$\Phi_{l,i}$	volume fraction of species l in layer i
Ω	combinatorial factor for the interfacial system
Ω_l	combinatorial factor for the reference system containing chains of type l

Subscripts and Superscripts

b	bulk properties
i,j	layer numbers i,j
l	denotes species type under consideration in the bimodal melt; $l = 1$ denotes the longer chain, $l = 2$ the shorter chains

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Density Profile of Terminally Adsorbed Polymers

Frank D. Blum* and Brijnaresh R. Sinha†

Department of Chemistry and Materials Research Center, University of Missouri—Rolla, Rolla, Missouri 65401

Frederick C. Schwab

Mobil Chemical Company, R&D Laboratory, P.O. Box 240, Edison, New Jersey 08818

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ABSTRACT: Specifically labeled terpolymers of 2-vinylpyridine, styrene, and deuterostyrene have been prepared by anionic polymerization. The deuterostyrene was deuterated in the methine position and placed either in the middle or at the end of the triblock terpolymer. The moderately low molecular weight polymers (ca. 20 000 g/mol, polydispersity ca. 1.4) were then adsorbed onto high surface area silica. The adsorption isotherm was measured from toluene solution to plateau at about 1.75 mg of polymer/m^2 of silica. The environment of the styrene segments in the terpolymer attached to the silica surface and swollen with toluene was probed with ^{2}H NMR. Comparison of ^{2}H NMR spin–lattice relaxation time, T_1, for the adsorbed polymer to that of the polymer in solution suggests that the local concentration of styrene segments near the middle of the polymer, i.e. next to the vinylpyridine segments, is about 0.11 g/mL. The concentration of segments located at the end of the polymer is estimated to be approximately 0.048 g/mL. These experiments suggest that the polymers are extended in a good solvent for styrene to about 4 times the styrene radius of gyration. The relaxation times (T_1 and T_2) of the surface-bound polymer were closer to each other than those for the homopolymer in solution, suggesting that the dynamics are rather different than in solution.

Introduction

The use of polymers as agents for improving colloidal stability is well-known.[1-4] In the absence of significant electrostatic forces, polymers may be used to achieve colloidal stability through entropic stabilization, based on the inability of the polymer segments on neighboring particles to pass through each other or intertwine upon close approach. A number of theoretical treatments have been used to describe the conformation of polymer molecules on solid surfaces including those based on self-consistent-field,[5,6] scaling,[7] or Monte-Carlo approaches.[8] These theories have been of importance in understanding

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* Author to whom correspondence should be sent.

† Present address: Union Carbide Corp., P.O. Box 8361, S. Charleston, WV 25303.

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the basic chemistry and physics of adsorbed macromolecules.

The properties of systems that require adsorbed polymers can often be improved with the use of copolymers instead of homopolymers. Block copolymers are often used and suited for study because these specifically tailored molecules may behave in a straightforward way if one segment adsorbs to the surface much better than the other. This may result in terminally attached polymers which have been treated theoretically for the case where one segment is strongly adsorbed and the other is not.[8-11] It is predicted that terminally attached polymers will have density profiles that depend on the coil radius of the chain, R, and the distance between the grafted sites on the surface, D.[7,9,10] The extreme configurations for random-coil polymers have been described as "mushrooms" ($D \gg R$) or "brushes" ($D \ll R$). In the mushroom case, the polymer coil occupies roughly a half sphere on the surface with a radius R. The brushes, on the other hand, are expected to have a much more extended conformation with a density profile that after an initial rise, is roughly flat and drops off suddenly at a distance, τ, proportional to molecular weight. This has not yet been experimentally verified. The chains in this regime have been called "stretched chains".[10] Milner et al.[11] have used self-consistent-field methods to calculate the concentration profile of brushes in a solvent. They predict a concentration profile of a parabolic form for high molecular weight brushes as opposed to a step function predicted by Alexander[9] and de Gennes.[10] Neither model has been conclusively verified.

In the past few years, there have been a number of experimental studies performed on block copolymers attached to solid surfaces. One system that has attracted attention has been block copolymer poly(2-vinylpyridine-*co*-styrene) (VPS). In addition, many similar systems with variations on this basic structure have also been studied. The adsorption of VPS on silica for both block and random copolymers in trichloroethylene has suggested that styrene does not adsorb on the silica surface and the presence of 2-vinylpyridine in the copolymer is necessary to achieve steric stabilization.[12] Hadziioannou et al.[13] have adsorbed VPS polymers on mica and used the surface force apparatus to probe the polymer–polymer interactions between coated surfaces at small separations in solvents of different thermodynamic quality. In a good solvent, toluene, they found that the onset of the repulsive interactions between the polymer-coated surfaces occurred at separations of about 10 R_g (radius of gyration value expected in solution). This suggested a very extended structure for the styrene segments. In contrast, in a poor solvent, cyclohexane, the repulsion occurs only at about 4 R_g, suggesting a much more compact structure. Qualitatively similar results have been found for copolymers with *tert*-butylstyrene as a comonomer with 2-vinylpyridine in several solvents.[14,15]

