Molecular Mobilities of Poly(*N*-alkylacrylamide) Resins As Studied by Solid-State ^{13}C–^{1}H Dipolar Dephasing NMR

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ABSTRACT: The molecular mobilities of poly(*N*-alkylacrylamide)s, prepared by the reactions of porous, lightly cross-linked beads of poly(methyl acrylate) (PMA) with mono-, di-, and trifunctional amines, were studied by measuring the NMR dipolar dephasing decay constant, T_{DD}. Fast segmental motion was observed for the side chains of poly(*N*-*n*-hexylacrylamide), while cross-linking caused the motion of the backbone to be relatively slow. By comparison, the motion of the side chains of poly(((thiophene-2-ylmethyl)amino)-glycidyl methacrylate) appeared to be sterically hindered by the presence of the bulky terminal thiophene-yl ring. For poly(*N*-(6-amino-*n*-hexyl)acrylamide) two types of side chains were detected: those with a terminal amino group exhibited the normal fast motion while others forming interchain cross-links had a slower motion. In contrast, the mobility of the side chains of poly(*N*-(2-(bis(2-aminoethyl)amino)ethyl)acrylamide), a product of PMA functionalized by reaction with the trifunctional tris(2-aminoethyl)amine, was highly restricted by the additional extra side chain cross-linking that accompanied the functionalization reaction and, to a lesser degree, the inter/intramolecular hydrogen-bond formation.

Introduction

Due to their academic and industrial importance, poly(*N*-alkylacrylamide)s and their copolymers have received considerable attention in recent years.[1–6] These polyacrylamides exhibit some unusual rheological properties that depend on the length of the pendent groups, their hydrophobicity, and the method by which the pendent groups are attached.[1] Because of the range of properties that can be realized, poly(*N*-alkylacrylamide)s have found applications as solid supports for peptide syntheses[4] and other chemical reactions as well as clinically for drug carriers and in drug delivery systems, among other uses.[6]

Research in this laboratory has shown that ammonium-bearing poly(*N*-alkylacrylamide) resins, obtained by functionalizing porous cross-linked poly(methyl acrylate) beads by reactions with various multifunctional amines, have potential use as bile salt binding agents for lowering blood cholesterol levels.[7–9] It is well-known that the molecular structure of polymeric resins plays an important role in such binding processes.[10] Systematic studies[7] of the binding of bilirubin by polyacrylamide resins showed that not only the hydrophobicity but also the length of the *N*-alkyl groups affects the binding characteristics. While the isotherms for the sorption of bilirubin by sorbents with long *N*-alkyl side chains, i.e., C_{10}, exhibited the conventional Langmuir shape, binding by those with shorter *N*-alkyl groups, i.e., C_2 or C_3, manifested a so-called "S-shape", indicative of positive cooperativity. Thus, indications are that hydrophobic interactions have an important role in the binding.

It seems likely that, in addition, the mobility of the *N*-alkyl side chain groups will be of importance in the binding. An increase in the flexibility should facilitate accessibility of the sorbate to the functional groups. In this regard, a particular concern is that the multifunctional amines used in the functionalization reactions can form additional intramolecular cross-links with a concomitant decrease in functionality and swellability of the resin. A previous kinetic study demonstrated that the increase in cross-linking restricted the diffusion of amine molecules within the polymer beads.[11] It was these considerations that prompted this investigation of the mobility of the polyacrylamide *N*-alkyl pendent groups.

NMR has long been employed to study molecular motion and has been applied extensively to the complex dynamics problems presented by macromolecules.[12] A large number of NMR parameters, including the strength of heteronuclear dipolar interactions, are sensitive to molecular motions.[13] The reduction in the strength of the dipolar interaction by molecular motions can be a measure of the amplitude of motions of frequency comparable to or greater than that of the dipolar interaction.

The intensity of ^{13}C–^{1}H dipolar interaction can be measured by a variety of NMR methods. For example, in a study of the molecular motions in polycarbonates, Schaefer and co-workers[14] derived the dipolar coupling between carbons and directly attached protons by dipolar rotational spin-echo ^{13}C NMR. The intensity of dipolar interaction can also be deduced from the rise of ^{13}C magnetization in cross-polarization experiments[15,16] and by ^{13}C–^{1}H dipolar dephasing NMR, a technique that is widely used for distinguishing carbon atoms in chemical structure determinations.[17–20] Although the latter method has been relatively less explored as a means of studying the molecular motions of polymers in the solid state, it has great potential.[21,22] This paper reports the use of ^{13}C–^{1}H dipolar dephasing NMR for the study, at room temperature, of the molecular motions of poly(*N*-alkylacrylamide)s prepared by the functionalization of cross-linked poly(methyl acrylate) beads by reactions with mono-, di-, and trifunctional amines.

