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Characterization of Absorbed Water in Perdeuterated Polycarbonate by Residual-Proton NMR

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ABSTRACT: The distance from the protons of water absorbed in a precipitated, perdeuterated polycarbonate powder to the ^{13}C-labeled carbonyl carbon is 5 ± 1 Å. This distance was determined by magic-angle spinning rotational-echo double-resonance ^{1}H NMR with ^{13}C dephasing. As shown by rotor-synthesized Hahn-echo dephashing, translational motion of the absorbed water is restricted in a nominally dry powder but not in an annealed film. Water in both powder and film undergoes rapid, nearly isotropic rotational reorientation. Water in the powder shares motions with a structural unit in the polycarbonate that is large enough to have a correlation time comparable to the rotor period.

Magic-angle spinning is sufficient to produce a high-sensitivity, high-resolution *proton* NMR spectrum of a perdeuterated solid.[1] The 1% residual protons are rare spins with a small chemical-shift anisotropy of 5 ppm or less. Minor spinning side bands arise primarily from the 3-kHz dipolar coupling to nearby deuterons. At high field, the residual ^{1}H NMR spectrum of perdeuterated polycarbonate[2] has three resolved isotropic shifts corresponding to three types of protons: aromatic, methyl, and water. There is about one fully protonated water molecule per 100 polymer repeat units. The water peak is at high field, indicating that water molecules are isolated from one another in an organic matrix.[3]

In this paper we determine the location and mobility of the water absorbed in [*carbonyl*-^{13}C]polycarbonate-d_{14} and natural-abundance ^{13}C polycarbonate-d_{14} using three ^{1}H NMR experiments: (1) rotational-echo double-resonance[4] (REDOR) with ^{13}C dephasing; (2) rotor-synchronized single-resonance Hahn-echo dephasing;[2] and (3) rotating-frame spin–lattice relaxation. Low levels of absorbed water are an inherent part of amorphous polycarbonate. The protons of absorbed water therefore offer a nonperturbative NMR probe of interchain polycarbonate organization. The range of this probe is determined in part by the mobility of individual water molecules. Specific advantages of residual ^{1}H NMR of perdeuterated polycarbonate over direct detection of deuterated water in protonated or deuterated polycarbonate include (1) the greater NMR sensitivity of ^{1}H over ^{2}H; (2) the improved resolution for the same distribution of isotropic shifts;[2] and (3) the 7-fold increase in dipolar coupling for ^{1}H–^{13}C compared to ^{2}H–^{13}C in REDOR dephasing experiments. The characterization of the location and mobility of water in polycarbonate that will be described below would not have been possible using ^{2}H NMR.

Experiments

Synthesis and Purification of Double-Labeled Polycarbonate. Carbon-13-labeled phosgene (1 M in benzene, 99 atom % ^{13}C) and perdeuterated Bisphenol A (nominal 98 atom % ^{2}H) were obtained from Isotec (Miamisburg) and Merck Stable Isotopes (Montreal), respectively. The average residual proton concentration was determined to be 1% by high-resolution, solution-state NMR.[2] The ratio of aromatic protons to methyl protons was 2:1 rather than the expected 4:3, indicating that the methyl groups had been preferentially deuterated. Both labeled materials were used as received. *N,N*-Dimethylaniline and triethylamine (Aldrich) were used without further purification. Twenty milliliters phosgene solution, 8.7 mmol of perdeuterated Bisphenol A, and 15 mL of toluene were mixed in a 100-mL single neck flask and cooled to −20 °C. Dimethylaniline (2.42 g, 20 mmol) was added to the mixture. The solution was allowed to warm to room temperature where it was maintained for 12 h. Dimethylaniline hydrochloride was removed by filtration after excess phosgene was evaporated under reduced pressure. After the solution was passed through a column packed with 70 g of silica gel (Grade 12, 28–200 mesh), the solvent was evaporated under vacuum. The Bisphenol A chlorocarbonate product formed in 73% yield. Further purification was achieved by recrystallization from hexane. Polycarbonate was formed in 96% yield by the condensation of Bisphenol A and Bisphenol A chlorocarbonate at low temperatures, as previously described.[5] The polymer was purified by reprecipitation from dichloromethane and 2-propenol. The average residual proton concentration of the perdeuterated polycarbonate remained at 1%, the same concentration as the starting monomer. A natural-abundance ^{13}C polycarbonate-d_{14} was also prepared.