A number of other experimental techniques for studying adsorbed polymers are available and many of these have been reviewed[16] and classified as either thermodynamic, spectroscopic (including scattering), hydrodynamic, electrochemical, or disjoining pressure. Though many advances in understanding them have been made, much more experimental work needs to be done to test the theoretical predictions and also to gain further insight into these systems. In the present study, we have probed the environment of two different triblock terpolymers,[17] namely poly(2-vinylpyridine–styrene–deuterostyrene) (VPSDS) and poly(2-vinylpyridine–deuterostyrene–styrene) (VPDSS), bound to silica surfaces and swollen with solvent. The two polymers differ in the positions of the label (deuteron), allowing the environment to be probed as a function of the contour length of the polymer. Since the longitudinal relaxation time, T_1, of the deuteron is sensitive to the local dynamics of the chain, a comparison of the solution relaxation time and that of the surface-bound segments provides a measure of the effective polymer concentration for the latter species. Differences in the transverse relaxation times (T_2) between bound and unbound polymer segments of a fairly large magnitude have already been demonstrated.[18,19] Much smaller differences in liquidlike spectra were used in this study to probe the relatively small differences between the two different labeled polymer segments.

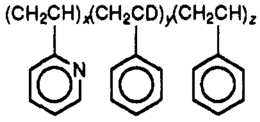
Table I
Molecular Weight and Monomer Distribution in VPS Polymers

designation	M_w[a]	M_w/M_n	S(H), wt %	S(D), wt %	VP, wt %
DS	265.5	2.5		100	
DS-L	8.8	1.9		100	
VPS-1	20.9	2.4	75.0		25.0
VPS-7	20.7	1.5	75.0		25.0
VPDSS	19.2	1.5	37.5	37.5	25.0
VPSDS	21.3	1.4	37.5	37.5	25.0

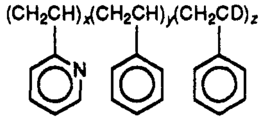
[a] From SEC in THF based on calibration with polystyrene in kilograms per mole.

Experimental Section

Polymer Synthesis and Characterization. α-Deuterated styrene was synthesized by preparing the Grignard reagent from α-bromostyrene followed by addition of deuterium oxide. The purity of the monomer was checked by ^{2}H and ^{1}H NMR and IR spectroscopy. Typically, deuteration levels for the monomer were found to be 80–90% deuterated in the methine position. The block polymers were prepared via "living" anionic polymerization techniques by sequential addition of monomer similar to methods used by Sigwalt et al.[20] The polymerizations were carried out in tetrahydrofuran (THF) at low temperatures (−78 °C) by using *sec*-butyllithium as the initiator. The vinylpyridine block was always added last because the pyridinyl anion is incapable of initiating styrene monomer. After termination with methanol the block polymers were isolated by precipitation in hexane. The structures of the polymers are given as


$(CH_2CH)_x(CH_2CD)_y(CH_2CH)_z$

VPDSS


$(CH_2CH)_x(CH_2CH)_y(CH_2CD)_z$

VPSDS

We note that in the absence of any molecular weight effects, the polymers differ only in the position of the deuteron.

The molecular weights of the polymers were determined by size-exclusion chromatography in THF, which is a good solvent for both polymer segments. The molecular weights reported are based on polystyrene standards, and no correction was made for the presence of the 2-vinylpyridine segments. The results for the polymers used in this study are given in Table I.

Adsorption. Due to its high surface area (200 ± 25 m^2/g), amorphous fumed silica, Cab-O-Sil M-5 (Cabot Corp., Tuscola, IL), was chosen as the model surface. This silica was first heated in a vacuum oven at 105 °C for 24 h to remove any adsorbed moisture, and then samples of it were weighed in centrifuge tubes. The surface area of the silica was found to be within experimental error of the nominal 200 m^2/g before and after heat treatment as determined by nitrogen adsorption. Cab-O-Sil consists of fused silica beads with diameters of about 140 Å each. Solutions of poly(2-vinylpyridine-*co*-styrene) (VPS) in toluene of varying concentrations were prepared. Known quantities of these solutions were then added into the tubes containing silica, which

