Dynamic Alternation between Inter- and Intra-Polymer Hydrogen Bonds in a Polymer Complex As Studied by Solid-State ^{13}C 2D Exchange NMR

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Received June 24, 1999; Revised Manuscript Received September 29, 1999

ABSTRACT: Solid-state ^{13}C two-dimensional (2D) exchange NMR has been applied to investigate dynamic alternation among three forms of hydrogen bonds in the poly(acrylic acid)/poly(ethylene oxide) (PAA/PEO) complex. The ^{13}C CPMAS NMR spectrum of the signal for the PAA carboxyl carbon in the complex is split into three peaks corresponding to three forms of hydrogen bonds, namely, the complex form, the dimeric form, and the free form. These three peaks coalesce into a single peak at temperatures above 346 K, showing that dynamic alternation of hydrogen bonds occurs in the complex. 2D exchange NMR spectra directly show that the dissociation−association of hydrogen bonds occurs at temperatures above 329 K, which is 7 deg higher than the glass transition temperature (T_g). The exchange rates are on the order of Hz and have a wide distribution. At the same time, it was found that PAA conformational transitions occur at a rate comparable to that of the hydrogen bond alternation. On the other hand, the PEO motion shows no apparent correlation to the hydrogen-bonding dynamics. It is concluded that the hydrogen-bonding dynamics is coupled to the segmental motion of PAA in the complex.

Introduction

For two dissimilar polymers to form a polymer complex, certain inter-polymer interactions such as hydrophobic, Coulomb, dipolar, and hydrogen-bonding interactions should cooperatively work between functional groups of the component polymers.[1] Among these interactions, the hydrogen-bonding interaction has attracted many researchers, and extensive studies on the complex formation primarily in the solution state have been done over the past two decades.[1−7] It was shown that the complex formation by hydrogen bonds is sensitive to temperature, concentration, medium, and chain length of component polymers.[1−5] In particular, the chain-length effect is interesting because it is a special character of a polymer.[3,4] When the chain length is less than a certain critical length, association−dissociation dynamic equilibrium of the inter-polymer hydrogen bonds occurs in the solution state. When the chain length is longer than the critical length, a stable polymer complex is formed by the cooperative inter-polymer hydrogen bonds, and a solid complex material is precipitated. This leads us to envisage that once the cooperative inter-polymer hydrogen bonds are formed, they will not be dissociated.[1,3,4] The macroscopic properties of the complex differ apparently from those of pure polymers.[8,9] For example, Smith et al. compared heat stability of the poly(acrylic acid)/ poly(ethylene oxide) (PAA/PEO) complex with those of pure polymers.[8] They concluded that weight retention of the complex is higher than those of pure polymers. This thermal stability was interpreted in terms of cooperative inter-polymer hydrogen bonds which alter the dynamics and structures of the component polymers.

Recently, Miyoshi et al. investigated the hydrogen-bonding structures of the poly(methacrylic acid) (PMAA)/PEO[10] and PAA/PEO[11] complexes using solid-state ^{13}C NMR. The ^{13}C NMR study showed that two kinds of hydrogen bonds appear in both complexes, namely, the complex form of inter-polymer hydrogen bonds between PAA (PMAA) and PEO and the dimeric form of intra-polymer hydrogen bonds among PAA (PMAA). In the PAA/PEO complex, Miyoshi et al. also found that some free carboxyl carbons exist, which do not participate in hydrogen bonding (the free form). In addition to the existence of the free form in the PAA/PEO complex, there is a salient difference in the temperature dependence of spectra for the two complexes. For the PMAA/PEO complex, an increase in temperature leads to an irreversible change in line shape for the carboxyl carbon. This suggests that irreversible rearrangements of the hydrogen bonds occur at higher temperatures. In contrast, for the PAA/PEO complex, the spectrum is temperature-reversible, showing that a dynamic dissociation−association reaction among the hydrogen bonds occurs. This finding is interesting because it has been considered that hydrogen-bonding alternation in the solid complex is a nonequilibrium one. To date, microscopic studies on the dynamic nature of hydrogen bonds in the complex have not been extensively been completed. It is of interest to extend the study of the PAA/PEO complex by undertaking an investigation on the dynamic aspects of hydrogen bonds using solid-state two-dimensional (2D) exchange NMR spectroscopy. It is demonstrated that the dynamic alternation of the inter- and intra-polymer hydrogen bonds does exist even in the stable solid complex, and its relation to the segmental motion of component polymers is discussed.

