Fast Magic-Angle Proton NMR Studies of Polymer Interfaces in Poly(ethyl acrylate)/Vycor Composites

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ABSTRACT: Fast magic-angle spinning solid-state proton NMR has been used to study the structure and dynamics of poly(ethyl acrylate) in bulk and polymerized in a Vycor glass with 40 Å pores. Bulk poly(ethyl acrylate) is a low-T_g material, and high-resolution solid-state proton NMR spectra are observed at ambient temperature because the dipolar interactions are averaged by the combination of chain motion and fast magic-angle sample spinning. The spectrum of the poly(ethyl acrylate)/Vycor composite shows signals in addition to those of the polymer that are assigned to water and surface hydroxyl groups in the porous glass. Integration of the composite and bulk poly(ethyl acrylate) signals reveals that the volume fraction of polymer in the pores is 0.56 and that the polymer occupies the central 30 Å in a 40 Å pore. Spin diffusion studies demonstrate that filling of the poly(ethyl acrylate)/Vycor is incomplete, and a fraction of the water in the pores is isolated from the polymer. Multiple-quantum NMR studies reveal a large difference in chain dynamics between the bulk poly(ethyl acrylate) and the porous glass composite, and 2D wide line separation NMR shows that the polymer is restricted at the surface of the pores but has bulklike mobility in the center of the pore.

Introduction

Polymer−solid interfaces are an important part of many technologically important materials, including composites and adhesives. The macroscopic behavior of these materials depends not only on the properties of the polymer and the solid but also on the nature of the polymer−solid interface. While such interfaces are important, they are often present at low concentrations and difficult to study by spectroscopic methods. It is important to study the properties of polymers at surfaces because it has been reported that the properties of the polymer at the interface can be very different from the bulk materials.[1,2]

NMR is a powerful tool for polymer characterization that has not been extensively used for the study of polymers at surfaces and interfaces because NMR is a relatively insensitive method, and the interfaces are often present at low concentrations. The second fundamental problem limiting the application of NMR is the separation of the bulk and interfacial signals in complex materials. In favorable cases the chemical shifts or relaxation rates of the surface or interface can be different from the bulk, but this is often not the case. These problems can be overcome with isotopic labeling using ^{13}C or ^{2}H,[2,3] but this requires the synthesis of new materials.

There have been some studies using solid-state NMR to study the structure and dynamics of polymers at surfaces.[3] The results from ^{13}C studies showed that the α-helical structure of poly-L-lysine and poly-L-glutamic acid are replaced by a more extended conformation upon adsorption.[4] More recently, the dynamics of poly(methyl acrylate)-d_3 have been investigated by ^{2}H NMR, and it has been reported that the polymer at the solid surface is restricted relative to the bulk while the polymer at the air surface has an enhanced mobility.[2,5] Solid-state NMR has also been used to study oligomers attached to solid surfaces.[3]

In these studies we use solid-state proton NMR with fast magic-angle sample spinning to study the structure and dynamics of poly(ethyl acrylate) in the bulk and polymerized in a Vycor glass with 40 Å pores. These composites are currently under consideration as optical devices for recording refractive index gradients to store holographic images.[6,7] The advantage of such a composite is that the rigid host matrix minimizes the shrinkage during polymerization and reduces the distortions from dimensional changes. We have found that high-resolution spectra can be obtained for the composites and that multiple-quantum NMR can be used to identify the glass−polymer interface. The results allow us to measure the fraction of polymer in the pores and to determine how homogeneously the glass has been filled with the polymer. The sensitivity in these experiments is very high because we are detecting protons, and the high signal-to-noise ratios observed here suggest that these methods will be applicable to a wide variety of lower surface area materials.

Materials and Methods

The Vycor glass (Corning) used in these studies has a porosity of 0.28, a surface area of 250 m^2/g, and an average pore diameter of 40 Å. Poly(ethyl acrylate)/Vycor composites were prepared by soaking Vycor pieces in a 20 mL solution of ethyl acrylate monomer (Aldrich, inhibitor removed) and 1% w/v Ciba initiator for 5 days. The sample was flood cured at 546 nm under a N_2 purge followed by overnight UV exposure in air. Near-IR before and after cure showed that ca. 5% of the monomer remained after exposure. A control sample was prepared by polymerization of an ethyl acrylate/initiator solution in a Petri dish using the same conditions as for the Vycor composite. The resulting polymer was pumped in a vacuum oven overnight at 60 °C.

