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Local Packing in Glassy Polycarbonate by Carbon−Deuterium Rotational-Echo Double-Resonance NMR. 2

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ABSTRACT: Continuing our work of measuring intermolecular distances in ^{13}C,^{2}H-labeled polycarbonate using rotational-echo double-resonance ^{13}C NMR with ^{2}H dephasing, we report average nearest-neighbor interchain ring−carbon to ring−deuterium and ring−carbon to methyl−deuterium distances of 2.6 and 3.2 Å, respectively. The short ring−ring distance indicates that the phenyl groups are tightly packed, consistent with the observation that cooperative intermolecular motion is required for ring flips.

The cooperative molecular motions that accompany ring flips in polycarbonate[1] are believed to be related to the polymer's low-temperature mechanical transition[2] which, in turn, is associated with toughness and high impact strength.[3] To determine the extent to which lattice reorganization is indeed correlated with the macroscopic properties of polycarbonate, a more complete description of the structure of the glass at the molecular level is needed. Computer simulations have provided valuable information about the microscopic structure of polycarbonate.[4,5] Such calculations benefit from a knowledge of the actual interchain distances in the glassy polymer.

A number of solid-state NMR experiments capable of measuring intermolecular distances have been developed recently.[6,7] The results of these experiments help to define local chain packing and can be used as starting coordinates for molecular dynamics simulations. In a previous paper, we reported an average intermolecular distance of 3.8 Å between carbonyl carbons and nearest-neighbor methyl groups in polycarbonate as determined by ^{13}C−^{2}H rotational-echo double resonance (REDOR).[8] In this paper we use the same REDOR pulse sequence to measure average interchain distances in polycarbonate between phenyl rings and between rings and methyl groups.

Experiments

Solids NMR Spectrometer. NMR experiments were performed using three channels of a four-channel spectrometer built around an 89-mm, vertical-bore superconducting solenoid operating at 7.05 T. The triple-turned, ^{1}H−^{13}C−^{2}H, transmission line probe used for the REDOR experiments has been previously described.[8] Samples were spun in zirconia rotors at speeds up to 5 kHz. Spinning stability to within ±2 Hz was achieved with active control. Power for the radio-frequency pulses was supplied by 1-kW Kalmus LP-1000, 600-W Kalmus 166-UP, and 1-kW ENI LPI-10 transmitters for ^{1}H, ^{13}C, and ^{2}H channels, respectively. The spectrometer was controlled by a four-channel Chemagnetics CMX-300 console.

REDOR. The ^{13}C−^{2}H REDOR pulse sequence is shown in Figure 1. A 3-ms, 62-kHz matched spin-lock cross-polarization transfer from protons to carbon was used for signal enhancement. The protons were then decoupled with 90-kHz continuous-wave radio-frequency irradiation. Dephasing 180° pulses were applied alternately on the carbon and deuterium channels. Carbon pulses were placed on the rotor period and deuterium pulses at t_1. A 180° pulse length was 8 μs for carbon and 6.4 μs for deuterium. XY-8 and XY-4 phase alteration schemes[9] were used for the carbon and deuterium pulse trains, respectively, to compensate for frequency offsets and pulse imperfections. The final 180° carbon pulse refocused isotropic chemical shifts. The signal was detected as an echo to avoid interferences from the radio-frequency pulses. The experiment performed with the dephasing ^{2}H pulses yields the REDOR-dephased signal, S, and that performed without the ^{2}H pulses, S_0. Decay of the ratio S/S_0 is due solely to ^{13}C−^{2}H dipolar coupling.

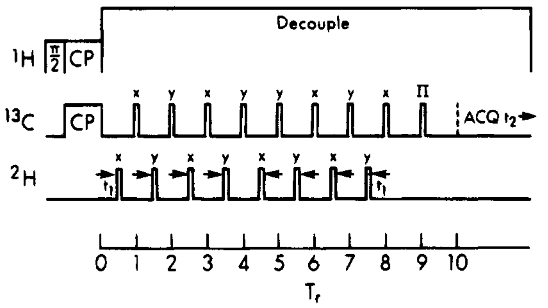

Figure 1. ^{13}C-observe, ^{2}H-dephase REDOR pulse sequence. Protons are used for signal enhancement via a cross-polarization transfer to carbons and then are decoupled. The effect of ^{13}C−^{2}H dipolar couplings on carbon = echo amplitudes, which is removed by magic-angle spinning, is reintroduced by 180° pulses applied alternately on the ^{13}C and ^{2}H channels. The phases of pulses on the carbon channel are varied according to the XY-8 scheme, and those on the deuterium channel, according to the XY-4 scheme. (See ref 9.)

