# Experimental Measurements of Local Mobility in Adsorbed Poly(dimethylsiloxane) Layers

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ABSTRACT: $^{13}$C NMR relaxation measurements have been used to investigate the changes in Brownian dynamics caused by polymer adsorption within a boundary region 5–15 Å from the adsorbate surface. Brownian dynamics within the boundary region have been found to be sensitive to the surface coverage (mass of polymer per unit area of surface). Dynamics measured approximately 7 Å from the surface are found to slow and then increase as chain surface density increases. This is believed to reflect the conformational state of the adsorbed chains, with chain segments lying relatively flat at low coverages and forming small, low-mobility loops and tails at intermediate coverages.

It is widely recognized that the study of chain behavior at solid surfaces is important to the understanding of important technological phenomena such as adhesion and lubrication. Most of these studies, theoretical, calculational, or experimental, have concentrated on the structures formed at the interface of the polymer melt or solution phase with the contacting solid. Theoretical models for solution/solid interfaces have been extensively reviewed[1,2] and will not be repeated here. Many computational simulations of chain organization at melt interfaces have recently appeared as well.[3] From such studies, it appears clear that the presence of an adsorbing substrate induces a very short-ranged organization of the contacting layer; in the case of polymer chains, this perturbation is manifest as a small increase in the segmental density, roughly 2–5 Å from the contacting wall, followed by a small density decrease in the next segmental layer.

While studies regarding the structure of the interface have been legion, very little attention has been paid to the influence of the perturbed structure on chain dynamics. It would appear reasonable that the molecular dynamics of adsorbed chains within the surface region might display interesting differences from bulk behavior, with dependencies on sticking energy, density, and the conformational state of the adsorbed macromolecule. Some recent computational work[4] on low-density melts has indicated that local dynamics, as measured by the center of mass diffusivity, suffer only a slight perturbation from behavior in the bulk. On the experimental side, there have been few studies of surface dynamics outside of shear measurements made on very thin films in a highly compressed geometry, which are complicated by the extraordinary organization of the liquid layer induced by the apparatus.[5] It would be most desirable to experimentally probe surface dynamics in situ, without such strong perturbations of the system.

Experimental measurements on surface properties are naturally made difficult by the relatively small number of molecules associated with the interface. The application of NMR techniques, however, appears promising, as information on Brownian dynamics is available through the time evolution of energy dissipation, the well-known spin–lattice ($T_1$), spin–spin ($T_2$), and rotating-frame spin–lattice ($T_{1\rho}$) relaxation times. In addition, the extraordinary chemical specificity afforded by the NMR chemical shift makes it possible to track behavior in different parts of a molecule, or several different molecules, simultaneously. Numerous studies have been made of interfaces with high surface area materials, with particular emphasis on the characterization of behavior within chromatographic supports. Gilpin and Gangoda determined the dependence of the spin–lattice relaxation time on bound chain length[6] and local viscosity[7] and thereby clearly established the sensitivity of the bound chain $T_1$ to the local environment. More recent work has shown that the relative degree of chain motion is dependent on surface chemistry, finding that polar molecules are able to increase the degree of bound chain motion by competing with the alkyl backbone for surface sites, thus driving the chain off the surface of the support.[8,9]

In studies of polymer interfaces, the pioneering work of Kaufman and Slichter[10] took advantage of the large difference in spin–spin relaxation times ($T_2$) between polybutadiene nuclei physically bound and those tethered to carbon black particles to measure the "bound fraction" in filled rubber, and many other studies have since exploited this phenomenon.[11] In recent work, Blum used selectively deuterated block copolymers to characterize mobility within an adsorbed layer, using spin–lattice relaxation times to estimate the shape of the adsorbed polymer segmental density profile.[12] Perhaps the most extensive studies to date have been the proton relaxation studies of Litvinov, which have concentrated on poly(dimethylsiloxane)/silica rubber.[13] These showed that the segments associated with the surface boundary region (estimated to be 8 Å in thickness) exist in a family of environments, as evidenced by a relatively broad temperature range (50 K) over which segmental mobility is "defrosted". These studies also suggested that segmental mobility within the boundary region was dependent on the volume fraction of filler, as determined by an appreciable decrease in the $T_2$ of the tethered segments with an increasing fraction of silica.

We seek to build upon these studies by more completely localizing measurements to the region limited to within approximately 5–15 Å from the surface. In so doing, our goal is to isolate the short-ranged phenomena that occur near the surface. We accomplish this by covalently binding and NMR spin probe of known chain length to the adsorbing surface and using measurements of spin–lattice relaxation times ($T_1$) to observe effects of the local environment on the relaxation dynamics of the probe *and* surrounding molecules.

