Interpolymer Complexation of Poly(acrylic acid) and Poly(acrylamide): Structural and Dynamic Studies by Solution- and Solid-State NMR

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ABSTRACT: Interpolymeric complexes of poly(acrylic acid) (PAA) and poly(acrylamide) (PAAm) at 60, 20, 5, and 0% ionization (α) were studied by 1H/13C solution-state and 13C solid-state cross-polarization magic angle spinning (CPMAS) NMR experiments. The solid-state NMR results support a model in which ionization (α or PD) alteration leads to conformation and segment changes along the PAA–PAAm polymeric backbone. Solid-state relaxation measurements show short $T_1$ values at high ionization ($α = 60\%$) but long $T_1$ values toward low ionization ($α \leq 20\%$). This is consistent with a model in which the PAA and PAAm polymers take on a stretched but mobile conformation at high ionization but become immobile and restricted at low ionization. Dynamic restriction of the polymer is attributed to symbiotic hydrogen bonding of the carboxyl group of PAA and the amide residue of PAAm to form interpolymer complexes. Other relaxation parameters such as $1H$–$13C$ cross-polarization times $T_{CP}(SL)$, proton spin–lattice relaxation times in the rotating frame $T_{1H}(H)$, and $13C$ dipolar-dephasing results are also consistent with this model.

I. Introduction

Understanding the structure and dynamics of inter-macromolecular complexes is of interest because of the occurrence of such structures in many systems of biological importance.1,2 The mechanism of complexation is an important prerequisite in predicting the microscopic structure and, through structure correlations, the macroscopic properties of these biopolymeric materials. Non-covalent binding forces derived from electrostatic, hydrogen bonding, and hydrophobic interactions have been attributed to be the main driving force for complexation of biopolymers.3–7 Investigations of the dynamics and structural characterization of the these materials may provide insight into the macromolecular organization, which, in turn, may reflect the infrastructure and dynamics of the complexation mechanism at a molecular level.

Interpolymer complexation between poly(ethylene oxide) and poly(acrylic acid) has been characterized previously by NMR techniques,9 although only the polymer blend of poly(acrylic acid)–poly(acrylamide) (PAA–PAAm) has been studied by this technique.9,10 Interpolymer complexation between PAA and PAAm has previously been characterized by fluorescence measurements using pyrene-labeled PAAm (py-PAAm) fluorescence probes.11,12 The results were interpreted in terms of the occurrence of weak or negligible interactions for PAA and py-PAAm at pH ≥ 7.0 and the occurrence of strong stable complexes at pH ≤ 4.5 (shown in Scheme 1). This report describes the investigation by NMR spectroscopy of intermolecular complexes of PAA and PAAm for various degrees of ionization of PAA in a comparative manner. The modes of binding interactions, i.e., complexation of the carboxylic and amide residues, are monitored by NMR relaxation parameters. Although only qualitative, the results of this study provide complementary but otherwise independent evidence on the cooperative binding nature of PAA–PAAm as reported previously by fluorescence techniques.11,12

NMR relaxation techniques were used to monitor motions in the mid-kilohertz and megahertz frequency range, which may provide clues on the impact strength of these materials.13–16 The main mechanism for $13C$ spin-lattice relaxation is due to $1H$–$13C$ dipole–dipole interactions, with smaller contributions arising from chemical shift anisotropy and spin rotation.17 For low molecular weight polymers in the solution state, the spectral density offers a correlation time ($\tau_c$) in the motional narrowing limit. In this limit, $\omega \ll 1/\tau_c$, $T_1$ is inversely proportional to $\tau_c$ and is field independent. In the solid state, however, the spectral density yields $\omega^2 T_2 < 1$, and $T_1$ is directly proportional to $\tau_c$ and is field dependent.17,18 An indication of fast segment mobility, as it relates to the correlation times for these polymers, is therefore expected to yield large $T_1$s in the solution state but small $T_1$s in the solid state.19,20 In our experiments, NMR spectra were measured by a fast inversion–recovery pulse sequence, and

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the $T_1$ parameters were calculated by fitting the data to eq 1.