Experimental Section

Materials. Porous, lightly cross-linked beads of poly(methyl acrylate) (PMA) were synthesized according to procedures described in detail elsewhere.[7] The reaction of PMA beads with *n*-hexylamine (Eastman) at 125 °C for 48 h was used to prepare poly(*N*-*n*-hexylacrylamide) (PMA–HAN). Poly(*N*-(6-amino-*n*-hexyl)acrylamide) (PMA–DNH) was prepared by the analogous reaction with 1,6-diaminohexane (Aldrich) at 130 °C for 24 h, and poly(*N*-(2-(bis(2-aminoethyl)amino)ethyl)acrylamide) (PMA–TREN) was obtained by the reaction with tris(2-aminoethyl)amine (TREN) (Aldrich) at 125 °C for 12 h.

Cross-linked beads of poly(glycidyl methacrylate), G5, were prepared by suspension polymerization, as described by Svec and co-workers,[23] using 39.0 g of glycidyl methacrylate (Aldrich)

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and 2.1 g (5 wt %) of bis(ethylene methacrylate) (Aldrich) mixed with 0.41 g of AIBN in 41 g of an inert phase consisting of dodecanol (10%) and cyclohexanol. The organic phase was suspended, by vigorous stirring, in a 1% aqueous solution of poly(vinylpyrrolidone) (MW = 360 000, Aldrich). The polymerization was performed under N_2 at 70 °C for 3 h, followed by a period of at least 8 h at 80 °C. Remaining soluble components were removed by repeatedly decanting with water and alcohol. The G5 was functionalized by the reaction with 2-(aminomethyl)-thiophene in DMF at 80 °C for 2 days to produce G5-NCS, poly(((thiophene-2-ylmethyl)amino)glycidyl methacrylate).

In every case the functionalized beads were washed with large amounts of deionized water, extracted with methanol in a Soxhlet extractor overnight and dried *in vacuo* at 40 °C for at least two days prior to study.

NMR Spectroscopy. Dipolar Dephasing (DDph). The samples were packed into a bullet-type zirconia rotor and spun at a speed of ca. 3 kHz. DDph experiments were performed with a Chemagnetics M-100 NMR spectrometer operating at a frequency of 25.1 MHz using a pulse sequence first proposed by Alla and Lippmaa.[17] As described by Alemany and co-workers,[20] in this pulse sequence a 90° proton pulse is followed by a 90° phase shift in the proton rf field so as to create the lock before the carbon rf field, whose magnitude satisfies the Hartmann–Hahn condition, and is applied for a contact time t_{cp}. Then both rf fields are turned off for a variable time, τ, during which the dipolar interactions between the carbons and protons induce the rapid dephasing of the carbon signal. Halfway through the τ period a 180° refocusing pulse is inserted along the spin-lock coordinate to remove linear phase distortions and to refocus long-term isotropic and anisotropic chemical shift spin order. Finally, carbon data acquisition is performed while the proton decoupler is on. A contact time of 1 ms, with a pulse delay of 3 s, yielded the optimum intensity ratios for the aromatic to aliphatic carbon signals of hexamethylbenzene. A 1K data file was zero filled to 2K before FT. The chemical shifts were referenced to TMS by setting the methyl resonance of hexamethylbenzene (HMB) at 17.4 ppm.

Direct Polarization with MAS (DP/MAS). To obtain the spectra of the mobile molecules, conventional one pulse ^{1}H NMR, i.e., direct polarization (DP), was also performed with two-level proton decoupling under MAS with a Chemagnetics CMX-300 NMR spectrometer. A pulse width of 4.3 μs was used with a pulse delay of 3 s between two successive pulse sequences.

Results and Discussion

T_{DD} and Molecular Motion. The DDph experiment is similar to a conventional cross-polarization (CP) experiment except for the introduction of a delay time, τ, before the application of the abundant spin, ^{1}H, decoupling pulse.[17,24,25] It is used to measure the rate at which a polarized carbon loses its magnetization upon termination of the proton locking.[20]

During the dipolar dephasing time period, τ, two interactions appear to dominate the time development of the ^{1}H spins:[19] (1) the evolution of the rare spin, ^{13}C, under its off-resonance and isotropic shielding Hamiltonians and (2) the heteronuclear dipolar coupling between ^{13}C and ^{1}H nuclei. Assuming that the MAS speeds are sufficiently rapid to average all shielding tensors to their isotropic values (which is generally the case for macromolecules in the solid state), the first interaction will result only in the introduction of a linear phase error for the entire spectrum. The intensity of the second interaction, $\langle b \rangle$, which has an r_{CH}^{-6} dependence, can be described by[13]

$$\langle b \rangle = \frac{4}{5}(\gamma_C \gamma_H \hbar^2 / r_{CH}^3)^2 \qquad (1)$$

where r_{CH} is the carbon–proton distance and γ_C and γ_H are the gyromagnetic ratios of ^{13}C and ^{1}H, respectively. Thus, the second interaction manifests itself as a dipolar dephasing time, τ, dependent attenuation for each type of spin. As a result, during the dephasing time the amplitude of the resonance of each spin decreases with a characteristic decay constant, T_{DD}, which depends on the strength of the dipolar interaction, the number of neighboring abundant ^{1}H spins, internal molecular motions, MAS rotation speeds, and spin diffusion. Unlike the effect of the first interaction, each particular spin type is affected differently by the second interaction and exhibits a characteristic decay constant, T_{DD}. Since the static heteronuclear interaction can be averaged through internal molecular motions, the derived values of T_{DD} can be a quantitative measure of the internal molecular motions of the nuclei.