Preparation of [*Carbonyl*-^{13}C]polycarbonate-d_{14} Powders and Films. Three different double-labeled samples were investigated, two powders and an annealed film. Powder **1** contained approximately one-fifth as much water as powder **2**. Powder **1** was obtained by dissolving the double-labeled polycarbonate in dry chloroform (1.5% polymer by weight) and reprecipitating drop by drop in methanol. The solid was then collected by suction filtration, air-dried overnight, and vacuum-dried for several days at 80 °C. The same procedure was repeated with chloroform exposed to room-temperature humidity to produce powder **2**. The film was made by compression molding powder **2** at 220 °C between polished chromium-coated plates and annealed by cooling freely in the press to room temperature. Differential scanning calorimetry indicated no crystallinity above the 1% level. Natural-abundance ^{13}C polycarbonate-d_{14} powder and annealed film were prepared similarly.

Solids NMR Spectrometer. Magic-angle spinning ^{1}H, ^{13}C, ^{2}H NMR spectra were obtained using three channels of a four-channel spectrometer built around an 89-mm, vertical-bore superconducting solenoid operating at 7.05 T. Multifrequency tuning was accomplished by the use of a coaxial transmission line connecting tuning components to a single, four-turn, 9-mm

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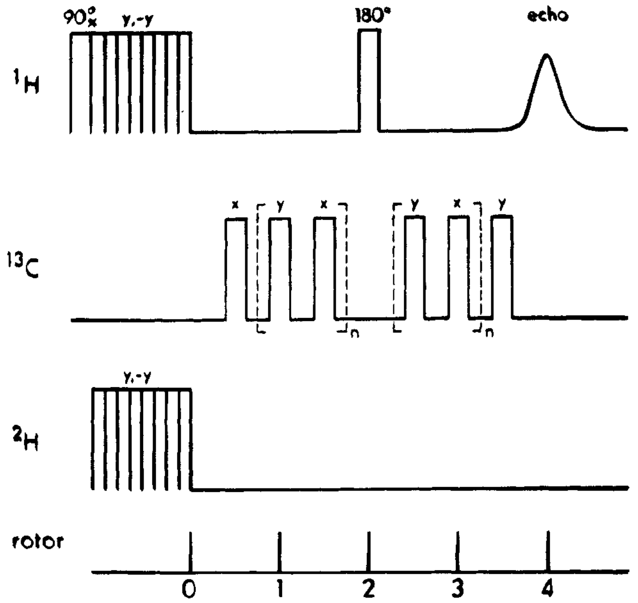

Figure 1. Pulse sequence for ^{1}H-observe, ^{13}C-dephase rotational-echo double-resonance NMR. A matched spin-lock ^{1}H$-$^{2}H depolarizing contact was used to enhance the water peak relative to the polymer proton signals. A single refocusing ^{1}H pulse occurs at the middle of the evolution period to refocus isotropic chemical shifts. The illustration is for four rotor cycles.

diameter solenoidal coil wound from 14-gauge, tinned bus wire. Only the coil is in the magnet. Chemagnetics pencil-shaped zirconia rotors were spun at speeds up to 5 kHz with ±2 Hz active control. An ENI LPI-10 1-kW transmitter was used for the deuterium channel, and Kalmus LP-1000 1-kW and 166-UP 600-W transmitter were used for the carbon and proton channels, respectively. The spectrometer is controlled by a four-channel Chemagnetics CMX-300 console.