Experimental Section

PAA and PEO were purchased from Aldrich Chem. Com. The molecular weight (Mw) of PAA and PEO are 900 000 and 20 000, respectively. PAA and PEO were separately dissolved in aqueous solution at pH = 2.0 (4 wt %) and mixed to 2/1 in monomer unit ratio. The polymer complex precipitated slowly and was collected, washed by water, and dried for 1 day at room temperature. The solid was further dried at 323 K under reduced pressure. The component ratio of the obtained PAA/PEO complex is 1.4/1.0 in monomer unit ratio.[11] The NMR

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10.1021/ma991012b CCC: $18.00

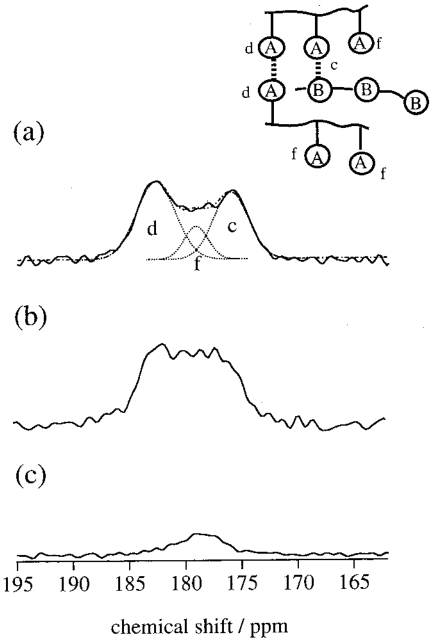


Figure 1. CPMAS NMR spectra for the carboxyl carbon of PAA in the PAA/PEO complex at (a) 303 K, (b) 346 K, and (c) 383 K. The observed line shape at 303 K was fitted to a sum (broken line) of three Gaussian peaks (dottted line), and the peaks are assigned to the dimeric form **d** (183.2 ppm), the free form **f** (179.5 ppm), and the complex form **c** (176.2 ppm) of the carboxyl carbon. The fractional ratios for the **c**, **f**, and **d** forms are 40%, 13%, and 47%, respectively. A schematical representation of three forms of hydrogen bonds in the complex is shown in the inset of Figure 1, where circle A denotes the carboxyl group on PAA and circle B is the oxygen on PEO.

experiment was carried out with a CMX-300 spectrometer operating at 300.3 MHz for ^1H and 75.5 MHz for ^{13}C. High-resolution solid-state ^{13}C NMR spectra were obtained by the combined use of high-power ^1H dipolar decoupling (DD) and magic-angle spinning (MAS). The radio frequency field strength was set to about 50 kHz for both ^1H and ^{13}C. The MAS frequency was set to 5.0 kHz. For the temperature range between 285 and 361 K, the cross-polarization technique (CP) was used with a contact time of 1 ms and a pulse-repetition delay of 6 s. For the temperature range between 361 and 383 K, molecular motion is significant; the conventional 90° pulse method was used at a repetition delay of 10 s, because CP was ineffective. The ^{13}C 2D exchange NMR spectra[12] were taken with 512 data points along t_2 and with 50−140 points of 50 μs along t_1. T_g for the complex was determined to be 323 K by differential scanning calorimetry (Mac Science DSC 3000S) at a heating rate of 5 K/min.