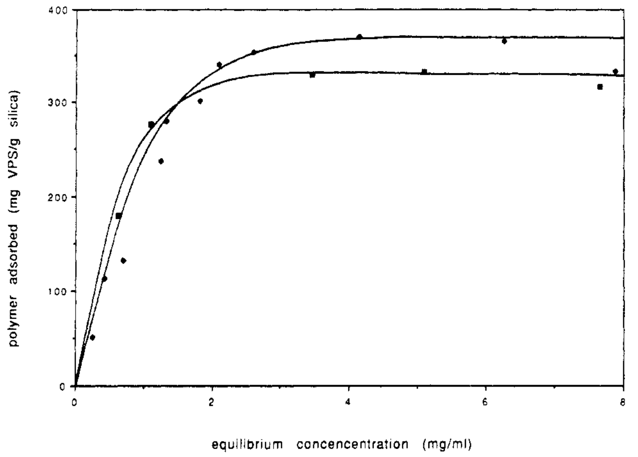


Figure 1. Adsorption isotherms for block poly(styrene-*co*-vinylpyridine) in toluene on Cab-O-Sil silica (♦) VPS-1 and (■) VPS-7. The curves are drawn to aid the eye.

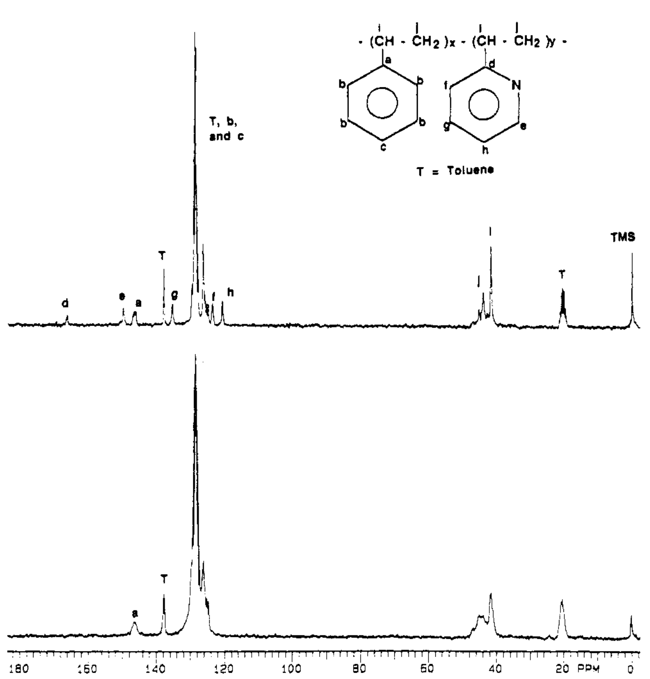


Figure 2. Carbon-13 spectra of VPS-1 (top) and VPDSS surface-bound onto silica (bottom) in toluene-d_8 at 80 °C.

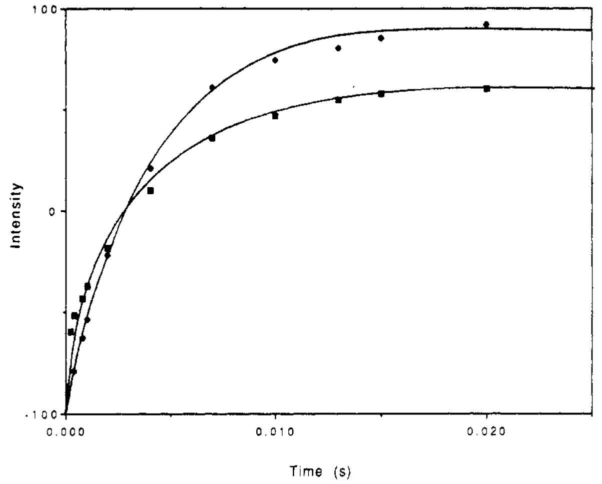


Figure 3. NMR response of styrene deuterons to the inversion-recovery sequence for (■) VPDSS and (♦) VPSDS adsorbed on silica and reswollen with toluene. Also shown are the single-exponential best fits in each case.

were allowed to equilibrate in a water bath for 48 h at 25 °C. The tubes were then removed and centrifuged. The concentration of polymer in the supernatant liquid was then determined gravimetrically after solvent evaporation. The amount of VPS adsorbed per gram of silica was then calculated from the knowledge of the initial and final concentration of VPS and the amount of silica used. The amount of VPS adsorbed per gram of surface was calculated and plotted against the equilibrium concentration of polymer in solution to obtain the adsorption isotherm. The isotherms obtained in this way were similar to those obtained by waiting only 24 h for equilibration.