NMR Experiments. The pulse sequence used for ^{1}H NMR with REDOR ^{13}C dephasing[5] is shown in Figure 1. Proton magnetization was produced by a 90° inspection pulse preceded by a ^{1}H$-$^{2}H matched spin-lock contact with depolarizing phase alternation.[6] The latter was used to drain polarization from polymer protons which have strong ^{1}H$-$^{2}H coupling and so reduce the spectral overlap between polymer and water peaks. Simplifying the water spectrum facilitates quantitation of the ^{13}C REDOR dephasing. A REDOR-dephased ^{1}H echo (S) was observed with dephasing ^{13}C pulses at $NT_r/2$ and NT_r. A full echo (S_0) was observed by omitting the dephasing ^{13}C pulses. A single 180° pulse was applied on the ^{1}H channel to refocus isotropic chemical shifts. Simple xy phase alternation[7] was used on the ^{13}C dephasing channel. Hahn-echo amplitudes for the water signal were obtained using a $90_x-\tau-180_y-\tau$ pulse sequence with τ equal to an integral number of rotor cycles. The time constant associated with the decay of the echo train is referred to as the water T_2. The proton rotating-frame, spin–lattice relaxation time, $T_{1\rho}$(H), was determing by varying the duration of a proton spin lock prior to data acquisition.

Results

REDOR. The residual aromatic and methyl protons in perdeuterated polycarbonate give rise to two of the observed ^{1}H NMR isotropic peaks. A low concentration of fully protonated absorbed water is responsible for the third (Figure 2). As noted before,[2] the water peak appears at high field, indicating that each water molecule is isolated in the organic matrix. This is true for all three of the samples examined. Powder **1** has the least water uptake (0.02%, by weight) and the annealed film has the most (0.2%). Powder **2** has an intermediate concentration of water (0.1%). Annealing has narrowed the width and increased the height of the methyl-proton peak of the film (Figure 2, bottom left).

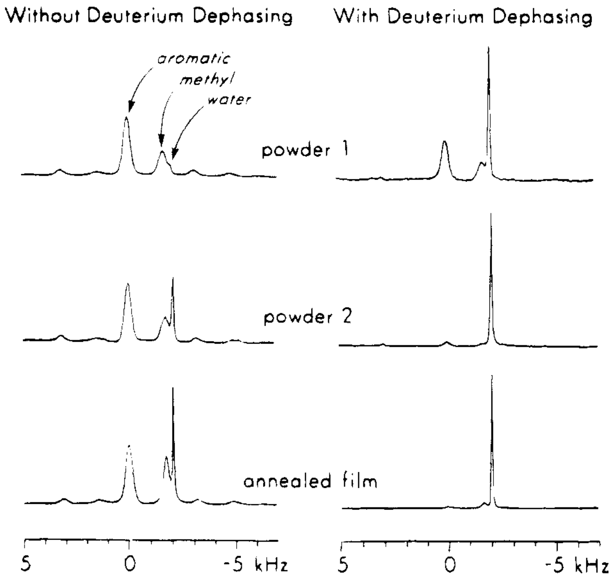

Figure 2. (Left) Rotor-synchronized 300-MHz ^{1}H Hahn-echo spectra of three [*carbonyl*-^{13}C]polycarbonate-d_{14} samples with magic-angle spinning at 3125 Hz. The echo was observed after two rotor periods with the refocusing pulse after the first rotor period. The spectra have been scaled for equal-intensity aromatic proton peaks which appear at 0-kHz offset. (Right) Full-echo ^{1}H-observe, ^{13}C-dephase REDOR spectra following eight rotor cycles of preparative ^{2}H dephasing for the three polycarbonates whose Hahn-echo spectra are shown on the left. The spectra have been scaled for equal-intensity water peaks. Magic-angle spinning was at 5 kHz.

