Dynamics of Poly(vinyl acetate) in Bulk and on Silica

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ABSTRACT: Quadrupole echo deuterium NMR has been used to probe the dynamics of poly(vinyl acetate-d_3) in bulk and at saturation coverage (from toluene) on silica at the solid−air interface. In bulk and at lower temperatures, the deuterium powder pattern of the labeled methyl group was found to be consistent with fast threefold jumps with a small asymmetry due to the interaction of the methyl deuteron with the carbonyl oxygen. This apparent asymmetry was a result either of a distortion in the C−C−D bond angle or a reduction of the axial symmetry of the electric field gradient along the C−D bond vector. At higher temperatures, the onset of backbone motion of the polymer caused the collapse of the powder pattern to a single broad resonance over a fairly small temperature range between 65 and 73 °C. The collapse was well above the glass transition temperature as measured by differential scanning calorimetry, T_g(DSC) = 32 °C, and can be considered the T_g(NMR). The differences in temperatures for these two experiments are due to their different time scales. For the PVAc-d_3 adsorbed at monolayer coverage on a silica surface, a small fraction was found to result in a collapsed powder pattern below the T_g(NMR). This fraction with enhanced mobility was believed to be located near the air−polymer interface. The powder pattern for the majority of the surface-bound polymer was found to collapse gradually with temperature, with a rigid component observable well above the temperature where the splittings for all of the bulk material had collapsed. Thus, from the deuterium NMR spectra, it is possible to deduce that on a surface, different segments from a single molecule exhibit a range of mobilities.

Introduction

Most applications of polymers involve composites, wherein the polymer is used in conjunction with other materials, typically solid fibers or fillers. Usually the fiber or filler is added as a reinforcement to the more flexible polymer matrix. The interaction of the polymer with the fiber/filler plays a crucial role in the physical properties of the composite system. Unfortunately, it is difficult to determine the role that this interaction plays because it is often limited to a molecular (interfacial) distance scale.

Since the distance scale for the behavior which characterizes the interfacial interactions is so small (on the order of 10−100 Å), spectroscopic techniques, rather than mechanical ones, will likely be the more sensitive investigative methods. Spectroscopic techniques usually influence our understanding of either the structure or the dynamics of interfacial layers, both of which contribute to physical properties in their own way. Traditionally, studies of chemical reactions at interfaces have outnumbered those on the mobility of these species. It is our contention that *both* play a very important role in the determination of the physical properties of the composites.

Magnetic resonance (NMR and ESR) studies have been particularly useful in the determination of both structure and dynamics of interfacial polymers. Magnetic resonance techniques are not impacted, to first order, by the presence of solid fillers or by the optical clarity of the sample. Consequently magnetic resonance is well suited for studies of filled systems. Both NMR and ESR have been used to probe the dynamics of polymers at interfaces. Their sensitivity limitations result in the use of high surface area samples and, often, in the use of spectroscopic labels. A limited number of reviews have dealt with NMR and ESR studies on adsorbed polymers.[1−6] These studies cover work which deals with a broad range of systems from the determination of trains, loops and tails in adsorbed, swollen polymers to the changes in mobility in the interfaces in polymer composites.

One of the more important polymers used in applications where surface interactions are critical is poly(vinyl acetate) (PVAc), which is often used in paints and adhesives. PVAc has been studied in bulk with NMR by several authors.[7−11] Proton relaxation rates T_1, $T_{1\rho}$, and T_2 for PVAc and PVAc-d_3 were studied by Hoch *et al.*[7] They found that the methyl rotation was rapid down to very low temperatures and that the NMR glass transition temperature, T_g(NMR), was significantly higher than that found by differential scanning calorimetry, T_g(DSC). This difference in T_g temperature was consistent with the frequency differences of the different experiments.[7,12] Blum *et al.*[8] used high-resolution ^{13}C NMR, ^{2}H NMR, and ESR, along with DSC, to probe the effect of diluents on the polymer dynamics. Swanson *et al.*[9] and Ganapathy *et al.*[10] used both ^{13}C and ^{1}H NMR to probe the dynamics in the presence and absence of water through relaxation and spin−echo lineshape studies. Finally, Schmidt-Rohr and Spiess[11] have used ^{13}C 2- and 4-dimensional studies to probe the behavior of the polymer above the T_g(DSC). They found that there was motional heterogeneity on short time scales, but that the system became homogeneous on longer time scales.

In this paper, we report deuterium NMR studies of methyl-labeled PVAc (PVAc-d_3) in bulk and in monolayer coverage adsorbed on silica. Even though the methyl group is attached to the side chain of the polymer, its motion can be an effective indicator of the polymer backbone motion. The backbone motion of the polymer further averages the deuterium quadrupole powder pattern beyond that of the methyl rotation. Of

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particular interest in this study is the behavior of the polymer near the T_g(NMR) for both the bulk and surface-bound polymer.

