spacing between them, respectively. The diffusion coefficient derived from the slope of plots of the echo attenuation $\ln[A(g)/A(0)]$ against $g^2\delta^2(\Delta - \delta/3)$ was proportional to the molecular weight raised to the minus second power, in good agreement with the predictions of the reptation model. However, because of the decrease of the nuclear relaxation time with the molecular weight, diffusion in polymer of very high molecular weight could not be detected by PFG NMR.

Kramer et al. measured the diffusion coefficient of polystyrene in an entangled system by forward recoil spectroscopy (FRES).[12-14] A beam of 3-MeV $^4He^{2+}$ ions was directed at a bilayer sample of DPS and PS at a glancing angle α (measured between the incident beam and the sample surface) equal to 15°. The energy of deuterons and protons recoiling from the surface at a scattering angle of 30° (measured between the direction of incidence and the scattering direction) was determined. The output of the detector provided a spectrum of number of recoiling particles versus energy. Since ^2H nuclei recoil with energies about 1.4 times greater than those of ^1H nuclei, recoiling ^2H and ^1H could be distinguished. The recoil energy of nuclei from below the surface was lower than that of nuclei from near the surface due to inelastic particle collision with electrons in the polymers. Therefore, a plot of the yield of ^2H nuclei versus energy could be converted to a plot of the atom fraction of ^2H versus diffusion depth. The diffusion coefficient was calculated from the Fickian diffusion equation:

$$\phi(x) = 0.5\{\mathrm{erf}\,[(h - x)/(4Dt)^{0.5}] + \mathrm{erf}\,[(h + x)/(4Dt)^{0.5}]\} \quad (4)$$

where $\phi(x)$ is the volume fraction of DPS at a depth x, D is the diffusion coefficient, and h and t are thickness of DPS and the diffusion time, respectively. A very low value of the diffusion coefficient can be measured by FRES. The spatial resolution of this technique is around 35 nm, which is much better than that of IRM (around 50 μm).

Recently, diffusion measurements using nuclear reaction analysis (NRA) were carried out by Chaturvedi et al.[15] When ^3He particles from a Van de Graaff accelerator were incident on a deuterium-labeled polymer layer, the polymer would emit α particles according to the nuclear reaction

$$^3He + {}^2H \rightarrow {}^4He + {}^1H \quad (5)$$

As the ^3He particles penetrated into the polymer, the reaction occurred at different depths. The energy of forward-emitted α particles was detected and found to decrease as the penetration depth increased due to inelastic electronic processes which decreased the energies of the incident ^3He particles as they penetrated into the sample and the α particles emitted from the sample. Therefore, the energies of the α particles provided a measure of the depth at which the reaction occurred. From the intensity of counts at different energies, a concentration versus depth profile of deuterium atoms was obtained from which the diffusion coefficient was calculated using the Fickian diffusion equation. The spatial resolution of NRA is around 10 nm. Thus diffusion in a very thin film is able to be carried out by this technique.

Techniques for measuring the diffusion coefficient in entangled polymer systems must have good spatial resolution. In that regard, surface-enhanced Raman scattering (SERS) seems ideal. SERS is a process in which the Raman scattering cross section of the 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. 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. As a result, SERS is surface selective. The scattering from a polymer film on a SERS-active substrate arises almost entirely from the first few molecular layers adjacent to the substrate as long as the film is less than ~1000 Å in thickness. Thus, SERS can be used for in situ, nondestructive characterization of polymer interfaces.

Although many theories of SERS have been reported, it now appears that two mechanisms are responsible for most of the enhancement.[17] One mechanism is associated with the large electric field that exists at the surface 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 the molecules immediately adjacent to the substrate, but enhancement due to electromagnetic mechanisms may extend a few molecular layers away from the metal surface.

Several applications of SERS to polymer systems have been reported. Allara et al. investigated SERS from poly(*p*-nitrostyrene) (PPNS) and polystyrene (PS).[18] In one case, PPNS films of different thickness were spin-coated onto aluminum substrates and silver island films 200 Å thick were deposited onto the polymer films. In the other case, a 100-Å-thick silver island film was deposited onto glass slides and then PS films of different thickness were spin-coated onto the silver films. In both cases, the SERS intensity initially increased as a function of the polymer film thickness. After the thickness of the polymer film reached a certain value, the SERS intensity depended on the morphological features of the silver island film.

