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Microscopic Dynamics in Chloral Polycarbonate by Cross-Polarization Magic-Angle Spinning ^{13}C NMR Spectroscopy

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ABSTRACT: The centerband of the ^{13}C dipolar powder pattern observed in a dipolar rotational spin-echo experiment on the resolved protonated aromatic carbon resonance of chloral polycarbonate at room temperature is more pronounced than the corresponding centerband for bisphenol A polycarbonate. We attribute this extra intensity to additional averaging of H–C dipolar interactions by restricted motions about ring and main-chain axes in chloral polycarbonate. None of the rings in the chloral polycarbonate main chain are observed to undergo motions such as full ring rotation or isotropic rotational reorientation.

Introduction

A broad distribution in the rates of molecular motions in chloral polycarbonate (abbreviated CPC) has been inferred from both NMR[1] and mechanical-loss spectroscopy.[2] All of the rings of CPC flip,[3] but at rates which differ by several orders of magnitude. The ring flips appear to be associated with other local and cooperative main-chain motions, whose rates also are broadly distributed.[3]

Li et al.[4] have observed an extremely narrow component of the ^{1}H NMR line shape of CPC just above T_g. Because flips, oscillations, and rotations about the phenyl-ring C_2 axis do not average strong H-2–H-3 and H-5–H-6 intra-ring ^{1}H–^{1}H dipolar couplings, the narrow component (2% of the total) was interpreted as indicating the presence of rings undergoing isotropic rotational reorientation. The increase in population of this narrow component with increasing temperature was then modeled on the basis of an increasing concentration of spatial defects. The models also suggested the presence of small amounts of isotropically reorienting mobile material at defect sites below the glass transition as well.[4] Such defect sites might permit conformational rearrangements of the main chain,[5] a process which has been cited as important to the macroscopic mechanical properties of polycarbonates in the glassy state.[6]

In this paper, we report the results of dipolar rotational spin-echo (DRSE), spin-lattice (T_1), and magic-angle slow-spinning ^{13}C NMR experiments on CPC at room temperature. These experiments all measure phenyl-ring ^{1}H–^{13}C dipolar coupling, an interaction which is partially averaged by ring flips, oscillations, and rotations. The DRSE spinning-sideband dipolar powder patterns for the protonated aromatic carbons of CPC have a pronounced centerband suggesting the possibility of extensive averaging of H–C dipolar coupling by molecular motion. Even though the population of isotropically reorienting rings in CPC can be expected to be much less than 1% at room temperature,[4] only about one-fifth of the free volume required for isotropic reorientation is needed for full rotation about the ring C_2 axis. The focus of this paper is the determination of whether the observed CPC dipolar centerband intensity is due to defect sites with sufficient free volume to permit rings to undergo full rotation at room temperature.

Experimental Section

Magic-Angle Spinning. Cross-polarization, magic-angle spinning ^{13}C NMR spectra were obtained at room temperature on a spectrometer built around a 12-in. iron magnet operating at a proton Larmor frequency of 60 MHz.[7] Half-gram samples were spun in a double-bearing rotor[8] at 1859 or 930 Hz. The long-term stability of the spinning speed was ±1 Hz.

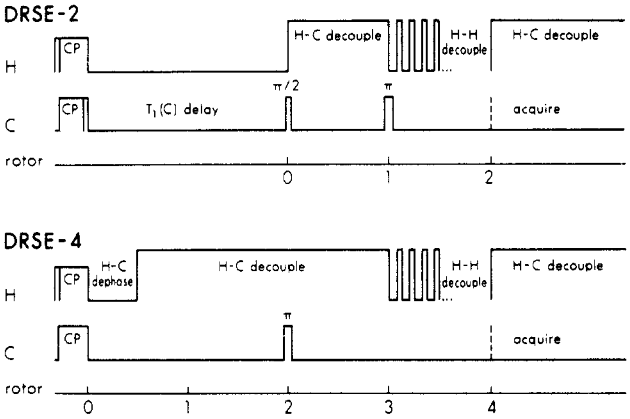

Figure 1. Pulse sequences for dipolar rotational spin-echo ^{13}C NMR.

