Characterization of Interchain Interactions in Perdeuterated Bisphenol-A Polycarbonate by Residual-Proton Solid-State NMR

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It has been postulated that interchain cooperativity of molecular motion is responsible for many of the useful engineering properties of bisphenol-A polycarbonate.[1] Previous experiments using solid-state NMR to probe this phenomenon have focused on interpreting the spectra of either a single deuterium[2,3] or a directly bonded carbon–proton pair on one chain.[4] In both instances, direct observation of dynamics is limited to a single chain; the effect of other chains on the properties of the detected nucleus must be inferred.

Study of the dipolar interaction of two nuclei, each on a separate polymer chain, leads more directly to information about the cooperative motions of interest. Detection of a proton–proton pair is preferable to that of a carbon–carbon pair due to the proximity of interchain protons and the excellent sensitivity arising from the large proton gyromagnetic ratio. However, the broad featureless NMR signal from protons at natural abundance is generally difficult to interpret. This problem can be circumvented by the use of perdeuterated compounds containing only residual protons.

The residual-proton NMR spectra of perdeuterated bisphenol-A polycarbonate (PC-d_{14}) and the bisphenol-A monomer (BPA-d_{16}) shown in Figure 1 were obtained at 60 MHz with 1852-Hz magic-angle spinning. A $90-\tau-180-\tau$ pulse sequence was used with τ equal to an integral number of rotor periods. The average level of residual protonation was quantified by solution-state NMR and found to be about 1% for both PC-d_{14} and BPA-d_{16}. In both samples the methyl groups were preferentially labeled. The ratio of aromatic signal to methyl signal was found to be 2:1 instead of the expected 4:3. At low concentration, protons behave as a rare spin-$^1/_2$ with the NMR spectrum dominated by heterogeneous rather than homogeneous interactions. Even at relatively low spinning frequencies, complete separation of sidebands is achieved, indicating that proton spin–spin communication is limited. Aromatic and methyl-proton resonances are almost resolved at 60 MHz, although the high-field peak of PC-d_{14} has an important contribution from water which is better resolved at 300 MHz (Figure 2, left). This water is exchangeable with D_2O and can be removed by heating the sample under vacuum. Upon exposure to the atmosphere the water is reabsorbed almost immediately. The resonance position of the water at higher field than that of the methyl protons is consistent with isolated water in an organic matrix.[5,6] The size of the residual water sidebands (Figure 2, top left) and their insensitivity to deuterium decoupling (spectrum not shown) indicate that the water is tumbling almost isotropically. Therefore, its predominant NMR interaction is intramolecular proton–proton dipolar coupling.

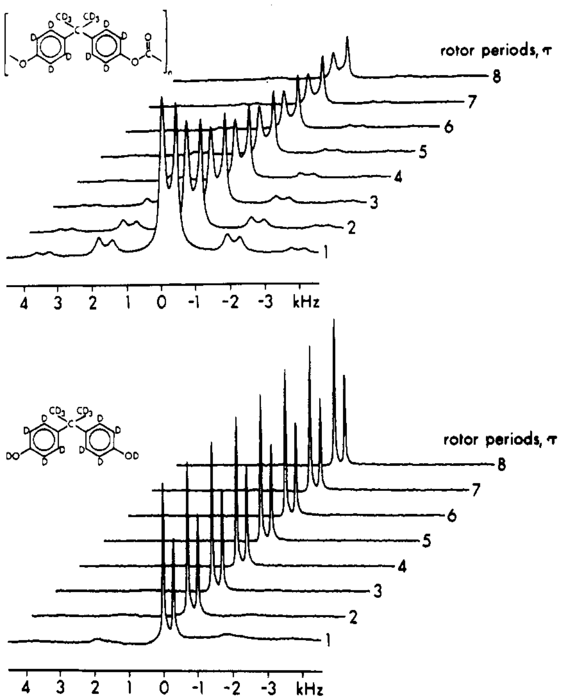

Figure 1. Residual-proton NMR spectra at 60 MHz with 1852-Hz spinning of polycarbonate-d_{14} (top) and bisphenol-A-d_{16} (bottom) obtained using a $90-\tau-180-\tau$ pulse sequence with τ equal to an integral number of rotor periods. The broad sidebands for $\tau = 1$ rotor period for bisphenol-A-d_{16} are due to clusters of exchangeable OH protons. The ppm scale is referenced to the aromatic-proton peak.