NMR Measurements. The NMR measurements reported were made at 18 °C for the surface-bound species and for the solutions on a Varian VXR-200 NMR spectrometer operating at 30.7 MHz for deuterons and 50.3 MHz for carbon-13. Modulated proton decoupling was used for the carbon-13 measurements. Solutions of deuteropolystyrene (DS) in toluene of several different concentrations were prepared along with samples with monolayer coverage of both terpolymers, washed with toluene, dried, and reswollen with toluene. Deuterium relaxation times (T_1 and T_2) were measured for the methine deuteron. The T_1 values were measured by using the inversion-recovery (180°-τ-90°) sequence and the T_2s with the CPMG method.[21] A pulse delay of 410 ms (greater than 5 times T_1) was allowed for the deuterons to achieve equilibrium magnetization after each data acquisition. Typically 2000 (surface) and 200 (solution) transients were taken for each time value of the relaxation measurements. The errors in the measurements of T_1 were about 3% and of T_2 about 10%. These estimates are based on both the precision estimated on individual runs plus the consistency of replicate runs. In addition to high-resolution liquid experiments, several wide-line experiments on these polymers were also made. Deuterium wide-line spectra using the solid echo sequence[22] with a 2-μs 90° pulse and 2-MHz band width were used on the bulk homopolymer to estimate the quadrupole coupling constant and to check for the presence of broad (solidlike) resonances on the swollen, surface-bound polymers.

Results

The adsorption isotherms for two of the copolymers are shown in Figure 1. Both are similar in nature and are not of the high affinity type exhibited for other polymer systems.[23,24] They plateau at 320 and 370 mg of polymer/g of silica for VPS-7 and VPS-1, respectively. When the nominal value of 200 m^2/g for the surface area of the silica is used, the plateaus correspond to 1.6 and 1.9 mg of polymer/m^2, respectively. The isotherms of the two polymers are similar and perhaps expected to be so because they have similar weight-average molecular weights.

The proton-decoupled carbon-13 spectra of VPS-1 and VPDSS surface-bound onto silica are shown in Figure 2 in toluene-d_8. The spectrum of the solution polymer is assigned in the figure on the basis of chemical shifts found in the literature.[25] The spectrum of the swollen polymer on the surface has resonances that are somewhat broader than those of the solution polymer. In addition, the resonances from the vinylpyridine are not observed in the surface-bound species, suggesting that these segments are somewhat immobile.

The segmental dynamics of the polymer was studied by using ^2H NMR of the deuterons labeled at the methine position. Some of the original spectra were shown previously[17] and are not repeated here. The response of the magnetization of the styrene deuterons to the inversion-recovery pulse sequence is shown in Figure 3 for terpolymers VPDSS and VPSDS, adsorbed on Cab-O-Sil and reswollen with toluene. A small resonance from the ring deuterons on the toluene (from natural abundant deuterons) was apparent, but because of chemical shift and T_1 differences, it could easily be distinguished from that of the polymer. It is important to note that the relaxation behavior can be fit with a single exponential in each case. Statistical analysis of both curves verified that, within

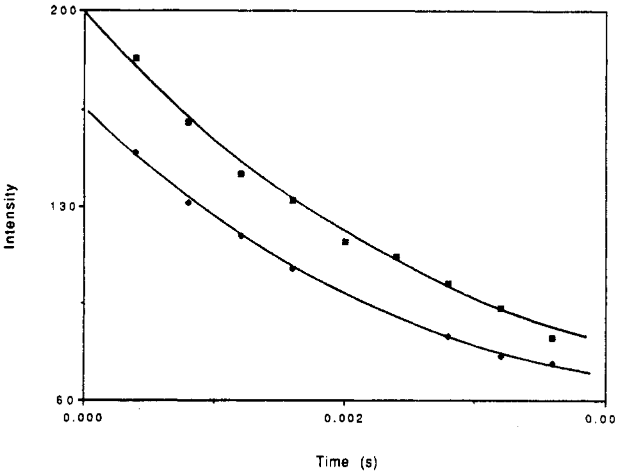


Figure 4. Response of styrene deuteron intensity to the CPMG sequence for (■) VPDSS and (♦) VPSDS adsorbed on silica and reswollen with toluene. Also shown are the single-exponential best fits in each case.

experimental error, multi- and biexponential behavior was not present. In addition, both curves suggest similar relaxation times. The T_1 values that describe the data are 3.63 ± 0.092 and 3.94 ± 0.089 ms for VPDSS and VPSDS, respectively. These values represent the averages of 3 runs each.