$$M(t) = M_1 \left[1 - \left(2 - \exp \left(\frac{-t}{T_1}\right)\right)\right] \left[\exp \left(-\frac{t}{T_1}\right)\right]$$

(1)

$M(t)$ is the peak intensity as a function of time $t$, $M_1$ is the normalization constant, $\Delta$ is the delay time, and $T_1$ is the spin–lattice relaxation time.17-21

Two other relaxation techniques used here are (1) the variable spin-lock contact time experiment and (2) the dipolar-dephasing experiment.13-15,18-20,22-24 For (1), a varied contact time was added to the basic CPMAS pulse sequence. The results were fitted to eq 2.

$$M(t) = \frac{M_1}{1 - \left(\frac{T_{CH}}{T_{1p(H)}}\right)^{\alpha}} \exp \left(-\frac{t}{T_{1p(H)}}\right) \left[\exp \left(-\frac{t}{T_{CH}}\right)\right]$$

(2)

$M(t)$ is the signal intensity as a function of contact time $t$, $M_1$ is the normalization constant, $T_{CH(SL)}$ is the cross-polarization time constant during the spin-lock period, and $T_{1p(H)}$ is the proton spin–lattice relaxation time in the rotating frame.22-24 The former relaxation parameter probes the static H–C dipolar interaction, whereas the latter monitors the rates of proton spin diffusion.

In the dipolar-dephasing experiment, (2), a time delay is inserted in the carbon channel of the CPMAS experiment after the $^1$H–$^{13}$C spin-lock period.14,20,25 The integrity of the signals after this period probes both the direct C–H dipolar coupling for a given $^{13}$C resonance and the diminution of this dipolar coupling due to segment dynamics. The parameters derived from these measurements can be interpreted in terms of the molecular motion of the polymer chains as a function of variables such as pH or ionization.

II. Experimental Section

A. Materials. Poly(acrylic acid) purchased from Polysciences was used without further purification with a manufacturer-specified molecular weight of $M_a = 90,000$.

The poly(acrylamide) sample was kindly supplied by American Cyanamid and had a number-average molecular weight, $M_n$, of 120,000. The polymer was purified by reprecipitating from aqueous solution using acetone as a nonsolvent.

B. Preparation. (1) Solution-State NMR Studies. Polymer samples were prepared by dissolving dried polymers in $D_2O$. Solution spectra were taken at ambient temperature (20 ± 2 °C) with chemical shifts referenced to TMS.

(2) Solid-State NMR Studies. Polymer solutions were prepared in triple-distilled water. Poly(acrylic acid) (PAA) was neutralized to various extents by adding a predetermined volume of standard sodium hydroxide solution. Equimolar (monomer mole) solutions of poly(acrylamide) and poly(acrylic acid) were mixed for about 24 h and subsequently freeze-dried to remove water completely. Solutions of poly(acrylic acid) neutralized to various extents were also freeze-dried.

Seven samples were prepared for the solid-state NMR studies: (1) PAAm, neutral; (2) PAA, degree of ionization ($\alpha$) = 60%; (3) PAA, $\alpha$ = 0%; (4) PAA–PAAm, $\alpha$ = 60%; (5) PAA–PAM, $\alpha$ = 20%; (6) PAA–PAAm, $\alpha$ = 5%; (7) PAA–PAAm, $\alpha$ = 0%. The PDs of the samples before freeze-drying were 7.0, 4.75, 3.85, and 3.5 for $\alpha$ = 60, 20, 5, and 0%, respectively.

C. Instrumentation. Solution- and solid-state NMR measurements were acquired by a Bruker AF-260 FT-NMR spectrometer, and the spectra were recorded on an HP 5890A digital plotter. Detailed experimental conditions are described in a previous report.26