Depolarization by matched ^{1}H$-$^{2}H contact enhances the water peak for all three samples relative to the polycarbonate aromatic and methyl-proton peaks (Figure 2, right). The water protons show no significant depolarization due to ^{2}H$-$^{1}H dipolar coupling. The ^{2}H-dephasing preparation makes detection of subsequent dephasing by the ^{13}C label easier by reducing spectral overlap in the ^{1}H NMR spectrum. The water molecules of all three samples are rapidly rotating in place, thereby reducing the ^{1}H$-$O$-$^{1}H dipolar coupling of about 30 kHz by a factor of 10, consistent with 5% spinning side band intensities under 2-kHz magic-angle spinning.[8] (See Figure 2 in ref 2 for a display of spinning side band intensities).

The observed ^{13}C REDOR dephasing of 50% in 35 ms for the water protons in powder **1** (Figure 3, solid squares) corresponds[9] to a motionally averaged ^{1}H$-$^{13}C dipolar coupling of about 30 Hz ($D \approx 1/NT_r$). This means that the full dipolar coupling is 300 Hz, which, assuming a single internuclear separation, translates[10] to a nearest-neighbor proton to carbonyl-^{13}C distance for each of these water molecules of 5 ± 1 Å. If a distribution of distances were present, the inverse cube-root weighted average determined by REDOR would be much more sensitive to short distances than to long ones. We assign an uncertainty in the ^{1}H$-$^{13}C coupling arising from unknown details of the motional averaging of no more than a factor of 2, which means an uncertainty in the ^{1}H$-$^{13}C distance of ±25%. The water-proton signal is REDOR-dephased by the ^{13}C label for the water-depleted powder **1** but not for the annealed film which has about the same dephasing as observed for a perdeuterated polycarbonate with no ^{13}C label (Figure 3, solid triangles and open circles). Powder **2** exhibits intermediate ^{13}C dephasing behavior (solid circles).

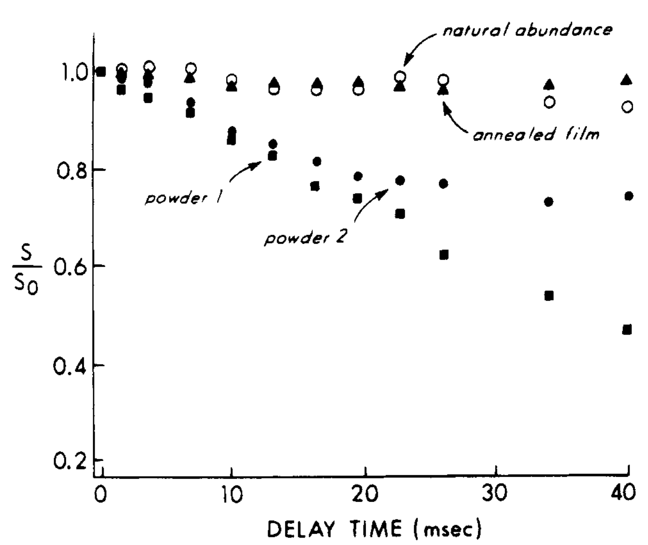

Figure 3. REDOR ^{13}C dephasing (S/S_0) for the water signal of [*carbonyl*-^{13}C]polycarbonate-d_{14} at 300 MHz for the three samples of Figure 2: powder **1**, solid squares; powder **2**, solid circles; annealed film, solid triangles. Magic-angle spinning was at 5 kHz. Dephasing arising from the natural-abundance level of ^{13}C in a polycarbonate-d_{14} powder is negligible (open circles). The natural-abundance ^{13}C polycarbonate-d_{14} had the same concentration of water as powder **2**.

