Conformation of Polystyrene Adsorbed from Cyclohexane onto Mica

Gnanarajah Thambo and Wilmer G. Miller*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received September 13, 1989; Revised Manuscript Received March 27, 1990

ABSTRACT: A spin-labeling technique has been used to study the conformation and mobility of polystyrene (PS) adsorbed onto mica from cyclohexane at 40 °C, and the results have been compared with those from the force-balance method. The effects of surface coverage, diluent, and temperature on polymer-surface interaction were investigated. For example, at saturation coverage more than 80% of the polymer segments were found to undergo fast motion, i.e., be in loops and tails, in the presence of the poor solvent, cyclohexane; the percentage decreased at low surface coverage. This is in contrast to poly(methyl methacrylate) (PMMA), which, after adsorption onto mica, did not show any fast motion in contact with the same solvent. Furthermore, when samples dried with saturation coverage were heated, PS on mica desorbed at a lower temperature than PS on silica. In addition, a significant amount of PS desorbs from mica into pure cyclohexane and even more into benzene, although desorption is a kinetically unfavorable process in the presence of neat solvents. Our results are consistent with those of the force-balance method, where it was found that PS interacts weakly with mica.

Introduction

Polymer-surface interaction is an important phenomenon both from the theoretical point of view and in practical applications, e.g., coatings, adhesives, etc. Techniques such as FTIR,[1] ellipsometry,[2] NMR,[3] and force balance[4] have been used to study this interaction. The conformation of adsorbed polymer has been modeled;[5-10] however, the theoretical predictions of the polymer segment distribution in loops, tails, and trains cannot be verified easily by these experimental techniques. As an alternative a spin-labeling technique has been used in recent years to study the conformation and mobility of polymers adsorbed on surfaces.[11-13] In this method ESR is used to monitor the motion of a spin label, a paramagnetic molecule, that is covalently attached to a known site on the polymer.[14-17] Generally, a stable nitroxide is used as the spin label. The rotational diffusion of the nitroxide, mediated by the segmental mobility of the polymer to which it is attached, can be determined by spectral line-shape analysis. The line shape of the ESR spectrum of the nitroxide free radicals varies with the rotational diffusion of the radicals over the range 10^{-11}-10^{-7} s in rotational correlation time. Segments in trains adsorbed on the surface display a motionally slowed line shape whereas segments in loops and tails show a motionally narrowed line shape, an easily recognized difference.[11-17] From a quantitative analysis of the ESR spectrum both conformation and correlation times can be determined. In addition, the relative strength of the polymer-surface interaction and the amount of adsorption can be obtained from ESR spectral data.

Recently, Klein, Israelachvili, and others studied the adsorption of polymers on mica by measuring the forces between two mica surfaces.[18-22] In this experiment the mica sheets, immersed in a polymer solution, were brought together or separated from each other and the force between them was measured against separation. Both attractive and repulsive forces were found. In addition, information about the adsorbed polymer layer thickness and its relationship to the radius of gyration of the attached polymer was also obtained. In one experiment polystyrene was allowed to adsorb from either a thermodynamically poor solvent, such as cyclohexane, or a good solvent, such as toluene.[20] Adsorption occurred from cyclohexane both below and above the Θ temperature, 34.5 °C. However, no adsorption of polymer was found even after 24-h incubation of mica in PS/toluene solution, and the force-distance profiles were unchanged relative to those in the polymer-free solvent. It was concluded that PS interacts very weakly with mica. Most of the adsorption experiments in the force-balance method were carried out with mica because of the smooth and transparent character of this surface. A diluent is present during measurement. Questions arise concerning equilibrium adsorption and aggregation of polymer in the very narrow gap width.

We have investigated the interaction of PS with mica and with fumed silica from cyclohexane and toluene using the spin-labeling technique. The effects of surface coverage, diluent, and temperature on the polymer-surface interaction are described. The emphasis is on a qualitative analysis of the conformation rather than a quantitative comparison with theory. The adsorption isotherm for PS-mica was determined. The desorption of PS from mica was also studied.

Experimental Section

Spin-labeled polystyrene was prepared by emulsion polymerization at 50 °C of styrene and (chloromethyl)styrene (Polysciences) in a 99.3:0.7 mole ratio using sodium dodecyl sulfate as emulsifier and persulfate as initiator. The polymer was precipitated with acetone, dried, and repeatedly precipitated from dimethylformamide (DMF) with methanol to remove surfactant. The yield was 65%. The nitroxide spin label, 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-*N*-oxy (Aldrich), was substituted on (chloromethyl)styrene. First, sodium hydride (50% oil dispersion, Alfa Products) and spin label (1:1; mol:mol) were allowed to react for 2 h in DMF at room temperature under a nitrogen atmosphere. After the reaction the amount required (1:1; mol of nitroxide:mol of (chloromethyl)styrene) was withdrawn and added to a flask that contained polymer/DMF solution. The spin-labeled polymer was precipitated after ca. 1 h from the reaction mixture with methanol. Any unreacted (chloromethyl)styrene was converted to the methyl ether by reaction with methanol and sodium hydride. The amount of (chloromethyl)styrene incorporated into the polymer and the amount of nitroxide substitution were determined by NMR and ESR, respectively. Spin-labeled PMMA was also prepared, using methyl methacrylate and methacryloyl chloride as starting materials.

