Segmental Motion of Surface-Bound Swollen Poly(methyl acrylate)-*d*

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ABSTRACT: Poly(methyl acrylate)-*d* (PMA-*d*), labeled in the backbone α position, was prepared and adsorbed from toluene on silica at a coverage of 0.38 mg of PMA-*d*/mg of silica. This coverage was roughly that of the maximum found in the adsorption isotherm. Comparisons of deuterium NMR spin−lattice relaxation time, T_1, and spin−spin relaxation time, T_2, for the adsorbed, swollen polymer at different temperatures were made to obtain information about the backbone motion of the surface-bound polymer. The results were consistent with a system where the fast local motions were similar to those in solution but the longer range segmental motions were more restricted than those in solution. The log-normal distribution yielded mean correlation times which were 4−10 times slower for the surface-bound species than that in solution. The Hall−Helfand (HH) model with two correlation times yielded *slow* correlation times more than an order of magnitude slower for the surface species. Compared to previous studies on terminally attached polymers which formed extended brushes, liquid-like segments of randomly attached homopolymers have significantly reduced *longer range* segmental motions.

Introduction

The behavior of homopolymers adsorbed at solid−liquid interfaces is much different from that of small molecules. Molecular motions of segments in adsorbed polymers may be affected by both the direct interaction of the segments with the surface and through covalent bonds with neighboring segments. Usually, homopolymers are randomly attached to the solid surfaces. For species with a strong attraction to the surface, some segments may be directly attached to the surface or are very close to other segments which are attached. These are known as trains and they are relatively immobile. The remaining segments which are also indirectly attached are typically further away from the surface. These are known as loops and tails and are generally much more mobile.[1] Thus, at an interface, which may be only a single polymer molecule thick, segments of greatly differing mobilities exist.

There are a variety of ways to characterize adsorbed polymers,[1] and many of these have been used to estimate some sort of “bound fraction”. For example, deconvolution of infrared spectra has been used to estimate the fraction of directly bound segments,[2−5] i.e., those which have direct attachment on the surface. On the other hand, electron spin resonance (ESR) and nuclear magnetic resonance (NMR) experiments have been used to estimate a bound fraction which includes both the directly bound segments and those close to the directly bound segments.[6−9] These have reduced mobility compared to those in loops or tails.

NMR has been a particularly useful technique for studying the mobility of adsorbed chains. A few reviews of its application to surface-bound polymers exist.[10−12] If the polymer segments are extended into the solvent region or there is significant solvent penetration into the polymer layer, NMR solution spectra may be appropriate to characterize the motion of the loops and tails of the adsorbed chains. Prior studies range from the verification that some segments are considerably constrained on the surface,[13] to an estimation of bound and unbound fractions[9] in homopolymer systems, and to a more quantitative estimate of the dynamics[14,15] in a block copolymer system.

In polymer solutions, NMR relaxation data have been interpreted using different models and distributions of correlation times[16−18] to gain insight about molecular motion at the segmental level. Yet few studies have quantified the segmental dynamics of surface-adsorbed homopolymer. Both proton and ^{13}C NMR relaxation times are difficult to use in many systems. For protons, incomplete knowledge of the interatomic distances complicates the estimation of correlation times. For ^{13}C spectra, lack of sensitivity and possible spectral overlap for immobile species are detrimental. Our approach has been to use ^{2}H NMR relaxation times to obtain motional information on the adsorbed polymer chains.

In this work, poly(methyl acrylate) (PMA) has been specifically labeled at the backbone α-position with deuterons. A label on backbone enables us to probe backbone dynamics. The deuterated PMA was adsorbed on a silica surface and then swollen in toluene. The backbone motion of the liquid-like segments, of the adsorbed PMA-*d* chains in this homopolymer system, was probed with deuterium NMR relaxation data. The results were fit with the log-normal distribution of correlation times and also the Hall−Helfand model to gain information about segmental motions in a swollen surface-bound homopolymer system.

Experimental Section

Methyl acrylate was purchased from Aldrich Chemical Co. (Milwaukee, WI) and distilled under reduced pressure before use. 1,4-Diazabicyclo[2.2.2]octane (DABCO) and deuterium oxide (D_2O) were also from Aldrich and used as obtained. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol before use, and all solvents were distilled before use.