Enhanced Raman scattering was observed from several hundred angstroms into the polymer film when the silver film was continuous. However, enhanced Raman scattering was observed only from the first few tens of angstroms of the polymer at the silver surface when the roughness features of the silver film were sharp. As a result, it was suggested that SERS might be useful for depth profiling the surface regions of polymer films.

Boerio et al. investigated SERS from poly(α-methylstyrene) (PMS) spin-coated on silver island films from methyl ethyl ketone solutions with different concentrations.[19] The results showed that the intensity of the SERS spectra was constant even though the thickness of the PMS films varied from ~300 to 2000 Å, indicating that SERS was an interfacial rather than bulk effect.

Venkatachalam et al. investigated SERS from polymer bilayers deposited onto silver island films.[20] Samples were prepared by spin-coating thin films of polymers such as polystyrene, poly(α-methylstyrene), poly(4-vinylpyridine), and diglycidyl ether of Bisphenol A onto silver substrates and then overcoating them with a much thicker film of a second polymer such as poly(4-styrenesulfonate) (PSS). The results obtained confirmed that SERS could be used for nondestructive characterization of the interface. Raman scattering was observed from both polymers as long as the film adjacent to the silver was less than ~100 Å thick. However, Raman scattering was observed only from the polymer adjacent to the silver but not from PSS when the film adjacent to the substrates was more than ~100 Å thick. These results confirmed that SERS is an interfacial effect and that the enhancement extends nor more than ~100 Å from the silver surface.

The foregoing results indicate that SERS can easily be used to distinguish between a polymer layer at the surface of a metal and another layer that is distant from the surface by ~100 Å. Moreover, SERS, like other techniques of vibrational spectroscopy, can easily be used to distinguish a hydrogenated polymer from its deuterated analogue. Therefore, SERS should be well suited for investigations of the interdiffusion of hydrogenated and deuterated polymers. The purpose of this paper is to describe some preliminary results we have obtained using SERS to investigate the interdiffusion of polystyrene and deuterated polystyrene.

II. Experimental Section

Substrates for SERS were prepared by slow thermal evaporation of silver island films onto glass slides. The glass slides were cleaned by immersion in 0.1 N NaOH solution for 1 h, removed, rinsed in 0.1 N HCl solution for 1 h, and blown dry in a stream of nitrogen. Silver was evaporated onto the slides at a rate of about 1 Å/s to a final thickness of ~40 Å in a vacuum chamber equipped with sorption, sublimation, and ion pumps and a quartz crystal oscillator thickness monitor.

Samples for this experiment consisted of bilayers of deuterated polystyrene (DPS) and polystyrene (PS) films. The PS and DPS were prepared in our laboratories by anionic polymerization. Two different samples of PS were prepared, having molecular weights of 70 000 and 20 000. Similar samples of DPS were prepared. However, the PS and DPS samples had polydispersities of ca. 1.05 and 1.12, respectively.

Thin films of PS were deposited onto the SERS substrates by spin-coating from solution in toluene and then dried for 1 day in a vacuum oven at room temperature. Thin films of DPS were deposited onto cleaned glass slides by spin-coating from solution in toluene. DPS films were floated off the glass slides onto the surface of a water bath and picked up on the PS-coated SERS substrates to form a bilayer. Bilayer films were dried in a vacuum oven at room temperature for 1 day to remove the water trapped between the layers. The samples were then allowed to interdiffuse for various times at 170 °C in a vacuum oven.[16]