Results and Discussion

Figure 1 shows the carboxyl region of the ^{13}C CPMAS NMR spectrum observed at 303 K for the PAA/PEO complex. The line shape was successfully fitted to a sum of three Gaussian functions as shown in Figure 1. The three peaks for the present PAA-rich complex are less obvious than those for PEO-rich complexes (Figure 3 in ref 11). We used the PAA-rich complex because it gives us stronger PAA signals. These three peaks have been assigned to the different forms of hydrogen bonding, namely, as the dimeric form (**d**), the free form (**f**), and the complex form (**c**).[11] A schematical representation of the three forms is also shown in the inset of Figure 1. At temperatures above 346 K, the signals coalesce into a broad signal (Figure 1b, c). As has been pointed out in ref 11, the line shape change can be explained by motional exchange between the three hydrogen-bonding forms. We applied 2D exchange NMR to further examine the motional exchange. Figure 2 shows 2D exchange NMR spectra for the carboxyl region at three temperatures obtained with a mixing time of 500 ms. At 303 K, only diagonal peaks were observed. At 329 K, three off-diagonal peaks appear between the peaks of **c** and **f**, **d** and **f**, and **c** and **d**. Hereafter, these cross-peaks are referred to as **cf**, **df**, and **cd**, respectively. The intensity of the **cd** peak ($I_{\mathbf{cd}}$) is ca. 10% of that of the diagonal peak **d** ($I_{\mathbf{d}}$). At 338 K, only the **cd** cross-peak is appreciable with a significantly enhanced intensity with respect to the diagonal peak ($I_{\mathbf{cd}}/I_{\mathbf{d}}$ = 40%). These cross-peaks can be ascribed to the exchange among the **c**, **f**, and **d** forms. The **cf** peak arises from dissociation−association process for the inter-polymer hydrogen bonds. The **df** peak indicates that dissociation−association of the intra-PAA hydrogen bonds occurs in the complex. The **cd** exchange peak shows that dynamic alternation between inter- and intra-polymer hydrogen bonds takes place in the complex. These exchanges require the three forms to be in close proximity to each other, and some free space exists to allow such hydrogen-bonding alternation. Indeed, the previous ^1H spin diffusion experiment has shown that the carboxyl groups forming the inter- and intra-polymer hydrogen bonds are homogeneously distributed in the complex, at 2−3 nm.[11] The dynamic alternation further requires molecular motion of the main and side chains in order to absorb the structural deformation originated from hydrogen-bonding alternation. Before we discuss molecular motion associated with hydrogen-bonding alternation, we will examine the hydrogen bonding dynamics at 329 K in more detail.

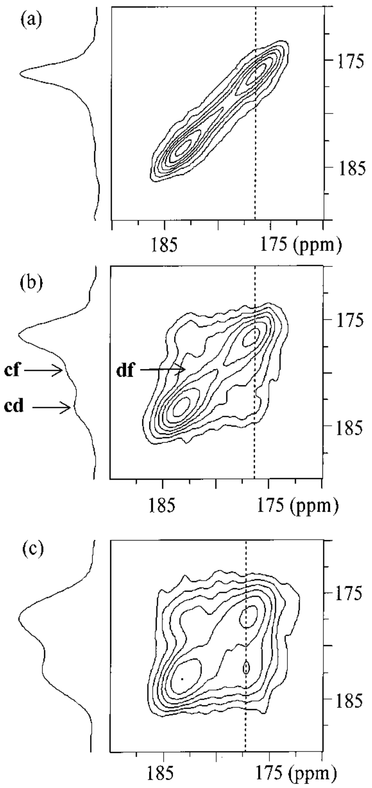


Figure 2. 2D exchange NMR spectra of the carboxyl region of PAA in the PAA/PEO complex at (a) 303 K, (b) 329 K, and (c) 338 K. The mixing time is 500 ms. The cross sections at the dotted lines are also shown. The 8 contour levels are drawn with exponentially spacing between 6 and 50% of the maximum spectral height. In (b), the **cf**, **df**, and **cd** exchange peaks are indicated by arrows.