Labeled Polycarbonates. Two blends were made containing 5% protonated polycarbonate with ^{13}C labels at the 3 and 3′ ring positions and 95% of a specifically deuterated polycarbonate, which was either [methyl-d_6]polycarbonate or (3,3′,5,5′-ring-d_4,methyl-d_6]polycarbonate. The [3,3′-ring-^{14}C$_2$]-polycarbonate was synthesized by Dr. Steve Bales (Dow Chemical Co., Midland, MI). The [3,3′,5,5′-ring-d_4,methyl-d_6]-polycarbonate was synthesized by Dr. R. J. Kern (formerly of Monsanto Co., St. Louis, MO) from monomer supplied by Merck Stable Isotopes. The [methyl-d_6]polycarbonate was a generous gift from Dr. Alan A. Jones (Clark University, Worcester, MA). The blends were made by coprecipitation in methanol from a chloroform solution containing 2.5% polymer (by weight). Under these conditions, nearest-neighbor effects in solution arise from interchain rather than intrachain interactions. The blends that result are homogeneously mixed with each ^{13}C-labeled chain completely surrounded by ^{2}H-labeled chains.[8]

Results

The ring-C3,3′ line of the ^{13}C-labeled polycarbonate is well resolved at 120 ppm (Figure 2). About 80% of this peak is due to ^{13}C label. The natural-abundance

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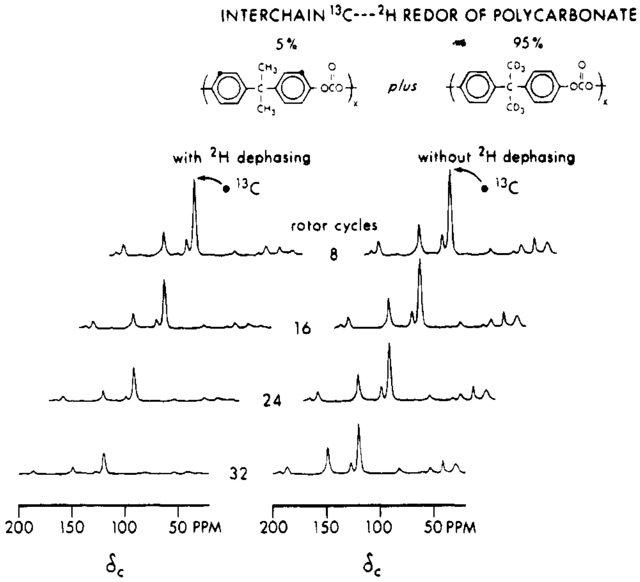

Figure 2. 75-MHz REDOR ^{13}C NMR spectra of a homogeneous mixture of 5% [3,3′-ring-$^{13}C_2$]polycarbonate and 95% [methyl-d_6]polycarbonate as a function of the number of rotor cycles of evolution of carbon magnetization with (left) and without (right) ^{2}H dephasing 180° pulses. The spectra were obtained using the pulse sequence of Figure 1 with $t_1 = T_r/2$ and 5-kHz magic-angle spinning.

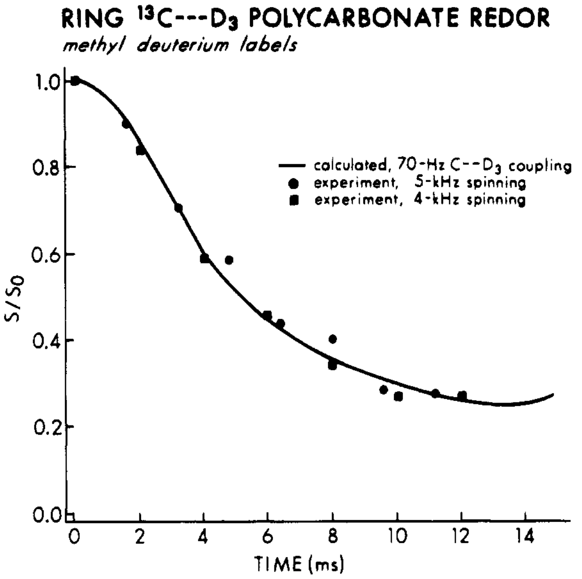

Figure 3. REDOR dephasing for the aromatic carbon of a homogeneous mixture of 5% [3,3′-ring-$^{13}C_2$]polycarbonate and 95% [methyl-d_6]polycarbonate. Spectra were obtained at 75 MHz using the pulse sequence of Figure 1 with $t_1 = T_r/2$ and either 4-kHz (squares) or 5-kHz (circles) magic-angle spinning. The calculated coupling of 70 Hz is based on an interaction between a carbon and a single rotating methyl group.