Adsorption studies of the spin-labeled polystyrene were carried out in cyclohexane at 40 °C, above the Θ temperature of 34.5 °C. The polymer was dissolved in cyclohexane at 40 °C, mica (Asheville Shoon Maker Mica Co., flaked and fractured to give a high surface area) was added, and the system was stirred for 24 h. The mica was then allowed to settle, the supernatant was removed, and the mica was washed for 5 min with 15 mL of cyclohexane, followed by a second similar wash, to remove the unattached polymer. All procedures were carried out keeping the sample at 40 °C. The samples were dried near 100 °C for 2 h in a vacuum oven, except for some used in desorption experiments which were not allowed to dry. The adsorption isotherm was determined by monitoring the amount of polymer on the surface and in the supernatant by either ESR or UV (218 nm) measurement. Paramagnetic impurities leached from the mica gave line broadening, which reduced the precision of the analysis by ESR. For comparison, PMMA was adsorbed onto mica from cyclohexane at 40 °C. Since the solubility of PMMA in cyclohexane at 40 °C is very low, the adsorption experiment was carried out with two different containers, one for PMMA and the other for mica in order to avoid direct contact of undissolved PMMA with mica. Here, a small vial containing PMMA in cyclohexane was submerged in a large Quapak bottle that held mica in cyclohexane at 40 °C under gentle magnetic stirring. After 24 h the vial was removed, the mica was allowed to settle, and analysis was made by ESR. PS was also adsorbed onto fumed silica (Cab-O-Sil M5, Cabot Corp.) from toluene. Cyclohexane was not used due to the difficulties in removal of silica from the suspension at 40 °C. The effect of temperature and diluent on the PS–silica interaction was determined by ESR.

The ESR spectra were measured on either a Varian E-3 or an IBM-Bruker ER-300 X-band spectrometer having temperature control accessories. NMR spectra were recorded on an IBM 200-MHz spectrometer. Scanning electron micrographs of mica were taken on a Hitachi S-450SEM instrument. The magnification ranged from 43 000 to 50 000. The specimens for SEM were prepared by a spin-coating technique using glass substrate. Optical micrographs for contact angle measurement were taken on a Nikon/PFM optical microscope at 350 magnification.

Results and Discussion

The amount of (chloromethyl)styrene in the polymer was kept to the level of nitroxide label needed to give adequate signal intensity. Additionally, if a considerably higher amount was used, cross-linking of the polymer occurred during the spin-labeling reaction. There was no evidence of cross-linking in the spin-labeled polymer subsequently studied. The composition of the polymer was analyzed by NMR after polymerization and isolation but before spin labeling by comparing the chloromethyl protons to the total aromatic protons. The polymer was found to contain 1.8 mol % (chloromethyl)styrene, more than double the monomer feed. ESR analysis using appropriate standards indicates about 1 in 12 (chloromethyl)styrene has a nitroxide substituted. Methanol-substituted product could not be positively identified by NMR. Intrinsic viscosity in chloroform[23] gave a molecular weight of 1.0×10^6. GPC analysis indicated a polydispersity of 3–4.

A. Adsorption of Polymer on Surfaces. When a polymer is adsorbed from solutions of different concentration, the surface coverage increases with concentration until a plateau region in the adsorption isotherm is reached. The segmental motion of the polymer near the polymer–surface interface may depend on the surface coverage. In order to study the effect of surface coverage on the mobility of polymer segments, PS was allowed to adsorb onto mica from PS/cyclohexane solutions of various concentrations at 40 °C, the unattached polymer removed, and the ESR spectrum taken and analyzed for any change in the spectral line shape.

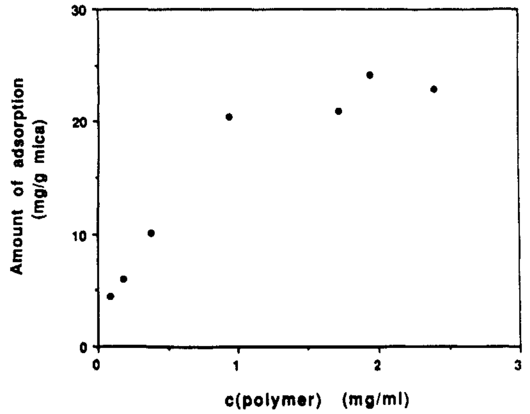

Figure 1. Adsorption isotherm for polystyrene on mica from cyclohexane at 40 °C. Concentrations given are the equilibrium concentrations of the unattached polymer.

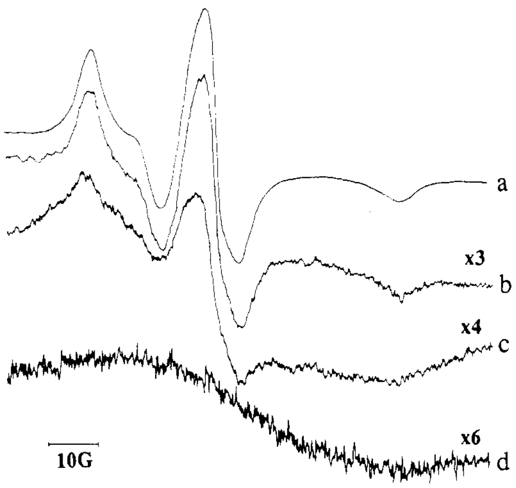

Figure 2. ESR spectra of polystyrene adsorbed onto mica from cyclohexane at 40 °C. The samples are dry and the spectra are taken at 23 °C. Equilibrium concentrations of unattached polymer before removal were (in mg/mL) (a) 1.94, (b) 3.75×10^{-1}, (c) 8.9×10^{-2}, and (d) 0 (pure mica surface).