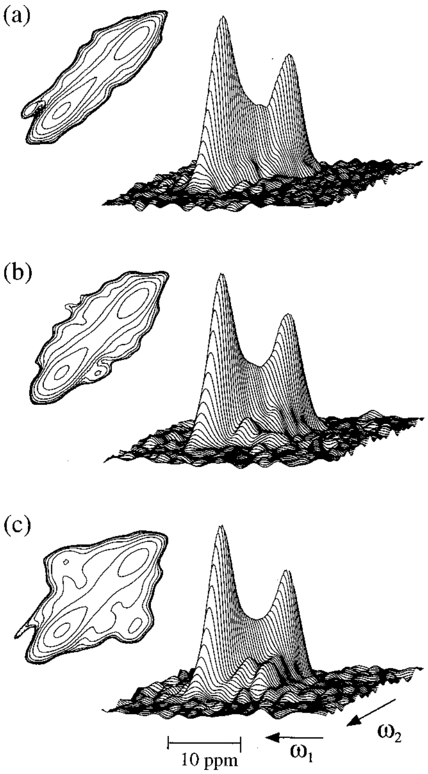
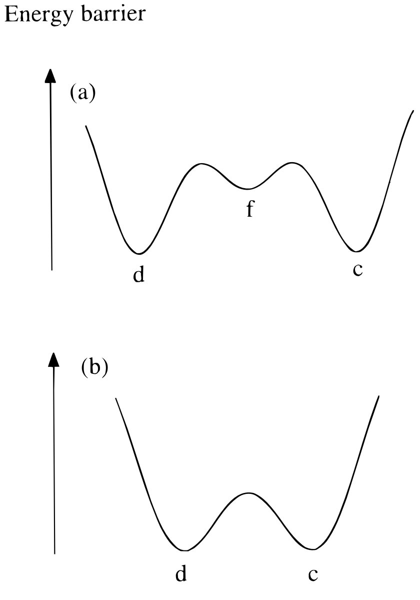


Figure 3. 2D exchange NMR spectra of the carboxyl region of PAA in the PAA/PEO complex at 333 K. The mixing time is (a) 10 ms, (b) 200 ms, and (c) 500 ms. The corresponding contour plots are also drawn.

Scheme 1



The mixing-time dependence of the carboxyl region of the 2D exchange NMR spectra at 329 K is shown in Figure 3. At a mixing time of 10 ms, no exchange peak is detected. At 200 ms, three cross-peaks are observed. The intensity of the **cd** exchange peak is the smallest. At 500 ms, intensities of the **cf** and **df** peaks increase less significantly than that of the **cd** peak. This suggests that the rates of the **cf** and **df** exchanges are similar or faster than that of the **cd** exchange. This leads us to invoke the potential curve as depicted schematically in Scheme 1a. At 338K, only the **cd** cross-peak is appreciable. Further, the **d** and **c** peak positions shift inwardly; a separation of 7.0 ppm at 329 K is reduced to 5.7 ppm at 338 K. These observations can be ascribed to coalescence of the **c** and **f** peaks and that of the **d** and **f** peaks due to fast **c** ↔ **f** and **d** ↔ **f** exchange motions, respectively. In other words, the exchange between **cf** and **df** at 338 K is fast enough to assume the potential curve shown in Scheme 1b. From the chemical-shift differences of these peaks (~300 Hz), the motional averaging of the peaks requires that the **c** ↔ **f** and **d** ↔ **f** exchange motions of the order of seconds at 329 K are accelerated more than 100 times at 338 K. Such a steep increase of motional frequency has also been observed for main-chain dynamics of polystyrene above T_g.[13]

