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Main-Chain Reorientation in Bisphenol-A Polycarbonate by ^{2}H−^{13}C Rotational-Echo Double Resonance

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The mechanically active ring flip in polycarbonate is often thought of in terms of a two-site, single-barrier process.[1] The relevant spatial coordinate for this process is not, however, the ring C_2 axis, but rather a generalized spatial coordinate that involves the positions of neighboring side groups and main chains, as well as the position of the phenyl ring.[2] Thus, a description of the ring-flip process is not straightforward because it depends on many chains. A useful quantitative parameter to help in this description is the average main-chain rotational reorientation angle, which measures the degree to which polycarbonate chains can wiggle in the glass. In the past, we characterized main-chain wiggling using dipolar rotational spin-echo (DRSE) NMR of the isopropylidene methyl carbons.[2,3] We determined that main-chain wiggles were on the order of 10°, a value consistent with the observed temperature dependence of various ^{2}H quadrupolar parameters in perdeuterated polycarbonate.[4,5] However, the DRSE experiment is complicated by the technical difficulty of decoupling methyl−proton ^{1}H−^{1}H interactions for extended periods. The purpose of this paper is to illustrate the direct measurement of main-chain wiggles in polycarbonate using ^{2}H−^{13}C rotational-echo double resonance[6] (REDOR).

The basis of the new measurement is the well-established idea that motion will reduce dipolar coupling and thus decrease REDOR dephasing. When we observe the REDOR dephasing of the natural-abundance methyl ^{13}C magnetization by the isopropylidene methyl deuterons in a methyl-d_6-labeled polycarbonate, wiggling of the main chain that reduces the directly bonded dipolar coupling will also reduce the ^{2}H−^{13}C dephasing. To measure the ^{2}H−^{13}C dephasing in polycarbonate, we used a two-dimensional REDOR experiment[7] in eight rotor cycles (Figure 1). Half of the π pulses were on the ^{13}C channel and were placed on the rotor periods. The other half were on the ^{2}H channel and were placed symmetrically at t_1/T_r (Figure 1). The t_1 parameter was varied from zero (which defines S_0) to $3T_r/16$ in increments of $T_r/32$ with T_r = 200 μs. Data for $t_1 = T_r/32$ were not obtained because of complications arising from the overlap of pulses with finite widths. Simple *XY* phase cycling[8] was used for both the 10-μs ^{13}C pulses and the 7.3-μs ^{2}H pulses. The initial carbon magnetization was obtained from a 50-kHz matched spin-lock transfer from the protons. Data acquisition began following a rotor-synchronized Hahn echo under 90-kHz proton decoupling. Additional details of the probe and spectrometer used in these experiments may be found in ref 9.

The two-dimensional REDOR experiment was performed on (ring-*3,3′,5,5′*-d_4)(methyl-d_6)Bisphenol A (supplied by Merck Stable Isotopes, Montreal) and the polycarbonate made from this labeled Bisphenol A. The ring protons of this polycarbonate are proximate to the isopropylidene methyl carbons[9] and so ensure a uniform cross-polarization transfer (Figure 2, bottom). In addition, there is no significant methyl−^{13}C to ring−^{2}H dipolar coupling and so no averaging effect of ring flips of varying angle[10] in polycarbonate on methyl−carbon REDOR dephasing. The ^{13}C-observed, ^{2}H dephasing for the methyl carbons (Figure 2, top) reaches the theoretical maximum[9,11] of 74% for N_c = 8 with the dephasing pulses at $3T_r/16$. In both systems the directly bonded ^{2}H−^{13}C dipolar coupling is averaged by fast C_3 rotation. The slower dephasing for ^{2}H-labeled polycarbonate compared to that for the corresponding ^{2}H-labeled crystalline Bisphenol A (Figure 3) is due to an additional reduction of the dipolar interaction as a result of main-chain wiggling.

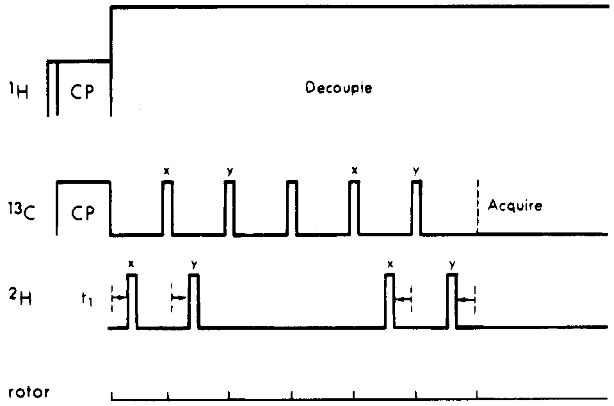

Figure 1. Pulse sequence for two-dimensional ^{13}C-observed, ^{2}H-dephase rotational-echo double resonance. The illustration is for four rotor cycles of dephasing. The carbon π pulse in the middle of the evolution period refocuses isotropic ^{13}C chemical shifts.