D. Solid-State NMR. Each sample (ca. 250 mg) described above was packed in a 7-mm-o.d. sapphire (Al2O3) rotor with Kel-F end caps (Doty Scientific). The high-power preamplifier for the CPMAS experiment was provided by IBM instruments, and the probe was designed by Doty Scientific. Carbon-13 cross-polarization magic angle spinning with high-power heteronuclear decoupling, ca. 40 kHz, was used to obtain high-resolution NMR spectra. The dipolar-dephasing, pulse sequence experiment provided proton-decoupled carbon resonance assignments. In this experiment, a 50-µs dephasing period was used. The CPMAS experiment consisted of matching the Hartmann–Hahn condition ($\gamma_B H_0 = (\gamma_B)H_0$), contact times of 1500–2000 µs, a pulse width for $^1$H of 5.8 µs, and recycled delays between 2 and 5 s (6 s for $^{13}$C $T_1$ measurements). Spinning rates were between 3 and 5 kHz, and chemical shifts were referenced to the methyl carbon of external hexamethylbenzene (Me, $\delta = 16.7$ ppm vs TMS). All measurements were taken at ambient temperature (20 °C).

III. Results and Discussion

A. Solution-State NMR. In the literature, tacticity analyses have been made for polyacrylates based on $^1$H and $^{13}$C-NMR results.27-33 For our experimental conditions (20 °C), only triad sensitivity could be observed at best. Figure 1, shows the $^1$H NMR spectra of (a) PAAm in $D_2O$ under neutral conditions, (b) PAA at $pD = 3.5$, (c) PAA at $pD = 7.0$, (d) PAA–PAAm at $pD = 3.5$, and (e) PAA–PAAm at $pD = 7.0$. These spectra all show a Pd dependence with significant resonance line broadening (line width, $W_{1/2} > 40$ Hz). Despite the occurrence of line broadening, resonance assignments are readily made based on the integrated area of the signals by literature comparison27,28,31,34,35 or by computer simulation analysis.36-41 For PAAm in $D_2O$ (Figure 1a), the broad resonance centered at 2.08 ppm is assigned to the $\alpha$-protons and the resonance at 1.53 ppm is assigned to the $\beta$-protons of the monomer unit, which are consistent with the 1:2 integration. The tacticity of PAAm has previously been assigned as a mixture of isotactic and syndiotactic species based on $^1$H NMR methods.28 Our result is not consistent with this but representative of a more complicated microstructure which will be discussed in the context of the $^{13}$C NMR result.

The $^1$H NMR spectrum for PAA at $pD = 3.5$ (Figure 1b) shows a more complicated resonance pattern with four distinct resonances centered at $\delta = 2.26, 1.80, 1.63,$ and 1.52 ppm; weaker signals are observed at 2.65, 1.97, and 1.50 ppm. The three resonances between 1.50 and 1.80 ppm are assigned to the $\beta$-protons, and the 2.26 ppm resonance is assigned to the $\alpha$-proton. Previous tacticity analysis of PAA at $pH = 2$ is consistent with our result here in which the triad distribution of the $rr$, $mr$, and $mm$ sequences is assigned to the methylene resonances at 1.80, 1.63, and 1.52 ppm, respectively.27,28 At $pD = 7.0$, the PAA $^1$H NMR spectrum shows two broad resonances centered at 1.96 ($\alpha$-proton) and 1.39 ppm ($\beta$-protons),
Figure 1. $^1$H (a–e, left) and $^{13}$C (a’–e’, right) solution-state NMR spectra in D$_2$O vs TMS for (a) PAAm, (b) PAA at pD = 3.5, (c) PAA at pD = 7.0, (d) PAA–PAAm at pD = 3.5, and (e) PAA–PAAm at pD = 7.0.

Figure IC. Tacticity assignment based on the $^1$H NMR results is difficult at this point because of the poor resolution of the signals. The sharp signal at 2.10 ppm is assigned to adventitious acetone.

A mixture of PAA and PAAm at pD = 3.5 (Figure 1d) shows a $^1$H NMR spectrum similar to that of the PAA $^1$H NMR spectrum at pD = 3.5 (Figure 1b). Proton resonances from the spectrum in Figure 1d indicate a downfield shift of the resonance at 2.26–2.31 ppm but otherwise minor differences in the chemical shifts of the other signals at 2.11, 1.83, 1.67, and 1.60 (shoulder) ppm. This $^1$H NMR spectrum can be characterized as the sum of $^1$H signals from the $^1$H NMR spectra of PAA at pD = 3.5 (Figure 1b) and PAAm (Figure 1a). Tacticity assignment based on the methylene resonances is similar to those of PAA–PAAm at pD = 3.5.42 In comparison, the $^1$H NMR spectrum for PAA–PAAm at pD = 7.0 (Figure 1e) shows broad structureless resonances at higher field (8.2/1.0 ca. 50 Hz): δ = 2.08 and 1.54/1.44 ppm. The $^1$H assignments are analogous to the other assignments; the upfield resonances are assigned to the $\alpha$-protons, and the downfield resonances are assigned to the $\beta$-protons. The chemical shifts are listed in Table 1.