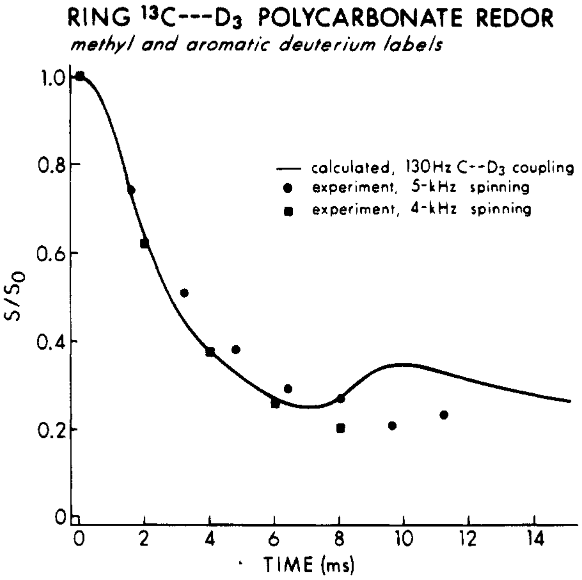

Figure 4. REDOR dephasing for the aromatic carbon of a homogeneous mixture of 5% [3,3′-ring-$^{13}C_2$]polycarbonate and 95% [3,3′,5,5′-ring-d_4,methyl-d_6]polycarbonate. Spectra were obtained at 75 MHz using the pulse sequence of Figure 1 with $t_1 = T_r/2$ and either 4-kHz (squares) or 5-kHz (circles) magic-angle spinning. The calculated coupling of 130 Hz is based on an interaction between a carbon and a single rotating methyl group.

^{13}C contribution can be estimated by comparison to the aromatic-carbon peak at 130 ppm. The REDOR S/S_0 as a function of total dephasing time for the 120 ppm peak in the [methyl-d_6]polycarbonate blend is shown in Figure 3. Dephasing results for the sample with both methyl and aromatic deuterons (the blend with 95% [3,3′,5,5′-ring-d_4,methyl-d_6]polycarbonate) are shown in Figure 4. Magnetization due to the ^{13}C label has decayed to 27% for dephasing by methyl deuterons only and to 20% for combined methyl and aromatic deuterons. The massive dephasing of the 120 ppm line by ^{2}H REDOR dephasing pulses can only arise from *inter*molecular ^{13}C$-^{2}$H interactions. The best-fit calculated curves (the solid lines in Figures 3 and 4) yield values for the apparent ^{13}C$-^{2}$H dipolar coupling of 70 Hz for the methyl-deuterated sample and 130 Hz for the sample with both methyl and aromatic deuterium labeling. The 60-Hz difference for the two blends is taken to be the contribution to the ^{13}C$-^{2}$H coupling from the aromatic deuterons. The ^{13}C$-^{2}$H couplings are compared to those obtained for the corresponding couplings in blends of [carbonyl-^{13}C]polycarbonate in Table 1. Coupling of the ring-^{13}C label is less than that of the carbonyl-^{13}C label to the methyl deuterons (70 Hz compared to 85 Hz) but more than the combined methyl and ring deuterons (130 Hz compared to 120 Hz). Thus, the ring deuterons are more strongly coupled to the ring-^{13}C label than to the carbonyl-^{13}C label.

As described previously,[8] REDOR calculations must take into account the spin statistics of the methyl group. Rapid methyl rotation results in dephasing by all three deuterons, so that the effect of the deuterated methyl group on a ^{13}C-labeled carbon will be that of a ^{2}H spin-3 system. For $I = 3$, there are 27 possible spin states with $m = \pm 3, \pm 2, \pm 1$, or 0. A methyl group with $m = \pm 1$ will cause carbon dephasing at half the rate of a group with $m = \pm 2$ and at a third of the rate of one with $m = \pm 3$. Deuterated methyl groups with $m = 0$ cause no dephasing. The calculated curves are a sum of three curves, reflecting the differences in dephasing rates arising from the different m values, weighted by the appropriate factors from the spin statistics. An offset of 0.26 was added to account for the 7 out of 27 states with $m = 0$.