NMR spectra were obtained on a Varian Unity NMR spectrometer at 400 MHz for protons using either a 4 or 7.5 mm magic-angle spinning probe from Chemagnetics. The fast magic-angle spinning proton spectra were recorded on the 4 mm probe with spinning speed regulation between 12 and 14 kHz using a Chemagnetics spin speed controller and 3 μs 90° pulses. The multiple-quantum spectra[8] were recorded using time proportional phase incrementation with a 12° phase shift and 64 increments in the t_1 dimension. Two-dimensional wide

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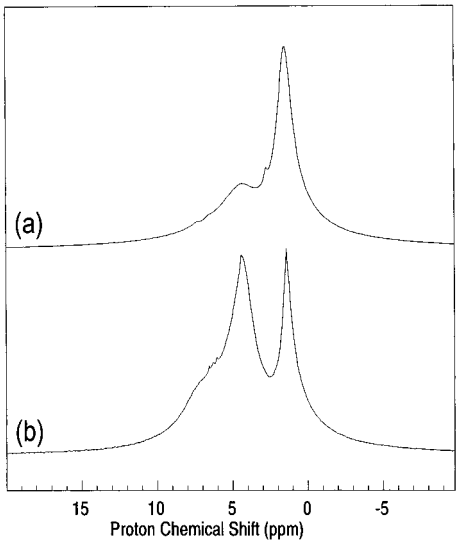

Figure 1. The 400 MHz proton NMR spectra of (a) poly(ethyl acrylate) and (b) poly(ethyl acrylate) in a Vycor glass acquired with magic angle spinning at 13 kHz.

line separation (WISE) NMR spectra[9] were recorded with the 7.5 mm probe with carbon detection and magic-angle spinning at 3 kHz. The 90° pulse widths were 4.5 μs for carbons and protons in the WISE experiments, and the data were recorded with 30 kHz sweep widths in the carbon dimension and 200 kHz sweep widths in the proton dimension. A cross-polarization contact time of 1 ms was used for all samples, and the 2D spectra for the Vycor composite were recorded with a 50 ms spin diffusion mixing time.

Results

Proton NMR with fast magic-angle spinning has been used to study bulk poly(ethyl acrylate) and its Vycor composite. Proton NMR is typically not used to observe the solid-state NMR spectrum of polymers because the lines are broadened by strong dipolar interactions between nearby protons.[10] We have found that high-resolution spectra can be obtained with fast magic-angle spinning for many polymers above T_g where the dipolar interactions are partially averaged by molecular motion. The fast magic-angle spinning also allows us to measure the polymer dynamics by multiple-quantum NMR and to identify polymer at the surface of the porous glass.

Figure 1 shows the 400 MHz proton NMR spectra of bulk poly(ethyl acrylate) and the Vycor composite obtained with 13 kHz magic-angle sample spinning at ambient temperature. The spectrum for poly(ethyl acrylate) (Figure 1a) shows two main peaks at 1.3 and 4.5 ppm, which can be assigned to the side chain methyl group and the remaining proton signals that are not resolved. The high field signal is resolved in the poly(ethyl acrylate)/Vycor composite (Figure 1b), but the lower field peak overlaps with the signal from the hydyoxyl groups and water at the surface of the pore.

The fraction of polymer and water in the pores can be estimated by taking the difference between the spectra shown in Figure 1. The results show that 55% of the total proton NMR signal is associated with the polymer, and the remainder is assigned to the water and surface hydroxyl groups. Correcting for the number of protons and the molar volumes of water and poly(ethyl acrylate) (18 and 77.4 cm^3/mol), we calculate that the volume fraction of polymer in the pore is 0.56. If we assume that the 40 Å pores are completely filled, this corresponds to the polymer occupying the center 30 Å of the 40 Å pore. The surface hydroxyl groups and water occupy the remaining 10 Å.