Experimental Section

Vinyl acetate-d_3 was prepared via the interchange reaction of deuterated acetic acid-d_3 and vinyl propionate. Acetic acid-d_3, 50 g (Aldrich, Milwaukee, WI), 150 g of vinyl propionate (Lancaster Synthesis Inc., Windham, NH), 1.2 g of mercuric acetate (Aldrich), 0.17 g of concentrated sulfuric acid (98%, Fisher, Pittsburgh, PA) and 0.001 g of hydroquinone (Eastman Kodak Co., Rochester, NY) were put into a three-neck flask. The reaction was heated to 90−94 °C for 2 h. Sodium acetate (2 g, Fisher) was added after reaction, and the resultant vinyl acetate-d_3 was collected by distillation at reduced pressure. A total of 31.9 g of vinyl acetate-d_3 was obtained after a second distillation at 73 °C using a spinning band column. The yield was about 45% based on the amount of acetic acid used. The product was verified by NMR and found to contain greater than 99% deuteration in the methyl position.

$$\mathrm{CD_3CO_2H + CH_3CH_2CO_2CH{=}CH_2 \xrightarrow[H_2SO_4]{(CH_3CO_2)_2Hg} CD_3CO_2CH{=}CH_2 + CH_3CH_2CO_2H}$$

The polymerization of poly(vinyl acetate-d_3) (PVAc-d_3) was carried out in an emulsion. Deuterated vinyl acetate-d_3 (6.3 g), double-distilled water (6.2 g), $K_2S_2O_8$ (0.007 g) (Fisher), and sodium dodecyl sulfate (0.007 g) (SDS, Aldrich) were mixed in a flask and flushed for about 5 min with nitrogen gas. Emulsion polymerization was carried out at about 70 °C for 3 h with stirring using a magnetic bar. The yield of polymer was approximately 75%.

The molecular weight of PVAc-d_3 was measured using an IBM (IBM Instruments Inc., Danbury, CT) refractive index detector, a SP 8700 pump (Spectra-Physics, San Jose, CA), and a 300 × 7.8 mm column with Phenomenex Phenogel of 5 μm particle size (Phenomenex, Torrance, CA). Measurements were performed at room temperature using tetrahydrofuran (THF, Fisher) as the solvent with a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained using polystyrene standards (Pressure Chemical Co., Pittsburgh, PA) of molecular weights ranging from 800 to 1 800 000 Da. The PVAc-d_3 sample had a molecular mass and polydispersity of 1200 kg/mol and 2.2, respectively, based on universal calibration corrections.[13]

The surface-bound PVAc samples were prepared on high-surface area Cab-O-Sil silica M5 (200 m^2/g, Cabot Corp., Tuscola, IL) from toluene solutions at room temperature. This high-surface area material was chosen to obtain good signal-to-noise spectra.[3,4] The silica with adsorbed polymer was centrifuged and washed with toluene. Due to the limited amount of the deuterated sample, a protonated PVAc sample, with a molecular mass of 120 kg/mol, was used to determine the full adsorption isotherm. The amount of PVAc adsorbed and the solution concentration were calculated from the mass of polymer dried from the supernatant solution. A maximum adsorbed amount of 0.31 mg of polymer/mg of silica was obtained for the protonated material and the result is shown in Figure 1. The shape of the isotherm was rounded because of its polydispersity.[14] The measurement of the adsorption isotherm for the protonated polymer was used to estimate the concentrations needed for the PVAc-d_3.

Solutions for adsorption of the PVAc-d_3 samples were prepared at concentrations to yield plateau coverage as shown in the PVAc adsorption isotherm. The adsorption amount for four samples is also shown for PVAc-d_3 in Figure 1. The adsorption amounts for these samples were determined from thermogravimetric analysis (TGA). All four samples were at maximum (plateau) coverage. The sample on which the NMR experiments were done had 0.36 mg polymer/mg of silica.

The NMR results shown were obtained, in Missouri, on a modified Varian VXR-400/S spectrometer operating at 61.395 MHz for deuterium. The spectra obtained were essentially independent of temperature cycling. The probe used was a fixed-frequency wide-line probe (Doty Scientific, Columbia, SC) with an 8 mm solenoid coil. The larger coil is advantageous because it allows more material to be observed than 5 mm coils, which is especially important when surface species are being detected. For the bulk PVAc-d_3, the quadrupole echo pulse sequence was used[15] with a 2.7 μs 90° pulse, 30 μs echo delay time, 4096 points, 1.024 ms acquisition time, 2 MHz sweep width, 6 s recycle time, and 256 scans with appropriate phase cycling. For the surface-bound material, the parameters were the same except that 2000 scans were used. The quadrupole echo spectra were taken with the delays adjusted so the echo maximum fell coincident with a data point and the spectra left-shifted to the echo maximum. Additional spectra (not shown) were taken at IBM at 76.7 MHz on a Bruker Instruments AM-500 spectrometer at temperatures down to −100 °C.