A direct hydrogen-exchange reaction[19] was chosen to prepare α-deuterated methyl acrylate. At room temperature methyl acrylate (8.32 g, 0.100 mol), deuterium oxide (33.99 g, 1.70 mol), and DABCO (1.61 g, 0.014 mol) were stirred in a 100 mL flask for 2 h. The deuterium oxide layer was removed with a separatory funnel. The remaining methyl acrylate-*d* was dried with sodium sulfate. The yield was around 70%. Proton and deuterium NMR indicated >90% deuteration in the α-position.

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Methyl acrylate-*d* (3.58 g, 0.041 mol) was polymerized in toluene (6.20 g, 0.067 mol) with 2,2′-azobis(isobutyronitrile) (0.06 g, 0.33 mmol) as the initiator. The solution was kept under nitrogen gas and bath-heated to 65 °C for 4 h. The yield of polymer was about 80%. The molecular mass of this poly(methyl acrylate)-*d* (PMA-*d*) was $M_w = 56$ kg/mol with a polydispersity of 2.1, as determined by gel permeation chromatography (GPC) based on polystyrene standards.

Protonated poly(methyl acrylate) (PMA) was used for the adsorption isotherm measurements as it was not practical to use the deuterated PMA. The protonated sample had a molecular mass $M_w = 100$ kg/mol and a polydispersity of 1.6. From this measurement an estimate of the concentration required for maximum in adsorbed amount (where the adsorption isotherm levels out) of the deuterated polymer could be made. The substrate used was high surface area amorphous fumed silica (Cab-O-Sil grade M-5, 200 m^2/g from Cabot Corp., Tuscola, IL). The solvent was toluene. The results showed that the maximum adsorbed amount was about 0.38 mg of PMA/mg of silica in toluene. Based on this information, an approximately 8 wt % solution of PMA-*d* was prepared and used to adsorb the polymer on Cab-O-Sil. An estimate of the amount adsorbed for this sample was based on thermogravimetric analysis (TGA) measurements. This yielded a coverage of 0.32 mg of PMA-*d*/mg of silica. Considering the molecular weight dependence of adsorption isotherms, this result seems reasonably consistent with that for the protonated material.

The surface-bound PMA-*d* at was swollen with toluene and placed in 5 mm NMR tubes. For comparison, a solution of PMA-*d* was also prepared in toluene. These two samples for NMR studies were designed to have similar polymer/solvent molar ratios. At low temperature, both have the same T_1 value, consistent with the notion that their fast segmental motion was similar (vide infra).

Deuterium NMR relaxation times T_1 and T_2 were obtained on a Varian VXR-200/S spectrometer operating at 30.7 MHz at a temperature range from 18 to 50 °C. The T_1 values were measured using the inversion−recovery (180°−τ−90°) sequence and the T_2's by the CPMG method. A pulse delay of at least $5T_1$ was used for the deuterons to achieve equilibrium magnetization after each data acquisition. Both the spin−lattice and the spin−spin relaxation data were fit to a single-exponential decay function. The spectra obtained under these conditions were "liquid-like".

Results and Discussion

For the T_1 measurements, the signal decay curves for either surface polymer or solution polymer could be satisfactorily characterized by single-exponential functions. For the T_2 measurements, deviations from single-exponential decay functions were found for the surface-bound polymer. These could be fit better with a biexponential function, but the results were not of high enough quality to make meaningful estimates of correlation times from a biexponential fit. Thus, we felt it was a reasonable approximation to fit all of the decay curves with single-exponential functions for consistency. Under the "liquid-like" conditions used, no observation of a "solid-like" component was observed. Thus, we were likely probing only the more mobile loops and tails.

The relaxation times for the polymer on the surface, swollen with solvent, were altered compared to those in solution, due to their adsorption on silica. Figure 1 shows the deuterium NMR relaxation times for the liquid-like segments of surface-bound PMA-*d* swollen in toluene and the polymer in toluene solution at different temperatures. The comparison was made for both the spin−lattice relaxation time, T_1, and the spin−spin relaxation time, T_2. Toluene is considered a thermodynamically good solvent for PMA-*d*.

Both T_1's and T_2's for the surface-bound PMA-*d* chains, swollen in toluene, were shorter than those of free polymer chains in solution. The effect of surface adsorption was much greater for the T_2's than the T_1's.

