Macromolecules **2001,** *34,* 7403−7410

Conformation of Adsorbed Random Copolymers: A Solid-State NMR and FTIR-PAS Study

Victor Nasreddine, Jamie Halla, and Linda Reven*

Department of Chemistry, McGill University, 801 Sherbrooke Street West,
Montreal, Quebec, Canada H3A 2K6

Received May 14, 2001

ABSTRACT: The properties of bulk and adsorbed polyethylene-*co*-acrylic acid (PEA) random copolymers were characterized by solid-state NMR and vibrational spectroscopy. FTIR-PAS (Fourier transform infrared photoacoustic spectroscopy) measurements show that the copolymers are chemisorbed to zirconia surfaces via the carboxylic acid sticker groups. The chain mobility, conformation, and morphology of bulk and adsorbed PEA were studied by ^{13}C CP-MAS, 2D WISE, and ^{1}H spin diffusion NMR experiments. The effect of the copolymer loading and acrylic acid content on these properties was examined. Whereas adsorbed PEA with a 5% w/w acrylic acid content contain transoid chain segments at all loadings, samples with higher acrylic acid contents (15 % w/w) only display an all-trans component at higher loadings where unbound acid groups are present.

Introduction

Polymer/solid interfaces are key to industrial applications ranging from protective coatings to photoresists.[1] The relationship between the conformational and dynamic features of adsorbed polymers to surface properties such as adhesion is of interest to these applications. Although vibrational spectroscopy has been commonly employed to investigate the conformational properties of polymers at interfaces, this technique does not provide dynamic information. Solution NMR techniques, based primarily on relaxation measurements, have been used to estimate the fraction of polymer bound to a surface.[1a,2] Although a large number of solid-state NMR techniques have been developed to probe polymer dynamics,[3] relatively few NMR studies have been carried out for adsorbed polymers at the solid/air interface due to sensitivity problems. A notable exception has been the solid-state NMR studies of adsorbed polymers and copolymers by Blum and co-workers.[4]

Copolymers containing acrylic acid have been used for many years to increase the adhesion of polymer films to metals. Most studies have focused on the mechanical properties (peeling tests, thermal stability) rather than the molecular level structure.[5] Gong et al. showed that a critical concentration of carboxylic acid sticker groups is required for optimal chain connectivity near the surface and a maximum in the fracture energy.[6] Theoretical studies of adsorbed random copolymers predict that the maximum fracture energy is associated with the chain conformation at the interface.[7] It was recently reported that the bonding of fatty acids and acrylic acid copolymers to alumina can be enhanced by pretreating the surface with zirconium alkoxides.[8] Likewise, we have found that whereas long chain carboxylic acids adsorb weakly to alumina, highly ordered self-assembled monolayers form on zirconia.[9] The high surface area zirconia substrate used in this study provided sufficient signal-to-noise for even 2D solid-state ^{13}C NMR experiments. Furthermore, the nature of the metal carboxylate surface bond could be easily determined by vibrational spectroscopy.[8,9]

In view of these results, as well as the wide industrial use of acrylic acid containing copolymers, we have chosen polyethylene-*co*-acrylic acid (PEA) random copolymers deposited on nonporous zirconia as a convenient system for a detailed solid-state NMR study of a strongly adsorbed polymer. The chain conformation of the polyethylene segments, determined from the ^{13}C chemical shifts, can be correlated with the interaction of the poly(acrylic acid) groups with the surface, as detected by infrared spectroscopy. Solid-state 2D wide-line separation (WISE) and ^{1}H spin diffusion NMR experiments are applied to probe the chain motion and morphology in the bulk and adsorbed states. The effect of copolymer loading and acrylic acid content on surface bonding, the chain order, mobility, and morphology are reported.

Experimental Section

Sample Preparation. Random polyethylene-*co*-acrylic acid (PEA) copolymers were used as-received (Scientific Polymer Products, Inc.). The two copolymers used (5% PEA and 15% PEA) contain 5 and 15 wt % acrylic acid, respectively. Nonporous zirconia (ZrO_2) powder (monoclinic, VP zirconium dioxide, Degussa Corp.) was calcinated at 400 °C to eliminate any residual organic impurities. The reported average primary particle size of this ZrO_2 is 30 nm, and the BET surface area is 40 m^2/g. Zirconia powder (2 g) was dispersed in 250 mL of xylene by sonication for 15 min. The copolymer solutions were prepared by dissolving the appropriate amount of polymer in 50 mL of warm xylene. A total of seven samples were prepared for each copolymer using 30, 60, 120, 200, 300, 600, and 900 mg of polymer. The copolymer solutions were added to the dispersed zirconia powder under stirring. The resulting mixture was refluxed with stirring for 1 day. The samples were washed a total of six times each by redispersing the powder in 40 mL of xylene with gentle heating, filtering, and then drying under vacuum after the final washing step. The samples studied along with the carbon content in percent weight (%C) determined from elemental analyses are summarized in Table 1.

Gel Permeation Chromatography (GPC). The molecular weights of the copolymers were determined by GPC. For the 5% PEA, $M_w \sim 7900$, and the polydispersity index is $M_w/M_n \sim 1.8$. For 15% PEA, $M_w \sim 1300$, and the polydispersity index is $M_w/M_n \sim 1.1$.

Differential Scanning Calorimetry (DSC). The crystallinity of the 5% and 15% PEA were 24% and 8%, respectively,

10.1021/ma010833p CCC: $20.00

Table 1. Samples, Preparation Loadings, and Adsorbed Amounts[a]

sample	preparation loadings, mg of polymer/g of ZrO_2	ads amount (% C)	sample	preparation loadings, mg of polymer/g of ZrO_2	ads amount (% C)
5%PEA bulk			100PEA5%	100	6.4
15% PEA bulk			100PEA15%	100	5.6
15PEA5%	15	2.4	150PEA5%	150	6.0
15PEA15%	15	2.2	150PEA15%	150	6.6
30PEA5%	30	3.1	300PEA5%	300	15.4
30PEA15%	30	3.2	300PEA15%	300	15.0
60PEA5%	60	4.8	450PEA5%	450	18.9
60PEA15%	60	4.5	450PEA15%	450	17.8

[a] % C is the percentage of carbon = [(wt C)/(wt polymer + wt zirconia)] × 100%.