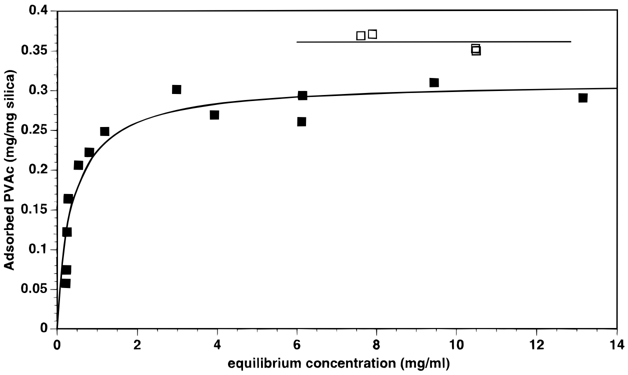

Figure 1. Adsorption isotherm for protonated PVAc (filled squares, 120 kg/mol) and adsorption amount for PVAc-d_3 (open squares, 1200 kg/mol).

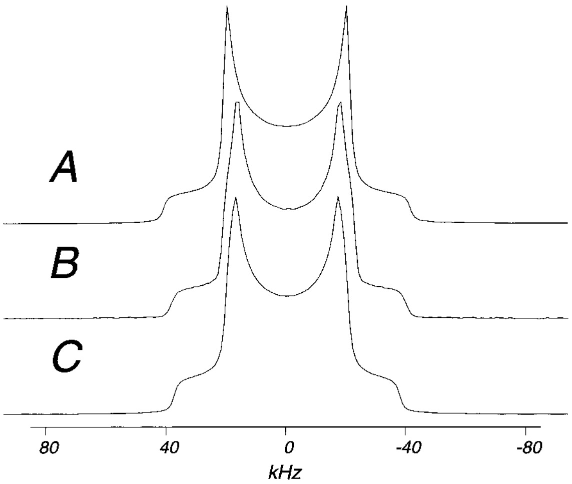

Figure 2. Simulated (A, C) and experimental (B) deuterium NMR quadrupole echo spectra of bulk PVAc-d_3 at 49 °C (NMR details given in Experimental Section). The simulated spectra are based on three-site tetrahedral jumps with equivalent (A) and distorted (C) sites (see text).

The spectral simulations and data reduction were done on an IBM RISC 6000 workstation. The data reduction and comparison were done using a commercial software package Felix (Biosym, San Diego, CA). The simulations were done using a FORTRAN program given to us by R. Wittebort[16] based on discrete jumps between deuterium sites.

Results

The experimental deuterium quadrupole-echo spectrum of PVAc-d_3 in bulk at 49 °C is shown in Figure 2B along with two simulations. The spectrum resembled a Pake powder pattern with a reduced splitting. To first order, the pattern was similar to that expected for a methyl group undergoing fast motions about its sym-

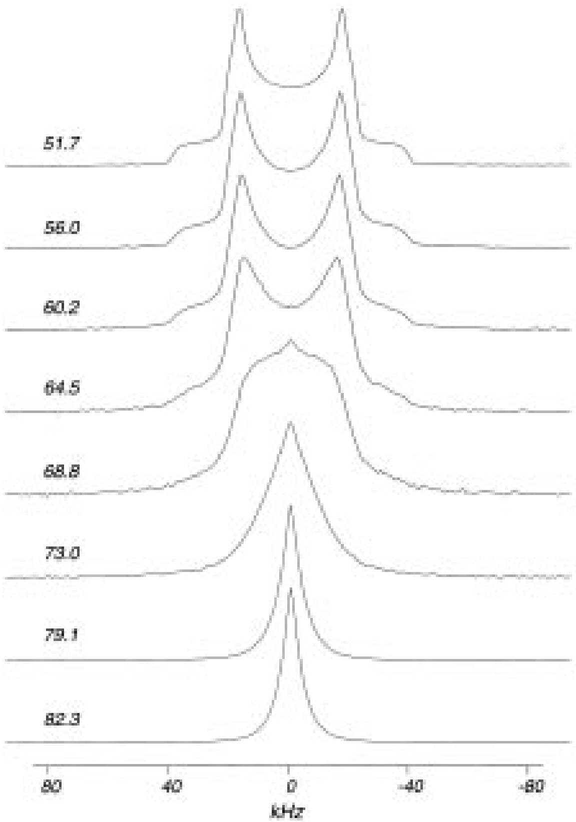

Figure 3. Deuterium NMR quadrupole echo spectra as a function of temperature for bulk PVAc-d_3. The temperatures are shown in °C.