Discussion

Coupling to Methyl Deuterons. The calculated ^{13}C$-^{2}$H couplings obtained by fitting the experimental data represent the strength of the carbon–deuterium interaction after motional averaging. The carbonyl and isopropylidene groups have only small-amplitude main-chain reorientational motion of less than 20° (root mean

Table 1. Intermolecular Dipolar Couplings from REDOR Dephasing

blend	$^{13}C-^{2}H$ dipolar coupling (Hz)
5% [3,3′-ring-$^{13}C_2$]polycarbonate *plus* 95% [methyl-d_6]polycarbonate	70[a]
5% [carbonyl-^{13}C]polycarbonate *plus* 95% [methyl-d_6]polycarbonate	85[b]
5% [3,3′-ring-$^{13}C_2$]polycarbonate *plus* 95% [3,3′,5,5′-ring-d_4, methyl-d_6]polycarbonate	130[c]
5% [carbonyl-^{13}C]polycarbonate *plus* 95% [3,3′,5,5′-ring-d_4,methyl-d_6]polycarbonate	120[b]

[a] From Figure 3; experimental uncertainty is ±15%. [b] From ref 8; experimental uncertainty is ±20%. [c] From Figure 4; experimental uncertainty is ±30%.

square).[10-12] In contrast, the phenyl rings undergo oscillations of about $\pm 30°$ superimposed on 180° flips about the C_2 axis.[11,13] The aromatic carbons (Figures 3 and 4) and carbonyl carbons (Figures 7 and 8 of ref 8) have comparable rates of REDOR dephasing, although only the former have large-amplitude motions. This result indicates that $^{13}C-^{2}H$ intermolecular distances are shorter for the aromatic rings than for the carbonyl group. In an earlier paper describing the residual-proton spectrum of perdeuterated polycarbonate,[14] we showed qualitatively that, based on the size of the spinning sidebands, short (less than 2 Å) $^{1}H-^{2}H$ intermolecular distances are present in polycarbonate. With REDOR we can make a more quantitative estimate of the ring–ring and ring–methyl interchain distances.

To obtain a distance from the REDOR dephasing, averaging of the dipolar coupling by molecular motion must be considered explicitly. The C_3 rotation of the deuterated methyl groups has been accounted for by using the $I = 3$ spin statistics described above. We must now include the effect of ring flips on the dipolar interaction. For the blend with deuterium at the methyl positions only (Figure 3), the REDOR results are consistent with dipolar coupling between the aromatic ^{13}C label and a single methyl group. If the sites before and after a ring flip are equivalent (that is, the labeled aromatic carbon toggles between couplings with two different methyl-d_3 groups), the fraction of $m = 0$ states would decrease from 0.26 to 0.13. The observed value of between 0.2 and 0.3 shows that 180° flips cause the aromatic ^{13}C to alternate between strong coupling with a methyl group and no strong coupling. This conclusion is also supported by X-ray data for a crystalline low molecular weight polycarbonate analogue[15] which shows a near-neighbor methyl group for one configuration of the ring but not for its flip side. Thus the effect of the ring flip is to reduce the interaction by about a factor of 2, so that the value of 70 Hz obtained from fitting the experimental dephasing corresponds to a 140-Hz $^{13}C-^{2}H$ coupling and a $^{13}C-^{2}H$ average distance of 3.2 Å. The average distance determined by REDOR is an inverse cube-root average given by $\langle 1/r^3\rangle = 2\pi\langle D_{\mathrm{full}}\rangle/\gamma_D\gamma_C h$, where the γ's are the deuterium and carbon gyromagnetic ratios, respectively, h is Planck's constant, and $\langle D_{\mathrm{full}}\rangle$ is the average full static dipolar coupling. This distance would be reduced slightly if additional motional averaging by main-chain wiggles and phenyl-ring oscillations were taken into account. We have assumed that the aromatic carbon lies on the C_3 axis of the closest CD_3 group, so that the 3.2-Å distance is from the carbon to the base of the rotational cone. This is the shortest-distance geometry.[8] We have also assumed that there is no distribution of packing distances[8] and consequently have probably underestimated the average distance because of the inverse cube-root weighting.