The response of the deuterons to the CPMG pulse sequence is shown in Figure 4 for the two deuterated polymers adsorbed on silica and swollen in toluene. The time dependence of magnetization was fit with a single-exponential decay constant, T_2, for both of the polymers. The time dependence of the magnetization could also be fit to a multiexponential decay for each case, but these fits are not significantly better statistically than a single-exponential fit. The CPMG behavior was also probed for time periods of 1 order of magnitude larger and smaller than the range at which the T_2 was measured (Figure 4). At time periods larger than that range, no signal was obtained from the adsorbed polymer while at time periods smaller than that range the peak intensities were virtually constant. Again the relaxation times for the deuterons in either polymer are similar. They have T_2s of 3.38 and 3.60 ms for VPDSS and VPSDS, respectively. The linewidths from the spectra suggest T_2 values that are similar, but not equal, to the measured T_2 values. For example, 2.70 ms (from linewidth) vs 3.38 ms (from CPMG) was found. The line shapes were slightly broader near the base than expected for Lorentzian shapes based on the width at half-height. The deviation from a Lorentzian was typically on the order of 10% or less. No solidlike components were found in wide-line spectra of these species.

In order to understand the dynamics of the adsorbed polymers, we have chosen to compare their behavior with labeled polystyrene (DS) in toluene solution. Three polymers have been used for this purpose, namely, a high (DS) and low (DS-L) molecular weight homopolymer plus the block terpolymer (VPDSS). In Figure 5, the relaxation times T_1 and T_2 have been plotted at 18 °C for the polymers in solution as a function of concentration. The concentration range was chosen to bracket the relaxation behavior of the polymer adsorbed to the surface. Rossler et al.[26] have measured deuteron relaxation times for the polystyrene–toluene system, but they do not report separate data for the α-deuteron. It is obvious from the figure that the relaxation times for the polymer in solution do not bear a 1:1 correspondence to those of the surface-bound polymer. The low molecular weight polymer has significantly larger relaxation times indicative of faster and/or more isotropic motions. The high molecular weight polymer and the block terpolymer have very similar relaxation data. For a given T_1 value the surface-bound polymer has a longer T_2 than the solution polymer. Shown as dashed lines on this plot are the behavior of the surface-bound polymers. The measured relaxation time of the surface-bound polymers fixes a location on the solution relaxation curves. Vertical extrapolation of these points yields a value on the concentration axis that will be used for comparison. This yields concentrations for the surface-bound polymers of 0.11 and 0.048 g/mL for VPDSS and VPSDS, respectively.

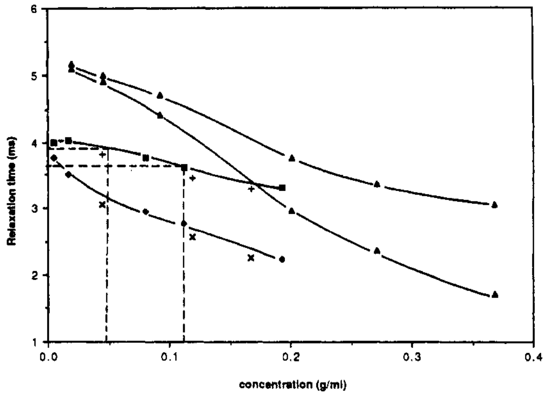


Figure 5. ^{2}H NMR relaxation times for DS ((■) T_1 and (♦) T_2), DS-L ((▲) T_1 and (△) T_2), and VPDSS ((+) T_1 and (×) T_2) in toluene solution. Also shown are the relaxation times for the surface-bound polymers and their extrapolations to the concentration axis (dashed lines).

Discussion

The plateau for copolymer adsorption (Figure 1) is about a factor of 2 lower than VPS block copolymers previously studied of similar molecular weight,[12] although no polydispersities were reported in that study. The lower affinity adsorption isotherms exhibited here are probably due to a combination of the relatively low molecular weight used here plus polydispersity effects.[27] Ideally, in the plateau region it is expected that the high molecular weight polymer is preferentially adsorbed on the surface.[27] At these molecular weights, the adsorption of homopolystyrene from 0.01 g/mL solutions on silica is on the order of 1 mg/m^2 from a poor solvent, cyclohexane.[28] Even though the polystyrene adsorption is of the same order of magnitude, our experiments confirm that the polymer is bound to the surface via the vinylpyridine groups. Liquidlike ^{13}C NMR studies of these polymers (Figure 2), adsorbed on the surface and swollen with toluene, show relatively narrow resonances for the styrene segments and none for the vinylpyridine. This supports the conclusion that the polymer is bound through the 2-vinylpyridine segments, which are broad because their motion is significantly reduced on or near the surface. Similar results were observed for poly(methyl methacrylate) on silica gel in deuterochloroform.[29] In addition, polystyrene does not effectively compete with more polar polymers in competitive adsorption studies.[30]