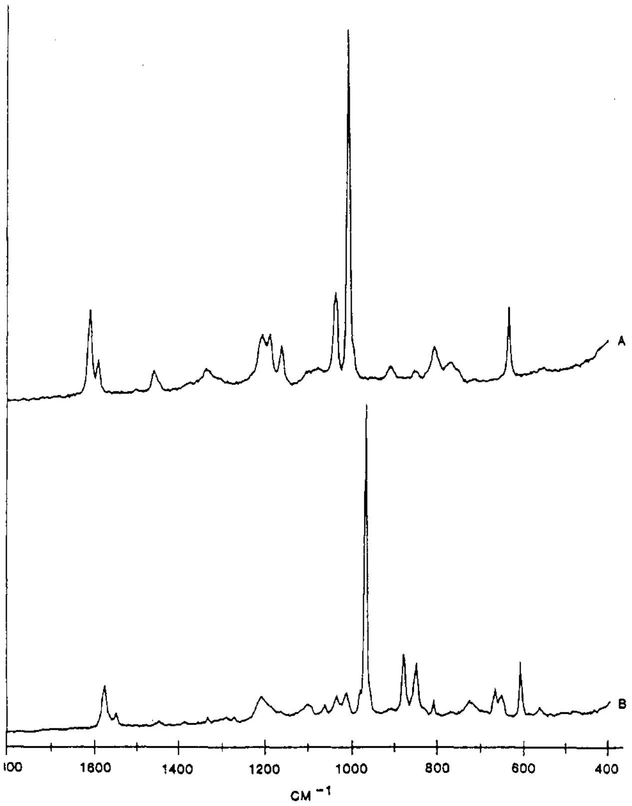

Figure 1. Normal Raman spectra of (A) polystyrene and (B) deuterated polystyrene.

To estimate the thickness of the organic films on the SERS samples, thick films of Ag (several hundred angstroms) were evaporated onto glass slides. Films of PS were spin-coated onto the Ag substrates from the same solutions and at the same speeds as were used to prepare the SERS samples. Films of DPS were spin-coated onto glass slides and then floated off the glass slide onto the surface of a water bath. The films were then picked up on the Ag substrates. The thickness of the polymer films was determined by using a Rudolph Research Model 436 ellipsometer to examine the Ag substrates before and after deposition of the polymer films.

SERS spectra were obtained with 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 with the 5145-Å line of the laser, a scan rate of 50 cm^{-1}/min, and a time constant of 10 s.

Normal Raman spectra were obtained with the same instrument and techniques that have been described elsewhere. The laser beam was focused onto a small amount of powdered sample supported in a glass capillary tube, and the scattered light was collected as described above. However, in this case the spectral slit width was ~2 cm^{-1}.

III. Results and Discussion

Results obtained from ellipsometry indicated that films of polystyrene and deuterated polystyrene spin-coated from 2% solutions in toluene onto thick silver films had thicknesses of approximately 1100 Å. Films spun from 5% and 10% solutions had thicknesses of approximately 3100 and 4800 Å, respectively.

The normal Raman spectra of polystyrene and deuterated polystyrene are shown in Figure 1. The observed bands are also summarized in Table I. Most of the

Table I
Tentative Band Assignments of PS and DPS[a]

DPS		PS		
NRS, cm^{-1}	SERS, cm^{-1}	NRS, cm^{-1}	SERS, cm^{-1}	assignment
1580 (M)	1585 (W)	1612 (M)	1615 (M)	$\nu(8a)$
1555 (M)	1585 (M)	1596 (W)		$\nu(8b)$
1211 (W)	1458 (W)	1458 (W)	1461 (W)	$\delta(CH_2)$
1105 (W)		1330 (W)		$\gamma_t(CH_2)$
		1210 (M)		$\nu(13)$
882 (M)	886 (M)	1196 (M)		$\nu(9a)$
852 (M)	858 (W)	1170 (M)	1172 (W)	$\nu(15)$
1018 (M)	1018 (M)	1040 (M)	1040 (M)	$\nu(18a)$
970 (S)	976 (S)	1012 (S)	1014 (S)	$\nu(1)$
		912 (W)		$\nu(17b)$
810 (W)		852 (W)		$\nu(10a)$
703 (W)				$\gamma_r(CH_2)$
670 (M)	829 (W)	806 (W)		$\nu(12)$
595 (M)	631 (W)	633 (M)	636 (W)	$\nu(6b)$