The adsorption isotherm is shown in Figure 1. A maximum of 24 mg per g of mica was adsorbed under the above conditions. The shape of the isotherm is likely influenced by the polydispersity, as narrow distribution polymers typically plateau more abruptly.[9] A companion study using a commercial PS of similar molecular weight gave the same plateau value, within experimental error, indicating that the small number of units introduced for the purpose of labeling had a negligible effect on the adsorption. The ESR spectra of dry PS–mica samples are displayed in Figure 2. The signal is significantly reduced in samples prepared with equilibrium solution concentrations of 0.1 mg/mL and below. The distortion seen in the spectra at high spectral gain is due to paramagnetic impurities in the pure mica which gave a broad spectrum (Figure 2d). Whenever possible this was corrected by a software subtraction routine. Otherwise, the ESR spectra consist of broad hyperfine lines whose overall line shapes are those expected from dilute spin labels undergoing slow tumbling motions with correlation times on the order of 10^{-7} s or longer. The hyperfine extrema $(2A_{zz})$ are separated by ca. 64 G and increase by ca. 0.5 G at the lowest surface coverage. All spin labels are motionally slowed. Inasmuch as the glass transition of bulk polymer is 100 °C, it is not surprising that all motions are slow even though no bulk polymer is present here.

Segmental motion in tails and loops appears in the ESR spectra when a diluent is added to the dry samples. The ESR spectra of the above samples, but now recorded in the presence of cyclohexane at room temperature, are shown in Figure 3. A motionally narrowed three-line spectrum dominates the spectra in all cases studied. A

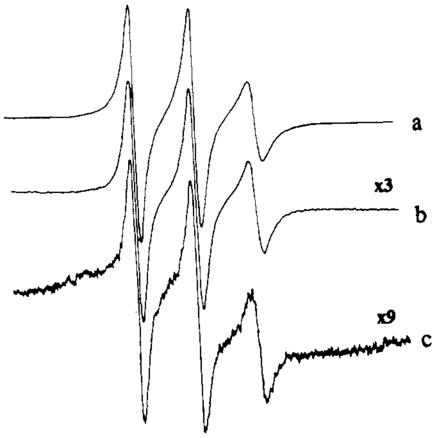

Figure 3. Same as Figure 2 except in the presence of cyclohexane. The diluent was added to the ESR tube that contained dry PS–mica sample.

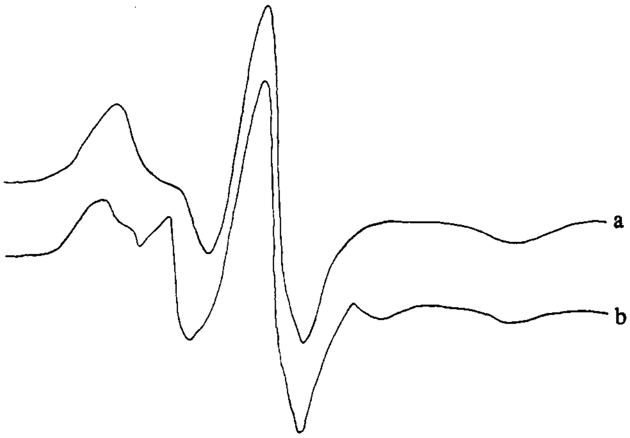

Figure 4. ESR spectra of PS–silica: (a) dry sample; (b) in the presence of cyclohexane. In contrast to PS–mica only a small fraction is in tails and loops.

detailed analysis of the low-field line shape was undertaken to detect any slow-motion component, as described in the Appendix. When the number of spins in the slow component is small, it becomes difficult to distinguish signal from base line, particularly in the presence of the much more intense fast component. Computer simulation shows that if less than 20% of the spins are in the slow component, they cannot be analyzed reliably by this approach. At saturation coverage no slow component was detectable. As the surface coverage was reduced, a slow component was detected. These results were further substantiated from desorption studies discussed in a later section. Thus the polymer takes on a more flattened conformation at low surface coverage. However, a significant fraction of the segments are still in loops even at the lowest surface coverage, about 20%, in contrast to the effect of surface coverage on conformation observed previously in a different polymer/surface system.[12]

The spectra of PS–silica, shown in Figure 4, exhibited substantial slow as well as fast component in the presence of cyclohexane with the hyperfine extrema of the slow component equal to that of the dry PS–silica sample. This can be characterized by a bimodal distribution of correlation times,[24] and the fractions undergoing fast and slow motion can be determined. Here, the fraction of the total segments in trains is ca. 95%.