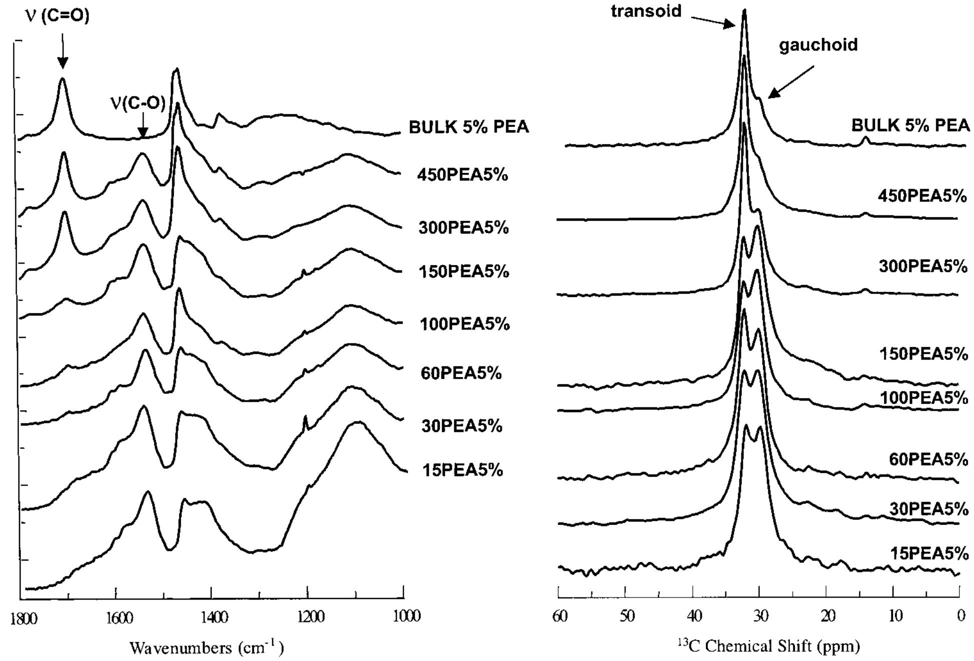

Figure 1. The 67.9 MHz ^{13}C CP-MAS NMR and FTIR-PAS spectra of the 5% polyethylene-*co*-acrylic acid copolymer in the bulk state and adsorbed on zirconia. See Table 1 for the loading amounts in the adsorbed polymer samples. A contact time of 3 ms, a spinning speed of 3 kHz, and 100 and 8000 acquisitions were used for the bulk and adsorbed polymer samples, respectively.

as determined by using a Perkin-Elmer differential calorimeter, DSC-7.

NMR. Solid-state ^{13}C NMR spectra (67.92 MHz) were recorded on a Chemagnetics CMX-270 NMR spectrometer with a 7 mm double-tuned fast magic angle spinning (MAS) Doty probe. Samples were spun at a rate of 3 kHz. A pulse delay of 3 s for both bulk (100 scans) and loadings (8000 scans) was used to acquire the ^{13}C CP-MAS spectra. For the ^{1}H$-^{13}$C cross-polarization (CP) experiments, ^{1}H 90° pulse widths between 3 and 4 μs and a contact time of 3 ms were used. Fully relaxed dipolar decoupled magic angle spinning (DD-MAS) ^{13}C NMR spectra were also acquired for the bulk polymers using a pulse delay of 600 s.

For the 2D wide-line separation experiments (WISE),[10] a ^{1}H 90° pulse was followed by a proton evolution period, t_1, consisting of 128 increments of 5 μs. After each t_1 period, cross-polarization followed by carbon detection with proton decoupling gives a carbon spectrum that is modulated as a function of t_1 by the free induction decay of the associated protons. A total of 1024 scans were required for each t_1 evolution period. A short contact time of 0.5 ms was used to minimize proton spin diffusion, which will equalize the proton line widths. The processed data sets contained 512 points in the F_2 (^{13}C) dimension and 1024 points in the F_1 (^{1}H) dimension. 2D WISE measurements with a spin diffusion mix time incorporated before the cross-polarization step were also carried out.

The dipolar filter[11] (spin diffusion experiment) destroys the magnetization of the rigid phase (at 33 ppm) in a manner similar to the classic Goldman−Shen experiment.[12] The magnetization of the more mobile component (at 31 ppm) is retained. Eight cycles of the dipolar filter with 10 μs delays between the pulses were used. After application of the dipolar filter the residual magnetization was stored on the $\pm Z$ axis (parallel to the magnetic field B_0) for a mixing time τ_m, during which spin diffusion occurs and eventually equilibrates the inhomogeneous distribution of magnetization. The intensities of the peaks were taken for each mixing time and corrected for longitudinal relaxation by measuring the signal decay for the same mixing time without the application of the dipolar filter.

FTIR-PAS. All spectra were run on powder samples of bulk and adsorbed polymers using a Fourier transform Mattson Research series 1 spectrometer equipped with a photoacoustic cell (MTEC model 300) at 1.0 cm^{-1} nominal resolution.

Results

^{13}C CP-MAS NMR and FTIR-PAS Spectroscopy.

The ^{13}C CP-MAS NMR and FTIR-PAS spectra of the bulk and adsorbed 5% and 15% polyethylene-*co*-acrylic acid random copolymers are shown in Figures 1 and 2. The ^{13}C CP-MAS NMR spectrum of polyethylene consists of a sharp peak at 33 ppm arising from all-trans polymer chains with restricted mobility within the crystalline regions and a broader peak at 31 ppm due to more mobile chains within the amorphous regions which contain gauche defects. The methylene carbon in this conformation is shielded relative to the all-trans one due to the γ-gauche effect.[13] The relative integrated