## Experimental Section

A carbon-13 spin label was used throughout this work to avoid possible complications due to spin diffusion and intermolecular

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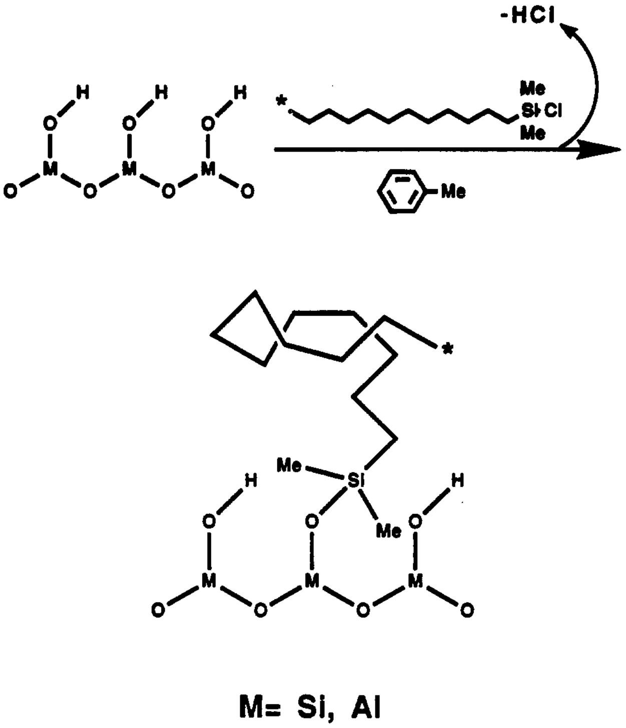
**Scheme I**
**Preparation of Surfaces**



dipolar coupling. Spin-labeled silica gel was prepared by slowly adding a dilute solution of [12-$^{13}$C]dodecyldimethylchlorosilane (MSD Isotopes, 99.2% atom 12-$^{13}$C) in toluene to a slurry of activated silica gel (Alfa; 310 m$^2$/g; average pore size 200 Å). This mixture was slurried at 50 °C for 2 days and followed by an increase in temperature of the mixture to 80 °C for 2 days (Scheme I). The material was then collected by filtration, washed exhaustively with cyclohexane, and dried in a vacuum oven; the presence of bound alkyl silane was confirmed via diffuse reflectance infrared spectroscopy. This reaction is a common and facile one and is typically used to create reversed-phase chromatography packings. The quantity of silane used was calculated to react with 4% of the surface hydroxyl groups, which have a surface density under the activating conditions of 4.6 groups/nm$^2$.[14]

Adsorbed polymer samples were prepared by slurrying the dried, spin-labeled silica gel in polymer solutions of between 0.001 and 0.3 volume fraction poly(dimethylsiloxane) (PDMS, Polysciences, 3900 molecular weight) in cyclohexane at room temperature for at least 1 week, followed by filtration and solvent wash. This results in a powder with a strongly bound polymer layer and can be quantitated gravimetrically. This material was then placed in an NMR tube and swollen with excess cyclohexane-$d_{12}$ prior to measurement. The 16-Å radius of gyration of the polymer[15] is much smaller than the average pore size of the substrate, and so transport to the entire surface should be facile. (It has been reported that the self-diffusion of chains in porous media is only moderately attenuated from that the dilute solution, even for chains whose hydrodynamic radii are larger than the pore diameters.[16]) Of greater concern is the effect of the slow equilibration of chains on surfaces, but our assumption is that the presence of a large volume fraction of solvent, along with the extremely high segmental mobility of the PDMS molecule, should allow proper equilibration over the sample preparation and storage times (weeks to months) used here. Because the presence of dissolved oxygen is not considered to become problematic for measurements of $T_1$s of less than 10 s,[17] the samples were not degassed.

All NMR measurements were performed on a Nicolet NT-300 spectrometer, operating at a frequency of 75.5 MHz for carbon-13. Spin–lattice relaxation times were measured by using a 180–$\tau$–90–5$T_1$ pulse sequence with proton decoupling; data were fit to a three-parameter relaxation model, from which $T_1$ is determined. Due to the large difference in chemical shift, relaxation times could be measured for the methyl groups of both the alkyl probe and the adsorbed polymer. The observed relaxation was characterized by a single exponential in all cases; the uncertainty in $T_1$ is 5–7%, as determined by performing multiple experiments. Spin–spin relaxation times were measured with the Hahn spin-echo sequence (90–$\tau$–180–5$T_1$). Due to the poor short-time (<100 $\mu$s) performance of our spectrometer, we could only reliably measure $T_2$ for slowly relaxing nuclei (i.e., those relatively far from the surface). Except where otherwise noted, the measurements were conducted at a temperature of 308 K.