[a] NRS = normal Raman spectra, SERS = surface-enhanced Raman spectra. S = strong, M = medium, W = weak.

observed bands were assigned to vibrations of the benzene rings and can be discussed in terms of Wilson's numbering system.[21] Normal Raman spectra of PS were characterized by a very strong band near 1012 cm^{-1} that was assigned to $\nu(1)$, the ring breathing mode. The medium-intensity bands near 1612 and 1040 cm^{-1} were assigned to $\nu(8a)$ and $\nu(18a)$, respectively. The medium-intensity band near 633 cm^{-1} was assigned to $\nu(6b)$, a radial ring stretching mode. The medium-intensity band near 1210 cm^{-1} was attributed to $\nu(13)$, a ring stretching mode. Medium-intensity bands near 1196 and 1170 cm^{-1} were assigned to $\nu(9a)$ and $\nu(15)$, which are CH in-plane bending modes, respectively. The weak band near 1596 cm^{-1} was assigned to $\nu(8b)$, a tangential ring stretching mode. Several bands related to modes of the polymer backbone were also observed in the normal Raman spectrum of PS. The band near 850 cm^{-1} could be the combination band of the CH out-of-plane bending modes $\nu(10a)$ from the ring and the CH_2 rocking modes $\gamma_r(CH_2)$ from the backbone. Two weak bands around 1458 and 1330 cm^{-1} were assigned to methylene deformation and twisting modes, respectively.

Differences in frequency between bands in the normal Raman spectra of PS and DPS were due to the replacement of hydrogen in PS by deuterium in DPS. The very strong band near 970 cm^{-1} in normal Raman spectra of DPS was attributed to $\nu(1)$, the totally symmetric ring breathing mode, while the same vibration mode was around 1012 cm^{-1} in the normal Raman spectra of PS. The band due to the ring stretching mode $\nu(8a)$ was observed near 1612 cm^{-1} in the PS spectrum and near 1580 cm^{-1} in the normal Raman spectrum of DPS. Bands near 882 and 852 cm^{-1} in the DPS spectrum were assigned to the CD in-plane bending modes $\nu(9a)$ and $\nu(15)$, respectively. The medium-intensity band near 595 cm^{-1} was assigned to $\nu(6b)$, a radial ring stretching mode. The bands related to the polymer backbone were also observed at lower wavenumbers in the DPS spectrum. Thus, bands due to the CD_2 deformation mode and the CD twisting mode were observed near 1211 and 1105 cm^{-1}, respectively.

SERS spectra obtained from thin films of PS spin-coated onto silver island films from 2%, 5%, and 10% solutions in toluene are shown in Figure 2. Only the bands related to $\nu(1)$, $\nu(18a)$, and $\nu(8a)$ are clearly visible in this spectrum, near 1040, 1014, and 1615 cm^{-1}, respectively. The broad bands near 1375 cm^{-1} and near 1600 cm^{-1} are related to graphitic species resulting from silver-catalyzed oxidative degradation of PS during intense laser irradiation.[19] The broad band near 940 cm^{-1} is related to a sulfite contaminant adsorbed onto the silver island films. It is interesting to note that the SERS spectra of PS shown in Figure 2 all have approximately the same intensity even though the films from which the spectra were obtained varied in thickness by a factor of approximately 4.5. These results emphasize that SERS is an interfacial rather than bulk effect.[19,20]