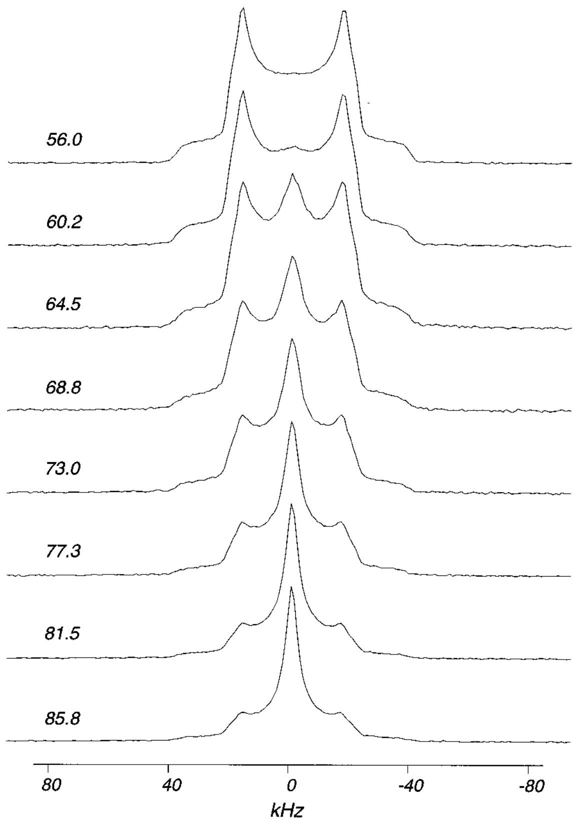

Figure 4. Deuterium NMR quadrupole echo spectra as a function of temperature for PVAc-d_3 at monolayer coverage on silica. The temperatures are shown in °C.

metry axis. However, upon closer examination, this spectrum had features not normally seen in deuterated methyl groups. The separation at the *base* of the "horns" between the two central features (*i.e.*, $\Delta\nu_q(90°)$) was about 43 kHz. At approximately 2/3 of the way up, the horns curve inward to a final separation of about 34.3 ± 1 kHz between the peaks. This effect is formally similar to that due to a nonzero asymmetry parameter. The simulated spectra were obtained by the method of Wittebort *et al.*[16] The first (Figure 2A) was for threefold jumps between sites with tetrahedral geometry (*i.e.*, each C−D bond was taken to be 70.5° off of the symmetry axis). The second (Figure 2C) was for threefold jumps with one C−D bond distorted from tetrahedral geometry by 5° (*i.e.*, 65.5° off of the symmetry axis). The exchange rate and quadrupole coupling constant were taken to be 10^{12}/s and 165 kHz, respectively. In the first case, the outer edges of the horns at a splitting of about 43 kHz were almost vertical, while the edges in the second case had an inward tilt similar to that found in the experimental spectrum.

Quadrupole echo NMR spectra for bulk PVAc-d_3 were taken as a function of temperature. At lower temperatures (not shown), the line shapes were similar to those in Figure 2B. The quadrupole splittings increased only slightly—to 36 kHz at −100 °C (not shown). Thus no major changes in the methyl group motion, to which the deuterium NMR spectra are sensitive, occurred in temperatures ranging from room temperature down to −100 °C. The rapid methyl reorientation for this polymer is known to persist well below this temperature.[7] For the higher temperature range, the spectra in Figure 3 show that at 64.5 °C, a definite broadening occurred and at 68.8 °C a spectrum indicative of intermediate-range motions was obtained. At 73.0 °C, no residual powder pattern was observed and by 79.1 °C, a relatively narrow resonance was found.

The quadrupole echo spectra of PVAc-d_3 at monolayer coverage on silica are shown in Figure 4. Additional scans were made for the surface spectra due to the dilution effect of the substrate.[4] At lower temperatures, the quadrupole splitting and shape of the horns were similar to those for the bulk sample, although the "middle" of the surface spectrum was a little higher in the bulk spectra. As the temperature was increased, the quadrupolar splittings decreased slightly. For the surface spectra, the changes with temperature were more gradual than in bulk. At 60.2 °C, there was a hint of a central component. At 64.5 °C, the narrow component was significant and clearly visible. We note that there was no narrow component in the bulk spectrum at 60.2 °C. As the temperature increased, the magnitude of the central component increased. In contrast to the bulk case, the central component occurred in addition to a residual powder pattern. In fact, a powder pattern component remained even at 85.8 °C, well above where all of the bulk material was narrowed.

It was found that the experimental spectra could be simulated based on the superposition of two components. The broad component was a residual Pake pattern and was based on the powder spectrum for the bulk sample at either 56.0 or 60.2 °C. The narrow component was based upon a single Lorentzian resonance. For the narrow component, Lorentzian resonances fit most of the spectra better than Gaussian ones. In some cases, an increase in width at the base of the narrow component would have provided a better match to the experimental spectra. The simulated spectra for the surface-bound species are shown in Figure 5. The fitting parameters are given in Table 1.