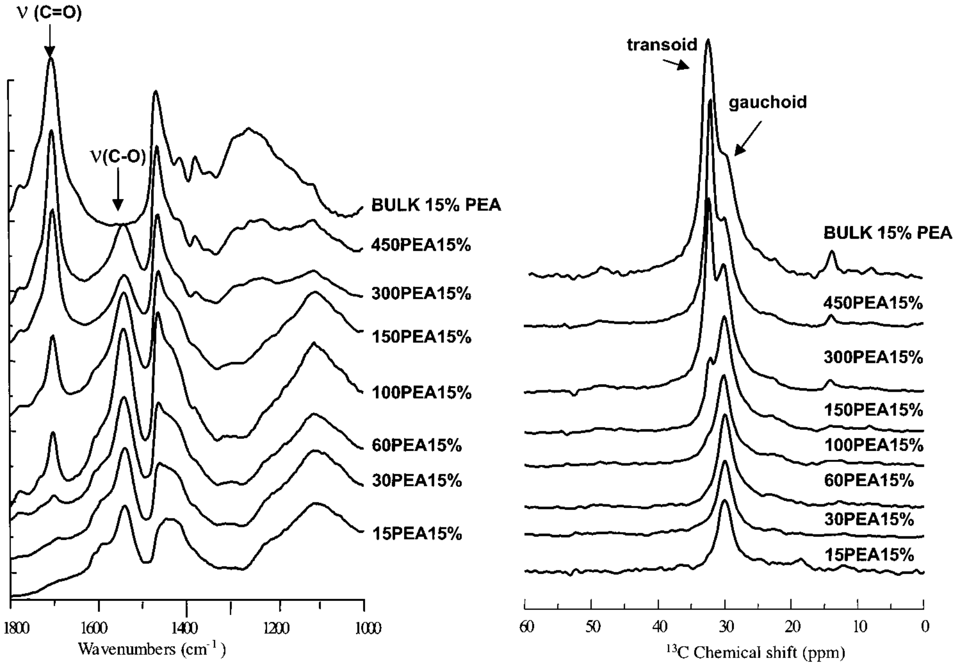

Figure 2. The 67.9 MHz ^{13}C CP-MAS NMR and FTIR-PAS spectra of the 15% polyethylene-*co*-acrylic acid copolymer in the bulk state and adsorbed on zirconia. See Table 1 for the loading amounts in the adsorbed polymer samples.

intensities of the crystalline and amorphous components, *I*(33)/*I*(31), were 2.7 and 2.0 for PEA5% and PEA15%, respectively. Fully relaxed ^{13}C DD-MAS NMR spectra were also acquired for the bulk polymers. The relative integrated intensities of the 33, 30, and 15 ppm peaks were 1.0, 0.89, and 0.036 for 5% PEA and 1.0, 1.14, and 0.049 for 15% PEA. The different relative intensities in the ^{13}C DD-MAS NMR spectra as compared to the spectra acquired with cross-polarization are due to the different cross-polarization efficiencies of the 33 and 31 ppm components. The intensities of the methyl peaks at 15 ppm reflect the low molecular weights of these copolymers ($M_w \sim 1300$ and 8000). The lower crystallinity of the copolymer with the higher acrylic acid content is due to the tendency of the acid groups to lie in the amorphous regions.[14]

The spectra of the adsorbed 5% PEA samples prepared with low loadings (15PEA5% to 150PEA5%) display resonances at 33 and 31 ppm which are of comparable relative intensities. Fully relaxed ^{13}C DD-MAS NMR spectra of the adsorbed samples showed similar relative intensities to the ^{13}C CP-MAS NMR spectra. Although these two peaks are assigned to chains in the crystalline and amorphous regions in bulk polyethylene, the 33 and 31 ppm resonances of the adsorbed copolymers are more properly described as arising from chain segments with a high trans content (transoid) and conformationally disordered chain segments containing a higher population of gauche defects (gauchoid). This distinction is important since we cannot refer to crystallinity (long-range order) in the case of the adsorbed polymers. The absence of a free acid C=O band at ~1700 cm^{-1} in the FTIR-PAS spectra with the simultaneous appearance of new bands in the carboxylate region indicates that all the carboxylic acid groups are bound to the surface in the samples with the lowest copolymer loadings. The chemisorption of the acid groups is indicated by the appearance of two broad intense bands in the C–O stretching region at ~1540 and ~1460 cm^{-1}, which are assigned to the asymmetric and symmetric C–O stretches of a chelating bidentate zirconium carboxylate surface bond.[8] These bands were assigned previously from isotopically labeled fatty acids on zirconia.[9] Note that the CH$_2$ scissoring band at 1470 cm^{-1} overlaps with the symmetric C–O stretch at ~1460 cm^{-1}.

In the 100PEA15% and 300PEA5% samples, a strong peak at 1704 cm^{-1} appears which is assigned to the C=O stretch of unbound carboxylic acid groups. Weak broad peaks for unbound acid groups may also be present in the lower loadings, 60PEA15% and 150PEA5%. The appearance of a strong free acid peak for adsorbed PEA5% at a loading which is 3 times higher than when it appears for adsorbed PEA15% reflects the relative acrylic acid contents of the two copolymers. The FTIR-PAS spectra of the highest loadings are similar to those of the bulk copolymers with the additional presence of the 1540 cm^{-1} asymmetric C–O stretching band due the chemisorbed polymer segments. Likewise, in the ^{13}C CP-MAS NMR spectra, the relative intensities of the transoid and gauchoid peaks at 33 and 31 ppm of the two highest loadings approach those of the bulk copolymers. In contrast to the 5% PEA samples, the ^{13}C CP-MAS NMR spectra of samples prepared with 15% PEA contain only one peak at 31 ppm when low loadings are used (15PEA15% to 100PEA15%). A 33 ppm transoid component first appears in 150PEA15%, a loading above which a free acid peak is present in the FTIR spectra. A similar correlation between the FTIR-PAS and ^{13}C CP-MAS NMR spectra is also evident for the 5% PEA. The intensity of the 33 ppm peak relative to that of the 31 ppm peak only increases in the 300PEA5% sample, the same loading at which a strong free acid peak appears in the IR spectra.

2D Wide-Line Separation (WISE) NMR. Qualitative information concerning the chain dynamics can be obtained from the WISE experiment which provides a correlation between chemical structure (^{13}C dimension) and mobility (^{1}H dimension).[10] In this 2D heteronuclear NMR experiment, each resolved ^{13}C resonance yields a proton wide-line spectrum which reflects the dipolar couplings of the protons in the proximity of the respec-