The relaxation time measurements of the surface-bound polymers help to infer a number of things about the polymers' environment. Since relatively narrow resonances were found, the environment of the deuterons is liquidlike as opposed to rigid or semirigid. The environment is far from that of a small molecule solution, which can be characterized by rapid and isotropic molecular

Table II
Relaxation Parameters from the HH Model

polymer	T_1, ms	T_2, ms	λ_1[a]	λ_0[a]	$J(0)$[b]	$J(\omega_0)$[b]	$J(2\omega_0)$[b]
VPDSS	3.63	3.38	9.51	6.611	1.54	1.48	1.34
solution	3.63	2.75	18.48	2.043	2.24	1.76	1.27
VPSDS	3.94	3.60	14.67	5.392	1.46	1.39	1.23
solution	3.94	3.25	20.68	2.939	1.75	1.52	1.19

[a] In units of 10^8 s^{-1}. [b] In units of 10^{-9} s.

motion. The anisotropic and/or slow motion of polymer molecules in solution is clearly established.[31] This is obvious from the inequality of the T_1 and T_2 for the same polymer. If one compares the relaxation times for the VPDSS and VPSDS polymers, it is found that in both cases the VPDSS polymer has shorter relaxation times. This suggests that the styrene segments near the vinylpyridine groups move slightly slower and/or less isotropically than those closer to the styrene end. The difference in relaxation times is easily measured because the precision of the relaxation time measurements is good especially for T_1. The difference between the relaxation times is not very large, suggesting that there is not very much difference between the dynamics of the two segments. Further support for this is found in the single-exponential relaxation behavior found for each sample. It is expected that some differences in mobility and concentration exist as a function of contour length along the polymer backbone. However, in the concentration region probed, small concentration differences would not yield large relaxation time differences. Therefore, our measurements would be representative of the average dynamics and concentrations of the labeled block.

In previous studies,[32] we have reported how a variety of models for molecular motion can be applied to NMR relaxation behavior. Several of these models were shown to adequately describe the relaxation behavior of polymers in dilute to semidilute solution. At higher concentrations, however, the models yield unphysical results. It was also noted that they appear to contain essentially the same physics. Whether by design or accident, they describe relatively fast motions, which dominate T_1, and slower motions, which dominate T_2. With respect to the present work, most of the models are difficult to apply to the surface–polymer data because of the closeness of the T_1 and T_2. The model of Hall and Helfand[33] (HH) does not appear to have this difficulty and is therefore used in this work.

The relaxation times for a deuterium nucleus attached to a carbon atom are dominated by electric quadrupole effects and given by[31,32]

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

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 (kilohertz) and $J(\omega)$ is the spectral density at various frequencies, with ω_0 being the Larmor (resonance) frequency. The quadrupole coupling constant was determined to be 165 kHz on the basis of the solid-state deuterium spectrum of the DS-L polymer. For the HH model, the spectral density is given by[33,34]

$$J(\omega) = 2A(\omega)\{[\lambda_0(\lambda_0 + 2\lambda_1) - \omega^2]^2 + [2(\lambda_0 + \lambda_1)\omega]^2\}^{-0.25} \qquad (3)$$

where

$$A(\omega) = \cos\{0.5 \tan^{-1} [(2(\lambda_0 + \lambda_1)\omega)/(\lambda_0(\lambda_0 + 2\lambda_1) - \omega^2)]\} \qquad (3a)$$

λ_0 and λ_1 are the two fitted parameters from the model which take the form of rates. In our previous work,[32] we interpreted these parameters as rates representative of the fast (short-range) and slow (long-range) motions of the polymer chains. We acknowledge that it is difficult, if not impossible, to distinguish between the spatial and temporal averaging of the C–D bond vectors on the basis of relaxation times alone. For bulk *cis*-1,4-polybutadiene a number of NMR techniques have been used to demonstrate that its motion is (as observed by NMR) "best modelled as rapid anisotropic segmental motion".[35] For polymers in dilute or semidilute regimes, this type of constraint is less likely. In the worst case, the results, in terms of rates for isotropic motion, of the HH or similar models can be used as a qualitative measure of the restricted motion of the C–D bond vector. If the motion is isotropic on the NMR timescale, then the rates themselves are valid for quantitative comparison.