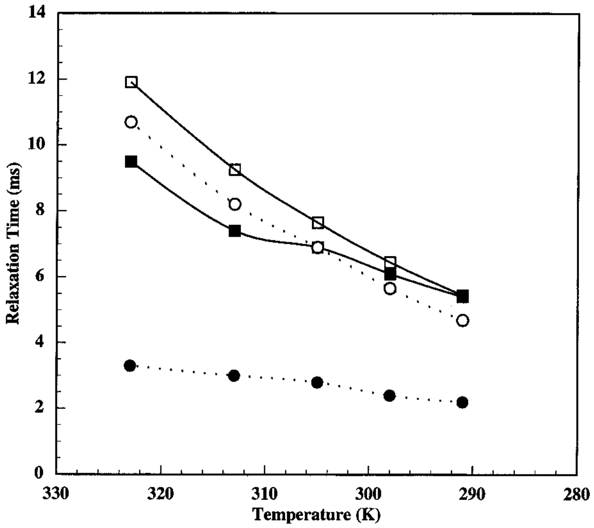

Figure 1. Deuterium NMR relaxation times for PMA-*d* ((□) T_1; (●) T_2) in toluene solution and ((■) T_1; (○) T_2) on silica swollen with toluene. The curves are drawn to aid the eye.

These results suggested that the mobility of the adsorbed PMA-*d* chains were restricted compared to those in solution. The T_1 values are dominated by fast (local) motions of the polymer chain while the T_2's are dominated by longer range, slower motions. Since the T_1 values of the adsorbed PMA-*d* chains were fairly similar to those in solution (in fact, at the lowest temperature measured, they were equal), the fast local motions of the liquid-like segments were believed to be similar to those in solution. These types of motions for the liquid-like segments did not appear to be greatly affected by attachment to the surface. This is also consistent with the surface T_1's being well characterized by a single-exponential function. Meanwhile, the longer range, slower motions of the liquid-like segments were significantly reduced due to adsorption. The deviations from single-exponential behavior for the T_2's were probably representative of a heterogeneous environment which the slower motions were more sensitive to.

The deuterium relaxation behavior is typically dominated by the electric quadrupole interaction. For an axially symmetric electric field gradient, the T_1 and T_2 values are given by[20]

$$1/T_1 = (3\pi^2/20)(e^2qQ/h)^2[J(\omega_0) + 4J(2\omega_0)] \qquad (1)$$

and

$$1/T_2 = (3\pi^2/40)(e^2qQ/h)^2[3J(0) + 5J(\omega_0) + 2J(2\omega_0)] \qquad (2)$$

where e^2qQ/h is the quadrupole coupling constant of 165 kHz as determined by the solid-state deuterium spectrum of bulk poly(methyl acrylate)-*d*, $J(\omega)$ is the spectral density, and ω_0 is the Larmor frequency. The spectral density is a measure of the relative amount of motion at a particular frequency and is defined by

$$J(\omega) = \int_{-\infty}^{\infty} G(t) \exp(-i\omega t)\, dt \qquad (3)$$

where $G(t)$ is an autocorrelation function that represents the correlation of the C−D bond vector axis at time 0 and t. Unfortunately, in a polymer system the relationship between experimental data and spectral densities is not so direct, nor can a unique correlation function be obtained by a reverse Fourier transformation of eq 3 because it is only sampled at a few points. It is therefore

Table 1. Distributions of Correlation Times for PMA-d_α from the Log-normal Function

	solution/toluene		surface/toluene	
T (K)	τ_0 (ns)	σ	τ_0 (ns)	σ
291	0.62	2.20	2.48	3.74
298	0.50	2.23	2.31	3.87
305	0.40	2.19	1.96	3.93
313	0.34	2.41	1.83	3.98
323	0.26	2.49	1.78	4.33
E_a (kJ/mol)	21		8.7	

appropriate to interpret the experimental data in terms of some type of motional model.

Distributions of correlation times have proved useful for analyzing polymer dynamics data. The asymmetric log χ^2 distribution proposed by Schaefer[16] has been used to fit many polymeric systems. Recently, O'Connor and Blum[18] have shown that a correction was required to obtain the true mean correlation time from that model. Another distribution function that we have preferred is the log-normal distribution[21] as it has well-defined moments and simple derivatives and gives physically reasonable results from low- and high-frequency T_1-T_2 data as well as solely high-frequency T_1 data.[18] The log-normal distribution is given by

$$G(\tau_r) = \frac{1}{\pi^{1/2}\sigma\tau_r} \exp\{-[\ln(\tau_r)/\sigma + \sigma/4]^2\} \tag{4}$$

with

$$\tau_r = \tau/\tau_0 \tag{5}$$

where τ_r stands for reduced correlation time, τ_0 mean correlation time, and τ the correlation time.