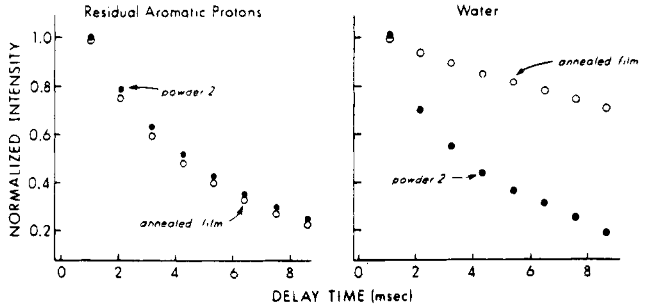

Figure 4. Residual aromatic-proton (left) and water-proton (right) Hahn-echo amplitudes for two natural-abundance ^{13}C polycarbonate-d_{14} samples with different thermal histories: powder (solid circles) and annealed film (open circles). The powder and film samples had the same water content as that of double-labeled powder **2** and annealed film, respectively. The decay of the methyl-proton magnetization (data not shown) was similar to that of the aromatic protons. Data were collected at 300 MHz with 1852-Hz magic-angle spinning using a $90_x-\tau-180_y-\tau$ pulse sequence with τ equal to an integral number of rotor cycles.

T_2(H) and $T_{1\varrho}$(H). The Hahn-echo T_2 of the polymer protons is the same for both powder and annealed film (Figure 4, left). However, the T_2 of the water protons in the powder is less than one-fifth of that for the annealed film (Figure 4, right). The $T_{1\varrho}$(H) of the polymer protons in the powder has a weaker radio-frequency field dependence[11] than that in the more densely packed annealed film (Figure 5, left). Only minor differences are observed in the radio-frequency field dependence of the water proton rotating-frame relaxation for powder and annealed film (Figure 5, right), although the relaxation rate for the water protons in the film has decreased relative to that in the powder.

Discussion

Polymer Microstructure, Chain Packing, and Bundles. To maintain a 5-Å, water-proton to ^{13}C-label internuclear distance in the REDOR experiment of Figure 3, all the water in powder **1** must be trapped in local regions defined by a few tightly packed polycarbonate chains. We refer to these regions of orientational order as "bundles".[12] Powder **2** exhibits an initial REDOR dephasing that we also assign to intrabundle water. This water accounts for about one-fourth of the total in powder **2**. The observed S/S_0 then plateaus with increasing dephasing time (Figure 3, solid circles). We conclude that three-fourths of the water in powder **2** (the fraction that does not dephase) is external to the bundles and so has no strong dipolar coupling to the ^{13}C-labeled carbonyl carbon. We refer to this water as "excess". The S/S_0 plateau (Figure 3, solid circles) shows that any exchange of excess water with the dephasing intrabundle water is slow on the 10-ms time scale of the REDOR experiment.

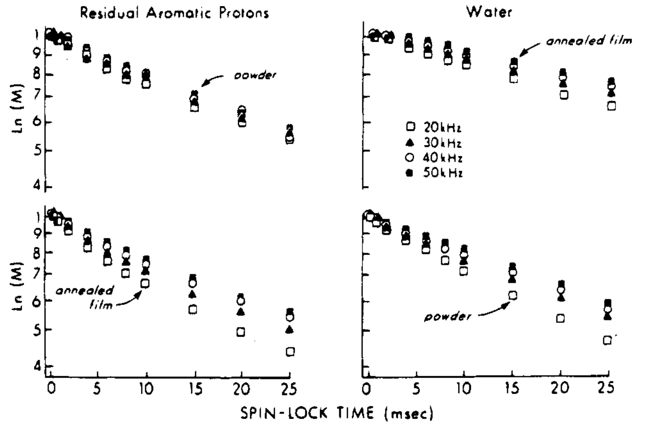

Figure 5. Residual aromatic-proton (left) and water-proton (right) spin-locked magnetization for a natural-abundance ^{13}C polycarbonate-d_{14} powder and an annealed film, as a function of ^{1}H radio-frequency field amplitude. The legend for symbols defining the spin-locking field amplitude applies to both left and right parts of the figure. The decay of the methyl-proton magnetization (data not shown) was similar to that of the aromatic protons. Data were collected at 300 MHz with 3125-Hz magic-angle spinning.