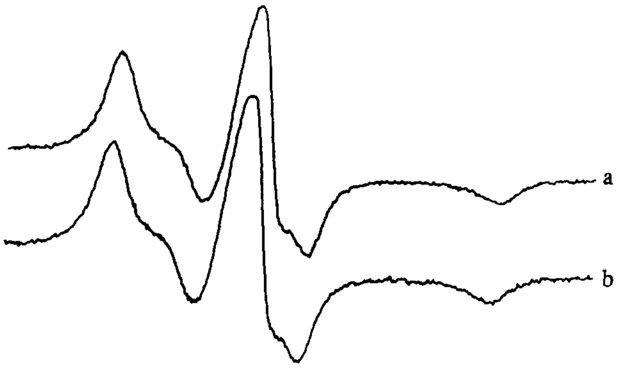

Figure 5. ESR spectra of PMMA–mica. The polymer was adsorbed from cyclohexane. The powder pattern spectrum of the dry sample (a) remains unchanged in the presence of cyclohexane (b).

Table I
Adsorption of Polystyrene from Toluene at 23 °C

equilib soln concn, mg/mL	amt of adsorp, mg/g of mica
10.00	4.8
1.00	3.0
0.10	negligible

Poly(methyl methacrylate) with its polar side chains is expected to adhere more strongly to mica than PS. This is confirmed in ESR experiments. The ESR spectrum of the dry PMMA–mica is the expected powder pattern type as shown in Figure 5a. Moreover, the appearance of the spectrum remained unchanged after the addition of cyclohexane (Figure 5b). The above results clearly indicate a weak PS–mica adherence. The effect of temperature on the mobility of the segments near the interface, which is discussed later, gives further evidence for this conclusion.

The amount of polymer adsorbed onto a surface depends on the solvent from which the polymer is adsorbed. Less polymer is usually adsorbed from a thermodynamically good solvent.[5] We studied the adsorption of PS onto mica from a thermodynamically good solvent, toluene, with three different concentrations. The results are shown in Table I. As expected, the amount of PS adsorbed from toluene was found to be lower, and the adsorption could not be detected from solutions of concentration lower than 1 mg/mL. In the case of cyclohexane the lower limit was 0.1 mg/mL. Even though the amount of PS adsorbed onto mica from a 1 mg/mL solution can be detected by ESR measurements on the washed sample, the unattached polymer remaining in solution is too dilute to be detected. Klein and co-workers[20] were not able to detect any PS adsorption from toluene with concentration of 1 mg/mL at 23 °C. The finite amount of adsorption detected in our study may be due to the larger surface area used for adsorption or to differences in the nature of the surfaces present. In the force-balance method the surface area of the metallic box holding the mica hemicylinders is larger than the surface area of the hemicylinders. Preferential adsorption onto the box at low polymer concentration would put a higher limit on the detectability on the mica. On the other hand, our mica was not only flaked but broken into small pieces so that it could be transferred to a 5-mm tube. Although the surface area of our mica is very large compared to the surface area of the container, it has an increased edge to face area. Polymer might preferentially adsorbed on the edges; however, the isotherm did not measurably depend on the degree of fracturing. Consequently, we take this as evidence of no preferential edge adsorption.

The comparatively larger amount of adsorption is a reason cyclohexane is preferred as solvent in the force-balance method. However, it is extremely difficult to prepare a homogeneous PS/cyclohexane solution and

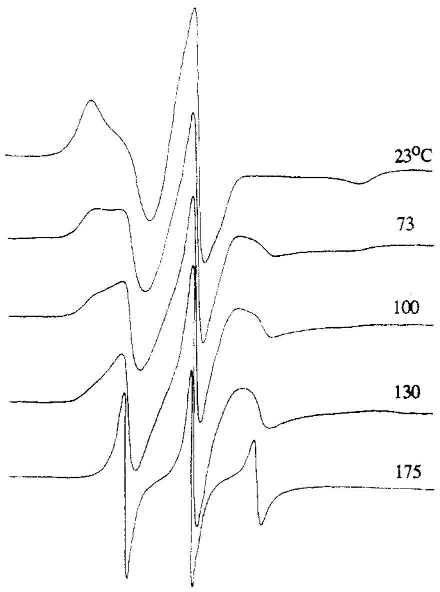

Figure 6. ESR spectra of bulk polystyrene as a function of temperature. The mobility of PS segments increases at a faster rate than when on mica or Cab-O-Sil (compare Figures 7 and 8) as the temperature is raised from 23 to 175 °C.

maintain it without phase separation at or below 34.5 °C. In the case of toluene, experiments can be run conveniently at room temperature.

Terashima et al.[25] developed a microbalance method suitable for determining adsorption isotherms. In this method, which is based on direct weighing of the amount of adsorbed polymer, a mica sheet was suspended from a microbalance, immersed in a beaker of polystyrene/cyclohexane solution so that adsorption occurs. The incubating solution was maintained at a constant temperature of 34.5 °C. The sheet was withdrawn from the beaker after a predetermined time, rinsed, and dried. Adsorption isotherms were determined for three polystyrene samples of different molecular weights. The plateau adsorption for polystyrene was found to be proportional to the square root of the molecular weight of the polymer. The proportionality is also true for other surfaces.[26] If the same proportionality constant is used in this work, we can estimate the average surface area for the mica used in our study. The calculated value for plateau adsorption is 7.7 mg/m^2. Hence, the surface area of our flaked and fractured mica is ca. 3.1 m^2/g. Assuming bulk density, 1.05 g/cm^3, this corresponds to a mean layer thickness of dry PS of 7.3 nm. By comparison, this molecular weight in cyclohexane has a diameter, $2R_g$, of 56 nm.