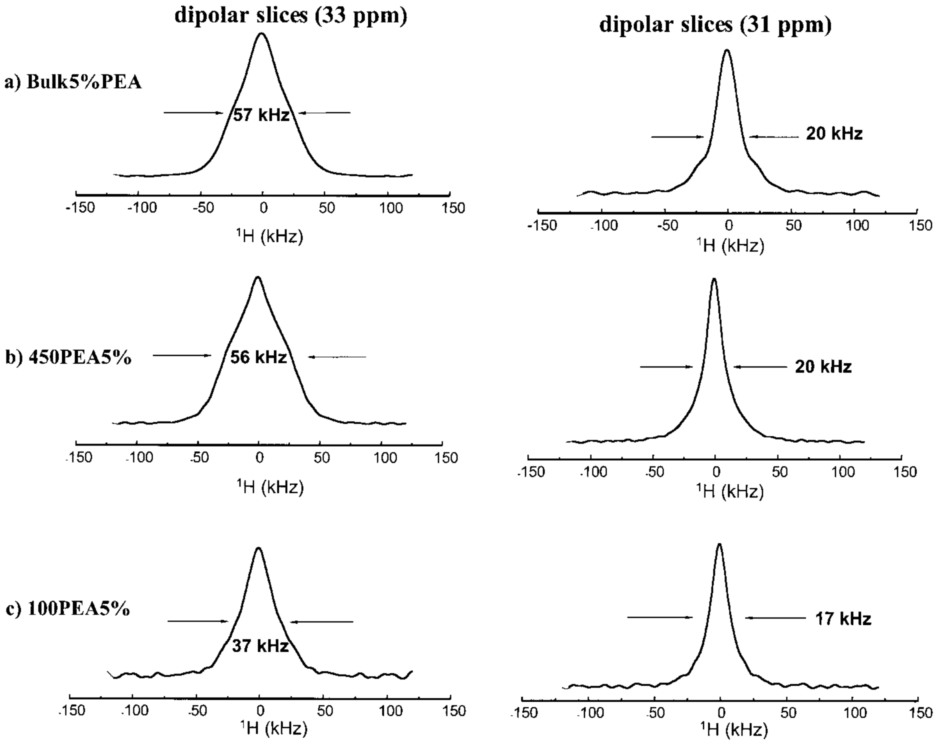

Figure 3. ^{1}H wide-line spectra for (a) 5% PEA, (b) 450PEA5%, and (c) 100PEA5%. The ^{1}H wide-line spectra shown correspond to the ^{1}H slices of the gauchoid and transoid components at 31 and 33 ppm in the ^{13}C dimension in the 2D wide-line separation (WISE) NMR experiments.

Table 2. ^{1}H Line Widths and Domain Sizes

	proton line widths at half-height, $\Delta\nu_{1/2}$ (kHz)		domains sizes (nm)	
sample	33 ppm	31 ppm	33 ppm	31 ppm
bulk PEA 15%	43	21	6 ± 1	5.5 ± 1
100PEA15%		21		
bulk PEA5%	57	20	6.5 ± 1	7 ± 1
100PEA5%	37	17	<2	<2
450PEA5%	56	20	8 ± 1	5 ± 1

tive ^{13}C nuclei. Since the ^{13}C chemical shift is sensitive to conformation, slices taken in the ^{1}H dimension in a 2D WISE spectrum allow separation of the broad proton resonances for ordered and disordered regions, which would completely overlap in the 1D ^{1}H NMR spectrum. In addition, the contributions from the protons associated with the metal oxide substrate are suppressed. In the WISE NMR spectrum of bulk polyethylene, the dipolar slice of the ^{13}C signal arising from the crystalline domains is a broad Gaussian peak with a typical line width of 50−70 kHz, whereas the slice corresponding to amorphous regions displays a motionally narrowed line shape with widths between 5 and 20 kHz.[10]

Figure 3 shows the 33 and 31 ppm dipolar slices extracted from the 2D WISE NMR spectra of 100PEA5%, 450PEA5%, 100PEA15%, and the bulk copolymers, and the line widths are listed in Table 2. Relatively short contact times (0.5 ms) were used to minimize spin diffusion which will tend to equalize the line widths. The WISE spectra indicate that the acrylic acid content affects the morphology and mobility of the copolymer. The widths at half-height of the crystalline (33 ppm) dipolar slices of the bulk 5% PEA were found to be 57−60, similar to that of bulk polyethylene. The dipolar slice of the crystalline component of the 15% PEA is 43 kHz.

The line widths of the highest loading, 450PEA5%, and bulk 5% PEA are comparable, reflecting a similar dynamic state. In 100PEA5%, the reduced line width of the 33 ppm transoid component (37 kHz) shows that the dipolar couplings of the transoid chain segments of the adsorbed copolymer is less than the crystalline regions of the bulk copolymer. However, the line width of the 31 ppm component indicates that the gauchoid chain segments of the adsorbed polymers experience dipolar couplings similar to the chains in the amorphous regions of the bulk copolymer. A similar trend is observed for the 15% PEA samples.

Spin Diffusion Experiments. ^{1}H spin diffusion experiments were used to determine the domain sizes of the crystalline and amorphous phases in the two copolymers and the ordered and disordered regions in the 100PEA5% and 450PEA5% adsorbed copolymer samples. Spin diffusion is the process by which nuclear magnetization is transported spatially through a solid sample via flip-flop transitions among dipolar coupled protons. In general, the first step of a spin diffusion experiment is to select the magnetization of one component and suppress the others via differences in mobilities or chemical shifts. The copolymer has two components of differing mobilities arising from the crystalline and amorphous regions. The dipolar filter experiment was used to select the magnetization of the more mobile amorphous component by suppressing the signal of the rigid component. Monitoring the transfer of magnetization from the mobile to the rigid component makes it possible to determine the length scales in polymers[15−20] and other heterogeneous materials.[21]

The spin diffusion experiment used consisted of four steps: (a) selection of the more mobile proton component via the dipolar filter, (b) a mixing step of variable duration, τ_m, in which the remaining magnetization spreads into neighboring spins, (c) transfer of the ^{1}H magnetization to ^{13}C spins via cross-polarization, and (d) a detection period in which the resolved ^{13}C signals

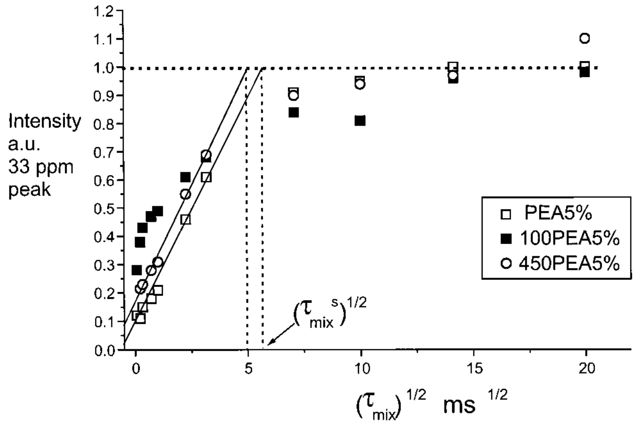

Figure 4. Plot of the peak intensity of the rigid component at 33 ppm (corrected for T_1 relaxation) against the square root of the mixing time for the bulk 5% PEA and the adsorbed copolymer samples 450PEA5% and 100PEA5%. The buildup signal is normalized against the average of the points in the plateau region.