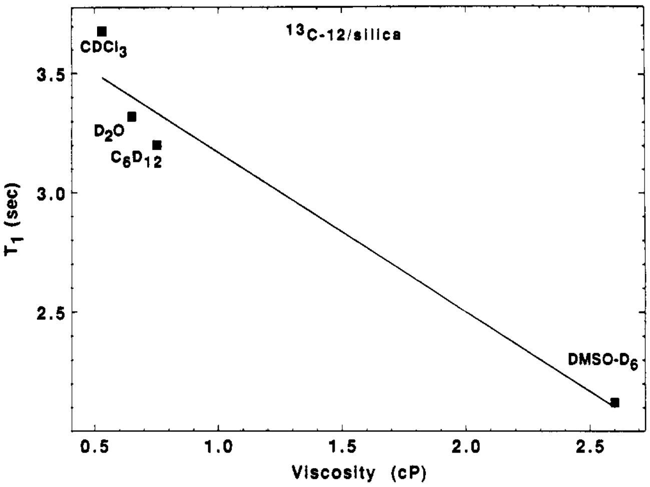


**Figure 1.** Dependence of the $^{13}$C spin–lattice relaxation time of a bound methyl probe on the local viscosity. Temperature: 308 K.

## Results

The effective interaction range of the dodecyl probe may be estimated by calculating the length that the terminal $^{13}$C nucleus extends from the surface. For low surface coverages, Monte Carlo calculations suggest that the average distance of a chain tail covalently bonded to a surface is not appreciably perturbed by the presence of the surface.[18] By using the freely jointed chain approximation, the RMS end-to-end distance may be estimated to be in the range of 7–8 Å.[19] If a "hard-sphere" approximation is used, such as that obtained from van der Waals parameters, a probe volume of roughly 500 Å$^3$ is obtained,[20] yielding a van der Waals radius of 9 Å. From these estimates, it appears reasonable that the surface probe samples predominantly those interactions within a length scale of 5–15 Å from the anchoring site. By comparison of spectra of the surface species taken in different solvents, it is observed that the characteristic probe resonance is in the fact a family of states, probably representing different surface sites on the silica. This is confirmed by measurements of the probe $T_2$, which yield a natural line width much narrower (30 Hz) than that observed (ca. 110 Hz).

The sensitivity of the spin–lattice relaxation time to local Brownian motion arises primarily from the time dependence of the carbon–hydrogen dipolar interaction.[18] We first confirmed this dependence by determining the surface probe $T_1$ in the presence of various small-molecule liquids (Figure 1), after the work of Gilpin and Gangoda.[7] The inverse relation of $T_1$ to medium viscosity indicates that the local probe dynamics are such that they fall within the regime of rapid dipolar motion, which is consistent with the viscosity[7] and temperature[21] dependence observed previously on this system. To firmly establish presence within the fast-motion regime for the adsorbed polymer samples, the location of the $T_1$ minimum was determined for one sample containing an adsorbed quantity of 0.27 g

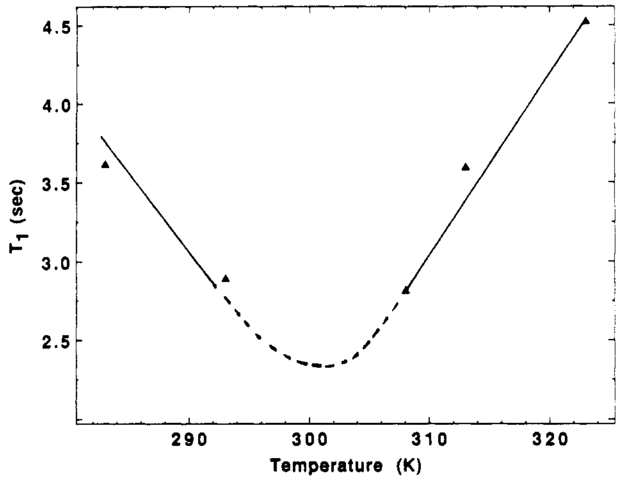


**Figure 2.** $T_1$ of the surface probe as a function of temperature, for a sample of 0.27 g of PDMS/g of silica gel.

**Table I**

| sample, g of PDMS/g of silica | temp, K | $T_1$ surface, s | $T_1$ bulk, s |
|---|---|---|---|
| melt/surface | 308 | 3.68 | 4.19 |
| | 318 | 3.92 | 4.26 |
| 1.09 | 298 | 2.83 | 3.88 |
| | 308 | 3.68 | 4.19 |
| 0.20 | 308 | 3.52 | 1.79 |
| | 323 | 5.49 | 2.60 |