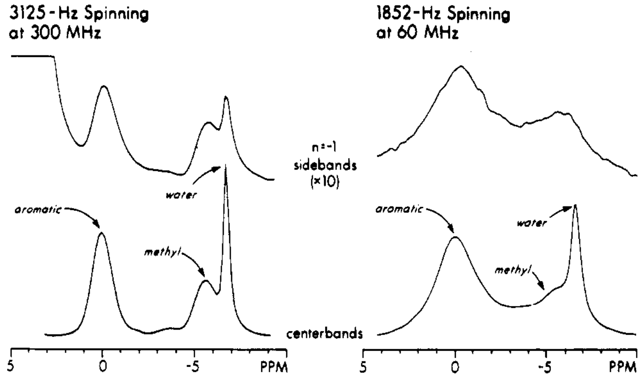

Figure 2. Proton NMR intensities of centerbands (bottom) and upper first spinning sidebands (top) for polycarbonate-d_{14} at 300 MHz (left) and 60 MHz (right). The relative contribution from water is less in the sidebands than the centerband. The ppm scale is referenced to the aromatic-proton peak.

The persistence of pronounced 60-MHz aromatic and methyl-proton sidebands with 1852-Hz spinning (Figure 1, top; Figure 2, right) requires an interaction strength greater than 2 kHz. This is much larger than either the average residual proton–proton dipolar coupling (cf. below) or the proton chemical shift anisotropy at low field. We attribute the kHz-range interaction in PC-d_{14} to proton–deuterium dipolar coupling. This is supported by the reduction of sideband intensity with on-resonance deuterium decoupling at 30 kHz (spectrum not shown). By contrast, the residual proton spectrum of perdeuterated bisphenol-A (BPA-d_{16}), the monomer precursor of PC-d_{14}, has no detectable spinning sidebands (Figure 1, bottom). Because intramolecular proton–deuteron distances are similar for both BPA and PC, the interactions giving rise to the proton sidebands in PC-d_{14} must be *inter*chain. This result leads to the unexpected conclusion that, for the phenyl rings and isopropylidene groups, the average packing in the glassy polymer is more dense than in the crystalline monomer.

The decay in intensity seen for PC-d_{14} as τ increases (Figure 1, top) defines the natural T_2 of the sample, which arises from the combined effect of molecular motion and

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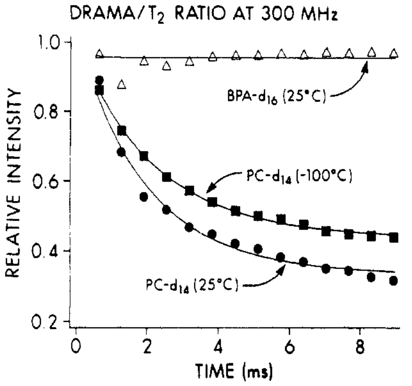

Figure 3. Ratio of DRAMA to T_2 signal intensities for the residual aromatic protons of polycarbonate-d_{14} and bisphenol-A-d_{16}. The intensities for the latter are influenced over the first rotor periods by contributions from the exchangeable protons (see Figure 1, bottom). All data were obtained at 300 MHz with 3125-Hz magic-angle spinning. DRAMA dephasing was achieved by 5-μs $\pi/2$ pulses placed at $^1/_4T_r$ and $^3/_4T_r$.

deuterium–proton dipolar coupling. If, in addition to the refocusing π pulse, two $\pi/2$-proton pulses are applied during each rotor cycle, further dephasing occurs due to reintroduction of the proton–proton dipolar interaction of isolated proton pairs that had been suppressed by magic-angle spinning. This effect has been described by Tycko and Dabbagh, and the pulse sequence has been given the name "DRAMA" for dipolar recovery at the magic angle.[7]

The ratio of the DRAMA signal intensity to the T_2 signal intensity removes the natural decay, leaving only the dephasing caused by proton–proton dipolar interactions. For BPA-d_{16}, the $\pi/2$ pulses have virtually no effect and the ratio is approximately one (Figure 3), which means that there are no significant proton–proton dipolar couplings. For PC-d_{14}, however, the denser packing introduces *inter*chain proton–proton interactions which cause the additional decay seen in the DRAMA/T_2 ratio (Figure 3). The DRAMA dephasing corresponds to an average proton–proton dipolar coupling of 350 Hz.[7] More than half of the protons are affected because of large-amplitude molecular motions in the polymer, not present in the crystalline BPA monomer, which allow each proton to come into contact with many different sites, thereby increasing the chance of a proton–proton dipolar coupling. At lower temperatures some of these motions are frozen out, reducing the number of protons which have H–H interactions. This causes the DRAMA/T_2 ratio to shift to higher values (Figure 3). The shift is limited because even at −100 °C most of the phenyl rings are still undergoing 180° flips at a rate that is fast compared to the 350-Hz proton–proton coupling.[2,4]

The conclusion that polycarbonate has shorter intermolecular distances than its crystalline monomer is based on both the DRAMA results and the comparison of BPA-d_{16} and PC-d_{14} spinning sidebands. Analysis of the results of heteronuclear NMR experiments on selectively labeled polycarbonates and computer simulations of proton–proton and proton–deuterium interactions are currently underway to extract accurate internuclear distances between polycarbonate chains in the glassy state. Results will be submitted to this Journal.

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References and Notes

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