The results of the fitting of the HH model to the data are reported in Table II. Also shown are the results for the homopolymer of styrene-*d* (DS) polymer in solution. For comparison, the solution and surface-bond relaxation results are reported for similar T_1 values. These are interpolated from Figure 5 for the solution data. Within the framework of the model, these results confirm that the T_1 values are dominated by the faster motions of the polymer chains while the T_2s are dominated by the slower motions. This can be verified in the spectral density terms, where $J(0)$ is the term representing the longer range slow motion. Comparison of the surface and solution data shows that the longer T_2 of the surface-bound species significantly changes the $J(0)$ values. Consequently, the view taken is of the swollen polymer on the surface in a local environment where the fast motions may be similar to those in solution, but the longer range motions are faster due to the fact that the polymers are somewhat extended in solution. Alternatively, it may also be possible that certain long-range motions are not possible for the bound polymer but are for the solution species.

Given that the T_1 is dominated by the local motions and that these should be similar to those experienced by the solution polymer, the T_1 has been used to give a rough estimate of the polymer concentration. From Figure 5 the polymer concentrations were estimated to be 0.11 and 0.048 g/mL for the styrene segments next to and away from the VP segments, respectively. The T_1 values of the adsorbed polymers were compared to solution T_1s of the higher molecular weight deuteropolystyrene (DS). We believe that this comparison is appropriate because the attachment of the polymer to the surface may make it behave more like a high molecular weight polymer. Moreover, the solution T_1s of VPDSS at different concentrations compared quite well with those of the solution T_1s of DS. For VPDSS in solution, micelle formation is likely.[36] Previously, we have obtained somewhat different results by comparison with the low molecular weight polymer (DS-L) in solution.[17] However, we feel that comparison with the DS data is more appropriate. A similar comparison has not been done for the T_2 data because of its dependence on slower motions which are apparent from the comparison with solution data.

From the concentration and the adsorption data it is possible to estimate the thickness of the swollen surface-bound polymer layer. For simplicity we assume the polymer adsorbed is 20 000 g/mol (75% of which is styrene) and has an adsorption plateau of 1.75 mg of polymer/m^2 of silica. This corresponds to an effective surface area of ca. 1900 Å^2/molecule. Based on the simple model of a uniform distribution of polymer segments, the effective volume occupied by the styrene on one molecule (including solvent) is 3.15×10^5 Å^3/molecule based on a average concentration of (0.11 + 0.048)/2 g/mL. The ratio of the volume to surface area yields the height of the styrene segments, which is about 166 Å. For comparison the radius of gyration of a styrene chain of the same size (15 000 g/mol) would have a R_g of ca. 42 Å in toluene solution.[37] It is therefore estimated that the chain extends to roughly 4 times the radius of gyration of the solution polymer.

Milner et al.[11] predict the density profile for polymeric brushes in a good solvent, $\Phi(z)$, to be parabolic in nature and given by

$$\Phi(z) = K(L^2 - z^2) \tag{4}$$

where K is a constant, L is the brush length, and z is the distance from the surface. This can be used to calculate the mean concentration in the lower ($0 < z < L/2$) and upper ($L/2 < z < L$) portions of the brush by integrating over z for each region. The ratio of $\langle \Phi\ (0 < z < L/2) \rangle$ to $\langle \Phi\ (L/2 < z < L) \rangle$ would then be 11:5. This value is quite close to the 11:4.8 from our analysis and is remarkable a agreement considering the degree of approximation in our model.

The accuracy of our estimate is limited by several factors. The smallness of the silica beads is a significant factor but is partially compensated by the fact that many beads are fused together. The molecular weights used are perhaps too low to conclusively distinguish between the mushroom and brush models. Further experimentation is needed on these systems, particularly with the use of higher molecular weight polymers and larger particles. However, the moderately low concentrations predicted from the data are in agreement with the proposal that the chains are significantly extended in toluene dispersions[13] and the predictions from the data seem realistic. Previous studies indicated[13] that repulsion between two coated surfaces occurs at about $10 \times R_g$ for similar polymers in toluene. The present results suggest a factor of 8. This value may be lower due to the curvature of the silica used in our study.

Other magnetic resonance studies of swollen, adsorbed polymers have been made and reviewed.[18,19,38-42] In contrast to the present work, these have often shown strong two-component relaxation behavior due to different environments along the polymer chain. Solid and liquid NMR echo studies have been used to count the fraction of bound segments.[18,19] This was based on the differences in relaxation times between the surface bound and unbound material. Grafting of ethylene oxide polymers and oligomers on silica in benzene also shows two-component behavior in NMR[38] as well as ESR[39] studies. The power of ESR spectroscopy has also been shown in a number of systems with labeled polystyrene, poly(vinyl acetate), or poly(methyl methacrylate),[40,41] including the effect of solvent systems, and types of surfaces. This technique has the advantage of sensitivity over NMR but suffers from the need of a bulky label. Silica-labeled poly(vinyl acetate) showed two-component motional behavior (fast and slow), while on titania the polymer was held tight and immobile on the surface.[40] In our work only single fast-component behavior was found for each type of polymer, and the difference between the two types was small. This is possibly due to the VP attachment point being near a narrow depletion layer, separating most of the styrene groups from the surface creating relatively uniform styrene segments.