The experimental relaxation data were fit by the log-normal distribution function and the results given in Table 1. This distribution function has usually been applied to flexible macromolecules in solution.[18,22] We extend these to a mobile polymer system attached to a solid surface. The model should be valid for at least a qualitative comparison of the segmental motions of the polymer in solution and at an interface.

For the fitted data, the log-normal distribution yielded mean correlation times, τ_0's. The τ_0's were consistent with the notion that the motions of the adsorbed chains were more restricted than in solution. The values of width parameter, σ, in the log-normal distribution for both the polymer in toluene solution and the surface-bound PMA-*d* swollen in toluene increased slightly with increasing temperature, although the increases were small. A more important aspect was that at the same temperature, the value of σ for the surface-bound PMA-*d* swollen in toluene was noticeably greater than that of the polymer in toluene solution. This implies a broader distribution of correlation times for the liquid-like segmental motions of the adsorbed polymer chain. The correlation times are shown in Figure 2 as a function of temperature. From these, apparent energies of activation, E_a, were calculated to be about 21 kJ/mol (5.0 kcal/mol) for the polymer in toluene solution and about 8.7 kJ/mol (2.0 kcal/mol) for the adsorbed one swollen in toluene. The value of E_a for PMA-*d* in toluene was similar to that for many common polymer solutions as determined by ^{13}C and ^{2}H relaxation measurements.[17,22,23]

It is appropriate to compare our work with other studies on swollen, adsorbed polymers where the correlation times were measured. The dynamics of poly(ethylene oxide) (PEO) end grafted to silica has been studied with both ESR[7,8,24] and NMR.[25] From ESR data, two components differing in mobility were found in benzene or chloroform, and these were assigned to species where the nitroxide label was near and away from the surface. Two components were also found with high-resolution ^{13}C and ^{1}H NMR relaxation experiments in benzene.[25] From both the ESR and NMR studies, relatively low apparent energies of activation were found for the faster surface-adsorbed component. In fact, the ESR results[8,24] yielded lower energies of activation for the surface species than for solution species. This is consistent with our result, although we have no clear explanation why the value of E_a for the surface-bound PMA-*d* was lower than that for the polymer in toluene solution. It is possible that the distribution of correlation times may complicate the interpretation of this value.

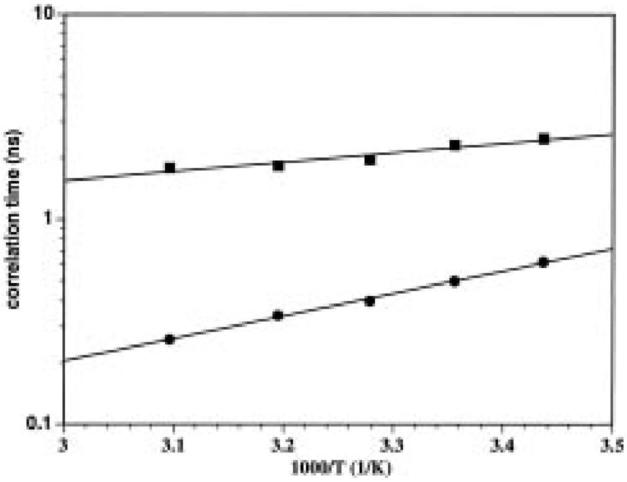

Figure 2. Temperature dependence of the mean correlation times, τ_c, from the log-normal distribution for PMA-*d* (●) in toluene solution and (■) on silica swollen in toluene.

Although many distribution functions[16,21,25−28] were derived to satisfy a number of experimental relaxation data for different polymer solution systems, more attractive theories[29−31] based on a molecular description of segmental motions have been developed. One which is frequently used to describe relaxation processes in polymer molecules is that of Hall and Helfand[29] (HH). The resulting correlation function was originally developed by Helfand and Weber[32]

$$G(t) = (t/\lambda_1) I_0 \exp(-t/\lambda_0) \exp(-t/\lambda_1) \tag{6}$$

and correspondingly the spectral density is given by[33]

$$J(\omega) = 2A(\omega)\{[\lambda_0(\lambda_0 + 2\lambda_1) - \omega^2]^2 + [2(\lambda_0 + \lambda_1)\omega]^2\}^{-0.25} \tag{7}$$

where

$$A(\omega) = \cos\{0.5 \tan^{-1}[(2(\lambda_0 + \lambda_1)\omega)/(\lambda_0(\lambda_0 + 2\lambda_1) - \omega^2)]\} \tag{8}$$

I_0 is a modified Bessel function, λ_0 is a rate constant for single-bond rotations, and λ_1 is a rate constant for cooperative transitions. Although precisely defined in the model, the transition rates are probably most significantly related to motions on different time scales. Thus λ_1 and λ_0 correspond to the rates of the fast (short range) and slow (long range) motions of the polymer chains, respectively.