The relative fractions of water and polymer filling the pores was calculated by assuming that the pores are completely filled, an assumption that can be tested using proton spin diffusion measured via the 2D exchange NMR.[11] Proton magnetization transfer in solids is a diffusive process, and the length scale of spin diffusion is approximately given by

$$L = \sqrt{\frac{6D}{R_1}}$$

where L is the length scale, D is the spin diffusion coefficient, and R_1 is the spin−lattice relaxation rate.[10] For polymers above T_g, the spin diffusion coefficient is approximately 0.05×10^{-15} m^2/s,[12] and the spin−lattice relaxation times for the protons in poly(ethyl acrylate) are ca. 1 s, giving a maximum spin diffusion length scale of 17 nm. This length scale is much larger than the diameter of the pores, so if the polymer and water are homogeneously distributed throughout the composite, then there should be complete equilibration of the magnetization of the water and polymer. If some pores are not completely filled, then the water in these pores will not be close enough to the polymer to exchange magnetization via spin diffusion.

Two-dimensional spin-exchange spectra are frequently used to measure internuclear distances because cross-peak buildup depends on the inverse sixth power of the distances.[11] In these experiments we are interested not in the initial buildup but rather in the final distribution of magnetization as the spin system approaches equilibrium.[13] For the samples where there is complete spin diffusion between all parts of the sample, the cross sections through the 2D spectra will all have the same line shape as the equilibrium spectrum. This behavior is illustrated in Figure 2 which shows the 2D exchange spectrum for poly(ethyl acrylate) with a mixing time of 0.25 s and an overlay of a cross section through the 2D spectrum at the frequency of the methyl protons and the equilibrium 1D spectrum. The spin system appears to have come to equilibrium after 0.25 s since identical line shapes are observed for the equilibrium spectrum and the 2D cross section.

Figure 3 shows a similar experiment with the poly(ethyl acrylate)/Vycor composite at a mixing time of 0.5 s where identical line shapes are not observed for the cross section through the 2D spectrum and the equilibrium 1D spectrum, demonstrating that spin diffusion is not complete. This shows that the sample is heterogeneous and that some of the water is not in close contact with the polymer. The composites were made by soaking the porous glass for 5 days in the monomer solution prior to polymerization. Evidently this is not long enough to completely fill the pores.

NMR can be used to study not only the molecular structure but also the dynamics through a variety of relaxation and exchange processes. The molecular dynamics are often measured via the NMR relaxation rates that are sensitive to polymer dynamics over a wide range of frequencies.[10] In these studies we have used multiple-quantum NMR with fast magic-angle sample spinning to measure the low-frequency dynamics of poly(ethyl acrylate) and poly(ethyl acrylate)/Vycor composites using the pulse sequence shown in Figure 4.[8] Multiple-quantum coherences are forbidden transitions