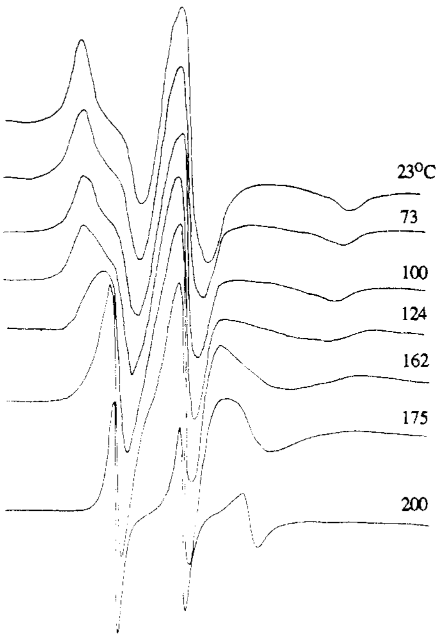

Figure 7. Effect of temperature on the ESR spectrum of polystyrene adsorbed onto mica (same sample as in Figure 2b). The temperature has to be raised to 175 °C before complete spectral narrowing occurs.

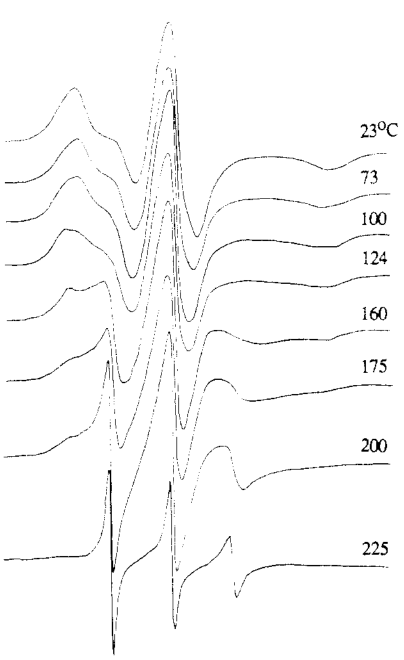

Figure 8. ESR spectrum of polystyrene adsorbed onto silica as a function of temperature. The effect of silica is still seen even at 225 °C. A motionally narrowed three-line spectrum appears at a temperature that is much higher than that of bulk PS or of PS–mica.

B. Effect of Temperature on the Mobility of the Adsorbed Segments near the Interface. The temperature dependence of the ESR line shape for the following samples was studied from room temperature up to 225 °C: bulk polystyrene, PS–mica, and PS–silica. In order to minimize the influence of surface coverage, the polymer–surface samples were analyzed at or near the plateau of the adsorption isotherm. The ESR spectra of the dry samples are shown in Figures 6–8. With increasing temperature the spectra of all three samples exhibited the typical features indicating the onset of spectral collapse and line narrowing. The separation of the hyperfine extrema steadily decreases, and a motionally narrowed three-line component slowly grows in. Of the three samples the segmental motion of the bulk polymer increases most rapidly with temperature. A complete line narrowing occurs at a higher temperature for PS–silica than for the other two samples. For instance, at 175 °C motionally narrowed three-line spectra are observed for bulk PS and PS–mica but not for PS–silica.

At room temperature the separations of the hyperfine extrema for bulk PS, PS–mica, and PS–silica are 66, 64, and 63.4 G, respectively. These values reduced to 64, 62, and 62 G, respectively, at 73 °C. This is in contrast to addition of small amounts of solvent to either bulk polymer or polymer adsorbed on a surface, where the separation of the hyperfine extrema stays constant and a motionally narrowed component appears,[12,24] or to the temperature dependence of strongly adsorbed polymers, where the separation of the extrema is constant over many degrees. The behavior of the spectra in Figures 6–8 is indicative of a broad distribution of correlation times with the mean value decreasing with increasing temperature, whereas the solvent effects are indicative of a biomodal distribution of correlation times.[12,24,27] Thus the adsorbed segments are dynamically moving on and off the surface, and the temperature needed for polymer/surface and bulk polymer to exhibit similar spectra is indicative of the strength of the polymer–surface interaction energy. Therefore, we conclude that polystyrene interacts more strongly with fumed silica than with mica.

The electron micrographs taken on ground mica showed that the particle size varies from 1 to 100 μm. Furthermore, the shape as well as the surface area was different for each particle. However, particles of fumed silica are spherical with particle size of 140 Å, but these particles are agglomerated during its gas-phase synthesis. Nevertheless, the surface area of silica is expected to be much larger than that of mica. Thus, even if the experiments are carried out under similar conditions, the amount of polymer adsorption may differ due to the nature of the surface. The mobility of the polymer segments on the surface is somewhat influenced by the difference in surface coverage. This is minimized above by studying the temperature effect at about equal surface coverage.