For molecules in a rigid lattice, dephasing due to strong dipolar coupling is most rapid for carbons having directly bonded protons, such as CH and CH_2. On the other hand, although methyl carbons have three directly attached protons, they usually experience only a moderate degree of C–H dipolar coupling because the rapid rotational motion tends to attenuate the dipole–dipole interaction. Since the effective dipolar interaction with neighboring groups is only small, nonprotonated carbons remain phase coherent for longer times.

Derivation of T_{DD} Values. Before the first rotational echo the intensities for carbons weakly coupled to protons follow a first-order exponential law, or Lorentzian shape, represented by

$$I = I_{(l)0} \exp(-\tau / T_{DD}) \qquad (2)$$

where $I_{(l)0}$ is the signal intensity at zero dipolar dephasing time. The slope of the plot of the logarithm of the peak intensity as a function of dipolar dephasing time τ gives T_{DD}. However, when the carbons are strongly coupled to protons, the signal decay frequently is modulated by the strong ^{13}C–^{1}H dipolar coupling, and in the short time limit the overall decay of the signal is better described by a second-order equation,[19,20] or Gaussian shape, as

$$I = I_{(g)0} \exp(\tau^2 / 2T_{DD}^2) \qquad (3)$$

where $I_{(g)0}$ is the initial intensity, at $\tau = 0$, of the second-order component. Hence, the slope of the plot of the logarithm of the peak intensity as a function of τ^2 gives T_{DD}. The experimental uncertainty in the T_{DD} values obtained by these methods is estimated to be ~5%.

The experimental data are often composed of a combination of first- and second-order components so that the observed intensity, I, is given by the summation of the signal intensities from the various carbon types in the sample, according to

$$I = \sum_i I_{(l)0}{}^i \exp(-\tau / T_{(l)DD}{}^{(i)}) + \sum_j I_{(g)0}{}^j \exp(-\tau^2 / (2T_{(g)DD}{}^{2(j)})) \qquad (4)$$

where i and j refer to the components with first- and second-order decay, respectively. In this case, the T_{DD} values can be obtained by a deconvolution approach or by a plotting procedure. For example, when the experimental decay is simply a combination of one Gaussian and one Lorentzian component, the latter can be extracted by performing a linear least squares fit to the slow decay and extrapolating the calculated intensities to zero delay time. These calculated intensities are subtracted from the corresponding observed values and then replotted as a function of τ^2 to obtain the T_{DD} of the second-order decay. Details of these methods will be presented in the text as needed.

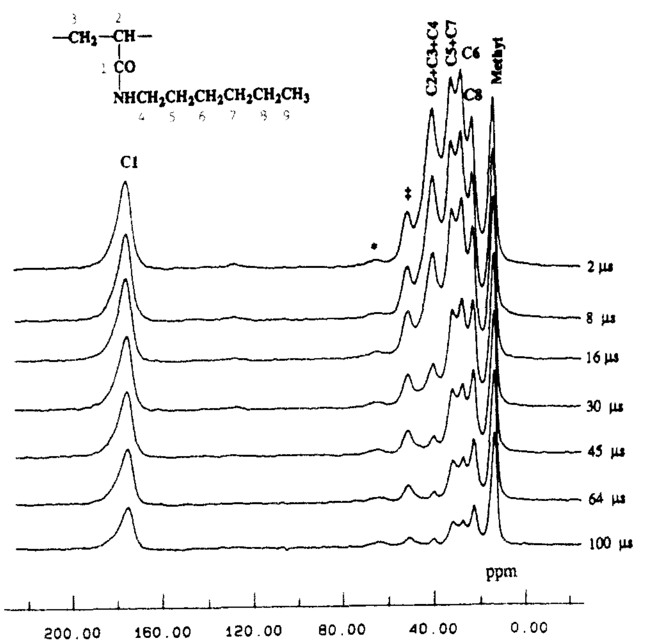

Figure 1. Selected ^{13}C CP/MAS spectra of PMA-HAN obtained with various dipolar dephasing times, as indicated on the spectra. The spinning sideband is labeled by * and the resonance corresponding to unreacted methoxy groups is marked by ‡.