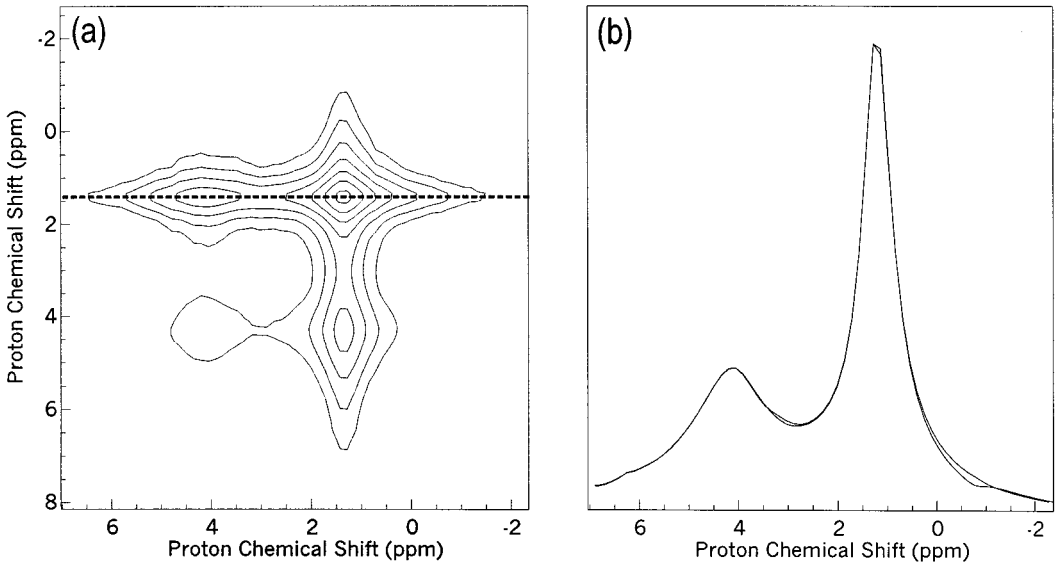

Figure 2. (a) 2D spin-exchange spectrum of bulk poly(ethyl acrylate) obtained with a mixing time of 0.25 s. (b) An overlay of a trace through the 2D spectrum (shown by the dotted line) and the equilibrium 1D spectrum.

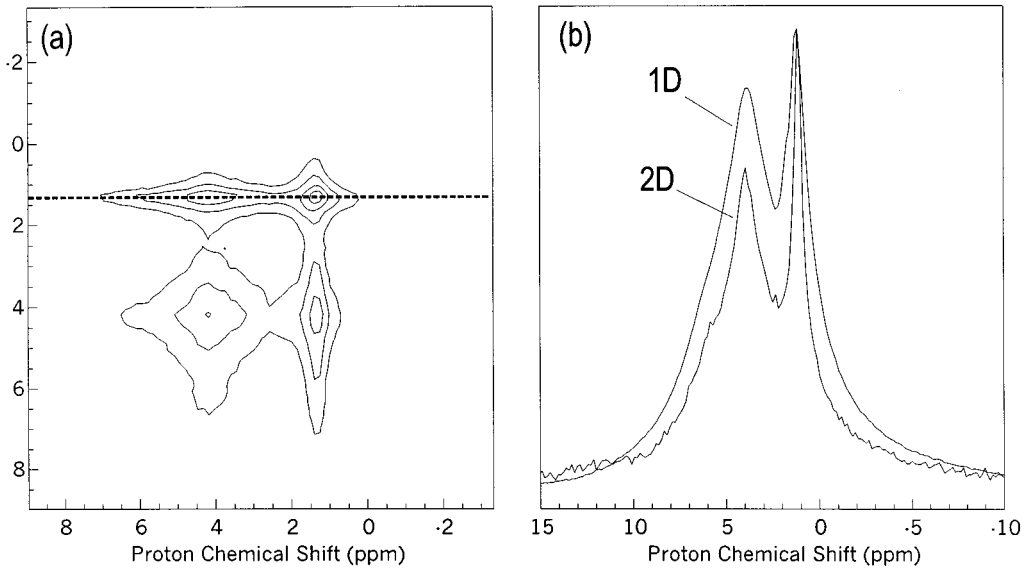

Figure 3. (a) 2D spin-exchange spectrum of the poly(ethyl acrylate)/Vycor composite obtained with a mixing time of 0.5 s. (b) An overlay of a trace through the 2D spectrum (shown by the dotted line) and the equilibrium 1D spectrum.

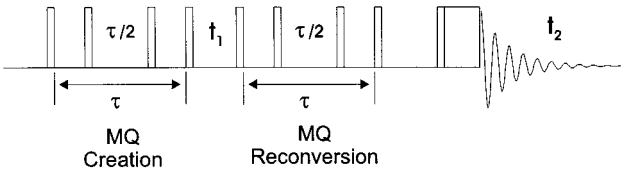

Figure 4. Pulse sequence diagram for the measuring the multiple-quantum spectrum with fast magic-angle spinning.[8] The pulses are applied synchronously with the spinning of the rotor. After creation of multiple-quantum coherences a t_1 period is allowed followed by reconversion of the multiple-quantum coherences into z magnetization. This magnetization is observed in the t_2 period following a 90° pulse and a spin-locking period.

that can be excited in solids when there are strong dipolar interactions.[14] In the fast magic-angle spinning version of this experiment the dipolar couplings that are averaged out by spinning are reintroduced using the DRAMA pulse sequence.[15] If the dipolar couplings are averaged by chain motion rather than sample spinning, as expected for polymers above T_g, then the excitation and reconversion of multiple-quantum coherences will be very inefficient, and no peaks will be observed.