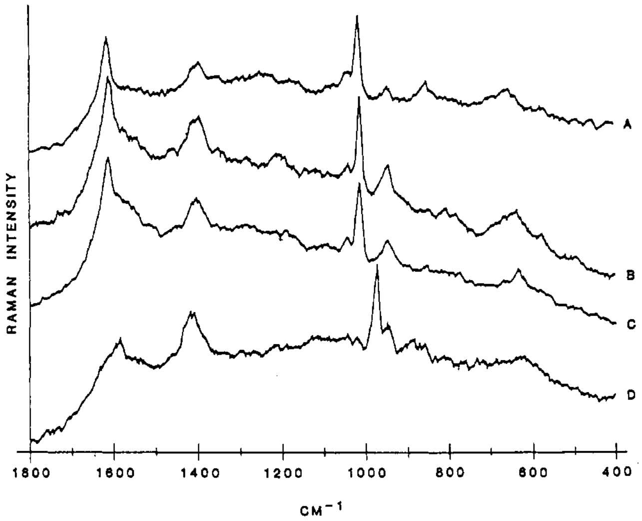

Figure 2. SERS spectra obtained from polystyrene spin-coated onto silver island films from (A) 2%, (B) 5%, and (C) 10% solutions in toluene. The SERS spectrum of deuterated polystyrene spin-coated onto a silver island film from a 2% toluene solution is shown in D. Molecular weight of both polymers was about 70 000.

The spectrum of DPS is also shown in Figure 2. Once again only three bands, assigned to $\nu(1)$, $\nu(18a)$, and $\nu(8a)$, were observed near 976, 1018, and 1585 cm^{-1}, respectively.

Initially, experiments were carried out on the polymers having molecular weight of 70 000. The SERS spectrum obtained from a bilayer consisting of a film of PS having a thickness of ~1100 Å overlaid with a film of DPS having a similar thickness is shown in Figure 3A. Only the bands characteristic of the PS layer adjacent to the silver surface are observed in this spectrum, near 1040 and 1014 cm^{-1}. Bands related to the DPS overlayer are not observed even though the thicknesses of the films were similar and DPS has approximately the same cross section for Raman scattering as PS. This demonstrates again that SERS is a relatively short-range effect.

The SERS spectra shown in Figures 3B-E were obtained from the specimen described above as a function of heating time at 170 °C. Before any heating, only the bands related to PS were observed near 1040 and 1014 cm^{-1}. At the beginning of the heating, the DPS layer may begin to diffuse into the PS layer. However, at a short diffusion time the DPS was not able to diffuse into the layers adjacent to the silver surface and was not adsorbed onto the silver substrate. Thus, no bands related to DPS were observed when the spectra were taken after heating the samples for 1 min (see Figure 3B). However, a new band related to DPS was observed near 970 cm^{-1} when the sample was heated for ~3 min, indicating that a certain amount of DPS was on the silver surface via diffusion. The intensity of this DPS band became almost the same as that of the PS band near 1014 cm^{-1} when the sample was heated for 4 min. No further changes in the relative intensities of the bands near 1014 and 976 cm^{-1} were observed as the heating time was increased beyond 4 min.

Since the Raman scattering cross section of PS is similar to that of DPS and SERS is a surface-selective effect, the SERS intensities of the bands near 1014 and 976 cm^{-1} should be proportional to the amounts of PS and DPS

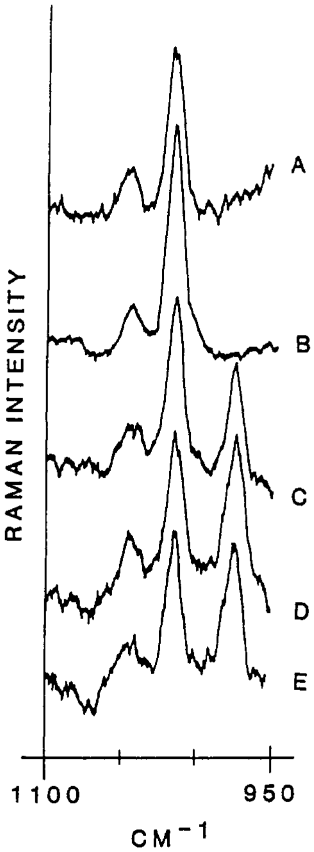

Figure 3. SERS spectra obtained as a function of heating time at 171 °C from a bilayer consisting of a film of polystyrene having a thickness of approximately 1100 Å overlaid with a film of deuterated polystyrene having a similar thickness. The heating times were (A) 0, (B) 1, (C) 3, (D) 4, and (E) 6 min. Molecular weight of both polymers was about 70 000.

located in the near-surface region. Since the intensities of bands characteristic of PS and DPS bands observed in the SERS spectra after heating for 4 min were similar, it was concluded that the amounts of DPS (via diffusion) and PS in the near-interface region were about the same.