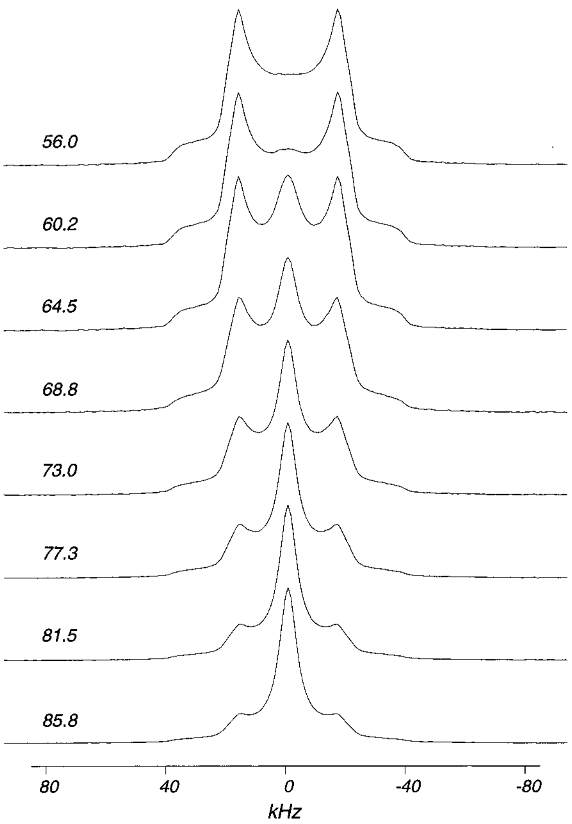

Figure 5. Simulated deuterium NMR quadrupole echo spectra as a function of temperature for PVAc-d_3 at monolayer coverage on silica. See text and Table 1 for simulation parameters.

Table 1. Fitting Parameters for the Central Lorentzian Component of the Simulated Surface Spectra

T (°C)	fraction[a]	half-width (kHz)[a]
56.0	0.07	20
60.2	0.08	15
64.5	0.18	10
68.8	0.21	8
73.0	0.29	7
77.3	0.41	7
81.5	0.54	7
85.8	0.62	7

[a] For the narrow component. The other component was based on the bulk powder pattern at 60.2 °C.

Discussion

In order to understand the dynamics of the backbone of PVAc-d_3 in bulk and on silica, it is first appropriate to consider the basic powder line shape observed at lower temperatures. A number of reviews on the use of deuterium NMR in polymer science have significant discussions on deuterium line shapes and polymer motions.[17−19] For the ($I = 1$) deuterium nucleus, the quadrupolar splitting, $\Delta\nu_q$, between the two different allowed transitions is given by[20]

$$\Delta\nu_q = (3/4)(e^2qQ/h)(3\cos^2\theta - 1 - \eta\sin^2\theta\cos^2\varphi) \qquad (1)$$

where e^2qQ/h is the quadrupole coupling constant (QCC), and θ and ϕ are the spherical polar angles for the orientation of the principal axis system for the electric field gradient tensor and the applied static magnetic field, $\mathbf{B}_0$, and η is the asymmetry parameter. Values for the QCC of methyl groups are typically on the order of 165−170 kHz[21−23] and have been proposed to vary for different positions of the methyl group (*vide infra*).

The line shapes observed at lower temperatures for PVAc-d_3 (Figure 2), especially the presence of the shoulders at about 43 kHz, were similar to those found in other samples including thymine-d_3[23] and [1,1,1,3,5,6-d_6]*n*-butyl 2,4,6-octatrienylideneimine.[24] Fast threefold jumping or rotational motions about the methyl group's (apparent) symmetry axis reduce the quadrupolar coupling to about 1/3 of its static value (41 kHz). For thymine-d_3, it was suggested that the interaction of the methyl deuterons with the carbonyl oxygen was anisotropic. That deuteron closest to the carbonyl oxygen experienced a change in both the QCC and η compared to the other two deuterons on the methyl group, which led to differences in QCC's and η's of as much as 6 kHz and 7%, respectively. The fast three-bond jumps in thymine averaged the QCC and η interactions, yielding a spectrum quite similar to that for PVAc-d_3. Other evidence of this effect has also been found in substituted acetic acids.[25,26] An alternative explanation was that the interaction caused a distortion from tetrahedral geometry[24] without a change in the axial symmetry of the electric field gradient. A neutron diffraction study of acetic acid[27] yielded bond angles for CCH of 112.3, 107.7, and 108.9° and HCH angles of 111.3, 108.6, and 108.1°. Clearly, the acetic acid parameters should be relevant to PVAc.

Based on our data, it is probably not possible to distinguish between the explanations proposed in the preceding paragraph. However, the bond angle distortion was easiest to simulate and was consistent with knowledge on the structure of acetic acid. The simulated spectrum in Figure 2C, which is in excellent agreement with the experimental spectrum, was based on a 5° variance from the tetrahedral angle for one of the C−D bond vectors. The distortion is undoubtedly due to the proximity of the C−D and carbonyl groups (ca. 2.5 Å). We have not observed this effect in the spectra of other methyl-labeled synthetic polymers such as poly(methylphenylsilane),[28] poly(α-methylstyrene),[29] or poly(methyl acrylate).[30] These methyl groups yield spectra more like that for tetrahedral jumps (Figure 2A). The apparent asymmetry was also not observed in perdeuterated polymers such as polypropylene[31] and poly(methyl methacrylate),[31] although its absence effect may be difficult to detect in the presence of overlapping deuterons.