Figure 5 compares the multiple-quantum spectra for the methyl groups of poly(ethyl acrylate) and the Vycor composite obtained with fast magic-angle spinning. Figure 5a shows that the double-quantum peak is barely visible above the noise for the bulk poly(ethyl acrylate) sample, as expected for a polymer above T_g when the dipolar couplings are averaged by chain motion. A higher signal-to-noise ratio is observed for the composite (Figure 5b), demonstrating that the chains are greatly restricted by incorporation into the porous glass. This is the first indication that the molecular dynamics are affected by incorporation into the rigid host matrix.

The multiple-quantum experiment demonstrates that there are differences in the chain dynamics of the composites and the bulk polymer. However, these experiments do not show if all of the chains in the channel are restricted or only if those in close proximity of the surface are restricted. We can distinguish between these possibilities using wide-line separation (WISE) 2D

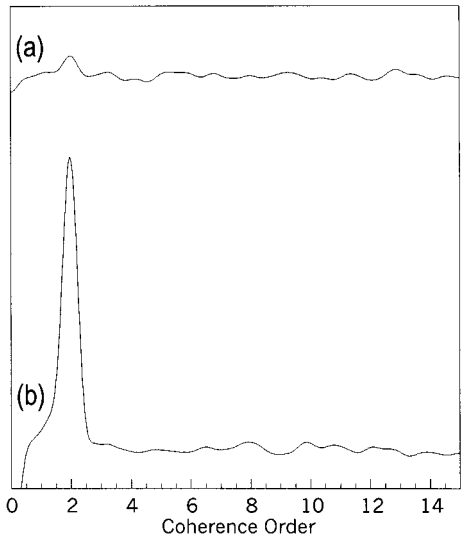

Figure 5. Multiple-quantum spectra of (a) bulk poly(ethyl acrylate) and (b) the poly(ethyl acrylate/Vycor composite). Only double-quantum signals are observed.

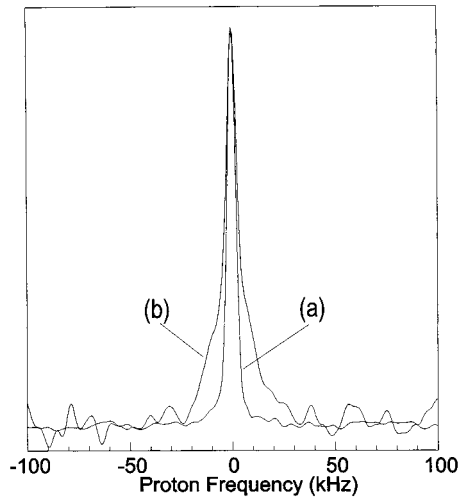

Figure 6. Cross sections through the 2D WISE spectra at the frequency of the methyl groups for (a) poly(ethyl acrylate) and (b) the Vycor composite.

NMR,[9] an experiment used to correlate the carbon chemical shifts and the proton line widths. If all the chains are restricted in the Vycor composite, then we will observe a broad proton line width associated with the poly(ethyl acrylate) methyl group. If only the surface chains are restricted, we will observe a composite line shape from the mobile and restricted chains.

Figure 6 compares cross sections through the 2D WISE spectra for bulk poly(ethyl acrylate) and the Vycor composites at the frequency of the methyl side chain carbon. Bulk poly(ethyl acrylate) has a T_g of −23 °C, and chain motion at ambient temperature averages the proton line widths from the 40 kHz value expected for rigid solids to 5.6 kHz. The comparable signal for the Vycor composite shows a more complex proton line shape with at least two components. The line shows a narrow component with the same line width as observed for bulk poly(ethyl acrylate) and a broader component that we attribute to material with substantially restricted mobility. This demonstrates that the dynamics of the polymer in the pore are heterogeneous, with some material having bulklike properties and some, presumably the material near the surface, having a restricted mobility.