No significant dephasing is observed for water in the annealed film (Figure 3, solid triangles). The film has twice as much water as powder **2**, and all of it appears to be interbundle water. If half of the water in the film behaved as the water in powder **2**, then the S/S_0 for the film would have shown 15% dephasing after 40 ms, or about half of the 30% dephasing observed for powder **2**. We conclude that annealing at $T < T_G$ removes trapped intrabundle water and so the primary source of $^1H-^{13}C$ dipolar coupling needed for REDOR dephasing.

Interbundle Motions and T_2. The difference in homogeneous, nonrefocusable T_2 behavior for water in powder and film (Figure 4) is determined by motions on the millisecond time scale of the rotor.[2] All other interactions for a pair of equivalent protons in a water molecule isolated in a perdeuterated polycarbonate matrix are heterogeneous and therefore refocusable. The nearly isotropic, reorientational motions of the water molecule itself are in the megahertz regime and are much too fast to be the source of the T_2 dephasing. The cooperative slow motions that cause T_2 dephasing for both polymer and water protons of the powder must also be present in the film because the polymer proton T_2 is the same in powder and film (Figure 4, left). These motions affect the relaxation of water localized in or near the bundles and so account for the short T_2 for *intra*bundle water in the powder (Figure 4, right). The increased water T_2(H) in the annealed film means an increased mobility of *inter*bundle water. We believe that the increase in the density of the glass caused by annealing decreases interbundle spacing. The closer packing of bundles apparently facilitates jumping of water from the surface of one bundle to the next. Thus, all water can exchange positions more readily in the film than in the powder.

Intrabundle Motions and $T_{1\varrho}$. We hypothesize that in the powder, the *intra*bundle free volume is sufficient to allow some chains to move independently, and thus at frequencies greater than 50 kHz. In the annealed film, tighter packing necessitates more cooperativity between chains to enable motion. The larger molecular units involved in cooperative motion in the film therefore result in a lower average frequency for motion in the 20−50-kHz regime, and this accounts for the stronger radio-frequency field dependence of $T_{1\varrho}$(H) of the annealed film relative to that of the powder (Figure 5, left). The increased interbundle mobility of water in the annealed film increases $T_{1\varrho}$(H), but less than it increases T_2(H) (compare Figure 4, right with Figure 5, right), presumably because some of the interbundle water motion is slower than 50-kHz main-chain rotational reorientation, but faster than 3-kHz magic-angle spinning.

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References and Notes

(1) Eckman, R. *J. Chem. Phys.* **1982**, *76*, 2767.
(2) Lee, P. L.; Schaefer, J. *Macromolecules* **1992**, *25*, 5559.
(3) Fyfe, C. A.; Randall, L.; Burlinson, N. *Chem. Mater.* **1992**, *4*, 267.
(4) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.
(5) Xiao, D.; Yee, A. F. *Macromolecules* **1992**, *25*, 6800.
(6) Schaefer, J.; Stejskal, E. O.; Garbow, J. R.; McKay, R. A. *J. Magn. Reson.* **1984**, *59*, 150.
(7) Gullion, T.; Baker, D.; Conradi, M. S. *J. Magn. Reson.* **1990**, *89*, 479.
(8) Afeworki, M.; Vega, S.; Schaefer, J. *Macromolecules* **1992**, *25*, 4100.
(9) Pan, Y.; Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1990**, *90*, 330.
(10) Gullion, T.; Schaefer, J. *Adv. Magn. Reson.* **1989**, *13*, 55.
(11) Steger, T. R.; Schaefer, J.; Stejskal, E. O.; McKay, R. A. *Macromolecules* **1980**, *13*, 1127.
(12) Lee, P. L.; Kowalewski, T.; Poliks, M. D.; Schaefer, J. *Macromolecules* **1995**, *28*, 2476.

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