The corresponding $^{13}$C NMR spectra under various ionization conditions are shown in Figure 1a’–e’. The chemical shifts are given in Table 1. The NMR spectrum for PAAm in D$_2$O shows six resonances centered at 187.4 (C=O); 36.3, 34.3 (C$_a$); and 30.0, 28.1, 26.3 ppm (C$_g$) (Figure 1a’). Based on the carbonyl resonances, our PAAm sample is consistent with a homopolymer (<5% hydrolysis).30,31 The methine, C$_a$, resonances show only two signals, short of the triad sensitivity reported by Lancaster which was obtained at 70 °C.50 The methylene resonances, C$_g$, are more diagnostic of triad sensitivity, however, with the 30.0 and 26.3 ppm signals assigned to the $rr$ and $mm$ configurations, respectively, and the 28.1 ppm signal assigned to the heterotactic ($rm + mr$) configuration.31,35 We make no attempts here to computer simulate these spectra to quantify the tacticity of the structure.

For PAA at pD = 3.5 (Figure 1b’) the $^{13}$C NMR spectrum shows carbon resonances at 182.4 (C=O); 45.2 (C$_a$); and 38.5, 37.9 ppm (C$_g$). Under less acidic conditions, pD = 7.0, the resonances broaden and shift downfield to 188.2 (C=O); 49.6, 49.0 (C$_a$); and 42.3, 40.6 (C$_g$) (Figure 1e’). Analysis of PAA by Chang consists of minimal fine structure at low pH.27 Furthermore, Schaefer analysis of PAA consists of a syndio-, hetero-, and isotactic sequence at high pH but mostly isotactic sequence at low pH.32 A pure Bernoullian atactic sequence for PAA has been suggested by Truong, which is more consistent with our results.30

The PAA–PAAm spectrum at pD = 3.5 (Figure 1d’) shows carbon resonances at 183.5, 182.7 (C=O); 45.5 (C$_a$); and 38.0, 38.1 ppm (C$_g$). At pD = 7.0 (Figure 1e’) the $^{13}$C

| Table 1. $^1$H and $^{13}$C Chemical Shifts and Carbon-13 Spin-Lattice Relaxation Times ($T_1$) for PAAm, PAA, and PAA–PAAm Mixture at Various Ionizations (pD) vs TMS |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | PAAm | PAA | PAA–PAAm | PAA–PAAm |
|                 | pD = 3.5 | pD = 7.0 | pD = 3.5 | pD = 7.0 |
| C=O (ppm)       | 187.4 | 182.4 | 188.2 | 183.5 | 187.8 |
| $^{13}$C $T_1$ (s) | 2.8 | 2.2 | 1.4 | 1.8 | 1.4 |
| $H_a$ (ppm)     | 2.08 | 2.26 | 1.96 | 2.31 | 2.08 |
| $C_a$ (ppm)     | 36.3 | 45.2 | 49.6 | 45.5 | 49.8 |
| $C_g$ (ppm)     | 34.3 | 48.9 | 49.1 | 48.3 | 45.8 |
| $^{13}$C $T_1$ (s) | 0.2 | 0.3 | 0.2 | 0.2 | 0.2 |
| $H_b$ (ppm)     | 1.53 | 1.80 | 1.39 | 1.83 | 1.64 |
| $C_b$ (ppm)     | 30.0 | 38.5 | 42.3 | 38.0 | 41.8 |
| $^{13}$C $T_1$ (s) | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 |
NMR spectrum for the PAAm–PAA polymeric mixture shows a more complicated chemical shift pattern. Resonances are observed at 187.8, 186.8, 183.1 (C=O); 49.8, 49.1, 48.3, 45.8 (Cα); and 41.8, 40.0 ppm (Cβ). Essentially, the two carbonyls from PAA and PAAm are observed in this spectrum, whereas at lower pD, only the carbonyl from PAA is resolved, with the splitting of this resonance indicative of complexation between the carboxylic group of PAA and the amide group of PAAm.

