Local Packing in Glassy Polycarbonate by Carbon–Deuterium REDOR NMR

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ABSTRACT: Carbon–deuterium internuclear dipolar couplings have been measured in a homogeneous mixture of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [*methyl*-d_6]polycarbonate using rotational-echo double-resonance NMR. The observed ^{13}C–^{2}H couplings can be interpreted in terms of intermolecular distances. The distance from the carbonyl carbon of one polycarbonate chain to the average deuterium position of the closest methyl group of the nearest-neighbor polycarbonate chain is 3.8 Å.

Introduction

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 around which the flip occurs but rather a generalized spatial coordinate that involves not only the position of the phenyl ring but also the positions of neighboring side groups and main chains.[2] Progress in understanding the lattice reorganization that gates the ring flip in polycarbonate has been made recently using computer simulations of cooperative motions in the solid state.[3] Naturally, these simulations benefit from realistic intermolecular starting coordinates. So far these coordinates have been limited to values determined approximately by energy minimization calculations[4] or by crystallography either for the bisphenol A monomer of polycarbonate or for low molecular weight crystalline analogues of polycarbonate.[5]

In this paper, we report the first of a series of NMR distance measurements on glassy polycarbonate itself. The goal of this work is to measure accurately interchain, internuclear distances to define local packing and so help make the connection between microscopic structure and macroscopic properties. Information about local packing will also provide starting coordinates for molecular dynamics of mechanically important motions. The NMR methods to be employed all involve recently developed hetero- and homonuclear dephasing techniques for measuring weak dipolar coupling between isolated pairs of spins in samples undergoing magic-angle spinning.[6-8] Carbon–deuterium heteronuclear couplings are measured by rotational-echo double-resonance (REDOR) and carbon–carbon homonuclear couplings by either dipolar restoration at the magic angle (DRAMA) or simple excitation for the dephasing of rotational amplitudes (SEDRA). The isolated spin pairs are introduced by isotopic labeling.

Experiments

Solids NMR Spectrometer. Magic-angle spinning ^{1}H, ^{13}C, and ^{2}H NMR spectra were obtained using a three-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-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 ±1-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 transmitters for the carbon and proton channels, respectively. The spectrometer is controlled by a three-channel Chemagnetics CMX-300 console.

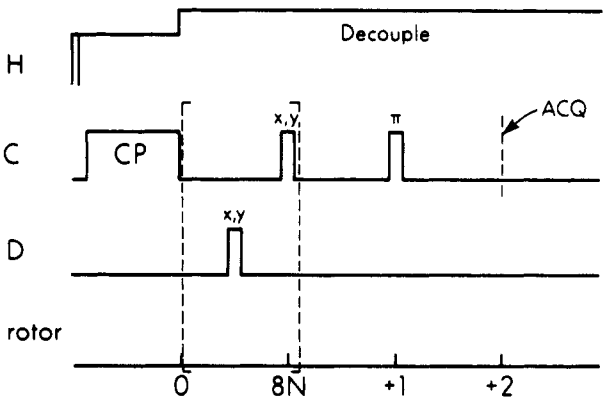

Figure 1. Pulse sequence for ^{13}C–^{2}H rotational-echo, double-resonance NMR with ^{13}C observation. The protons provide the initial carbon magnetization by a matched cross-polarization transfer at 50 kHz and then are removed from the experiment by resonant decoupling at 90 kHz. The phases of the ^{13}C and ^{2}H π pulses follow xy-8 and xy-4 phase-alternation schemes, respectively.

REDOR NMR. The pulse sequence used for distance measurements is shown in Figure 1. Carbon magnetization is produced by a matched proton–carbon spin-lock transfer at 50 kHz. The protons are then removed from the remainder of the experiment by 90-kHz resonant decoupling. Transverse carbon magnetization is dephased by rotor-synchronized π pulses on both carbon and deuterium channels.[9] The fully compensated, basic repeat sequence is eight rotor cycles in length with ^{13}C π pulses placed on the rotor periods and ^{2}H π pulses on the half rotor periods. The phases of ^{13}C π pulses are varied according to the xy-8 phase-alternation scheme, and those of the ^{2}H π pulses by the xy-4 phase-altenation scheme.[10] Data acquisition begins two rotor periods after dephasing, following a single ^{13}C π pulse one rotor period earlier to eliminate phase accumulation due to isotropic chemical-shift offsets. Data acquisition can be either synchronous with the rotor to eliminate spinning sidebands or asynchronous with the rotor for a spectral display with spinning sidebands. The version of REDOR that was used in these experiments was performed in two parts: once with the dephasing ^{2}H π pulses (S) and once without them (S_0). The resulting normalized carbon signal is S/S_0.