are recorded. The domain size is proportional to the square root of the product of the spin diffusion constant and the time for spin diffusion to eliminate the initial polarization gradient. The plot of the intensity of the more rigid component, I(33 ppm), vs $(\tau_m)^{1/2}$ (Figure 4) confirms that spin diffusion occurs between the amorphous (mobile) and crystalline (rigid) regions. In many polymer studies of this kind, a sigmoidal shape is observed due to the presence of a significant interphase. However, this was not the case for our data. Using the initial rate approximation,[16] the domain sizes of the mobile region were calculated using the following equation:

$$d_{\text{mobile}} = 2\epsilon(D_{\text{eff}}\tau^{s}_{\text{m}}/\pi)^{1/2}/F_{\text{rigid}} \qquad \text{where } F_{\text{rigid}} = 1 - F_{\text{mobile}}$$

In the initial rate approximation, the parameter $(\tau^{s}_{m})^{1/2}$ is determined from a fit of the points in the initial linear range and extending this line to find the value of $(\tau_m)^{1/2}$ where the line intersects with $I = 100\%$, at $\tau_m \rightarrow \infty$. The parameter ϵ in the equation designates the number of orthogonal directions relevant for the diffusion process. Its value depends on the morphology and is 1 for polymers with lamellar morphology as is the case for polyethylene and which was assumed for the copolymers. The square root of the effective spin diffusion coefficient is defined as

$$\sqrt{D_{\text{eff}}} = \frac{\sqrt{D_{\text{mobile}}D_{\text{rigid}}}}{(\sqrt{D_{\text{mobile}}} + \sqrt{D_{\text{rigid}}})/2}$$

The diffusivity D is proportional to the strength of the dipolar couplings and to the square of the average distance among nearest protons r_{HH}. The strength of the dipolar coupling is proportional to the full width at half-height $\Delta\nu_{1/2}$ of a proton in a ^{1}H wide-line spectrum. For $\Delta\nu_{1/2} > 5$ kHz, the spin diffusion coefficient can also be estimated using the following equation:

$$D = \frac{\Delta\nu_{1/2}(r_{\text{HH}})^2}{3}$$

with the line width being in kilohertz and the separation in nanometers.[16,22] For $\Delta\nu_{1/2} < 5$ kHz, a relationship between the spin–spin relaxation time, T_2, and the diffusion coefficient has been established.[19] Other useful formulas for the diffusion coefficients of the rigid and mobile components have been discussed by Demco and co-workers.[19b]

In addition to the diffusion coefficients, the estimate of the domain sizes from spin diffusion experiments depend strongly on the assumed values for the volume fractions, F_{mobile} and F_{rigid}. For polyethylene, the volume fractions are normally found from the crystallinity as measured by X-ray diffraction, DSC, or a fully relaxed DD-MAS ^{13}C NMR spectrum. However, the crystallinities of the polyethylene-*co*-acrylic acid random copolymers, as measured by DSC, vs the fully relaxed DD-MAS ^{13}C NMR spectra differ greatly. Whereas DSC measurements gave crystallinities of 24% and 8% for the 5% and 15% PEA, respectively, the integrated intensities of the transoid and gauchoid components from the fully relaxed DD-MAS ^{13}C NMR spectra yielded much larger crystallinities of 52% and 47%, respectively. A source of error is that the ^{13}C chemical shifts are due to conformational differences, which are not necessarily correlated with crystallinity. However, a 2D WISE experiment with a mix time incorporated,[22] which takes into account both conformation and mobility, gave a similar result. This large discrepancy may be due to the presence of the acid groups which hinder the formation of large crystalline domains combined with the fact that DSC will only detect crystalline domains greater than 2–5 nm, depending on the polymer. A similar situation was reported for a closely related random copolymer, 20% poly(ethylene-*co*-methacrylic acid).[22] Whereas the WISE experiment detected 50% crystallinity, X-ray diffraction indicated a 25% crystallinity in a poly(ethylene-*co*-methacrylic acid) with a 20% methacrylic acid content. The large difference between these two techniques was attributed to the diffraction limit of ca. 1.5 nm for polyethylene.[22] Since the spin diffusion experiment is actually probing the transfer of magnetization from the mobile gauchoid chains to the less mobile transoid chain segments which may be located in very small crystalline domains not detected by DSC, it is more appropriate to use the volume fractions as derived from NMR. The volume fractions from the fully relaxed DD-MAS ^{13}C NMR spectra along with the proton line widths extracted from the WISE experiments were used to calculate the domain sizes. Using the more exact expressions to calculate the spin diffusion coefficients by Demco and co-workers,[19b] these values are 6.5 and 7 nm for the rigid and mobile domains of 5% PEA and 6 and 5.5 nm for the for the rigid and mobile domains of 15% PEA. Although we would expect larger crystalline domains for the copolymer with the lower acrylic acid content, the rigid component domain sizes for 5% PEA and 15% PEA are the same within experimental error. These domain sizes are slightly larger than the 4.2 and 4.0 nm values measured in the 20% poly(ethylene-*co*-methacrylic acid) sample using a WISE experiment with a variable mix time. A similar analysis was performed for the adsorbed copolymers, 100PEA5% and 450PEA5%. The higher loading had domain sizes comparable to those of the bulk copolymer, 8 and 5 nm for the rigid and mobile components, which is further evidence that the highest loading is bulklike. In the case of the lower loading, 100PEA5%, it was not possible to fully suppress the component at 33 ppm using the same dipolar filter conditions. The proton line shape for the transoid component extracted from the 2D WISE experiment (Figure 3) shows a triangular proton line shape. This type of line shape may be due to a superimposition of narrow and broad components. Such line shapes can arise from a motional gradient along the chain, as observed for long chain fatty acid monolayers bound to ZrO_2,[9] or microheterogeneities within domains, as observed for core–shell polymers.[23]

Discussion

Structure at Low Coverage. The information derived from solid-state NMR (conformation, mobility, and morphology) in combination with FTIR (sticker attachment) provides a detailed view of the adsorbed copolymer structure as a function of loading and sticker density. Polymers that are randomly attached to a surface may adopt train conformations, loop conformations (double tethered chains or chains between two trains), and tails.[1] At low coverages, adsorbed homopolymers tend to maximize the interaction with the surface by forming train conformations. In the case of a copolymer, the adsorbed structure will depend on the selectivity of the solvent and the relative surface affinities of the two components. Whereas the poly(acrylic acid) forms strong ionic bonds with the zirconia surface, polyethylene can only interact via van der Waals interactions. The copolymer was adsorbed from a solvent that is selective for polyethylene. During the adsorption process, the acrylic acid groups will bind to the surface while the polyethylene segments will loop out into the favorable solvent environment. Upon drying, the final conformation of the polyethylene segments will depend on the topological constraints created by the strongly bound poly(acrylic acid) segments. The average distance between adsorption sites will be influenced by the solution conformation of the copolymer. Energetically unfavorable chain conformations may be kinetically trapped by the irreversible adsorption of the carboxylic acid sticker groups.