The above results are consistent with the previous observation that PS–mica interaction is weaker than that of PS–silica. Moreover, this study is again consistent with the results of Klein and co-workers,[20] who found little or no adsorption of PS onto mica from either cyclohexane or toluene.

C. Desorption of Polystyrene from Mica. Samples of PS–mica, where the PS had been preadsorbed to saturation coverage (24 mg/g of mica) at 40 °C in cyclohexane followed by drying at 110 °C, were monitored for desorption in neat solvents. In cyclohexane at 23 °C, below the Θ temperature, a negligible amount desorbed in 24 h no matter what volume of cyclohexane was used. When desorbed at 40 °C, now above Θ, 8 mg of PS per g of mica, or about one-third of the PS on the mica, was desorbed in 24 h when 0.5 g of PS–mica was in contact with 100 mL of cyclohexane. This is an unusually large desorption rate. After extraction in cyclohexane at 40 °C, the sample was further extracted at 23 °C with benzene, a good solvent. After 24 h an additional 4 mg of PS per 0.5 g of PS–mica was extracted. Repeated extraction with benzene eventually desorbed 80% of the PS. However, it was also noted that the separation of the hyperfine extrema at room temperature was 63.4 G in bulk PS, 64.0 G in monolayer, dry PS–mica, and ca. 67 G in monolayer, dry PS–silica. Typically, the magnetic parameters are a function of the dielectric constant,[28] and nitroxide-labeled polymers adsorbed onto surface of dielectric constant higher than that of the bulk polymer show a larger separation of the extrema. This was not the case with PS–mica. However, the dried sample had been annealed at 110 °C so rearrangement may have occurred. Since PS adsorbs weakly from cyclohexane even though it is a poor solvent for PS, pure PS on mica might not wet mica. Hence in the annealing at 110 °C rearrangement may lead to islands of PS with many chains not in contact with the mica. This would make desorption much easier.

The approximate contact angle at the PS–mica interface was determined by placing a polystyrene pellet on a freshly cleaved mica sheet followed by heating at 130 °C. The sheet was then allowed to cool, and the contact angle was estimated from the optical micrographs taken at the interface. It was found to be about 30°, showing that polystyrene above T_g spreads on a mica surface.

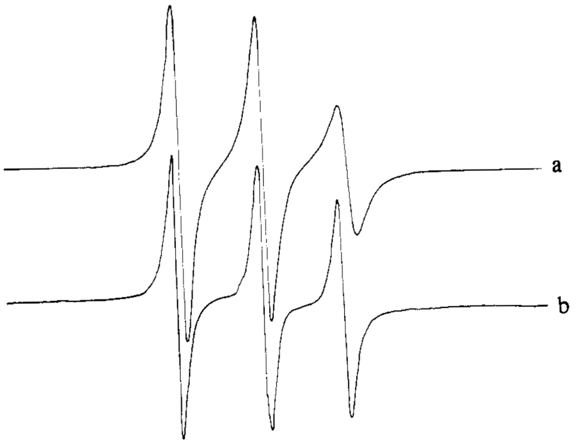

Figure 9. Spectra showing anisotropic motion of the nitroxide attached to polystyrene adsorbed on mica whether in the presence of (a) a poor solvent, cyclohexane, or (b) a good solvent, benzene.

Additional desorption experiments were undertaken in which the PS–mica sample was not dried, but rinsed and then desorbed in a fixed volume of solvent. The results were the same as with the dried, annealed samples. Thus any annealing does not appear to affect the polymer conformation on the surface. This is further confirmed by the finding that the hyperfine extrema separation was not affected by annealing.

The spectra line shape of the adsorbed PS in the presence of either cyclohexane or benzene, Figures 3 and 9, shows anisotropic nitroxide motion, as the low-field line is more intense than the central line. As this is not generally observed in polymer–diluent systems when no surface is involved,[12] it indicates that the adsorption affects the PS chain dynamics even though the adsorption is very weak with a preponderance of monomeric units in loops and tails.

Polystyrene on mica has previously been observed to desorb when in contact with cyclopentane.[22] Desorption of polymer from surfaces into neat solvents is only seen if the adsorption is very weak. Both our data and the force-balance data show clearly that polystyrene on mica in the presence of a poor solvent is very weakly adsorbed, with most of the polymer segments extending out into the solvent at saturation coverage.

Summary

The spin-labeling technique and the force balance show polystyrene to be weakly adsorbed on mica from cyclohexane at 40 °C. The conformation of the polymer was shown to be dependent on surface coverage, with a smaller fraction of the polymer segments in loops at lower surface coverage. The effect, however, is not nearly as pronounced as in more strongly adsorbed chains. Poly(methyl methacrylate) was found to adsorb much more strongly to mica than polystyrene. Polystyrene was found to adsorb more strongly on silica than on mica. Adsorbed polystyrene was found to desorb in the presence of neat solvents such as cyclohexane and benzene. The very loose binding of PS to mica suggests that bridging between mica sheets in the force-balance measurement is highly likely.

Acknowledgment. This work was supported in part by funds from the Midwest Transfer Development Institute and by the Center for Interfacial Engineering (NSF).