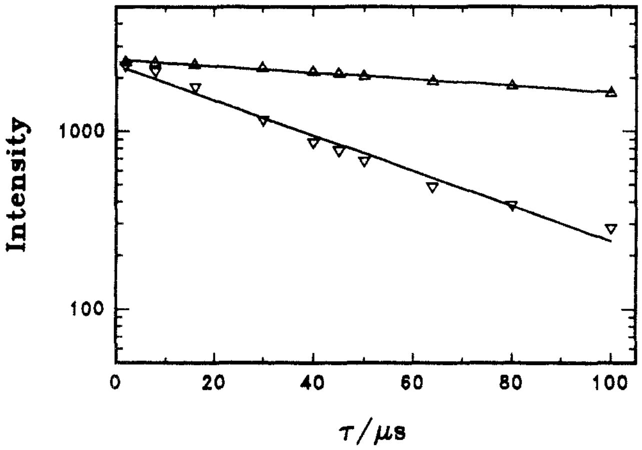

Figure 2. Plots of ln I as a function of dipolar dephasing time, τ, for various carbons of PMA-HAN (C9 (△); C5 + C7 (▽)).

Poly(*N*-*n*-hexylacrylamide) (PMA-HAN). A stack plot of the solid-state NMR spectra of PMA-HAN obtained by the dipolar dephasing experiment with various τ values is given in Figure 1. The plots of ln I as a function of τ, based on eq 2, show linear relationships for all of the peaks (Figures 2 and 3) except for the one assigned to carbons C2 and C3, i.e., the backbone CH and CH$_2$ groups, respectively, which also overlaps with the peak for the side chain C4 carbon. Separate T_{DD} values for this composite peak were obtained by use of deconvolution methods, with a combination of one Gaussian component and one Lorentzian (based on eq 4), that yielded two values, 18 and 77 μs, assigned to carbons C2 + C3 and C4, respectively. The T_{DD} values obtained for the various carbon species of poly(*N*-*n*-hexylacrylamide) are summarized in Table I.

Due to the cross-linking, the backbone of PMA-HAN is relatively rigid and the ^{13}C–^{1}H dipolar interactions remain sufficiently strong so that, in the absence of a proton locking field, the magnetization of the CH and CH$_2$ signals dephase rapidly by destructive interference,[20] yielding a short T_{DD} (18 μs). The large value of T_{DD} (129 μs) obtained for the carbonyl carbon is expected because it has no directly bonded protons. Since the ^{13}C–^{1}H dipolar interaction has an r_{CH}^{-6} dependence (eq 1), coupling of the carbonyl carbon with the nearest protons on adjacent carbons ($r > 2.0$ Å) is much smaller than for those carbons directly bonded to protons ($r \approx 1.1$ Å). Consequently, after the heteronuclear decoupling pulse is turned off, the carbonyl carbon retains its phase coherence for longer times, yielding a large value for its T_{DD}.

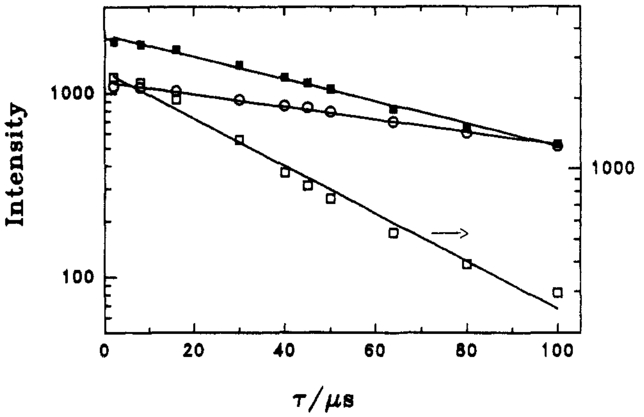

Figure 3. Plots of ln I as a function of dipolar dephasing time, τ, for various carbons of PMA-HAN (C1 (○); C6 (□); C8 (■)).

Although three protons are directly attached to the terminal methyl of the side chain *N*-hexyl group (C9), at room temperature the methyl group rotates freely about its C$_3$ axis and, hence, experiences less dipole–dipole interactions than other proton-bonded carbons.[26] Nevertheless, the derived T_{DD} value (235 μs) for this methyl is much larger than the normal value (50–125 μs) in the solid state.[27] Thus, it is unlikely that this reduction results from the rotational motion alone; some other motional mechanism must be operative. Since macromolecules in the solid-state cannot experience an overall tumbling motion, this attenuation of the strength of the dipolar interactions must reflect some form of segmental motions. This is supported by the fact that the T_{DD} values of all of the methylene groups of the side chain (Table I) are more than twice that for the CH$_2$ of the polymer backbone and by the progressive increase in T_{DD} values, hence weaker dipolar interactions, along the side chain carbons. The failure of the T_{DD} value of C4 (77 μs) to follow this order is probably a reflection of fact that one of the neighboring atoms is a nitrogen to which only one proton is attached.