If we assume that the average diffusion distance of DPS layers was equal to the thickness of the original PS layers, the macroscopic diffusion coefficient D can be calculated by the equation[8]

$$\langle x^2 \rangle = 2Dt \tag{6}$$

where $\langle x^2 \rangle$ is the mean-square displacement (or the average diffusion distance) in some direction during a time t. In this experiment, the average diffusion distance was around 1100 Å and the diffusion time was around 4 min. Thus, the diffusion coefficient of DPS obtained here was around 0.25×10^{-12} cm^2 s^{-1}, which was lower than the value obtained by others (1.4×10^{-12} cm^2 s^{-1}) by a factor of ~6.

Equation 6 is strictly applicable to a material diffusing into an infinite matrix. However, in the experiment described above, the PS matrix films were only about 1100 Å thick. It was considered that increasing the thickness of the PS matrix layer would result in an increase in the accuracy of the measurement of the diffusion coefficient. Therefore, a similar experiment was carried out except that the PS matrix film was deposited by spin-coating from a 5% instead of 2% solution. This resulted in an increase in the thickness of the matrix layer from 1100 to ~3100 Å. The results are shown in Figure 4.

Initially, only the bands characteristic of PS were observed near 1040 and 1014 cm^{-1}. However, after heating for 3 min, the band characteristic of DPS appeared near 976 cm^{-1}. The intensity of the band near 976 cm^{-1} increased somewhat as the heating time was increased from 3 to 5 and then to 10 min but no further increases were observed thereafter. Substituting $t = 600$ s and $x = 3100$ Å into eq 6, the diffusion coefficient was found to be approximately 0.8×10^{-12} cm^2 s^{-1}, which was within a factor of 1.8 of the value obtained previously (1.4×10^{-12} cm^2 s^{-1}) by others.

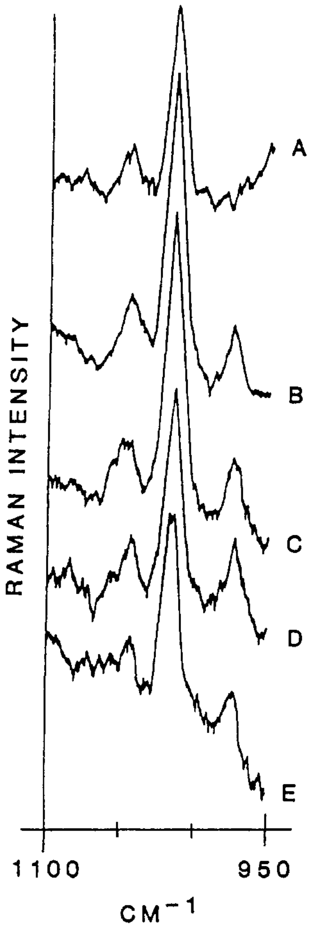

Figure 4. SERS spectra obtained as a function of heating time at 171 °C from a bilayer consisting of a polystyrene film having a thickness of about 3100 Å overlaid with a film of deuterated polystyrene having a thickness of about 1100 Å. The heating times were (A) 0, (B) 3, (C) 5, (D) 10, and (E) 15 min. Molecular weight of both polymers was about 70 000.

When the experiment was repeated but the thickness of the PS matrix layer was increased to about 4800 Å, the SERS spectra shown in Figure 5 were obtained. In this case the time required for an equilibrium concentration of DPS to be reached at the silver surface was about 20 min. The calculated diffusion constant was about 1.0×10^{-12} cm^2 s^{-1}, which was only different from the values obtained by others by a factor of about 1.4.