Labeled Polycarbonates. The [*carbonyl*-^{13}C]polycarbonate was the generous gift of J. Michael Hewitt (Eastman Kodak Co., Rochester, NY). This is the same polymer that was used in previous chemical-shift tensor experiments by Henrichs and Hewitt and their co-workers.[11] The [3,3′,5,5′-*ring*-d_4,*methyl*-d_6]-polycarbonate was synthesized in 1982 by R. J. Kern (Monsanto Co., St. Louis, MO) from monomer supplied by Merck Stable Isotopes. The polymer has a weight-average molecular weight of approximately 30 000. The [*methyl*-d_6]polycarbonate was the generous gift of Alan A. Jones (Clark University, Worcester, MA)

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and was described earlier in connection with experiments measuring the temperature dependence of local motions in polycarbonate.[12] Mixtures of polycarbonates (5% ^{13}C labeled and 95% ^{2}H labeled) were formed from 2.5% (by weight) solutions of polycarbonate in chloroform by dropwise precipitation in excess methanol.

Results

REDOR Calibration. The ^{13}C signal of an isolated ^{13}C–^{2}H pair in the REDOR experiment with dephasing ^{2}H π pulses shown in Figure 1 is

$$S(nT_R) = {}^1/_3[1 + 2\cos(2\bar{\omega}_D nT_R)] \quad (1)$$

where $\bar{\omega}_D$ is the effective dipolar coupling,[9] n is the number of rotor periods over which the dephasing occurs, and T_R is the rotor period. Because a single ^{2}H has three possible spin states ($m = -1, 0, 1$), one-third of the ^{13}C magnetization arises from ^{13}C's paired with deuterons with $m = 0$. This magnetization is unaffected by the REDOR dephasing pulses. The remaining two-thirds of the magnetization arises from carbons coupled to deuterons for which $m = \pm 1$. This ^{13}C magnetization dephases at twice the rate for a heteronuclear spin pair both of spin $^1/_2$. In the absence of ^{2}H π pulses, $\bar{\omega}_D$ is zero.

For a methyl-d_3 group undergoing fast internal rotation about its C_3 axis, the motionally averaged ^{13}C–^{2}H dipolar coupling is identical for each of the three deuterons. Therefore, the carbon and deuterium can be considered an isolated effective spin pair. However, the possible combinations of spin states of the deuterons ($M = -3, -2, -1, 0, 1, 2, 3$ with relative populations of 1, 3, 6, 7, 6, 3, 1, respectively) change the fraction of ^{13}C magnetization unaffected by REDOR dephasing from $^1/_3$, or 33%, to $^7/_{27}$, or 26%. Components of the remaining 74% dephase at 2, 4, or 6 times the spin $^1/_2$ pair rate, depending on the total spin state, M, so that

$$S(nT_R) = {}^1/_{27}[7 + 12\cos(2\bar{\omega}_D nT_R) + 6\cos(4\bar{\omega}_D nT_R) + 2\cos(6\bar{\omega}_D nT_R)] \quad (2)$$

This expression was used to calculate the dependence of S/S_0 on the total dephasing time, nT_R, shown in Figure 2 as the solid curve. The calculation was performed assuming a ^{13}C–^{2}H dipolar coupling of 250 Hz and so is applicable to two-bond ^{13}C–CD_3 carbon–deuterium coupling with the methyl group undergoing fast internal rotation and the entire molecule undergoing ultrafast, small-amplitude isotropic reorientation (cf. below). Experimental and calculated REDOR dephasing for zinc bis([1-^{13}C]methylacetate-d_3) (Isotec, Inc.) recrystallized with a 7-fold excess of natural-abundance zinc acetate, are in agreement (Figure 2, solid circles and squares). Dephasing for undiluted double-labeled zinc acetate is greater than 74% (Figure 2, open circles) because of combined intra and intermolecular ^{13}C–^{2}H coupling.

Mixing of Polycarbonate Chains. In solution, the root-mean-square end-to-end distance of a linear, flexible, freely jointed chain of length L, composed of N segments each of length a, is

$$R_F = aN^\nu = a^{(1-\nu)}L^\nu \quad (3)$$

where ν is a universal exponent which depends on polymer–solvent interactions.[13] Real polymer chains which rearrange through hindered rotation about skeletal covalent bonds can still be described as freely jointed if the segment length is identified with the effective rigid-unit length.[14,15] For a good solvent $\nu = {}^3/_5$; for a Θ solvent, $\nu = {}^1/_2$. The concentration for interchain coil–coil overlap is given by