These results demonstrate that the dipolar dephasing method can be used effectively in the characterization of such segmental motions, known to have correlation frequencies of the order of 10 kHz.[28]

Poly(((thiophene-2-ylmethyl)amino)glycidyl methacrylate) (G5–NCS). A stack plot of DDph CP/MAS ^{13}C NMR spectra with peak assignments for the G5–NCS sample is shown in Figure 4. As expected, the plots of ln I as a function of τ for the quaternary carbons (C1 and C8) both showed good fit to eq 2, yielding T_{DD} values of 159 and 163 μs, respectively. The marginally larger T_{DD} value of C1 relative to that for PMA-HAN probably reflects differences in the extent of cross-linking. For the CH$_2$ and CH groups corresponding to C9 + C10 + C11, C4 + C5, and C6 + C7, linearity was achieved only with plots of ln I as a function of τ^2 (Figure 5), which yielded T_{DD} values of 25, 16, and 14 μs, respectively. Derivation of the T_{DD} values for the peak corresponding to C2 + C3, which overlaps with the resonance of a CH$_2$ (C3) group, with a strong dipolar interaction, and a quaternary carbon (C2), without directly bonded hydrogens, required the use of eq 4 and yielded two T_{DD} values, 20 and 118 μs.

Table I. Dipolar Dephasing Decay Time Constants, T_{DD} (μs), Where the Values in the Parentheses Were Obtained by Deconvolution Methods Based on Eq 4

resins	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	methyl
PMA–HAN	130	18	18	(77)	42	43	42	67	235	235
G5–CNS	159	(118)	(20)	16	16	14	14	163	25[a]	60
PMA–DNH	178	(18)	(18)			(14, 20, 34)			(16,49)	n/a
PMA–TREN	carbonyl;[b] 126, 92, 40				methylene and methine: 16					

[a] Value for the peak of C9 + C10 + C11. [b] In the order from the downfield to upfield peaks.

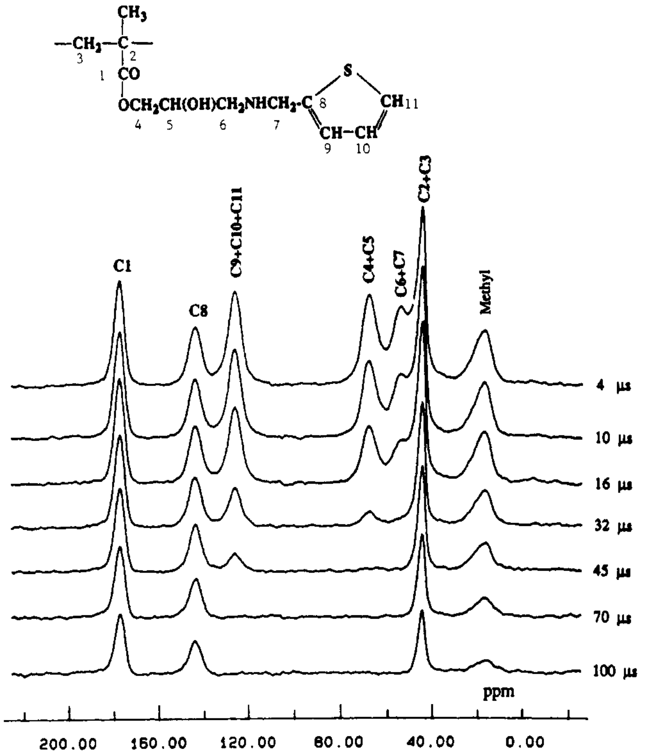

Figure 4. Selected ^{13}C CP/MAS NMR spectra of G5–CNS obtained with various dipolar dephasing times.

Somewhat unexpectedly, a less satisfactory linear relationship was found for the plot of ln *I* as a function of τ for the methyl group (Figure 6). Apparently, some methyl groups undergo a second-order decay in this case, indicating that some of the methyl groups in the polymeric beads may experience a hindered rotation. On the other hand, this may reflect the fact that the resonance of the methyl groups is very sensitive to their tacticity.[29]

It is of interest to notice that the T_{DD} values for the carbons of the side chain of G5–CNS, except those for the thiophene-yl ring, are shorter than those for the corresponding carbons of the PMA–HAN side chain, suggesting that it is less mobile. The polymer matrix apparently hinders the motions of the thiophene-yl group, which is certainly bulkier and heavier than the methyl group. Since the T_{DD} values for C9, C10, and C11 of the thiophene-yl ring (25 μs) are longer than that for a conventional rigid tertiary carbon (<20 μs), the ring must be undergoing some form of motion. For example, it may be a random oscillatory motion of the thiophene-yl ring along the C7–C8 σ bond, which is known to lie in the general frequency range of tens of hertz[30] and hence does not reduce dipolar interaction very effectively.