Finally, we note that scattering experiments provide spectroscopic evidence for the structure of surface-bound polymers. Of these, neutron scattering, under proper contrast matching, can yield the density profile of the polymer attached to the surface.[43,44] While these types of experiments are very informative and productive, the present technique offers a different probe of structure. That probe is along the contour length of the polymer. In principle, similar specific labeling could be used with proper contrast matching and neutron scattering to compare with our results for block copolymers.

Conclusions

^{2}H NMR has been used to probe the environment of a polymer segment attached to a surface. Selective deuteration of vinylpyridine–styrene block copolymers was used to obtain information on the motion as a function of position (i.e., contour length). The adsorbed polymers show that the behavior of the styrene segments is similar to those of a polymer in solution. The conformation of the polymer is also shown to be rather extended in agreement with other experimental results. On the basis of the comparison of the T_1 behavior of the surface-bound and solution polymers, the local concentration of the surface-bound polymer was found to be 0.11 and 0.048 g/mL for the styrene segment next to and away from the VP segments, respectively. This suggests a conformation of styrene extended to 4 times the normal R_g. Comparison of the T_2 values provides a quantitative measure of the differences in long-range motions of the polymers. Unfortunately, the lack of theoretical understanding of polymer segmental dynamics limits the overall usefulness of the technique. However, the technique does provide a rather different view of the environment of an attached polymer.

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Synthesis and Characterization of Poly(diarylamines). A New Class of Electrochromic Conducting Polymers

Jean Guay, Royston Paynter, and Lê H. Dao*

Laboratoire de Recherche sur les Matériaux Avancés, INRS-Energie, Institut National de la Recherche Scientifique, CP 1020, Varennes, Québec, Canada, J3X 1S2

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ABSTRACT: The electropolymerization of diphenylamine and *N*-phenyl-1-naphthylamine leads to the formation of poly(diphenylamine) (poly(DPA)) and poly(*N*-phenyl-1-naphthylamine) (poly(PNA)), respectively, with the incorporation of the aryl groups into the polymer backbone. The polymer films were characterized by cyclic voltammetry, spectroelectrochemistry, FTIR, and XPS. Poly(DPA) shows two reversible, stable electrochemical processes in its voltammogram, while poly(PNA) displays only one set of redox peaks. These two polymers exhibit very interesting optical properties; poly(DPA) films reversibly change color from pale yellow to yellow to green to blue when the potential (vs Ag/AgCl) is swept from 0.0 to 1.2 V, and poly(PNA) films change from pale yellow to red to blue between 0.0 and 0.8 V vs Ag/AgCl. XPS, spectroelectrochemistry, and FTIR measurements indicated the presence of polarons and bipolarons. Electrical conductivities of 2 Ω^{-1} cm^{-1} and doping levels as high as 53% were obtained for poly(DPA). Poly(PNA) shows a lower conductivity (10^{-3} Ω^{-1} cm^{-1}) and a lower doping level (30%).

Introduction

Recently, poly(aniline) has become of great interest owing to its good electrical conductivity and environmental stability.[1] This polymer can be obtained by electrochemical or chemical oxidation of aniline[2] in aqueous acidic[3] or organic media[4] and results from a head-to-tail coupling between oxidized species.[5] Poly(anilines) with alkyl[2,6] and aryl[7] substituents on the aromatic ring and alkyl,[8,9] benzyl,[10,11] and aryl[12-14] substituents on the nitrogen have also been successfully prepared. Because of the preferential head-to-tail polymerization mechanism, only anilines with an aryl substituent on the para position (e.g., 4-aminobiphenyl) can be polymerized, and the resulting polymer has a structure intermediate between that of poly(aniline) and poly(*p*-phenylene).[7] A similar structure was also reported for poly(diphenylamine), which was obtained by the electrochemical polymerization of diphenylamine via a 4,4′ C–C phenyl–phenyl coupling mechanism.[15,16]

In this paper, we report the synthesis and characterization of two electrochromic conducting polymers, poly(*N*-phenylaniline) (poly(DPA)) and poly(*N*-naphthylaniline) (poly(PNA)), obtained by electro-

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* To whom correspondence should be addressed.

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