At low loadings, the sticker groups of the copolymer with the higher acrylic acid content, 15% PEA, are all attached to the surface, and the polyethylene segments have an apparent mobility and a gauche/trans population similar to the amorphous regions of the bulk polymer, based on the proton line widths and ^{13}C chemical shifts. This implies the formation of more looped conformations rather than flat, extended train structures which would be expected to have a larger trans content as well as a reduced mobility. Such train conformations have been reported for physisorbed polyethylene on silica.[24] In contrast to polyethylene, the PEA copolymers are strongly chemisorbed to the zirconia surface. The sticker groups attach to the surface with a random distribution, giving rise to a predominance of short looped segments rather than flat trains.

In the case of the adsorbed copolymer with a lower acrylic acid content, 5% PEA, the ^{13}C NMR data show that certain chain conformations are strongly favored. Even at the lowest loadings, the adsorbed 5% PEA always contains a transoid component. Furthermore, the relative intensities of the transoid and gauchoid components remain constant with increasing coverage until most available surface sites are occupied. The occupation of most of the binding sites is indicated by the appearance of the FTIR band for unbound COOH groups. In a recent study, Wegman and co-workers covalently attached 5%, 10%, and 15% PEA to silica gel via glycidoxypropyl and aminopropyl linkages for use in reverse-phase liquid chromatography.[25] They also observed by solid-state ^{13}C NMR a higher trans content for the 5% PEA as compared to the copolymers with higher acrylic acid contents. The average number of methylene groups between the sticker groups in 5% PEA is much larger than in the 15% PEA. In a crude approximation, assuming an even distribution of acid groups, the 15% PEA and 5% PEA have on average ~30 and ~100 methylene groups, respectively, between sticker groups. In the case of molecular surfactants, 30 methylene units are sufficient for forming looped surface structures with all-trans segments. Allara and co-workers reported the formation of tightly folded, looping structures when the dicarboxylic acid, $HO_2C(CH_2)_{30}CO_2H$, was adsorbed on a silver surface.[26] The IR spectra showed components for all-trans CH_2 segments and a short sequence of conformationally disordered CH_2 groups. The fold was estimated to consist of at least six methylene groups, and thus the all-trans chain segments consisted of 12 methylene groups each. Since polymer chains are much more restricted in regards to surface rearrangements as compared to small molecules and there is a distribution of chain lengths between the sticker groups in a random copolymer, such tightly folded structures are unlikely. In the adsorbed 5% PEA samples, the polyethylene chain segments between sticker groups may be long enough for some folding to occur. Alternatively, a portion of the chain segment between sticker groups could lie flat on the surface, as in the case for physisorbed polyethylene, giving rise to the trans component observed at low coverages. However, the former case is both energetically and entropically more favorable. The selectivity of the solvent and the different surface affinities for the two components should reduce the occurrence of flat polyethylene trains. In either case, the all-trans regions would be very small, as supported by the spin diffusion studies. These proposed structures are illustrated schematically in Figure 5.

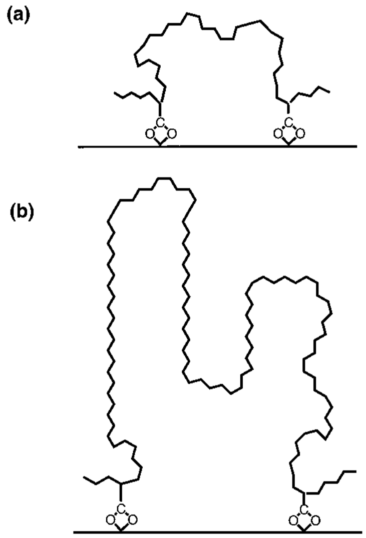

Figure 5. A schematic diagram showing the conformations adopted by low loadings of (a) 15% PEA and (b) 5% PEA.

Structure of Adsorbed Copolymers at High Loadings. As the loading is increased, a free acid peak at 1704 cm^{-1} appears in the FTIR-PAS spectra of both adsorbed copolymers, indicating that some sticker groups are not bound to the surface. A transoid component appears in the solid-state ^{13}C NMR spectra of the adsorbed 15% PEA at a loading (150PEA15%), above which a strong signal for unbound sticker groups is first detected in the FTIR-PAS spectra (100PEA15%). In the case of copolymer chains with a higher sticker content, transoid chain segments only occur after occupation of the surface sites by other polymer chains. A related trend is observed for the adsorbed 5% PEA. The relative intensities of the transoid and gauchoid components remain constant with increasing coverage (15PEA5% to 150PEA5%). A large increase in the trans content occurs at 300PEA5%, the same loading at which a large IR band for unbound sticker groups appears. Thus, the trans content of the surface-bound copolymer chains appears to be strongly determined by the average length of the segment between the sticker groups. Only when the loading is increased such that the incoming chains are forced to adopt more extended loop and tail conformations does the trans content increase. At the highest high loadings, the adsorbed copolymers, which consists of extended loops and tails as well as polymer that is not directly adsorbed to the metal oxide surface, appear to be bulklike in terms of the chain conformation, mobility, and morphology. The majority of the polymer chains are no longer subjected to the perturbation caused by the surface.

Mobility of the Adsorbed Copolymers. Recent experimental work shows that polymer chain mobility may be greatly altered near a surface or interface.[27] If the chain mobility at the polymer surface is different than in the bulk, there are consequences for adhesion, friction, fracture, and other properties relevant to the performance of a polymer coating or an adhesive layer. For example, the welding of two glassy polymers would be affected by a lower glass transition temperature at the surface which would lead to more chain entanglements and thus better adhesion than expected for a polymer below its bulk T_g.[27b] The exact meaning of the “surface mobility” must be considered in relation to its effect on the polymer properties. A recent theoretical study of the surface and interior mobility of a polyethylene thin film found an enhanced mobility on a local segmental level at the surface but a diminished diffusivity in the direction normal to the surface.[28] In the case of supported films, the mobility maybe enhanced or restricted, depending on the film thickness and the nature of the interaction of the polymer with the solid surface.[4,27a]