Carbon Dipolar Sideband Patterns. Carbon dipolar line shapes were characterized by dipolar rotational spin-echo (DRSE) ^{13}C NMR at 15.1 MHz. This is a two-dimensional experiment[9] in which, during the additional time dimension, carbon magnetization is allowed to evolve under the influence of H–C coupling while H–H coupling is suppressed by homonuclear multiple-pulse semiwindowless MREV-8 decoupling.[10] Dipolar echoes form at the end of each rotor period. The cycle time for the homonuclear decoupling pulse sequence was 33.6 μs, resulting in decoupling of proton–proton interactions as large as 60 kHz. Sixteen MREV-8 cycles fit exactly in one rotor period. Isotropic ^{13}C chemical shifts were refocused by a ^{13}C π pulse after the first rotor cycle so that the total evolution period had one rotor cycle for C–H modulation with H–H decoupling and one rotor cycle with complete C–H decoupling (Figure 1, top). The dipolar modulation was preceded by a spin-editing T_1(C) delay period which was varied from 0 to 150 ms. This delay was not synchronized to the rotor. A 16-point Fourier transform of the modulated intensity of any peak resolved by magic-angle spinning in the chemical-shift dimension yielded a 16-point dipolar spectrum, scaled by the MREV-8 decoupling, and broken up into sidebands by the spinning.[11]

The C–H dipolar modulation with H–H decoupling was sometimes preceded by a spin-editing period during which transverse carbon magnetization was dephased by H–C interactions with no H–H decoupling. This dephasing period was typically of the order of 100 μs. Only magnetization from carbons with weak coupling to protons survived. In this situation, dephasing due to chemical shift anisotropy was avoided[12] by a refocusing π pulse (Figure 1, bottom), which increased the total length of the DRSE experiment from two to four rotor periods (Figure 1, bottom).

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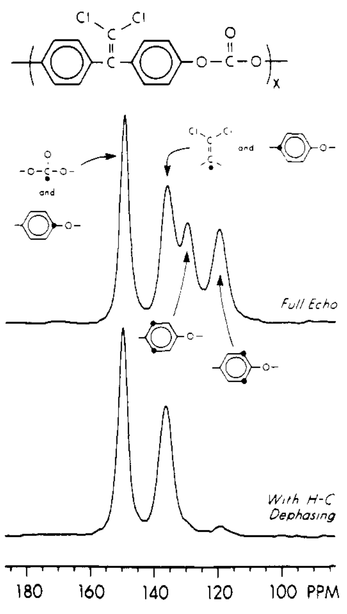

Figure 2. 15.1-MHz cross-polarization magic-angle spinning ^{13}C NMR spectra of chloral polycarbonate. Both spectra were taken with the DRSE-4 pulse sequence of Figure 1. The 50-kHz cross-polarization matched spin-lock transfer was made in 2 ms. The full-echo spectrum (top) had H–C decoupling throughout the echo-formation period. The bottom spectrum was obtained with a 60-μs H–C dephasing period during the first rotor cycle and H–C decoupling for the remainder of the four rotor cycles.

Materials. The PC used in these experiments was commercial Lexan pellets manufactured by General Electric. The CPC was an experimental material generously supplied by Dr. Elizabeth Williams (General Electric Co., Schnectady, NY). Low-molecular-weight components in this sample were removed by fractionation in chloroform. The NMR sample of PC was machined from a solid cylinder melt pressed above T_g and annealed by slow cooling to room temperature in the press. The NMR sample of CPC was cold-pressed powder.

Results

Line Assignments. The full ^{13}C NMR spectrum of CPC consists of four lines (Figure 2, top) of approximately equal integrated intensity. The two lines at higher field (120 and 130 ppm, respectively) are diminished in intensity by an order of magnitude by a 60-μs, H–C dephasing period (Figure 2, bottom). These lines arise from protonated aromatic carbons; the specific assignments shown in Figure 2 were made by analogy with PC line assignments.[13] The lowest field resonance (150 ppm) is a combination line arising from the carbonyl carbon and from the oxygen-substituted, nonprotonated aromatic carbon. The remaining line at 135 ppm is assigned to the 1,1′-phenyl carbons and the main-chain olefinic carbon. No resolved peak is observed for the chlorine-substituted olefinic carbon because of dipolar coupling to a quadrupolar nucleus at low H_0.[14]

Dipolar Coupling and Dipolar Powder Patterns. The intensities of the protonated aromatic carbons of CPC are a strong function of the length of the dipolar evolution period in a DRSE experiment, while those of the nonprotonated carbons are only slightly affected (Figure 3). Similar results have been described before for PC.[3] Fourier transforms of the modulated intensities of protonated aromatic carbons yield dipolar powder patterns for both CPC and PC. As mentioned in the Introduction, the pattern for CPC has a more pronounced centerband than that for PC (Figure 4). The intensity of the centerband increases with the length of a T_1(C) delay preceding dipolar modulation (Table I).