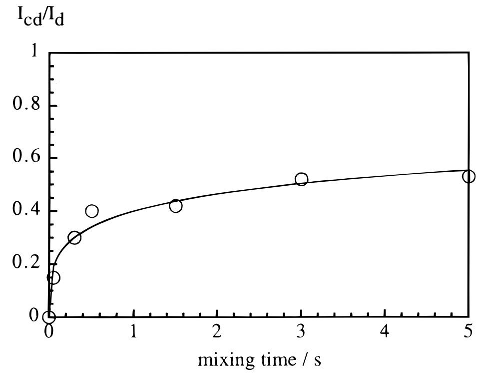


Figure 4. Mixing-time dependence of the cross/diagonal peak ($I_{\mathbf{cd}}/I_{\mathbf{d}}$) intensity ratio. The solid line is the best-fit curve to eq 4 with $k_{\mathbf{cd}} = 1.08 \pm 0.18$ Hz and $b = 0.29 \pm 0.04$, when a two-site exchange between the **c** and **d** forms is assumed (Scheme 1b).

We further investigated the mixing-time dependence of the exchange peak at 338 K to determine the **cd** exchange rate. The observed intensity ratio ($I_{\mathbf{cd}}/I_{\mathbf{d}}$) is plotted in Figure 4, which shows non-single-exponential behavior. The intensity ratio reaches 0.5 at a mixing time of 5 s. This suggests that, within 5 s, not all carboxyl groups participate in the exchange. As Figure 1b,c shows that three ^{13}C signals coalesce into one signal at higher temperatures, all carboxyl groups should participate in bond alternation at these temperatures. The nonexponential behavior, therefore, can be explained by a distribution of exchange rates arosen from motional heterogeneity in the complex.

Assuming a simple two sites exchange model for the **cd** exchange, the intensity ratio ($I_{\mathbf{cd}}/I_{\mathbf{d}}$) depends on the mixing time (t_{m}) as[14]

$$\frac{I_{\mathbf{cd}}}{I_{\mathbf{d}}}(t_{\mathrm{m}}) = \frac{P_{\mathbf{c}}k_{\mathbf{cd}}[1 - \exp(-2\epsilon t_{\mathrm{m}})]}{(\epsilon - \delta^2) + (\epsilon + \delta^2)\exp(-2\epsilon t_{\mathrm{m}})} \quad (1)$$

where

$$\epsilon = (\delta^2 + P_{\mathbf{c}}P_{\mathbf{d}}k_{\mathbf{cd}}{}^2)^{1/2} \quad (2)$$

and

$$\delta = {}^1/_2[k_{\mathbf{cd}}(P_{\mathbf{c}} - P_{\mathbf{d}}) + R_{1\mathbf{c}} + R_{1\mathbf{d}}] \quad (3)$$

In eq 1, $k_{\mathbf{cd}}$ is the exchange rate, R_{1x} and P_x represent the spin−lattice relaxation rate and the fractional population of the form x (x = **c** or **d**), respectively. Fractional populations of the **c** and **d** forms were obtained from the spectrum at 338 K to be $P_{\mathbf{c}} = 0.45$ and $P_{\mathbf{d}} = 0.55$. The T_1 values for the **c** and **d** forms were measured to be 14.3 ± 1.2 and 15.2 ± 0.6 s at 338 K,

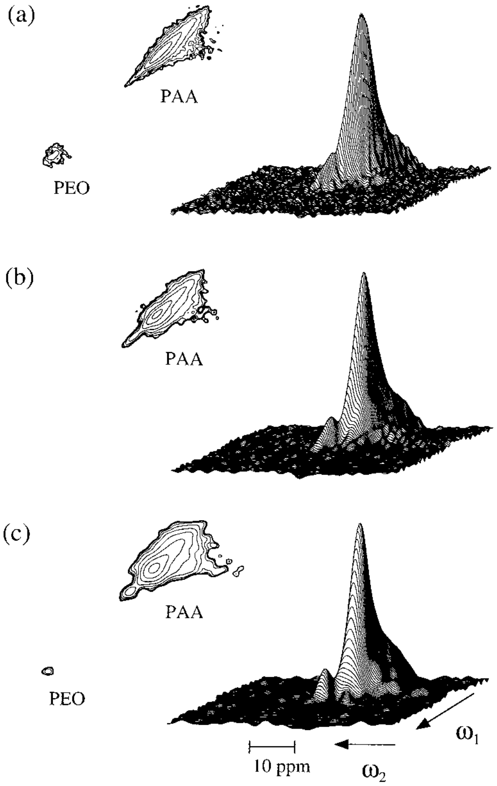


Figure 5. 2D exchange NMR spectra for the aliphatic region in PAA/PEO complex at (a) 303 K, (b) 329 K, and (c) 338 K. The corresponding contour plots are also drawn.