The 13C T1; spin-lattice relaxation times are listed in Table 1; measurements could not be obtained for PAAm in D2O, owing to the excessive number of accumulations needed to obtain adequate signal-to-noise. The T1; values for the carbonyl resonances for PAA at pD = 3.5 and pD = 7.0 (2.8 and 2.2 s, respectively) do not indicate any significant changes. This same trend (T1; of 1.4 and 1.8/1.4 s, respectively) is observed for the carbonyl resonance of PAA–PAAm at pD = 3.5 and pD = 7.0. The relaxation times for the carbon atoms of the aliphatic backbone show a similar behavior in which the T1; s do not show any significant variation with pD changes.

Relaxation pathways for polymeric samples may be linked to a number of intermolecular processes: the interactive process of polymer complexation, a chain self-coiling mechanism, a pH effect on ionity, residual H2O, and/or segment conformational perturbation. The trend-free T1; relaxation results in Table 1 suggest that segment mobility is just one of many other mechanisms for relaxation in the solution state. Our results were not conclusive since these values show only minor deviation with little connection between long correlation times (short T1; s) and restricted mobility at low pD. These effects must be deconvoluted to arrive at any conclusion about mobility and relaxation time in the solution state.

We make no attempts here, however, to quantify these contributions. Finally, the inconclusive result in solution-state studies of this work compared to that of the fluorescence work may be attributed to the difference in experimental conditions. The luminescence studies used dilute concentrations of the polymer, whereas the NMR solution-state measurements required higher concentrations to produce acceptable signal-to-noise. These and other differences in experimental conditions may have resulted in relaxation measurements more representative of ionization effects and concentration factors rather than conformation and mobility.

B. Solid-State NMR. The 13C CPMAS and dipolar-dephasing (DD) spectra for samples of PAAm, PAA (α = 0, 60%), and PAA–PAAm (α = 0, 5, 20, 60%) are shown in Figure 2, with spectra a–g corresponding to the CPMAS spectra and spectra a’–g’ corresponding to the dipolar-dephasing spectra. In general, the alkyl resonances, Cα and Cg, are broad and difficult to resolve. Based on the 13C NMR assignment above and assignments of other polyacrylates in solution and in the solid state, the intense signal downfield is assigned to the Cα resonance, with the shoulder upfield assigned to the Cg resonances. Chemical shifts are listed in Table 2 together with the spin–lattice relaxation times, T1;.

The 13C CPMAS spectrum for PAAm under neutral conditions (Figure 2a), shows four resonances with the following assignments: C=O, 180 ppm; Cα, 51/42 ppm; and Cg, 37 ppm (shoulder).

Under dipolar dephasing, the broad resonance centered at 42 ppm is suppressed, while the resonances at 180 and 51 ppm are affected only slightly.

Spectra 2b, b’ and c, c’ show the CPMAS and DD spectra for PAA at α = 0 and 60% and are consistent with the CPMAS spectra obtained by Fyfe. The dipolar-dephas-
Carbon-13 CPMAS NMR Chemical Shifts and Relaxation Times $T_1$, $T_{CH(SL)}$, and $T_b(H)$ for PAAm, PAA, and PAA–PAAm Polymers at Various Ionizations ($\alpha$) vs External Hexamethylbenzene (Me$_6$, $\delta$ = 16.7 ppm)