Bulk PVAc-d_3. For the bulk PVAc-d_3, the powder pattern spectrum was found to collapse between 65 and 69 °C. As the temperature was increased, significant narrowing occurred over the next 10°. The narrowing was indicative of the additional mobility of the polymer, undoubtedly due to the onset of backbone motions that average the residual quadrupole interaction. The transition, roughly centered around 67 °C, was consistent with the NMR glass transition temperature, T_g(NMR). Even though 2-D NMR experiments on PVAc at about 50 °C suggest a motional distribution that was 3 decades wide,[11] the T_g(NMR) was still fairly narrow. The T_g(NMR) was about 40 °C above that measured by DSC, T_g(DSC) = 32 °C.[13] It is well known that T_g(NMR) is greater than T_g(DSC) because of the different frequencies associated with the different techniques.[12] Typically, DSC scans are made on the order of several degrees per minute so that the time scale is on the order of Hz or less. For PVAc-d_3 in particular, the collapse

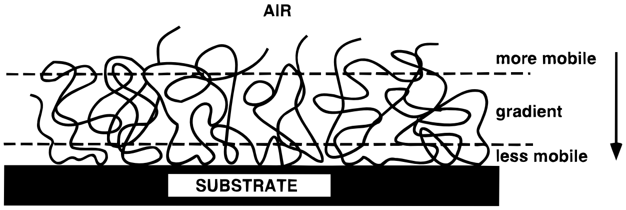

Figure 6. Schematic representation of the motional gradient in the surface-bound polymer.

of the deuterium powder pattern implies motion faster than the order of the reciprocal splitting (*ca.* 40 kHz). The T_g(NMR) was consistent, at that frequency, with other mechanical, dielectric, and NMR data.[7]

The methyl reorientation dominates the spectra at the lower temperatures. The methyl rotation is fast and does not "freeze out" until −223 °C (from T_1) and −250 °C (from $T_{1\rho}$).[7] At higher temperatures, but still below T_g(NMR), the 1-dimensional powder spectra did not exhibit any significant effects from backbone or side-chain motions, even though there is a reported β transition for this polymer in the range of −30 to 10 °C.[32] Others have found that the ^{13}C carbonyl chemical shift tensor was not altered from its rigid lattice values below 35 °C.[10] Multidimensional NMR spectra confirm that the carbonyl group shows little motion on a time scale on the order of 1 ms at 27 °C, but much reorientation at a time scale of 100 ms.[11] That study also showed that the motion in bulk PVAc was heterogeneous in terms of its distribution.

Surface PVAc-d_3. For the surface-bound polymer, the changes with temperature were considerably different than for the bulk polymer. Instead of a relatively distinct transition from a powder pattern to a narrower central component, the mobile component increased gradually with temperature. The gradual increase seemed consistent with a distribution of mobilities (environments) even more heterogeneous than that of the bulk polymer. It seems logical that there would be a distribution of mobilities within any given polymer molecule. Polymer segments nearer to the surface (*e.g.* in trains) are probably more restricted because of the interaction of the carbonyl group with the silica surface. As the distance from the surface increases, the mobility of the polymer segments (*e.g.*, in loops and tails) would also be expected to increase.

In order to explain the effects observed in the surface spectra, we propose the following model. The adsorbed monolayer has a motional gradient. Segments near the surface are relatively immobile due to adsorption of segments onto the silica surface, probably through the carbonyl group. Their mobility is significantly less than those in bulk over the range studied. At the polymer−air interface, the mobility is enhanced relative to bulk because there are fewer restrictions at this interface. Segments in between these two extremes have intermediate mobilities which vary from one side to the other. A representation of the proposed model is shown schematically in Figure 6.

On the basis of the deuterium NMR lineshapes, the spectra can be divided into rigid or mobile components. The appropriate time scale for the division is on the order of the reciprocal of the residual quadrupole splitting (on the order of 40 kHz). This division, in effect, puts a constraint on our observations. Motions much faster than 40 kHz result in a narrow resonance while those slower result in a Pake pattern. Motions in the intermediate region result in intermediate line shapes, but with significantly reduced intensities.[33] This effect was observed in the spectra of bulk PVAc-d_3 (Figure 3). For the same number of scans, the S/N ratio is measurably lower in the spectra from 64 to 70 °C than in the others. Both the collapse of the powder pattern and reduction in intensity are indications of motion in the intermediate regime. The reduction in intensity has also been observed in other methyl-labeled small-molecule systems[22,34] where the effect was substantially more severe than in this study. The effect was less significant in the current study because of the broad distribution of correlation times in the polymeric PVAc-d_3, as compared to the other systems. This distribution reduces the fraction of intermediate motion species present at any temperature. For the surface-bound polymer (Figure 4), the S/N reduction was not observed, an indication that it has an even wider range of mobilities (*vide infra*). Given these limitations, it is still possible to use the results of Table 1 to help understand the component contributions to the surface spectra. Below the T_g(NMR), the contributions to the line shape from the mobile components are small, but nonzero until 64.5 °C. Above 64.5 °C, the mobile component fractions jump from several percent to 20−30%. This component is a sizable proportion of "motionally enhanced" species below T_g(NMR). The fraction of the mobile component continues to grow with increasing temperature, but even at fairly high temperatures (*e.g.*, 85.8 °C) only 62% are motionally narrowed. About 38% of the segments are still rigid on the NMR time scale.