In the case of adsorbed PEA copolymers, the polyethylene segments become more conformationally disordered and apparently more mobile upon adsorption due to the random binding of the sticker groups to the surface which increases the available free volume between chains. However, it is important to note that an increased free volume alone will narrow NMR lines without an increase in mobility. Packing and mobility are often correlated, but when adsorbed on a surface, the polymer chains might be rigid, yet loosely packed. A reduction of the interchain dipolar interactions due to low surface coverages will lead to reduced line widths. Wide-line proton NMR studies of polyethylene inclusion compounds show that the proton line width of a rigid isolated polyethylene chain is approximately 30% smaller than that of chains located in the rigid crystalline regions of bulk polyethylene.[29] The transoid component of the adsorbed 5% PEA at low loadings showed a reduced line width of 37 kHz as compared to the line width of 57 kHz for chains located in the crystalline domains of the bulk copolymer. The proton line widths of the gauchoid components in both adsorbed copolymers, ~20 kHz, are similar to the amorphous regions of the bulk copolymers. If the reduced proton line widths are primarily due to enhanced mobility, this behavior contrasts sharply with that observed in a solid-state ^{13}C NMR study of physisorbed polyethylene. Inoue and coworkers compared the conformation and dynamic behavior of ^{13}C-labeled polyethylene samples that were solution-crystallized, melt-quenched, and adsorbed on silica gel.[24] Although the polyethylene adsorbed on silica gel had the largest mobile component at 30 ppm, the methylene chain motion of this component was found to be much more restricted than the chains in the noncrystalline regions of both the melt-quenched and solution-crystallized bulk polyethylene. The authors suggested that two components with different molecular motions were present. First, there are directly adsorbed chains with mostly trans and some gauche conformations (16:1) which are frozen on the NMR time scale, and second, there is adsorbed polyethylene not in direct contact with the surface which is undergoing rapid transitions between trans and gauche conformations, similar to the amorphous regions of bulk polyethylene. However, this motion is more restricted than that of the amorphous regions of bulk state. The difference in the motional behavior of the adsorbed polyethylene copolymer vs the homopolymer, as described above, is due to the disordering effect of the sticker binding. ^{13}C NMR relaxation studies of the adsorbed PEA copolymers are currently underway for a more definitive characterization of the relative mobilities.

Chain Conformation of Adsorbed Copolymers. There has been relatively little work, either theoretically or experimentally, concerning the role of the chain conformation on the fracture energy of polymer films on solid surfaces. Experimental work shows the existence of an optimal sticker concentration which gives a maximum in the fracture energy. Below this optimal sticker concentration, the fracture energy increases with sticker concentration. Above this maximum, an increasing sticker concentration decreases the fracture energy due to cohesive failure.[6] In regards to the relation of chain conformation to this behavior, Gutman and Chakraborty argued that a sticker concentration higher than optimal leads to the formation of a flat polymer layer, giving rise to a second diffuse interface between the near-surface chains and those further away from the solid surface.[7a] They propose that the locus of failure is at this second interface. On the basis of experimental work, Brogly and co-workers have recently proposed a model for the adhesion of ethylene vinyl acetate copolymers to alumina in which the chain conformation plays a role.[30] Vibrational studies to determine the orientation of the functional groups were combined with molecular dynamics simulations to obtain the polymer conformation in the adsorbed state. The proposed adsorption mechanism consists of a balance between a high probability to establish interfacial interaction (at low sticker group content) and a low probability for the chain to change in conformation in order to interact (at high sticker group content).[30d] This picture also leads to an optimal sticker concentration for maximum adhesion.

Poly(ethylene-*co*-acrylic acid) is commonly used as an adhesion promoter for polyethylene coatings on metal and paper surfaces. Simmons and Chakraborty have theoretically investigated the use of random heteropolymers as adhesion promoters between a homopolymer melt and a solid surface.[7b] The conformation of the random heteropolymer as a function of coverage and fraction of adsorbed segments was examined. At low coverages of the heteropolymer, the optimal parameters for adhesion combine a relatively high adsorbed fraction with long loops extending away from the surface to promote entanglements with the bulk homopolymer. At higher coverages, a separate random heteropolymer phase may develop depending on the segment−surface and segment−segment interaction strengths, creating the potential to fail at either the solid−polymer (adhesive failure) or polymer−polymer interface (cohesive failure).

Since adhesion studies of PEA laminates as a function of acrylic acid content have been reported mostly for alumina surfaces,[5] we cannot directly compare our results with these studies or the theoretical studies described above. The stronger binding of carboxylic acids on zirconia or zirconium alkoxide treated surfaces as compared to alumina[8] may influence the average chain conformation. The adhesion of PEA films to alumina increases with both acrylic acid content and crystallinity.[5a] Our spin diffusion and WISE NMR measurements show that for thick layers of PEA on ZrO_2 the morphology and crystallinity are similar to the bulk copolymers. The maximum adhesion of high-density polyethylene (HDPE) to alumina/PEA laminates was found when high molecular weight PEA with a medium acrylic acid content (∼13 wt %) was used for the adhesion layer. However, for low-density polyethylene (LDPE), high molecular weight, low acrylic acid content PEA layers (∼3 wt %) performed better.[5a] Whether there is any correlation between these adhesion measurements and the chain conformation and sticker attachment as measured by NMR and FTIR, respectively, would require a similar study of PEA adsorbed on alumina. Previous FTIR studies of the interaction of PEA with alumina have employed solution cast films.[5b,c] However, direct comparisons between hot pressed laminates vs solution cast films may not be valid.[5b]

In summary, the influence of the acrylic acid content on the conformation and mobility of chemisorbed ethylene−acrylic acid random copolymers was studied by solid-state NMR and FTIR photoacoustic spectroscopies. The chain conformation of the adsorbed random copolymer is most strongly influenced by the acrylic acid content rather than the coverage. These studies will be extended to alumina to determine the influence of the metal oxide substrate on the chain conformation and to examine whether correlations with adhesive properties exist. Relaxation measurements and variable temperature experiments are currently underway to further explore the dynamic properties of these adsorbed copolymers.

Acknowledgment. Support for this research was provided by the Natural Sciences and Engineering Research Council (NSERC) and an FCAR equipe grant. The authors thank Professor Thomas Ellis and Craig Hyett of the Université de Montreal for access to the FTIR-PAS spectrometer. We also thank Dr. Fred Morin for useful discussions.

References and Notes

(1) (a) Fleer, G. J.; Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993. (b) Wool, R. P. *Polymer Interfaces: Structure and Strength*; Hanser/Gardner: New York, 1995. (c) Jones, R. A. L.; Richards, R. W. *Polymers at Surfaces and Interfaces*; Cambridge University Press: Cambridge, 1999.