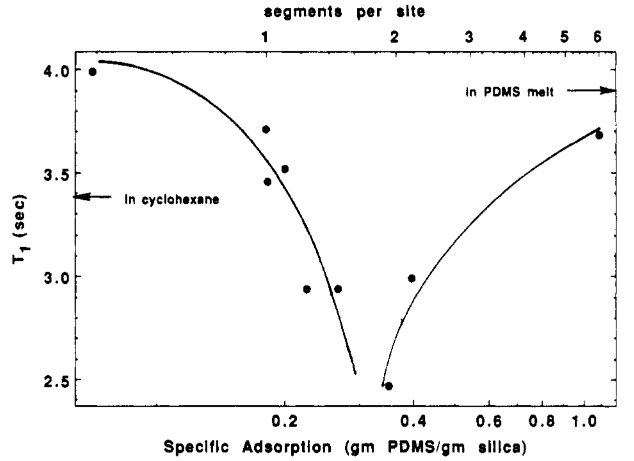


**Figure 3.** Dependence of the surface probe $T_1$ on surface coverage. The minima reflects a minima in mobility within the solid/solution interface and not the minima due to the dipolar nature of the nuclear relaxation (see text). Values of the surface $T_1$ in contact with pure solvent cyclohexane and in pure PDMS are illustrated.

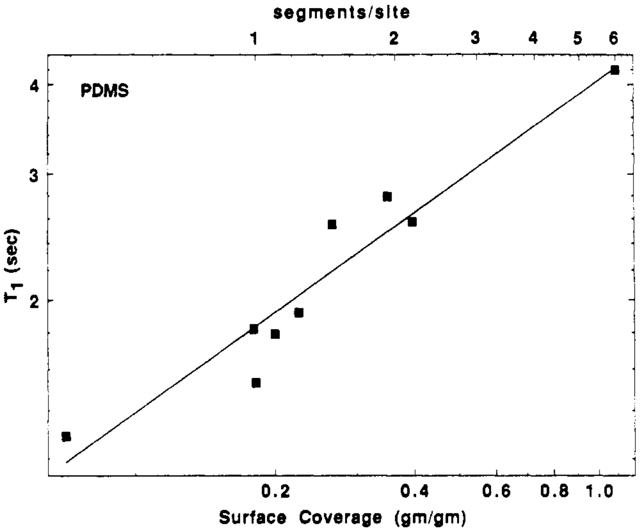


**Figure 4.** $T_1$ of adsorbed poly(dimethylsiloxane). The increase in $T_1$ with coverage indicates that chain motion becomes less restricted as the thickness of the adsorbed layer increases.

of polymer/g of silica gel. As Figure 2 illustrates, at 308 K this system does indeed lie within the fast-motion regime, although somewhat near the dipolar minimum (within 5–10 K). To ensure that *all* the systems studied are on the rapid-motion side of the dipolar minimum, the temperature dependence of $T_1$ was determined for a variety of samples (Table I). In all cases, the change in $T_1$ is consistent with rapid motion. As further evidence, we note that the line width, and the field independence of the $T_1$ of a very similar system, also supports placement within the regime of fast motion.

Spin–spin relaxation measurements of the adsorbed polymer systems show two-component relaxation behavior characteristic of adsorbed systems above the polymer glass transition temperature. $T_2$s of the slowly relaxing component of the adsorbed PDMS ranged from 30 to 260 ms, depending on surface coverage. This represents a difference in the mobile-phase $T_1$ and $T_2$ of over 20 times. Although the equivalence of $T_1$ and $T_2$ is normally considered a requirement for placement within the regime of motional narrowing for small molecules, the inequivalence of $T_1$ and $T_2$ is well established for polymer dynamics and is probably due to the contribution of low-frequency modes to $T_2$ as discussed by Schaefer.[22]

Since the probe and the adsorbed polymer are in the fast-motion regime, the spin–lattice relaxation times represent a direct measure of Brownian mobility. The $T_1$s of the bound probe are plotted versus polymer surface coverage in Figure 3. For comparison, the $T_1$s of the probe in contact with pure solvent and with an undiluted polymer melt are included. At very low coverages, the probe $T_1$ is significantly *higher* (by up to 21%) than the case where the surface is in contact with only the pure solvent cyclohexane. This increase in mobility may be caused by a driving of the ends of the nonpolar alkyl probe further from the oxide surface by the polar PDMS molecules. This extension from the surface would be expected to result in faster local motion, as has been well-documented in chromatographic systems.[9] The fact that the dynamics are so increased indicates that the probe does not interact significantly with the polymer chains, suggesting that most of the segments exist in trains lying flat on the oxide surface, or at least in structures smaller than the 7–15-Å characteristic length of the probe nuclei.