Appendix. Bimodal Composition Analysis with Highly Unequal Spin Populations

It is frequently desirable to decompose an ESR spectrum that is a superposition of a motionally narrowed (fast

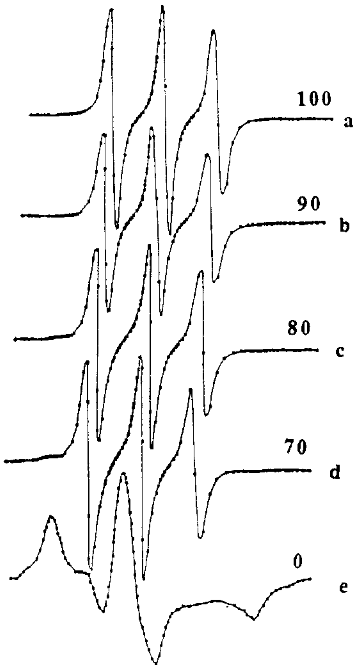

Figure 10. Composite spectra (b–d) simulated from mixing a motionally narrowed (fast) component (a) with a motionally slowed component (e). The percentage of fast component is indicated.

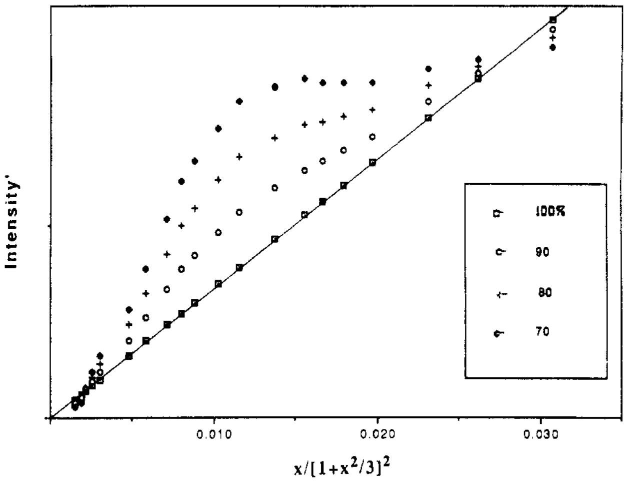

Figure 11. Spectra in Figure 10 plotted according to eq A-1. Deviation from linear behavior increases as the amount of slow component increases.

component) and a motionally slowed spectrum into the fractions of spins in each component. If the fast component does not dominate the spectral line shape, it can be subtracted from a digitized spectrum by simulating it through use of the Kivelson equation[28] and input of spin concentration, rotational correlation time, and line width. This plus double integration of the composite spectrum allows the population distribution to be determined sometimes with as little as 1 or 2% of fast-component spins. Analysis becomes much more difficult when the slow component is present in minor amounts. This is illustrated in Figure 10, where motionally narrowed (Figure 10a) and motionally slowed (Figure 10e) spins have been added to produce simulated spectra (Figure 10b–d) with the fraction of fast-component spins indicated. If experimental spectra such as b, c, or d are observed, retaking at much higher gain reveals the presence of the slow component at the low-field (left portion) end and sometimes at the high-field end, while making the dominate, central three lines go completely off scale. It is a quantitative or semiquantitative analysis under these conditions of interest here.

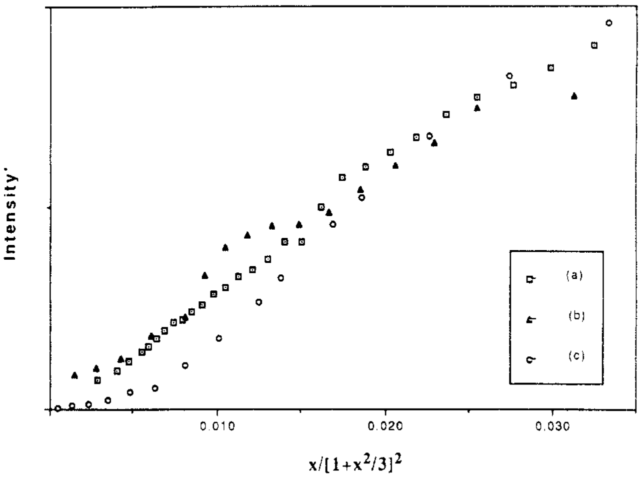

Figure 12. Data from Figure 3 plotted according to eq A-1.

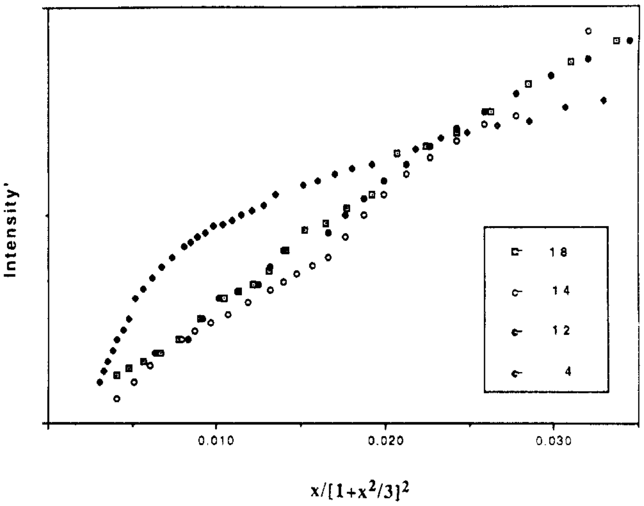

Figure 13. Sample from Figure 3a was desorbed by using either cyclohexane or benzene (see text). The amount of polymer remaining on the mica (mg of PS/g of mica) is indicated.