Poly(*N*-(*n*-6-aminohexyl)acrylamide) (PMA–DNH). A stack plot of selected NMR spectra of PMA–DNH is shown in Figure 7. For the peaks assigned to the carbonyl resonance (C1) the plot of the logarithm of the intensities as a function of the dipolar dephasing time, τ, gave a linear relationship, yielding a T_{DD} value of 178 μs, i.e., somewhat larger than the corresponding value for PMA–HAN.

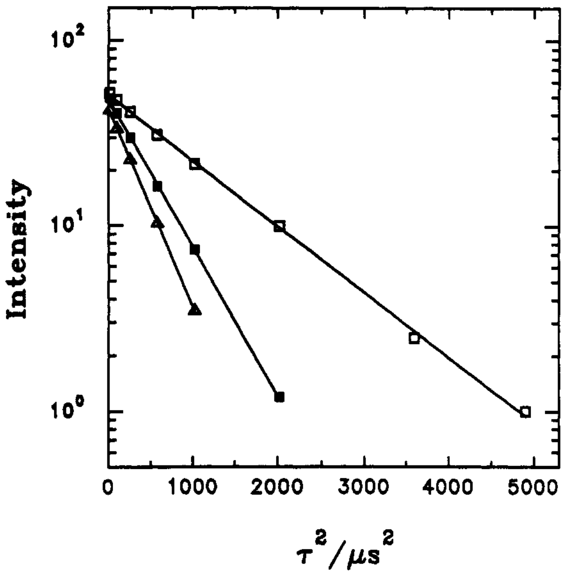

Figure 5. Plots of ln *I* as a function of τ^2 for the various carbons of resin G5–CNS (C10 + C11 + C12 (□); C5 + C6 (▲); C7 + C8 (■)).

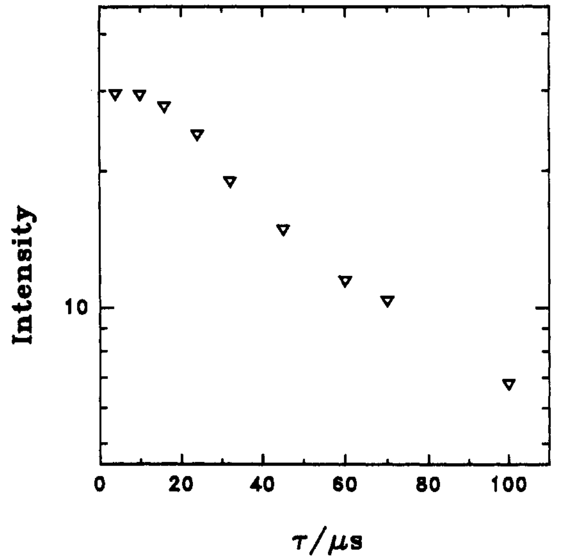

Figure 6. ln *I* of the methyl group of resin G5–CNS as a function of dipolar dephasing time, τ, showing the nonlinearity at short τ's.

Due to severe overlap of the methylene and methine resonances in the range of 25–45 ppm, the T_{DD} values of the various individual carbons could not be derived by direct methods. In fact, the Lorentzian-type decay exists for the peak at ~27 ppm, assigned to carbons C5–C8, because as τ is as long as 80 μs, the intensity of the resonance can still be noticed. In order to obtain the T_{DD} value of the Lorentzian-type decay, a plot of the logarithm intensity as a function of dipolar dephasing time with $\tau \geq 45$ μs[31] showed linearity, and the slope of this line yields a T_{DD} value of 34 μs. When this value was used in eq 4 by a curve-fitting routine, it was found that the best fit to the data, as shown in Figure 8, occurred when two Gaussian-

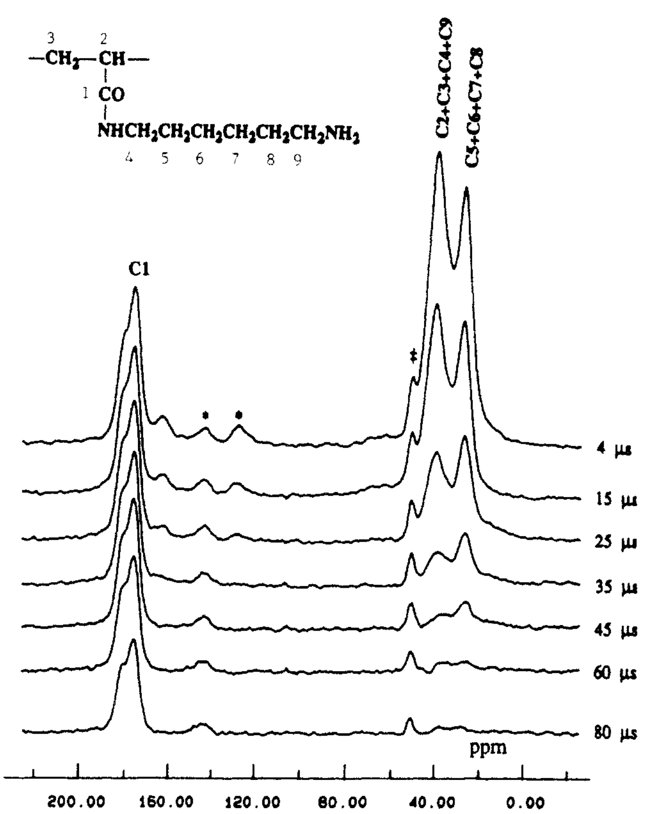

Figure 7. Selected ^{13}C CP/MAS with dipolar dephasing spectra of PMA–DNH. The resonances of the cross-linking agent, divinylbenzene, are labeled by * and those of the unreacted methoxy groups by ‡.