<table>
<thead>
<tr>
<th></th>
<th>PAAm $\alpha = 0%$</th>
<th>PAAm $\alpha = 60%$</th>
<th>PAA–PAAm $\alpha = 0%$</th>
<th>PAA–PAAm $\alpha = 5%$</th>
<th>PAA–PAAm $\alpha = 20%$</th>
<th>PAA–PAAm $\alpha = 60%$</th>
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<tr>
<td>C=O (ppm)</td>
<td>180</td>
<td>177</td>
<td>186</td>
<td>178</td>
<td>178</td>
<td>181</td>
</tr>
<tr>
<td>$T_1$ (s)</td>
<td>37</td>
<td>18</td>
<td>13</td>
<td>44</td>
<td>37</td>
<td>33</td>
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<tr>
<td>$T_{CH(SL)}$ (\mu s)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1406</td>
<td>932</td>
<td>1485</td>
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<tr>
<td>$T_b(H)$ (ms)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.9</td>
<td>2.6</td>
<td>1.5</td>
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<tr>
<td>$C_\alpha$ (ppm)</td>
<td>51</td>
<td>40</td>
<td>45</td>
<td>40</td>
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<td>41</td>
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<tr>
<td>$T_1$ (s)</td>
<td>42</td>
<td>34</td>
<td>23–21</td>
<td>14–8</td>
<td>58</td>
<td>36</td>
</tr>
<tr>
<td>$T_{CH(SL)}$ (\mu s)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>98</td>
<td>104</td>
<td>124</td>
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<td>$T_b(H)$ (ms)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
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<td>$C_\beta$ (ppm)</td>
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<td>34</td>
<td>40</td>
<td>34</td>
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<td>34</td>
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<td>$T_1$ (s)</td>
<td>31</td>
<td>14</td>
<td>6</td>
<td>30</td>
<td>26</td>
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<tr>
<td>$T_{CH(SL)}$ (\mu s)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>85</td>
<td>48</td>
<td>116</td>
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<td>$T_b(H)$ (ms)</td>
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<td>--</td>
<td>5.7</td>
<td>4.2</td>
<td>4.0</td>
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As mentioned earlier, the PAAm CPMAS spectrum shows an anomalous resonance at 51 ppm which persists upon dipolar dephasing. Magnetization survival after a 50-\mu s dipolar-dephasing period is associated with carbons having weak $^1$H–$^{13}$C dipolar coupling because of inefficient polarization transfer, e.g., quaternary carbon, or rapid rotation along the C–H bond.14,20,25 We attribute the perseverance of the resonance of 51 ppm to the latter; i.e., the terminal segments of the PAAm backbone undergo rapid random fluctuation, causing ineffective H–C dipolar coupling.46 With the exception of the PAAm, 51 ppm resonance, all other alkyl resonances are suppressed upon dipolar dephasing, suggesting that the motion involved along the polymeric backbone is not significant enough to diminish the H–C dipolar coupling.

Differences in line broadening and resolution in the CPMAS spectra of PAA at $\alpha = 0$ and 60% may originate from various stages of hydrogen bonding, ionic environment, and/or conformational arrangement as a result of the degree of ionization ($\alpha$). At high ionization, the PAA possesses repulsive Coulombic interactions among the –COO– groups along the polymeric backbone which give rise to resolved $C_\alpha$ and $C_\beta$ resonances.11,12,42 Moreover, ionization in the medium to low range (see Scheme 1) may contribute to different polymeric environments, giving rise to multiple signals, i.e., greater broadening.45 For the PAA–PAAm CPMAS spectra at $\alpha = 0$, 5, and 20%, the line broadening and resonance pattern are similar, in contrast to PAA–PAAm at $\alpha = 60\%$.

The $T_1$ values were determined for polymeric samples at various degrees of ionization. The signal intensities of the $T_1$ stacked plots were fitted to eq 1, and Figure 3 shows a representative curve fit for the $C_\alpha$ resonances of PAA–PAAm at $\alpha = 60$, 20, 5, and 0%; the $T_1$ values are listed in Table 2. Carbon-13 $T_1$ relaxation values for PAAm (Table 2) fall between 31 and 37 s except for the anomalous resonance at 51 ppm, which possesses a $T_1$ of ca. 5 s. Short relaxation times for this resonance are consistent with a PAAm terminal group undergoing rapid fluctuation with correlation times in the order of the Larmor frequency (~60 MHz). $T_1$s for the other resonances in PAAm are longer than those of PAA at $\alpha = 0$ and 60%. The $T_1$s for PAA at $\alpha = 0$% are 18 (177.3 ppm), 21–23 (40 ppm), and 14 s (34 ppm shoulder) and those for $\alpha = 60$% are 13 (186 ppm), 8–14 (45 ppm), and 6 s (40 ppm). It is noted that since the alkyl resonances overlap, the best $T_1$ estimates for $C_\alpha$ and $C_\beta$ are a composite of the $T_1$ values for the overlapping signals. Because of severe line broadening of the signals in the CPMAS spectrum, the $T_1$ values are expected to have error limits of 20%.