(2) (a) Cosgrove, T.; Barnett, K. G. *J. Magn. Reson.* **1981**, *43*, 15. (b) Cosgrove, T.; Griffiths, P. C. *Adv. Colloid Interface Sci.* **1992**, *42*, 175.

(3) Schimdt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: New York, 1994.

(4) (a) Lin, W. Y.; Blum, F. D. *Macromolecules* **1998**, *31*, 4135. (b) Blum, F. *Annu. Rep. NMR Spectrosc.* **1994**, *28*, 277. (c) Blum, F. D. *Colloids Surf.* **1990**, *45*, 361.

(5) (a) Smarook, W. H.; Bonotto, S. *Polym. Eng. Sci.* **1968**, *8*, 41. (b) Ulren, L.; Hjertberg, T.; Ishida, H. *J. Adhes.* **1990**, *31*, 117. (c) Stralin, A.; Hjertberg, T. *Surf. Interface Anal.* **1993**, *20*, 337. (d) Guezenoc, H.; Segui, Y.; Thery, S.; Asfardjani, K. *J. Adhes. Sci. Technol.* **1993**, *7*, 953. (e) Lee, J. H.; Kim, H. W.; Pak, P. K.; Lee, H. B. *J. Polym. Sci., Part A* **1994**, *32*, 1569. (f) Brack, H. P.; Risen, W. M. *J. Mater. Chem.* **1997**, *7*, 2355. (g) Cho, C. K.; Cho, K.; Park, C. E. *J. Adhes. Sci. Technol.* **1997**, *11*, 433. (h) McEnvoy, R. L.; Krause, S.; Wu, P. *Polymer* **1998**, *39*, 5223.

(6) (a) Gong, L.; Friend, A. D.; Wool, R. P. *Macromolecules* **1998**, *31*, 3709. (b) Lee, I.; Wool, R. P. *Macromolecules* **2000**, *33*, 2680.

(7) (a) Gutman, L.; Chakraborty, A. K. *J. Chem. Phys.* **1994**, *101*, 10074. (b) Simmons, E. R.; Chakraborty, A. K. *J. Chem. Phys.* **1998**, *109*, 8667.

(8) (a) Aronoff, Y. G.; Chen, B.; Lu, G.; Seto, C.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 259. (b) VanderKam, S. K.; Bocarsly, A. B.; Schwartz, J. *Chem. Mater.* **1998**, *10*, 685.

(9) Pawsey, S.; Yach, K.; Halla, J.; Reven, L. *Langmuir* **2000**, *16*, 3294.

(10) (a) Zumbulyadis, N. *Phys. Rev. B* **1986**, *33*, 6495. (b) Tekely, P. *Macromolecules* **1993**, *26*, 7363. (c) Claus, J.; Schmidt-Rohr, K.; Adam, A.; Boeffel, C.; Spiess, H. W. *Macromolecules* **1992**, *25*, 5208. (d) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.

(11) Egger, N.; Schmidt-Rohr, K.; Blümich, B.; Domke, W. D.; Stapp, B. *J. Appl. Polym. Sci.* **1992**, *44*, 289.

(12) Goldman, M.; Shen, L. *Phys. Rev.* **1966**, *144*, 321.

(13) Tonelli, E. *NMR Spectroscopy and Polymer Microstructure*; VCH Publ.: New York, 1989.

(14) (a) Otocka, E. P.; Kwei, T. K. *Macromolecules* **1968**, *1*, 244. (b) MacKnight, W. J.; Taggart, W. P.; McKenna, L. *J. Polym. Sci. Symp.* **1974**, *46*, 83.

(15) Blümich, B. *Adv. Mater.* **1991**, *3*, 237.

(16) Claus, J.; Schimdt-Rohr, K.; Spiess, H. W. *Acta Polym.* **1993**, *44*, l.

(17) Cai, W. Z.; Schimdt-Rohr, K.; Egger, N.; Gerharz, B.; Spiess, H. W. *Polymer* **1993**, *34*, 267.

(18) Landfester, K.; Boeffel, C.; Lambla, M.; Spiess, H. W. *Macromolecules* **1996**, *29*, 5972.

(19) (a) Mellinger, F.; Wilhelm, M.; Spiess, H. W. *Macromolecules* **1999**, *32*, 4686. (b) Demco, D. E.; Johansson, A.; Tegenfeldt, J. *Solid State NMR* **1995**, *4*, 13.

(20) Hu, W. G.; Schmidt-Rohr, K. *Polymer* **2000**, *41*, 2979.

(21) De Paul, S. M.; Zwanziger, J. W.; Ulrich, R.; Wiesner, U.; Spiess, H. W. *J. Am. Chem. Soc.* **1999**, *121*, 5727.

(22) Chin, Y. H.; Kaplan, S. *Magn. Reson. Chem.* **1994** *32*, S53.

(23) Landfester, K.; Boeffel, C.; Lambla, M.; Spiess, H. W. *Macromolecules* **1996**, *29*, 5972.

(24) (a) Inoue, D.; Kurosu, H.; Chen, Q.; Ando, I. *Acta Polym.* **1995**, *46*, 420. (b) Yamanobe, T. In *Solid State NMR of Polymers;* Ando, I., Asakura, T., Eds.; Elsevier: Amsterdam, 1998.

(25) Wegmann, J.; Albert, K.; Pursch, M.; Sander, L. C. *Anal. Chem.* **2001**, *73*, 1814.

(26) Allara, D. L.; Atre, S. V.; Elliger, C. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1852.

(27) (a) Jones, R. A. L. *Curr. Opin. Colloid Interface* **1999**, *4*, 153. (b) Jones, R. A. L.; Richards, R. W. *Polymers at Surfaces and Interfaces*; Cambridge University Press: Cambridge, 1999; pp 50−4.

(28) Doruker, P.; Mattice, W. L. *Macromolecules* **1999**, *32*, 194.

(29) Hori, Y.; Tanigawa, T.; Shimada, S.; Kashiwabara, H. *Polym. J.* **1981**, *13*, 293.

(30) (a) Brogly, M.; Nardin, M.; Schultz, J. *J. Adhes.* **1996**, *58*, 263. (b) Brogly, M.; Bistac, S.; Schultz, J. *Macromolecules* **1998**, *31*, 3967. (c) Brogly, M.; Bistac, S.; Schultz, J. *Macromol. Symp.* **1999**, *141*, 129. (d) Broglie, M. *Rev. Metall./Cah. Inf. Technol.* **2001**, *98*, 75.

MA010833P