Next, a series of experiments was carried out on bilayers prepared from the polymers having molecular weight of about 20 000. The SERS spectra shown in Figure 6 were obtained as function of heating time at 170 °C from a bilayer consisting of a film of PS having a thickness of approximately 3200 Å overlaid with a film of DPS having a similar thickness. The results obtained here were similar to those described above except that the diffusion time was greatly reduced and equilibrium was reached in only about 1.5 min. Using eq 6 and assuming that the diffusion distance was 3200 Å, a value of 5.7×10^{-12} cm^2 s^{-1} was calculated for the diffusion coefficient. The value obtained by others was about 17×10^{-12} cm^2 s^{-1}.

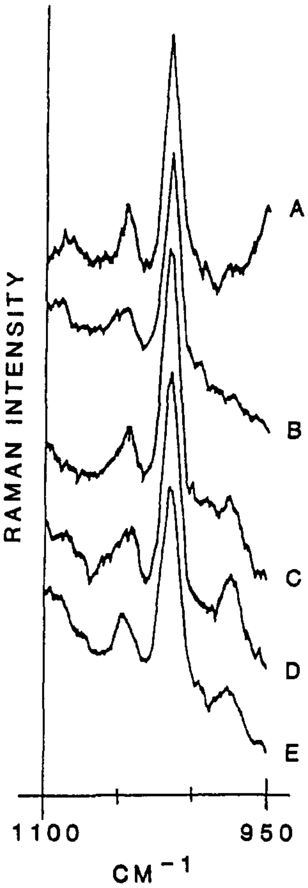

Figure 5. SERS spectra obtained as a function of heating time at 171 °C from a bilayer consisting of a polystyrene film having a thickness of about 4800 Å overlaid with a film of deuterated polystyrene having a thickness of about 1100 Å. The heating times were (A) 0, (B) 5, (C) 10, (D) 20, and (E) 30 min. Molecular weight of both polymers was about 70 000.

When the experiment was repeated but the thickness of the PS matrix was increased to 5100 Å, the results shown in Figure 7 were obtained. In this case the time to reach equilibrium was about 2.5 min and the calculated value of the diffusion constant was about 8.7 × 10^{-12} cm^2 s^{-1}. This value was only lower by a factor of 2 from those reported by others. The experimental value of the diffusion constant was thus much larger than for the higher molecular weight samples.

Equation 6 was derived for the random-walk distance assuming unrestricted Brownian motion. Strictly speaking, this equation may not really apply to diffusion in systems of entangled molecules. However, use of this equation provided a simple method for calculating an approximate value of the diffusion coefficient, and this value was in good agreement with the diffusion coefficient obtained by others using a variety of techniques. Moreover, the time required to prepare and analyze the samples was short and only a few milligrams was required for the SERS experiments.

There are several limitations to the analysis described here. One is the assumption that the Raman scattering cross section is the same for PS and DPS. Another is that the SERS enhancement is the same for the mode $\nu(1)$ near 1014 cm^{-1} in PS and 976 cm^{-1} in DPS. However, these two assumptions are both considered reasonable.

The two principal questions regarding the use of the SERS technique concern the nature of the diffusion process being characterized and the use of eq 6 for determining the diffusion constant from a measurement of the width of a diffusion-broadened interface. It is certainly appropriate to questionn whether the diffusion process under investigation is a bulk diffusion process or is a thermally activated process in which chemisorbed PS molecules are replaced at the silver surface by DPS molecules and vice

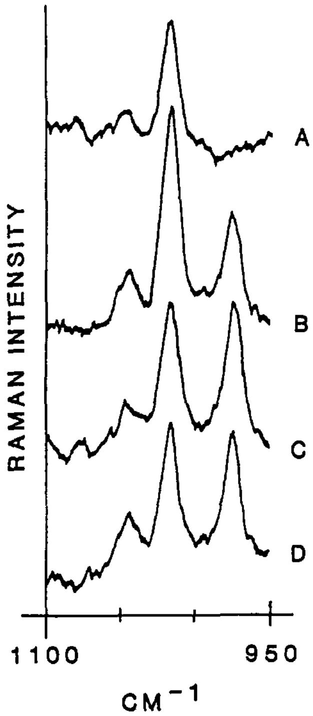

Figure 6. SERS spectra obtained as a function of heating time at 171 °C from a bilayer consisting of a polystyrene film having a thickness of about 3200 Å overlaid with a film of deuterated polystyrene having a thickness of about 3200 Å. The heating times were (A) 0, (B) 40, (C) 90, and (D) 200 s. The molecular weight of both polymers was approximately 20 000.