For the PAA–PAAm polymeric mixture at $\alpha = 0$, 5, 20, and 60%, the $T_1$ values decrease systematically as ionization increases. For example, at $\alpha = 0\%$, $T_1$s for the C=O, $C_\alpha$, and $C_\beta$ resonances are 44, 58, and 30 s, respectively, while those at $\alpha = 0\%$ are 19/21, 17, and 6 s, respectively; $T_1$ values for PAA–PAAm at $\alpha = 5$ and 20% fall between these two limits.

The spin–lattice relaxation results suggest that the extent of ionization plays an important role in the conformation and motional behavior of the polymer. The $T_1$ results for PAAm show that the carbonyl resonance has a relaxation time similar to that of its $C_\alpha$ and $C_\beta$ resonances (neglecting the 51 ppm resonance). This is consistent with PAAm nondependency on ionization effects. In comparison, the $T_1$ values of PAA at 60 and 0% do show a strong correlation to ionization changes. For example, between 60% and 0% ionization, the carbonyl relaxation time increases by 38% (13 to 18 s), with a similar result for the alkyl resonances. The $T_1$ variation for PAA–PAAm also shows a similar trend with more pronounced differences. A more detailed study would involve decon-
volution of the other relaxation factors by a variable-
temperature study, but, qualitatively, the results discussed
below are sufficient to describe the interpolymer com-
plexation process.

Qualitative analysis of the $T_1$ result for the interpolymer
PAA–PAAm complexes must take into consideration
contributions due to ionization effects and segment
mobility. If the $T_1$ result for the homopolymer PAA is
used as a baseline reference for the contribution due to
ionization effects and other relaxation mechanisms, then
differences between the two systems, homopolymer PAA
and interpolymer complexes PAA–PAAm, should reflect
contributions only due to segment dynamics as a result of
complexation. The $T_1$ results in Table 2 show a large
deviation between the two ionization limits for PAA–
PAAm compared to that of PAA. Qualitatively, all else
being equal, we attribute the increase of $T_1$ at lower
ionization ($\alpha = 0\%$) for the PAA–PAAm system relative
to the homopolymer PAA system to the longer correlation
times associated with the complexation process, thereby
restricting the segment mobility of the interpolymer
complex.$^{14,18}$

Contact times ranging from 50 to 6000 $\mu$s were used for
the variable contact time experiment of PAA–PAAm at
$\alpha = 60, 20, 5, \text{ and } 0\%$. Figure 4 shows a representa-
tive $^{13}$C magnetization buildup and decay for the $C_\beta$
resonances with $T_{\text{CH(SL)}}$ and $T_{1\beta(H)}$ values listed in Table 2. The
results show that maximum magnetization polarization is
approached fastest for $\alpha = 0\%$ and slowest for $\alpha = 60\%$.
Magnetization buildup depends on the strength of the
C–H dipolar interaction, which is also influenced by
molecular mobility between the two dipoles.$^{13-16,18-20,22,48}$
The rapid growth of the $^{13}$C signals, short $T_{\text{CH(SL)}}$, at
lower ionization therefore is diagnostic of the strong C–H
dipolar interaction as a result of restricted mobility, while
the longer $T_{\text{CH(SL)}}$ values at high ionization are consistent
with rapid segment dynamics, resulting in weak C–H
molecular coupling. Thus our relaxation results suggest that
the polymeric chain undergoes rapid contortion at high
ionization ($\alpha = 60\%$), resulting in less efficient cross-
polarization of the abundant $^1$H spins to the rare $^{13}$C spins
but restricted mobility of the chain at lower ionization ($\alpha
= 0\%$), yielding strong H–C dipolar coupling, and efficient
$^1$H to $^{13}$C polarization transfer. This systematic trend for
the $T_{\text{CH(SL)}}$ values under the different ionization
conditions shown in Table 2 is in agreement with the spin–
lattice relaxation result and polymeric model established
by the fluorescence study.