Discussion

NMR is frequently used for materials characterization because it provides atomic level structural and conformational information, and the relaxation rates are sensitive to the chain dynamics over a wide range of time scales. However, because of the low sensitivity of NMR and the difficulty in separating the bulk and surface-adsorbed layers, NMR has not been extensively used to study polymer surfaces and interfaces. We have shown that the spectra of many polymers can be observed by proton NMR with fast magic angle at temperatures above T_g where the dipolar interactions are partially averaged by chain motion.[13] Proton NMR has a high sensitivity, making it possible to study many types of materials. With the high signal-to-noise ratios observed in our experiments with high surface area materials (250 m^2/g), it appears that it will be feasible to study materials with a much lower surface area. In addition, if we can obtain a high-resolution spectrum with rapid sample spinning, then many of the experiments designed to measure the structure and dynamics of solution samples (such as 2D exchange) can be used to characterize the structure and dynamics of polymers at surfaces and interfaces. With the recent introduction of even faster sample spinning (ca. 35 kHz), we anticipate that many more materials will be amenable to analysis by these methods.[16]

These solid-state proton NMR experiments allow us to measure the structure and dynamics of the bulk polymer and the material polymerized in the channels of the porous glass. Vycor composites are currently under consideration as optical devices for recording refractive index gradients, and to maximize the strength of the refractive index gradients, it is important to fill the pores completely. These studies show that the central 30 Å of the 40 Å pores are filled with poly(ethyl acrylate), and there remains some fraction of the polymer that is not in close contact with water lining the pores even after soaking the porous glass for 5 days in the initiator/monomer solution. This conclusion is based on spin diffusion experiments and assumes that there is efficient spin diffusion between the surface water layer and the polymer. We have observed such spin diffusion in other samples using $^{29}S-^{1}H$ 2D WISE NMR where magnetization exchange between the protons near the surface silicon atoms and the polymer can be observed (unpublished). The NMR spectra provide an easy way to measure the volume fraction of polymer in the pore, making it possible to monitor the effectiveness of other filling strategies or surface treatments aimed at increasing the amount of polymer in the pore.

The dynamics of the polymer in the pore is of great concern as low-T_g materials are often required for recording refractive index gradients to allow for monomer diffusion during recording. We did not measure the T_g in these studies, but rather the low-frequency (kilohertz) dynamics of polymers in the porous glass. Under these conditions the bulk poly(ethyl acrylate) was sufficiently mobile that only weak double-quantum signals could be observed, while the poly(ethyl acrylate) in the Vycor composite gave very strong signals. The 2D WISE experiments show that the dynamics of the polymer are not homogeneous but that the Vycor composite contains material with bulklike dynamics and some material with restricted dynamics.

The dynamics of polymers in thin films and at surfaces has been the subject of several studies. It has been observed that the thickness in thin polystyrene films on silicon changes at temperatures below the bulk T_g, suggesting that the thin films are more mobile than the bulk material.[1] Similar result are reported for poly(methyl methacrylate) on a gold surface, while an increase in T_g is reported for poly(methyl methacrylate) on silicon that is attributed to a decreased mobility from hydrogen bonding between the polymer and the surface.[17,18] ^{2}H NMR has been used to investigate the dynamics of poly(methyl acrylate)-d_3 adsorbed on silica, and it has been reported that the dynamics are more complex than the bulk material.[2,5] The ^{2}H NMR results show that the polymer at the solid surface is more restricted than the bulk material while the polymer at the air interface is more mobile than the bulk. While the structure and dynamics of other polymers in porous glasses have not been extensively investigated, it has been reported that a new peak is observed in the dielectric spectrum of poly(propylene glycol) that is assigned to material with restricted mobility at the surface of the pores.[19]

The NMR data reported here for the poly(ethyl acrylate) composites demonstrate that the chain dynamics are restricted by incorporation into the porous glass. The 2D WISE experiments show that only a fraction of the polymer in the pore is restricted while the material in the center of the pore has a bulklike mobility. The behavior of the poly(ethyl acrylate) in the composite is similar to that reported for poly(methyl acrylate) in that both surface-restricted and bulklike material are observed.[2,5] We believe that the change in the molecular dynamics is related to the hydrogen bonding between the poly(ethyl acrylate) and the water and surface hydroxyl groups at the surface of the pores.

In summary, we have developed new NMR methods for the study of polymers at surfaces and applied them to the study of photopolymers for holography. Fast magic-angle spinning is easy to implement and provides information about the volume fraction of polymer in the pores, the completeness of filling, and the dynamics of polymers at the surface of the porous glass.

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