respectively. For simplicity, we assume $R_{1\mathbf{c}} = R_{1\mathbf{d}} = 0.068\ \mathrm{s}^{-1}$. To describe the non-single-exponential behavior, we replace the single-exponential function of $\exp(-k_{\mathbf{cd}}t_\mathrm{m})$ by a stretched exponential function of $\exp[-(k_{\mathbf{cd}}t_\mathrm{m})^b]$ $(0 < b \leq 1)$.[15] Equation 1 then becomes

$$\frac{I_{\mathbf{cd}}}{I_{\mathbf{d}}}(t_\mathrm{m}) = \frac{9 - 9\exp[-(k_{\mathbf{cd}}t_\mathrm{m})^b]}{11 + 9\exp[-(k_{\mathbf{cd}}t_\mathrm{m})^b]} \qquad (4)$$

The solid line in Figure 4 shows the best fit to eq 4 with $k_{\mathbf{cd}} = 1.08 \pm 0.18$ Hz and $b = 0.29 \pm 0.04$. The obtained b value corresponds to a distribution width over 3 decades. This value shows that the local structure of the complex is exceedingly heterogeneous. To examine the local heterogeneity, we measured ^{13}C $T_{1\rho}$ at 338 K and observed a single-exponential decay curve for both main and side chains on the individual component polymers (data not shown). This result indicates that the local heterogeneity affecting hydrogen-bonding alternation is not in the range of ~50 kHz governing the $T_{1\rho}$ relaxation process. The heterogeneity of the hydrogen-bonding alternation may be associated with much slower dynamics.

To investigate slow main-chain motion around T_g (323 K), we examine the 2D exchange NMR spectra of the main-chain region of the PAA/PEO complex at three temperatures at a mixing time of 500 ms. For PEO, the 2D exchange pattern shows a rounding shape at 303 K (Figure 5a). The ^{13}C line width of PEO reaches a ^{13}C maximum at 323 K, due to the interference[16,17] between ^{1}H DD and the segmental motion of PEO. Therefore, the observed shape at 303 K should be attributed to homogeneous line broadening caused by the interference between ^{1}H DD and the molecular motion. At 329 K, the PEO signal is no longer detected in the 2D spectrum, due to dynamics in line broadening and the short ^{13}C T_1 (120 ms). This T_1 value indicates that dynamics in PEO is on the order of 10^7 Hz at 329 K. Therefore, at least two motional modes with frequencies on the order of 10 kHz and 10 MHz are present in PEO. We therefore conclude that these frequency components cannot directly affect dynamic alternation of hydrogen bonding in the ~Hz range. The 2D spectrum for PAA at 303 K shows only diagonal components. Off-diagonal components begin to appear at 329 K and are significant at 338 K (Figure 5c). This shows that the slow conformational transition[18] of PAA on the order of Hz is present in the complex, and the rate coincides to the rate of the hydrogen-bonding alternation. We therefore conclude that the PAA conformational transition has an important role on the dynamic alternation of hydrogen-bonding. Indeed, for the PMAA/PEO complex, the hydrogen bonding alternation is temperature-irreversible. This should be explained by the rigidity of PMAA.[10]

To conclude, the dynamic alternation between inter- and intra-polymer hydrogen bonds above T_g for the PAA/PEO complex is detected for the first time. One should be careful enough to adopt the frozen inter-polymer hydrogen-bonding model for the polymer complex to explain the observed macroscopic properties.[8,9]

Acknowledgment. T.M. is thankful for Research Fellowship of the Japan Society for the Promotion of Aid for Science Research.

References and Notes

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MA991012B