Other magnetic resonance studies have probed the mobility relative to the effect of fillers. Most studies, such as those with filled elastomers have traditionally been used to identify tightly and loosely bound rubber molecules.[1−6] Only a few studies have probed polymer dynamics at the solid−air interface. ESR studies on labeled polystyrene[35,36] have shown decreased mobility for the adsorbed polymers compared to bulk material. Extension of this technique to labeled PVAc[37] showed that some PVAc surface segments were solidlike well above temperatures where the bulk segments were liquidlike. For poly(isopropyl acrylate) (PIPA) on silica, CP-MAS NMR[2,5,38] techniques showed that at less than saturation coverages, the resolution of the polymer resonances increased (*i.e.*, linewidths decreased) with increased amounts adsorbed. The effect was consistent with a decreased mobility with increased surface coverage. That work[38] also suggested that saturation coverage from toluene was roughly the distance scale over which this motional alteration was active. However, the sensitivity of these experiments was not sufficient to address the mobility issue more quantitatively. Litvonov and Spiess[39] have also found similar behavior for deuterated poly(dimethylsiloxane) (PDMS) on Aerosil (silica) particles. In their study, the crystallinity of the PDMS and the presence of unattached chains complicated the interpretation of their results. Their results, like ours, show the advantage of using the collapse of the deuterium powder spectrum to probe segmental dynamics.

It is of relevance to interpret our results in terms of the dynamic properties of filled PVAc systems. For *in-situ* prepared PVAc−silicon dioxide dispersions,[40] increased widths of dielectric and mechanical relaxations suggested the presence of motionally hindered chains. These were believed to be due to the interaction of the polymer chains with the silicon-containing network. Follow-up studies using PVAc−fumed silica[41] showed a much smaller effect. The transition temperatures and breadths of the relaxations were found not to have changed substantially, compared to bulk PVAc. The lack of an effect was believed to be due, in a large part, to the significantly reduced surface area found in the fumed silica compared to the *in-situ* prepared material. Other mechanical studies[42,43] have shown that while the transition temperatures for the main relaxation did not change much with the addition of a filler, their intensity was substantially reduced. It was proposed that many chains in the composite did not participate in the relaxation process. In essence, some chains, presumably those near the surface had a higher glass transition temperature and a separate tan δ peak. Our present results are direct confirmation of a gradation in terms of mobility.

Finally, we note that our results are in reasonable agreement with simulations of polymer dynamics of surface-absorbed polymers.[44−46] These predict both the slowing of polymer segments near the surface and increased breadth of the relaxation phenomena.

Conclusions

The deuterium NMR spectra of methyl-labeled PVAc-d_3 at lower temperatures were consistent with methyl group jumps between nonequivalent C−D sites. The interaction of the methyl deuterons with the carbonyl oxygen was probably responsible for the shoulders observed in the lineshape of the bulk material. For the bulk material in the region around 65−73 °C, the deuterated methyl group was a good reporter of polymer backbone motion. The T_g(NMR) occurred about 40 K above that found for T_g(DSC)—a result consistent with the much higher frequency of the NMR experiment as expected based on time−temperature superposition principles.

Surface-bound PVAc-d_3 at monolayer coverage showed significant spectral differences from bulk. Although just above room temperature, the surface material showed similar quadrupolar splittings to bulk, and the middle of the spectrum was filled in. These spectra were modeled with the addition of a central Lorentzian component. In contrast to bulk, the T_g(NMR) transition was much broader. Some of the material appeared to be much more mobile than bulk. We speculate that this more mobile component was associated with material near the polymer−air interface. Some of the material remained “glassy” on the NMR time scale at the highest temperatures studied. We associated these components with segments nearer to the polymer−silica interface.

This study clearly demonstates the existence of motional heterogeneity in the surface-bound material. This heterogeneity has been inferred as a result of other experimental work, as well as theoretical studies. The differences in the dynamics of the polymer segments within a single polymer molecule defined a motional gradient set up within the polymer layer.