Coupling to Aromatic Deuterons. When the dipolar coupling is between the aromatic ^{13}C and an aromatic ^{2}H, either labeled ring can undergo a 180° flip. When the deuterated ring flips, one deuterium is exchanged for another. The $^{13}C-^{2}H$ interaction changes when the spin states of the two deuterons are different. Of the possible combinations of deuterium spin states, $^{1}/_{3}$ have a flip-averaged effective spin quantum number of $m_{\mathrm{eff}} = 0$, $(-1 \leftrightarrow 1,\ 0 \leftrightarrow 0,\ 1 \leftrightarrow -1)$, $^{4}/_{9}$ have $m_{\mathrm{eff}} = \pm ^{1}/_{2}$, and $^{2}/_{9}$ have $m_{\mathrm{eff}} = \pm 1$. Using these spin statistics to fit the 60-Hz part of the decay in Figure 4 attributed to aromatic deuterons yields an interaction of 135 Hz ($^{9}/_{4} \times 60$ Hz). When the ring with the ^{13}C label flips, the situation is the same as described above for a ring carbon interacting with a methyl group where only one ring site has a $^{13}C-^{2}H$ dipolar coupling. The resulting factor of 2 gives a value for the ring–ring $^{13}C-^{2}H$ dipolar coupling of 270 Hz, which corresponds to a distance of 2.6 Å. As is the case with the ^{13}C coupling to methyl deuterons, including consideration of motional averaging by main-chain wiggles and phenyl-ring oscillations will reduce the estimated $^{13}C-^{2}H$ distance. However, the REDOR dephasing plateau value of 0.20 (Figure 4) is less than that expected from either methyl or aromatic deuterium spin statistics (0.26 and 0.33, respectively). This indicates that there is a next-nearest-neighbor contribution to dephasing which, if it were included, would increase the $^{13}C-^{2}H$ intermolecular distance estimated from the REDOR experiment.

Table 2. Intermolecular Distances for Polycarbonate and a Low Molecular Weight Crystalline Analogue of Polycarbonate

	polycarbonate[a] (Å)	crystalline analogue[b] (Å)
carbonyl ^{13}C to methyl ^{2}H or ^{1}H	3.8[c]	3.9
ring ^{13}C to methyl ^{2}H or ^{1}H	3.2	3.7
ring ^{13}C to ring ^{2}H or ^{1}H	2.6	3.2

[a] Determined by $^{13}C-^{2}H$ REDOR NMR; uncertainty in the distance is taken as ±0.4 Å and includes geometrical unknowns and experimental error as described in ref 8. [b] Determined by X-ray crystallography.[15] [c] From ref 8.

Packing. Table 2 summarizes the intermolecular distances in polycarbonate as determined by $^{13}C-^{2}H$ REDOR. Also listed are the comparable $^{12}C-^{1}H$ distances for the diphenol carbonate of 2,2′-bis(4-hydroxylphenyl)propane which is a low molecular weight analogue of polycarbonate.[15] In all cases the average interchain distances are about the same in the crystal and in the glass, even though the density of the crystal is 1.31 g/cm^3 compared to 1.20 g/cm^3 for the polymer.[15] However, density comparisons can be deceiving. The crystalline model compound has a higher mole fraction of oxygen than the polymer and many easily packed ends, both of which increase density without affecting the distances of Table 2. In addition, a 7% difference in density suggests only 2% differences in linear packing distances. The conclusion that the phenyl rings are densely packed is consistent with our earlier observations of tight packing in perdeuterated polycarbonate[14] and with the need for cooperative lattice motions to enable phenyl-ring flips.[1]

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References and Notes

(1) Schaefer, J.; Stejskal, E. O.; Perchak, D.; Skolnick, J.; Yaris, R. *Macromolecules* **1985**, *18*, 368.
(2) Nielsen, L. E. *Mechanical Properties of Polymers*; Reinhold Publishing Corp.: New York, 1962; p 125.
(3) Boyer, R. F. In *Polymeric Materials. Relationships Between Structure and Mechanical Behavior*; American Society for Metals: Metals Park, OH, 1975; p 308.
(4) Romiszowski, P.; Yaris, R. *J. Chem. Phys.* **1991**, *95*, 6738.
(5) Hutnik, M.; Gentile, F. T.; Ludovice, P. J.; Suter, U. W.; Argon, A. S. *Macromolecules* **1991**, *24*, 5962.
(6) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.
(7) Gullion, T.; Vega, S. *Chem. Phys. Lett.* **1992**, *194*, 423.
(8) Schmidt, A.; Kowalewski, T.; Schaefer, J. *Macromolecules* **1993**, *26*, 1729.
(9) Gullion, T.; Baker, D.; Conradi, M. S. *J. Magn. Reson.* **1990**, *89*, 479.
(10) Poliks, M. D.; Gullion, T.; Schaefer, J. *Macromolecules* **1990**, *23*, 2678.
(11) Schaefer, J.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. *Macromolecules* **1984**, *17*, 1479.
(12) Lee, P. L.; Schaefer, J. Main-Chain Reorientation in Bisphenol-A Polycarbonate by ^{2}H$-^{13}$C Rotational-Echo Double Resonance. *Macromolecules*, submitted for publication.
(13) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Colloid Polym. Sci.* **1987**, *265*, 815.
(14) Lee, P. L.; Schaefer, J. *Macromolecules* **1992**, *25*, 5559.
(15) Henrichs, P. M.; Luss, H. R.; Scaringe, R. P. *Macromolecules* **1984**, *22*, 2731.

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