Finally, the $T_{1\beta}(H)$ values for these samples do not show
significant variation for the different ionization conditions,
suggesting that polymeric chain dynamics are not near
the 40-kHz domain of the spin-locking field used in the
experiment and further that the proton spin diffusion has
equilibrated.

IV. Conclusions

The interaction between two polymers, PAA and PAAm,
which undergo complexation has been investigated by
NMR techniques in this report. The following summarizes
the behavior of the interpolymer complexes as reflected
by the NMR results. The average structure of PAAm
does not have any pD dependence as suggested by the
similarities of the $T_1$ values for the different resonances
of PAAm. The average structure of PAA, on the other
hand, is ionization dependent; at high pD or ionization,
it exists in the ionized form which affects the polymeric
backbone in two ways. First, the Coulombic repulsion
tends to stretch the polymer segments, and as a result,
this leads to the second effect, namely, rigidity of the
polymer. We do not observe this in our relaxation results,
however.

As the pD decreases or as $\alpha$ approaches zero, the ionized
form of the carboxyl group becomes protonated. Less
"ionized form" leads to less Coulombic interaction, which
leads to the contraction of the polymeric segments and
increased segment mobility. Our relaxation data suggest
that at 60% ionization we are already in this regime of
increased segment mobility. As the ionization decreases,
H-bonding processes become operative and influential
on the behavior of the polymer segments. At low enough
ionization, the H-bonding network begins to accumulate
due to the contraction of the polymers. Thus the
contracted form now becomes immobile, and a point is
reached in which the contracted form is less mobile than
the extended form which exists at higher ionization. This
picture of restricted mobility of the polymer segment is
consistent with the systematic trend observed in both the
$T_1$ and $T_{\text{CH(SL)}}$ result.

When PAA and PAAm are mixed to form an inter-
polymer complex, there is a parasitic relationship; that is,
PAA dictates the configuration of the complex. At high
pD, the two polymers act independently and there is no
interaction between the two polymers, but at low ioniza-
tion, PAA is deionized and either can intramolecularly
H-bond to itself or can intermolecularly H-bond to PAAm
as reflected in the relaxation results. As the intermolecular
interaction becomes efficient, the PAAm takes on prop-
erties associated with PAA.

For the homopolymer, the $T_1$ result will not only have
contributions from the model discussed above but also
have contributions from other factors such as the pD effect
on ionicity, tactility, and/or residual H$_2$O interaction. We
use the relation results for this system to provide a
reference point for the interpolymer complexation process.
That is, if we compare the relaxation results of the
homopolymer at the two extreme conditions, $\alpha = 60$ and
0%, to that of the interpolymer complexes under these
same conditions, then we can qualitatively assert that the
differences in the $T_1$ results are due to the segment
dynamics of the latter. The results here indicate longer
$T_1$ for the PAA–PAAm system at 0% ionization than that
of PAA homopolymer, which is consistent with a more
effective complexation process of PAA to PAAm. Inter-
pretation of the $T_{\text{CH(SL)}}$ result is consistent with this
model.

In conclusion, the solid-state NMR studies of poly-
(acrylic acid) and poly(acrylamide) at various ionization
support a polymer model in which at low levels of ionization
the PAA–PAAm solutions form an interpolymer complex
resulting in a relatively rigid polymeric mixture exhibiting
slow chain motions. At high levels of ionization, the PAA–PAAm complexes exist as random polymeric chains with rapid segment dynamics. Although the solution-state NMR studies were not conclusive, due to concentration effects or the nature of the H-bond in these materials, the solid-state CPMAS studies are consistent with the model established from fluorescence studies. Moreover, the results here show that interpolymer complexation is very strong in the solid state. Finally, the results demonstrate that CPMAS NMR is a powerful experimental technique for investigation of the effect of interpolymer complexation on segmental motion and macromolecular dynamics in the solid state.

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References and Notes
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