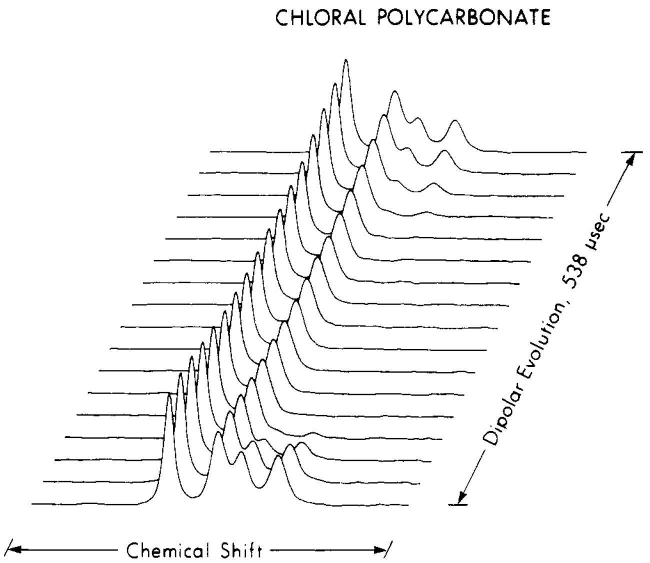

Figure 3. Dipolar rotational spin-echo ^{13}C NMR spectra of chloral polycarbonate as a function of the H–C dipolar evolution time with H–H decoupling. The DRSE-4 pulse sequence of Figure 1 was used with no preparatory H–C dephasing during the first rotor cycle. Each spectrum was the accumulation of 4000 scans. Magic-angle spinning was at 1859 Hz.

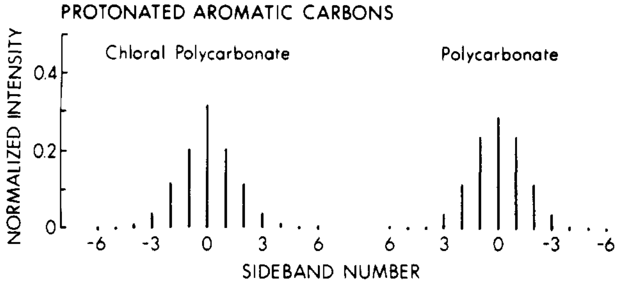

Figure 4. Dipolar powder patterns for chloral polycarbonate (left) and bisphenol A polycarbonate (right). Both patterns were obtained with the DRSE-2 pulse sequence of Figure 1 with the T_1(C) delay equal to zero.

Table I
Dipolar Rotational Sideband Intensities[a,b] for Chloral Polycarbonate

T_1 (C) delay, ms	percentage of initial magnetizatn	n 0	1	2	3	4
0	100	0.312	0.203	0.114	0.037	0.007
50	75	0.331	0.185	0.122	0.042	0.006
100	62	0.330	0.167	0.116	0.050	0.018
150	50	0.353	0.154	0.131	0.052	0.018

[a] Using the DRSE-2 pulse sequence of Figure 1. [b] Semiwindowless MREV-8 multiple-pulse decoupling. The scale factor is 0.54. Magic-angle spinning was at 1859 Hz.