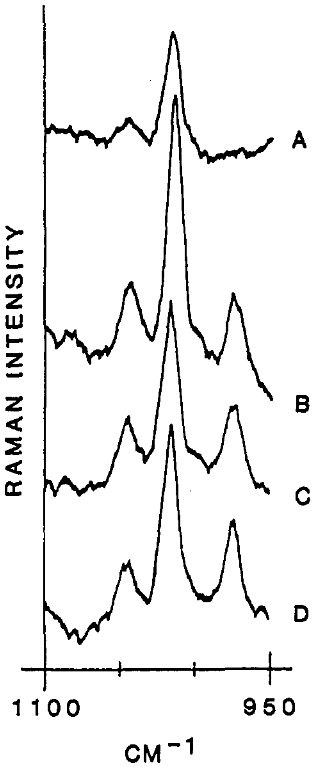

Figure 7. SERS spectra obtained as a function of heating time at 171 °C from a bilayer consisting of a polystyrene film having a thickness of about 5100 Å overlaid with a film of deuterated polystyrene having a thickness of about 3200 Å. The heating times were (A) 0, (B) 90, (C) 150, and (D) 300 s. The molecular weight of both polymers was approximately 20 000.

versa. In this regard, it is interesting to consider the results of Otto,[22] who investigated SERS from monolayers of pyridine adsorbed onto cold-deposited silver films and then overcoated with several monolayers of pyridine-d_5. Initially, only the SERS from pyridine was observed but after the specimens were annealed at elevated temperatures, bands characteristic of pyridine-d_5 appeared. However, replacement of physisorbed pyridine by physisorbed pyridine-d_5 was much faster than replacement of chemisorbed pyridine.

In the present case, the SERS spectra of PS and DPS are very similar to the normal Raman spectra. As a result, there can be little doubt that both polymers are physisorbed onto the silver surface. Therefore, the diffusion process under observation is most likely the replacement of physisorbed PS by DPS and the measured diffusion constant is characteristic of a bulk rather than an interfacial process.

Equation 6 is strictly applicable to a thin film of material diffusing into a semiinfinite matrix. In the experiments described here, the films of diffusant (DPS) and the matrix (PS) were both only a few thousand angstroms in thickness. However, we consider that the experimental configuration used here was close enough to the model used in the derivation of eq 6 to justify the use of the equation here.

A significant improvement in accuracy was obtained by increasing the thickness of the matrix layer. However, there is a limit to the thickness of the matrix layer that can be considered. If the thickness of the matrix layer is more than about 10 times that of the diffusant layer, then the signal to noise ratio for the bands in the SERS spectra characteristic of the diffusant layer will be too low to permit accurate intensity measurements.

IV. Conclusions

Surface-enhanced Raman scattering was used to investigate diffusion in deuterated polystyrene/polystyrene bilayers deposited on silver island films. When SERS spectra were obtained from the as-prepared bilayers, only bands characteristic of the polystyrene layer adjacent to the silver surface were observed. No bands due to the deuterated polystyrene film, which was separated from the silver surface by the polystyrene film, were observed, indicating that SERS is an interfacial rather than a bulk effect. After heating the bilayer samples at 170 °C for several minutes, a band characteristic of deuterated polystyrene appeared, indicating that deuterated polystyrene was diffusing to the surface regions of the silver. After heating for several additional minutes, equilibrium was reached and no further changes were observed in the relative intensities of the bands due to polystyrene and deuterated polystyrene. The diffusion coefficient was calculated from the equilibrium time and the thickness of the polystyrene film. Values that were within a factor of 2 of literature values were obtained when the polystyrene films were relatively thick. As expected, the diffusion constants were higher for lower molecular weights. This technique for measuring diffusion constants has the advantage of being relatively simple. Little sample material is required and the time required to analyze the samples is short.

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