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References and Notes

(1) Douglass, D. C.; McBrierty, V. J. *Polym. Eng. Sci.* **1979**, *19*, 1054.
(2) Blum, F. D. *Colloids Surf.* **1990**, *45*, 361.
(3) Cosgrove, T.; Griffiths, P. C. *Adv. Colloid Interface Sci.* **1992**, *42*, 175.
(4) Blum, F. D. In *Characterization of Composite Materials*; Ishida, H.. Ed.; Manning Publications: Greenwich, CT, 1994; pp 64−79.
(5) Blum, F. D. *Annu. Rep. NMR Spectrosc.* **1994**, *28*, 277.
(6) Hommel, H. *Adv. Colloid Interface Sci.* **1995**, *54*, 209.
(7) . Hoch, M. J. R.; Bovey, F. A.; Davis, D. D.; Douglass, D. C.; Falcone, D. R.; McCall, D. W.; Slichter, W. P. *Macromolecules* **1971**, *4*, 712.
(8) Blum, F. D.; Dickson, J. E.; Miller, W. G. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 211.
(9) Swanson, S.; Ganapathy, S.; Kennedy, S.; Henrichs, P. M.; Bryant, R. G. *J. Magn. Reson.* **1986**, *69*, 531.
(10) Ganapathy, S.; Chacko, V. P.; Bryant, R. G. *Macromolecules* **1986**, *19*, 1021.
(11) Schmidt-Rohr, K.; Spiess, H. *Phys. Rev. Lett.* **1991**, *66*, 3020.
(12) McCall, D. C. *Acc. Chem. Res.* **1971**, *4*, 223.
(13) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley Interscience: New York, 1989.
(14) Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 559.
(15) Davis, J. H.; Jeffrey, K. P.; Bloom, M.; Valic, M. F.; Higgs, T. P. *Chem. Phys. Lett.* **1976**, *42*, 390.
(16) Wittebort, R. J.; Olejniczak, E. T.; Griffin, R. G. *J. Chem. Phys.* **1987**, *86*, 5411.
(17) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(18) Jelinski, L. W. *Annu. Rev. Mater. Sci.* **1985**, *15*, 359.
(19) Spiess, H. W. *Annu. Rev. Mater. Sci.* **1991**, *21*, 131.
(20) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961.
(21) Jelinski, L. W.; Sullivan, C. E.; Torchia, D. A. *Nature* **1980**, *284*, 531.
(22) Beshah, K.; Olejniczak, E. T.; Griffin, R. G. *J. Chem. Phys.* **1987**, *86*, 4730.
(23) Hiyama, Y.; Roy, S.; Guo, K.; Butler, L. G.; Torchia, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 2525.
(24) Wann, M.-H.; Harbison, G. *J. Chem. Phys.* **1994**, *101*, 231.
(25) Jackisch, M. A.; Jarrett, W. L.; Guo, K.; Fronczek, F. R.; Butler, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 343.
(26) Jarrett, W. L.; Guo, K.; Jackisch, M. A.; Butler, L. G. *J. Magn. Reson.* **1989**, *82*, 76.
(27) Jöhnsson, P.-G. *Acta Crystallogr. B* **1971**, *27*, 893.
(28) O'Connor, R. D.; Blum, F. D.; Ginsberg, E.; Miller, R. D. *Polym. Prepr. (Am. Chem. soc., Div. Polym. Chem.)* **1994**, *35* (1), 417.
(29) O'Connor, R. D.; Blum, F. D.; Ginsberg, E.; Miller, R. D., to be submitted.
(30) Lin, W.-Y.; Blum, F. D., to be submitted.
(31) Early, T. A. *J. Magn. Reson.* **1987**, *74*, 337.
(32) Bershtein, V. A.; Yegorov, V. M.; Yemel'yanov, Y. A. *Polym. Sci. USSR* **1985**, *27*, 2757.
(33) Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* **1981**, *42*, 381.
(34) Beshah, K.; Griffin, R. G. *J. Magn. Reson.* **1989**, *84*, 268.
(35) Liang, T. M.; Dickson, P. N.; Miller, W. G. in *Polymerization Characterization by NMR and ESR*; Woodward, A. E., Bovey, F. A., Eds.; ACS Symposium Series 142; American Chemical Society: Washington, DC, 1980; p 1.
(36) Thambo, G.; Miller, W. G. *Macromolecules* **1990**, *23*, 4397.
(37) Nietering, K. E.; Miller, W. G. In *Molecular Characterization of Interfaces*; Ishida, H., Kumar, G., Eds.; Plenum: New York, 1985; p 145.
(38) Blum, F. D.; Funchess, R. B.; Meesiri, W. *Solid State NMR of Polymers*; Mathias, L., Ed.; Plenum: New York, 1991; p 271.
(39) Litvinov, V. M.; Spiess, H. W. *Makromol. Chem.* **1991**, *192*, 3005.
(40) Fitzgerald, J. J.; Landry, C. J. T.; Pochan, J. M. *Macromolecules* **1992**, *25*, 3715.
(41) Landry, C. J. T.; Coltrain, B. K.; Landry, M. R.; Fitzgerald, J. J.; Long, V. K. *Macromolecules* **1993**, *26*, 3702.
(42) Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 396.
(43) Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6067.
(44) Chakraborty, A. K.; Adriani, P. M. *Macromolecules* **1992**, *25*, 2470.
(45) Shaffer, J. S.; Chakraborty, A. K. *Macromolecules* **1993**, *26*, 1120.
(46) Mansfield, K. F.; Theodorou, D. N. *Macromolecules* **1989**, *22*, 3143.

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