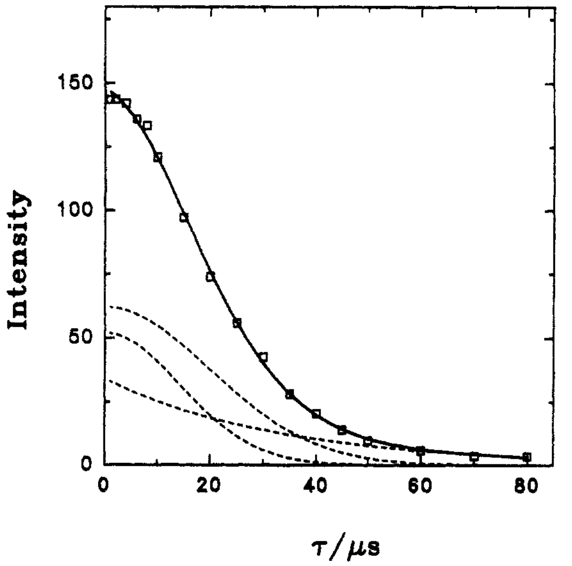

Figure 8. Curve fitting results for the C5 + C6 + C7 + C8 peak in the spectra of PMA–DNH (experimental data (□); components (- - -); the fit (—)).

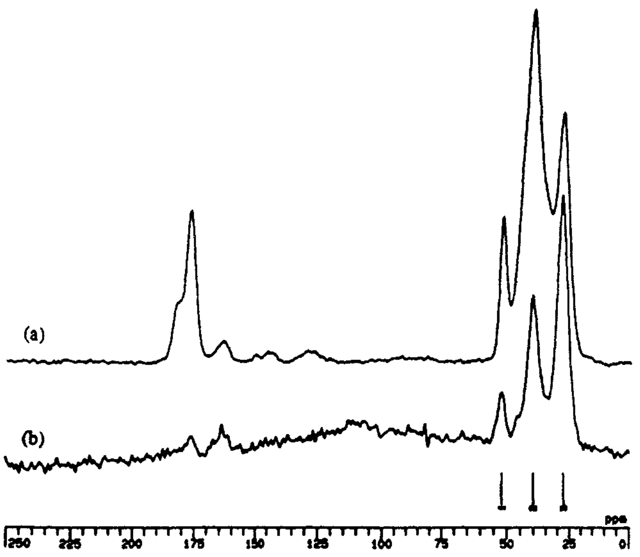

Figure 9. NMR spectra of poly(*N*-(6-aminohexyl)acrylamide) obtained by (a) CP/MAS with 512 transients and (b) DP/MAS with 256 transients.

type decays were used. This yielded two second-order decay constants (14 and 20 μs) given in Table I. A similar procedure was followed for the peak at ~40 ppm (assigned to carbons C2, C3, C4, and C9). In this case, assuming that the T_{DD} values of the backbone carbons remain the same as those for PMA–HAN that was prepared from the same PMA beads, the T_{DD} values thus obtained are reported in Table I.

As expected, the T_{DD} values for carbons C5–C8 of the side chain are longer than for those of the backbone, in keeping with greater segmental mobility. The occurrence for PMA–DNH of two types of the side chain motion, as evidenced by the additional short T_{DD}, is consistent with the presence of two kinds of pendent groups. As shown previously,[11] in addition to the desired functionalization product having the amino group at the end of the side chain, in the reaction of PMA with the difunctional amine, DNH, some of the DNH reacts so that both amino groups are attached to the backbone. Obviously, the mobility of the former side chains is greater than that of those that act as cross-links.

A DP/MAS experiment reveals considerable mobility of the side chains of PMA–DNH in the solid state. A solid-state NMR spectrum obtained by DP/MAS is actually like that obtained for samples in solution since this experiment detects signals for the mobile carbons only, i.e., those having short $T_1(^{13}C)$ values. Without cross-polarization transfer no signal will be detected for rigid carbons in the solid state[32] due to the extremely large T_1 values. The major differences between the ordinary CP/MAS spectrum (Figure 9a) and the DP/MAS spectrum (Figure 9b) are the absence of the resonance of the carbonyl group, at 176 ppm, and the attenuation of the peak at ~40 ppm. Because of the cross-linking, the backbone is rigid, so the T_1 values of carbons in the backbone are too large to permit polarization of the nuclei without cross-polarization transfer. The intensity of the resonance of carbons in the backbone is thus greatly attenuated, and only those carbons which are in the mobile side chains will be observed. On the other hand, the intensities of the resonances of the side chain methylene carbons (~27 ppm) remain relatively unchanged, which confirms that most of the side chains are sufficiently mobile to permit spin–lattice relaxation that is sufficiently efficient to reduce the T_1 values.