Unlike the results for experiments performed on rigid synthetic and biological solids,[15] about 10% of the CPC protonated aromatic carbon magnetization survives the 60-μs H–C dephasing (Figure 2, bottom). The dipolar powder pattern for the residual signal at 120 ppm has only a centerband and first spinning sideband (Figure 5, right). This pattern differs from that for the nonprotonated aromatic carbon line at 150 ppm under the same conditions (Figure 5, left). Magnetization surviving an H–C dephasing period necessarily is associated with carbons that have weak ^1H–^{13}C dipolar coupling. Particularly weak H–C coupling for the residual protonated aromatic carbon magnetization is revealed by the slow polarization transfer observed under matched spin-lock

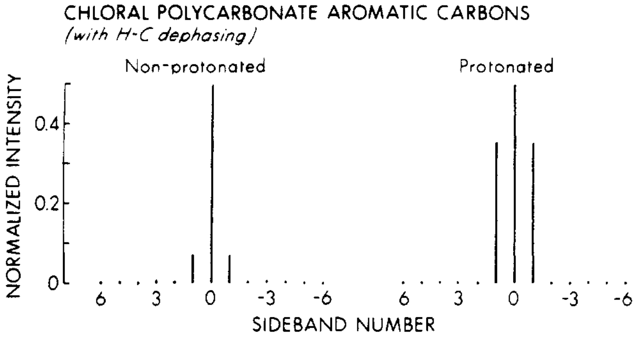

Figure 5. Dipolar powder pattens for chloral polycarbonate obtained with the DRSE-4 pulse sequence of Figure 1. The period for H-C dephasing (with no H-H decoupling) was equal to 60 μs. The pattern on the left is for the non-protonated aromatic carbon line at 150 ppm, and that on the right is for the residual signal at 120 ppm surviving the H-C dephasing.

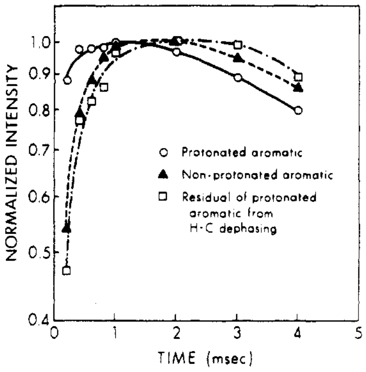

Figure 6. Matched spin-lock cross-polarization transfer kinetics for chloral polycarbonate. The transfer is slowest for those protonated-aromatic carbons surviving a 60-μs H-C dephasing period with no H-H decoupling.

Hartmann-Hahn conditions (Figure 6, open squares).

Chemical-Shift Sidebands. First and second chemical-shift spinning sidebands are resolved for the 120-ppm line of CPC and PC by spinning at 930 Hz (Figure 7, top). Both of these rotational spin-echo spectra were obtained with the DRSE-4 pulse sequence (Figure 1, bottom) but with full H-C decoupling during all four rotor cycles. An initial 60-μs H-C dephasing period changes the n_1/n_0 ratio of integrated intensities from 0.2 ± 0.1 without dephasing to 0.5 ± 0.1 with dephasing (Figure 7, bottom). The H-C dephasing period also essentially eliminates the $n = -1$ spinning sideband.

Discussion

Weak Dipolar Coupling in CPC. The pronounced centerband intensity in the protonated aromatic carbon CPC dipolar powder pattern of Figure 4 can result from molecular motion in either of two ways: a few CPC rings undergoing full rotational reorientation about their C_2 symmetry axes or many CPC rings undergoing restricted oscillations and wigglings about several axes. In both situations, the rate of ring motion cannot be in the 10-MHz regime because the centerband intensity is not associated with a short T_1(C) (Table I). In the latter situation, the average amplitude of restricted motion must be greater than that observed for PC[3] to account for the extra CPC dipolar centerband intensity.

Both of these explanations are consistent with the slow cross-polarization transfer rate for the aromatic carbon magnetization selected by H-C dephasing (Figure 6). The first explanation is consistent by virtue of motionally averaged H-C dipolar coupling and the second by virtue of selection through dephasing of H-C internuclear directions lying near the magic angle. However, the ring full-rotation explanation is not consistent with the dipolar powder pattern of the residual protonated aromatic carbon magnetization observed following H-C dephasing (Figure 5, right). Because of motional averaging, carbon magnetization of a free rotor would be unaffected by the H-C dephasing and would have an n_1/n_0 dipolar sideband ratio of less than 0.1.[3] The CPC experimental value of n_1/n_0 (with H-C dephasing) is 0.7 (Figure 5, right).