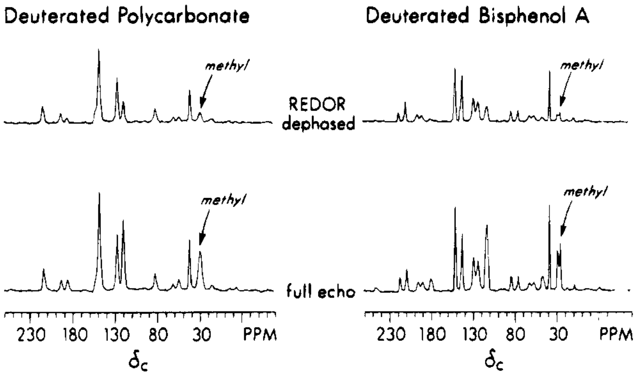

Figure 2. 75-MHz cross-polarization magic-angle spinning ^{13}C NMR spectra of (ring-*3,3′,5,5′*-d_4)(methyl-d_6)polycarbonate (left) and the corresponding labeled crystalline Bisphenol A (right) in an 8-cycle two-dimensional, dipolar modulation REDOR experiment (Figure 1), where the dephasing ^{2}H pulses are placed at fractions of a rotor cycle measured by t_1/T_r equal to 0 (bottom) and $^3/_{16}$ (top). Multiple methyl−carbon lines are observed in the spectrum of the crystal because there are four molecules in the unit cell. The full-echo spectra have been scaled so that the methyl−carbon peak height for polycarbonate matches the lower field methyl−carbon peak height for Bisphenol A. Dephasing is identical for both low- and high-field methyl−carbon lines of Bisphenol A. Magic-angle spinning was at 5 kHz.

If we assume that the wiggling can be represented by isotropic excursions from equilibrium of the vector connecting the methyl ^{13}C to the center of the triangle defined by the three methyl ^{2}H, then the ratio of dipolar coupling for wiggling polycarbonate relative to rigid

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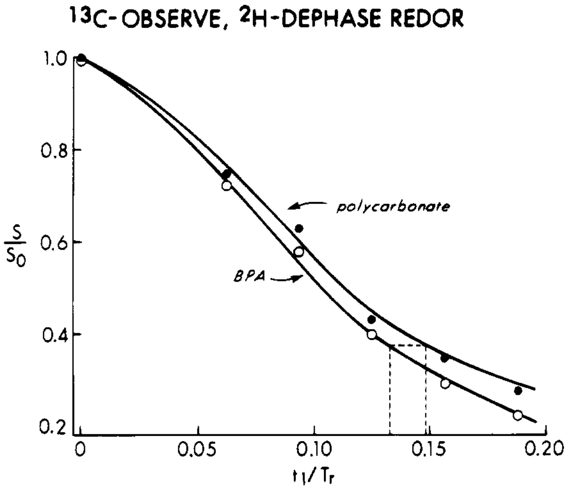

Figure 3. REDOR dephasing for the samples of Figure 2. The dephasing for the methyl–carbon line of glassy polycarbonate is slower than that of crystalline Bisphenol A. The time, t_1, required to reach $S/S_0 = 0.4$ for polycarbonate is about 10% greater than that for crystalline Bisphenol A (dotted-line construction).

Bisphenol A is equal to $1 - 3\langle\sin^2\theta\rangle/2$, where θ is the angular deviation from the equilibrium position.[3] The observed 10% decrease in dipolar coupling (Figure 3) leads to $\theta = \pm 15°$, essentially the same result obtained by DRSE.[2] Despite the need for isotopic labeling, the REDOR experiment has several significant advantages over DRSE: greater accuracy, technically easier execution, and, most importantly, no Larmor frequency constraint. DRSE is only practical at low field, where chemical-shift sidebands do not complicate the analysis despite the slow-spinning conditions necessary for large dipolar sidebands.[3] REDOR works equally well at high and low field. Thus, a CD_3 group can be used as a sensitive probe for REDOR detection of wiggling motions in a variety of glassy polymers, with the magnetic field selected to provide the optimum resolution and sensitivity for the natural-abundance ^{13}C NMR spectrum.

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References and Notes

(1) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(2) Schaefer, J.; Stejskal, E. O.; Perchak, D.; Skolnick, J.; Yaris, R. *Macromolecules* **1985**, *18*, 368.
(3) Schaefer, J.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. *Macromolecules* **1984**, *17*, 1479.
(4) Smith, P. B.; Bubeck, R. A.; Bales, S. E. *Macromolecules* **1988**, *21*, 2058.
(5) Tse, T. Y.; Vold, R. L.; Hoatson, G. L. 35th Experimental NMR Conference, Asilomar, CA.
(6) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.
(7) Gullion, T.; Schaefer, J. *Adv. Magn. Reson.* **1989**, *13*, 57.
(8) Gullion, T.; Baker, D.; Conradi, M. S. *J. Magn. Reson.* **1990**, *89*, 479.
(9) Schmidt, A.; Kowalewski, T.; Schaefer, J. *Macromolecules* **1993**, *26*, 1729.
(10) Hansen, M. T.; Blümich, B.; Boeffel, C.; Spiess, H. W.; Morbitzer, L.; Zembrod, A. *Macromolecules* **1992**, *25*, 5542.
(11) Schmidt, A.; McKay, R. A.; Schaefer, J. *J. Magn. Reson.* **1992**, *96*, 644.

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