In analysis of many experimental spectra where all spins are motionally narrowed, the low-field line up to the first maximum can be fitted well to a Lorentzian line shape, even though proton hyperfine broadening does occur. There are several ways in which a Lorentzian first-derivative line shape[29] can be plotted in a linear manner. When plotted in this manner, deviation from linear behavior indicates a slow component. Those involving logarithms or square roots of intensity were found to be less sensitive to detection of a slow component than that in the form given by eq A-1, where (intensity)' is the first-derivative intensity,

$$(\text{intensity})' = m[x/(1 + x^2/3)^2] \qquad \text{(A-1)}$$

m is a constant, and x is $2(H - H_r)/H_{pp}$, where H is the magnetic field, H_r the resonance field, and H_{pp} the peak-to-peak first-derivative line width. Such plots for the spectra in Figure 10 are shown in Figure 11. Data from Figure 3 are plotted in this manner in Figure 12, and desorption data in Figure 13. By adding in spins from the motionally slowed spectrum, one can estimate the fraction of slow component even with noisy spectra. As the intensity from the slow component becomes comparable to noise, the scatter increases, but it is still possible to detect the slow component even if only semiquantitatively down to ca. 20% slow component in these dilute spin systems. It is clear that at lower polymer adsorption a larger fraction of the spins are in the motionally slowed component, whether viewed from the adsorption (Figure 12) or the desorption (Figure 13) data.

References and Notes

(1) Parfitt, G. D.; Rochester, C. H. In *Adsorption from Solution at the Solid/Liquid Interface*; Parfitt, G. D., Rochester, C. H., Eds.; Academic Press: New York, 1983; p 3.

(2) Besio, G. J.; Prud'homme, R. K.; Benziger, J. B. *Macromolecules* **1988**, *21*, 1070.

(3) Blum, F. D.; Funchess, R. B. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 54.

(4) Tabor, D.; Winterton, R. H. S. *Proc. R. Soc. London, A* **1969**, *312*, 435.

(5) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619; **1980**, *84*, 178.

(6) Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1985**, *18*, 1882.

(7) de Gennes, P.-G. *Macromolecules* **1982**, *15*, 492.

(8) Patrick, R. L. In *Treatise on Adhesion and Adhesives*; Marcel Dekker: New York, 1967.

(9) Lipatov, Yu. S.; Sergeeva, L. M. In *Adsorption of Polymers*; Halsted Press: New York, 1974.

(10) Mittal, K. L. In *Adsorption at Interfaces*; American Chemical Society: Washington, DC, 1975.

(11) Robb, I. D.; Smith, R. *Polymer* **1977**, *18*, 500.

(12) Liang, T. M.; Dickson, P. N.; Miller, W. G. In *Polymer Characterization by ESR and NMR*; Woodward, A. E., Bovey, F. A., Eds.; ACS Symposium Series 42; American Chemical Society: Washington, DC, 1980; p 1.

(13) Miller, W. G.; Rudolf, W. R.; Veksli, Z.; Coon, D. L.; Wu, C. C.; Liang, T. M. In *Molecular Motion in Polymers by ESR*; Boyer, R. F., Keinath, S. E., Eds.; Harwood Academic: New York, 1978; p 145.

(14) Friedrich, C.; Laupretre, F.; Noel, C.; Monnerie, L. *Macromolecules* **1981**, *14*, 1119.

(15) Bullock, A. T.; Cameron, G. G.; Krajewski, V. *J. Phys. Chem.* **1976**, *80*, 1792.

(16) Brown, I. M.; Sandreczki, T. C. *Macromolecules* **1985**, *18*, 2702.

(17) Sandreczki, T. C.; Brown, I. M. *Macromolecules* **1984**, *17*, 1789.

(18) Klein, J.; Luckham, P. F. *Macromolecules* **1984**, *17*, 1041.

(19) Israelachvili, J. N.; Adams, G. E. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 975.

(20) Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almog, Y. *Macromolecules* **1984**, *17*, 204.

(21) Luckham, P. F.; Klein, J. *Macromolecules* **1985**, *18*, 721.

(22) Klein, J. *Makromol. Chem., Macromol. Symp.* **1986**, *1*, 125.

(23) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1975.

(24) Veksli, Z.; Miller, W. G. *Macromolecules* **1977**, *10*, 686.

(25) Terashima, H.; Klein, J.; Luckham, P. F. In *Adsorption from Solution*; Rochester, C., Ottewill, R. H., Eds.; Academic Press: London, 1983.

(26) Takahashi, A.; Kawaguchi, M.; Hirota, H.; Kato, T. *Macromolecules* **1980**, *13*, 884.

(27) Morrisett, J. D. In *Spin Labeling, Theory and Application*, Berliner, L. J., Ed.; Academic Press: New York, 1976; p 307.

(28) Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1094.

(29) Wertz, J. E.; Bolton, R. J. In *Electron Spin Resonance: Elementary Theory and Practical Application*; Chapman andHall: New York, 1986; p 33.