Poly(*N*-(2-(bis(2-aminoethyl)amino)ethyl)acrylamide) (PMA–TREN). The DDph experiments confirmed, as expected, that intramolecular cross-linking is even more pronounced in the reaction of PMA with the trifunctional molecule, tris(2-aminoethyl)amine (TREN), to prepare PMA–TREN, than in the preparation of PMA–DNH. As shown in Table I, for the methylene and methine groups the T_{DD} values of the main chain carbons are similar to those for the side chain, ca. 15 μs. This short T_{DD} value indicates that the $^{13}C-^{1}H$ dipolar coupling is strong and dominates the relaxation process, suggesting that in some way the mobility of the side chains is strongly restricted. Because of the overlap of the NMR peaks (Figure 10), the

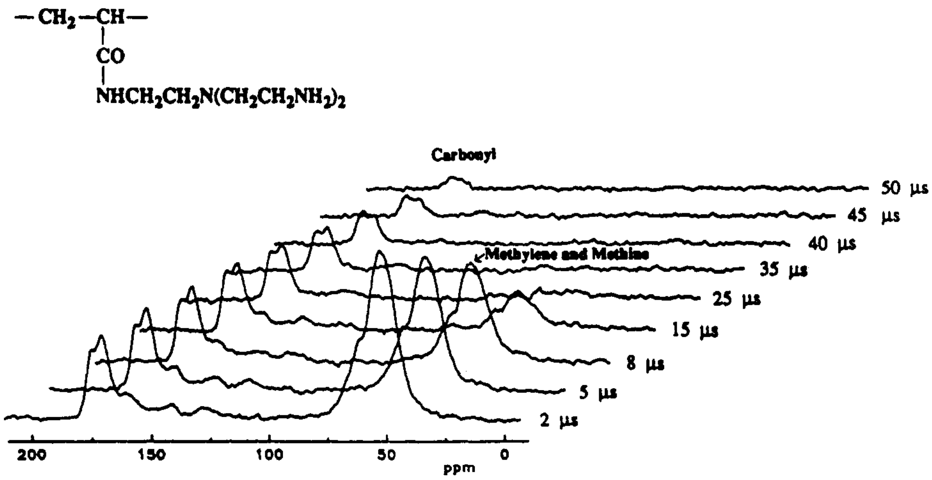

Figure 10. Selected ^{13}C NMR spectra for PMA–TREN obtained with CP/MAS using dipolar dephasing that show the fast decay in the methylene and methine resonances.

T_{DD} values of the individual carbon nuclei could not be determined.

Such restricted side chain mobility is inconsistent with a previous report that acid/base titrations of PMA–TREN, prepared by similar methods, showed a functionality of 6.4 mmol of free amino groups/g of dry polymer.[7] While this is significantly less than the 15.0 mmol/g (ignoring the cross-linking agent) expected if no additional cross-linking accompanied the reaction, if *each* added TREN molecule formed a cross-link the theoretical maximum functionality would be 3.9 mmols of TREN/g of polymer, or 7.8 mmol of free amino groups/g (of which 3.9 mmol is the central tertiary amino group which does not undergo functionalization reaction with PMA). Obviously, most of the TREN molecules are incorporated either as cross-links, with at least two of the three primary amino groups attached to the backbone, or attached in an intramolecular manner.

The evidence for hindrance of the mobility of the side chains, indicated by T_{DD} data, requires some interaction of the free amino groups. For example, they can form physical cross-links by hydrogen-bonding. This is supported by the observation that the fitting of the carbonyl resonances of PMA–TREN yielded three T_{DD} values, 126, 92, and 40 μs, in the downfield to upfield order, respectively. The unusually short T_{DD} value (40 μs) for a carbonyl group, that has no directly bonded hydrogen, requires efficient dipolar dephasing such as would result from the formation of hydrogen bonds. The dipole–dipole interactions (which are proportional to r_{CH}^{-6}) between the carbonyl carbon and its nearest proton(s) are stronger. Consequently, the carbon magnetization will dephase faster, yielding shorter T_{DD} values.

Conclusion

The results demonstrate that a detailed picture of the segmental motions of poly(*N*-alkylacrylamide)s, prepared by functionalization reactions of poly(methyl acrylate) (PMA) with mono-, di-, and trifunctional amines, can be obtained by application of the NMR techniques which yield characteristic dipolar dephasing decay times, T_{DD}. These methods will undoubtedly find utility in the study of a wide range of other polymeric systems.

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