Table 2. Relaxation Parameters of ^{2}H Fit by the HH Model

T (K)	T_1 (ms)	T_2 (ms)	λ_0[a]	λ_1[a]	$J(0)$[b]	$J(\omega)$[b]	$J(2\omega)$[b]
A. Solution/Toluene							
291	5.45	4.69	3.51	39.6	11.8	10.6	8.73
298	6.45	5.66	3.87	54.2	9.59	8.82	7.41
305	7.65	6.90	4.56	71.5	7.71	7.24	6.30
313	9.25	8.20	4.06	112	6.57	6.09	5.18
323	11.91	10.70	4.40	181	4.99	4.67	4.04
291	5.40	2.20	0.225	36.9	49.0	12.3	8.40
B. Surface/Toluene							
298	6.10	2.40	0.201	47.2	45.8	10.9	7.45
305	6.90	2.80	0.218	61.2	38.7	9.61	6.59
313	7.40	3.00	0.217	70.7	36.1	8.96	6.14
323	9.50	3.30	0.193	115	35.4	6.93	4.80

[a] In units of 10^8 s^{-1}. [b] In units of 10^{-10} s.

The results of fitting the data with the HH model are reported in Table 2. These results clearly show that the segmental motions of the polymer changed with adsorption. The values of λ_1 (fast motions) were quite similar for the solution and surface-bound polymer. The slower motions, represented by λ_0, were at least an order of magnitude faster for the solution than for the adsorbed polymer. The spectral density terms at zero frequency, $J(0)$, representative of the relative amount of longer range, slower motions, also confirm this. A comparison of the surface and solution data showed a significant increase in the $J(0)$ values with adsorption while the values of $J(\omega)$ and $J(2\omega)$ were quite close for both the solution and surface polymer.

The HH model was also used for the interpretation of relaxation data from deuterium-labeled styrene segments of a block copolymer poly(styrene-*b*-2-vinylpyridine) (SVP).[14,15] When SVP was adsorbed on silica and swollen with toluene, the styrene segments formed extended brush structures with the vinylpyridine attached to the surface in a collapsed state. A comparison of the λ_1 values for SVP and PMA show that the shorter range motions of the adsorbed swollen styrene segments were slower than those of PMA. This seems reasonable because, based on the solution data, the styrene segments have a lower inherent mobility in toluene. However, values of λ_0 for the longer range motions were *faster* for the adsorbed styrene segments in SVP than for those of PMA. Thus, the mode of attachment and the resulting structures influence the dynamics significantly. In particular, we believe that reduced segment–segment interactions due to the extended nature of the SVP brushes resulted in their enhanced longer range segmental motions relative to an adsorbed homopolymer.

Finally, the picture that emerged was that the liquid-like segments of PMA-*d* on the surface existed in local environments where the fast motions were *similar* to those in solution. In contrast, the longer range motions of the surface-bound polymer were significantly *slower* than those in solution. The breadth of the correlation time distributions were also broader for the surface polymer, presumably indicative of more motionally heterogeneous environments. This was undoubtedly due to the attachment of some of the polymer segments to the surface.

Conclusions

Deuterium relaxation times have been shown to be an effective probe of the motion of liquid-like polymer segments at interfaces. In toluene, the fast local motions of the liquid-like segments of the adsorbed PMA-*d* were similar to those in solution. The longer range, slower motions were significantly reduced compared to solution. The mean correlation times, obtained from fitting the relaxation data to a log-normal distribution of correlation times, were 4–10 times slower for the surface species. When the Hall–Helfand model was used, the slower correlation times for longer range motions were found to be over an order of magnitude slower for the surface species. Both models are in qualitative agreement. The apparent energy of activation from the mean correlation times was unexpectedly lower for the surface species. This may be due to the undoubtedly more complicated dynamics on the surface and requires further study. Finally, this study also highlights differences in the dynamics of adsorbed homopolymers from those terminally attached with extended brush structures. Compared to these, the longer range motions of the homopolymer segments were significantly reduced.

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