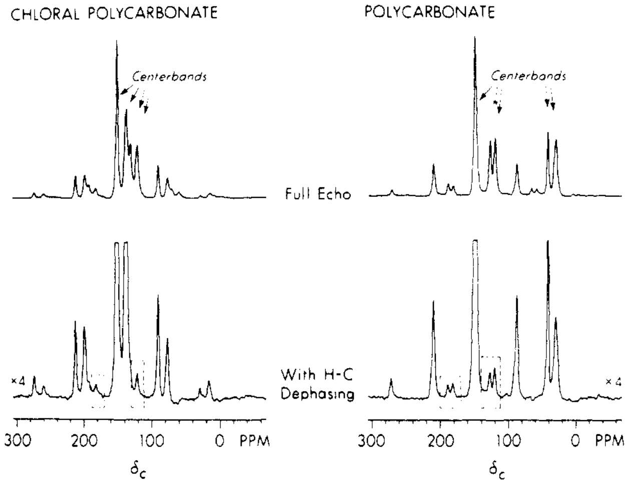

Figure 7. Cross-polarization magic-angle spinning ^{13}C NMR spectra of chloral polycarbonate (left) and bisphenol A polycarbonate (right). Both spectra were obtained by using the DRSE-4 sequence of Figure 1. The full-echo spectrum (top) was obtained with H-C decoupling throughout the four-cycle echo-formation period. The bottom spectrum was obtained with a 60-μs period for H-C dephasing with no H-H decoupling. The boxes highlight the intensities of the centerbands and first spinning sidebands ($n = 1$) of the protonated, aromatic carbon resonances after H-C dephasing. Magic-angle spinning was at 930 Hz.

Magic-Angle Slow Spinning. The ring full-rotation explanation is also not consistent with the slow-spinning results. Because the protonated aromatic carbon chemical-shift tensor is approximately axially symmetric and because it has one element approximately colinear with the C-H internuclear direction, full rotation about the ring C_2 axis takes this tensor element onto the surface of a 60° cone. Fast molecular rotation would therefore collapse the chemical-shift anisotropy,[3] and the CPC aromatic carbon magnetization selected by H-C dephasing would show no significant spinning sidebands. Because a sizeable first spinning sideband is observed (Figure 7, left box), the ring full-rotation explanation is eliminated. We therefore attribute the pronounced centerband intensity to additional averaging of H-C dipolar interactions by restricted motions about ring and main-chain axes. However, there is a remote possibility that the extra CPC dipolar centerband intensity is not due to extra motion at all but rather arises from a long-T_1(C) contribution from the nonprotonated, chlorinated olefinic carbon in CPC. Such a contribution could arise if a combination of quadrupolar and dipolar coupling, partially averaged by molecular motion, happened to result in a 1-kHz wide line centered near 130 ppm. This line would represent about 5% of the integrated intensity of the protonated aromatic carbon resonances and would contribute only to the centerband in a dipolar rotational spin-echo experiment.

Upper Limit on Full-Rotor Population. The results of ^{2}D, ^{1}H, and ^{13}C NMR experiments[16-18] have already established that none of the phenyl rings of PC are full rotors below T_g. We can use this conclusion to estimate an upper bound on the concentration of full rotors in CPC. If only 5% of the CPC protonated aromatic carbon magnetization remaining after an H–C dephasing of 60 μs arose from rings undergoing full rotation and the remaining 95% behaved the same as that from PC rings, then the n_1/n_0 chemical-shift sideband ratio for CPC (with H–C dephasing) would be reduced from the observed value of 0.5 (Figure 7, bottom left) to a value of 0.4. This difference would be just detectable with the present experimental error. Because the residual magnetization after dephasing is 10% of the total, the upper limit on the population of rings undergoing full rotation at room temperature in CPC is 0.5%. The true population could be much lower.

Nature of Defects in Glassy CPC. In the CPC glass, all sites are engaged in a variety of local and cooperative motions with reorientation rates dependent on local packing. In a complex system such as this, there is no single type of microscopic defect determining macroscopic properties. The small fraction of sites at which rings are isotropically reorienting near T_g, for example, is noticeable only because of the peculiarities of motional averaging in the NMR experiment. Nearby sites, which may be equally important to the properties of the glass but which are just slightly more densely packed, have disproportionately less motional averaging of dipolar coupling and so are simply less obvious in NMR spectra.

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