As the surface density increases, the polymer segments are driven from the surface into loop and tail configurations, which create a region of reduced mobility that is reflected by the decreasing $T_1$ of the surface probe. Figure 3 shows that the polymer loops begin to cause an attenuation in Brownian mobility at a surface coverage of about 0.2 g of PDMS/g of silica. At a surface density of about 0.35 g of PDMS/g of silica, the $T_1$ passes through a minimum. Due to the proximity of our system to the $^{13}$C *dipolar* minimum, it is conceivable that this behavior represents a continuous decrease in the mobility of the probe. However, as noted previously, the temperature dependencies of the $T_1$s of these samples always support the presence on the fast-motion side of the dipolar minimum. Although the proximity of this system to the dipolar minimum may cause the simple linear dependence of the $T_1$ to the Brownian dynamics of the system to break down, all of the evidence collected supports the contention

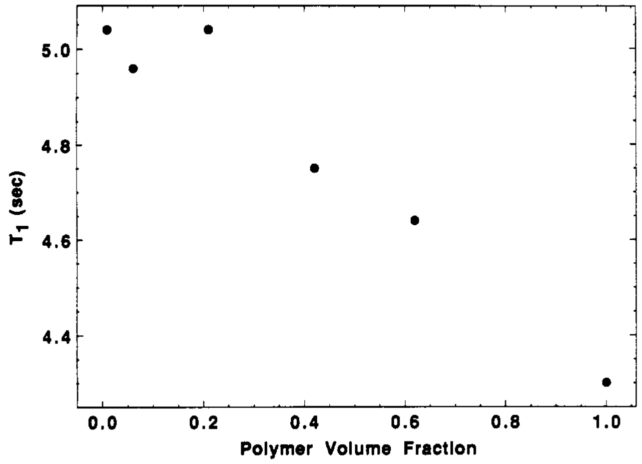


**Figure 5.** $T_1$ of 3900 molecular weight PDMS as a function of polymer volume fraction. Solvent: cyclohexane. Temperature: 308 K.

that the observed minimum in $T_1$ represents a true minimum in probe mobility.

This minimum probably reflects that point at which the adsorbed loops and tails have a thickness large enough to interact with the probe but are in general too small to explore the rapid motions available to bulklike chains due to their relatively short lengths. As the surface density of chains increases beyond this range, the average loop and tail size will become larger, with a concomitant increase in the mobility of these moieties. It is interesting to note that our results indicate that Brownian dynamics within the boundary region are substantially slower in cases of moderate surface coverage than when the surface is in contact with a large reservoir of the pure melt. This underscores the influence of polymer *conformation* on interfacial dynamics.

This change in mobility of the loops and tails can be clearly seen in the dependence of the adsorbed PDMS $T_1$ on surface coverage. Figure 4 shows that the polymer $T_1$ increases rapidly with surface coverage, reflecting a profound increase in mobility as the segments comprising the boundary layer increase in size and thereby spend a smaller fraction of time within the motionally restricted boundary region. It must be emphasized, however, that the segments never completely lose memory of the surface, as can be seen by comparing the $T_1$s of the bound polymer to those obtained in solution (Figure 5). Only at the highest surface coverage (1.09 g of PDMS/g of silica) does the polymer $T_1$ of 4.19 s become comparable to $T_1$s obtained in the liquid state, and then only to the $T_1$ measured in the pure melt (4.20 s).

There has been for some time an interest in estimating the thickness of the immobilized polymer layer in colloidal and composite systems. This study suggests that backbone architecture, rather than surface binding energy, is the key consideration in restricting local mobility at a surface. Although the PDMS chains are tenaciously bound to the silica substrate, the resultant interfacial regime is quite small and quite fluid. Polymer chains of greater stiffness would probably show both a larger boundary region and a greater decrease in fluidity.

## Conclusions

We have shown that the Brownian dynamics within an adsorbed polymer layer are highly sensitive to the extent of surface coverage, and therefore presumably the chain conformation. At very low surface coverages, the chains apparently adopt an extremely flat profile, with few loops or tails longer than approximately 5–15 Å. The extent of motion at a fixed distance from the surface is determined by the size of the loops and tails. The average segmental mobility has been shown to increase dramatically with surface coverage, although some residual influence of surface binding persists to even the highest surface coverages. Chain architecture, and not sticking energy, appears to be the most important factor in determining the fluidity of the boundary region.

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