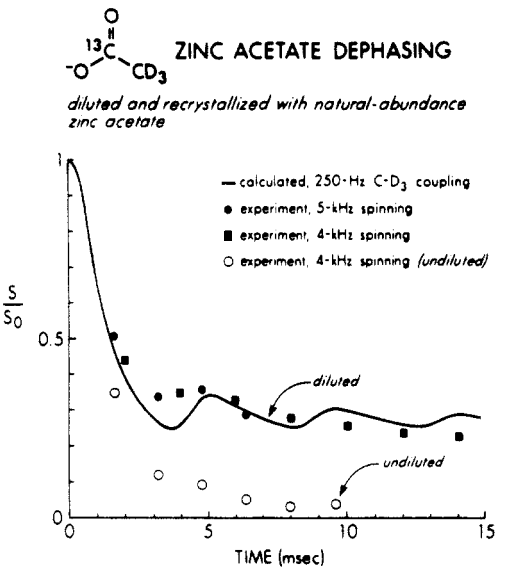

Figure 2. REDOR dephasing for the carbonyl carbon of zinc bis([1-^{13}C]methylacetate-d_3) using the pulse sequence of Figure 1. The total dephasing time is nT_R, where n = 8, 16, 24, ... and T_R is the rotor period. The open circles (T_R = 200 μs) correspond to a fully enriched sample. The solid circles (T_R = 200 μs) and squares (T_R = 250 μs) correspond to a 7-fold dilution of the ^{13}C-^{2}H-labeled zinc acetate by natural-abundance zinc acetate.

$$c^* = N/R_F^3 = L^{(1-3\nu)}/a^{(4-3\nu)} \quad (4)$$

where the solution concentration is expressed as the number of rigid units per unit volume.[13] The overlap concentration defines the condition for which the nearest neighbors of each effective rigid unit are from other chains rather than from the same chain. This condition depends on the molecular weight (represented by the chain length) and the chain flexibility (represented by the length of a rigid unit). For polymers like polyethylene, the effective rigid-unit length can be derived from the monomer repeat unit;[14] for polycarbonate, the assignment is less obvious. The effective rigid unit probably consists of about one monomer repeat but could be longer.[16] We denote by f the ratio M_a/M_m, where M_a and M_m are the molecular weights of the effective rigid unit and the repeat unit, respectively. We assume that f also represents the ratio of the lengths of an effective rigid unit and a repeat unit. Because $L = (M_n/M_m)l_m$, where M_n is the number-average molecular weight of the chain, and $a = fl_m$, we can rewrite eq 4 as

$$c^*\ (\mathrm{g/dL}) = (10^{26}/N_A)M_m l_m^{-3}(M_n/M_m)^{(1-3\nu)}f^{(3\nu-3)} \quad (5)$$

where N_A is Avogadro's number and the repeat unit length is expressed in angstroms. The overlap concentrations for two solvent conditions and two molecular weights typical for polycarbonates are plotted in Figure 3. The length of the repeat unit was taken as 13 Å. For a given effective rigid-unit segment length, the major factor determining the coil overlap condition is the solvent quality described by ν. For an f of the order of 1, interchain penetration occurs when a polycarbonate blend is prepared by solvent precipitation from a solution concentration of 2–3 g/dL, assuming a ν of about $^1/_2$ for the precipitating mixed-solvent conditions. Interchain mixing will also be more likely to occur upon rapid precipitation, as the chains which are thorougly mixed under good-solvent conditions will be kinetically trapped.

If ^{13}C-labeled polycarbonate coils are isolated from one another, the average concentration of ^{13}C-labeled rigid segments in a sphere of radius corresponding to the coil

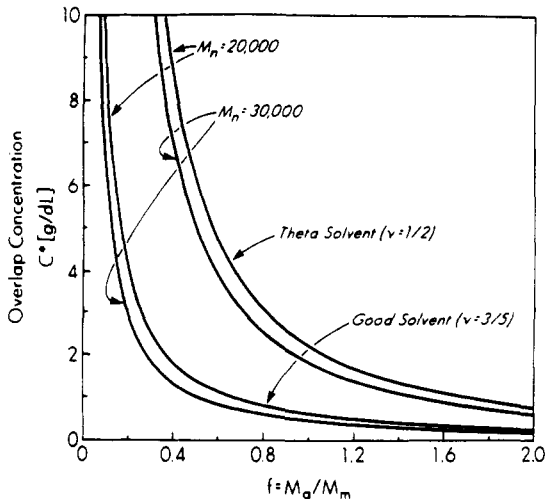

Figure 3. Calculated coil–coil overlap concentration, c^*, as a function of the ratio of the molecular weight of the chain's effective rigid unit to that of the chain's monomer repeat unit.

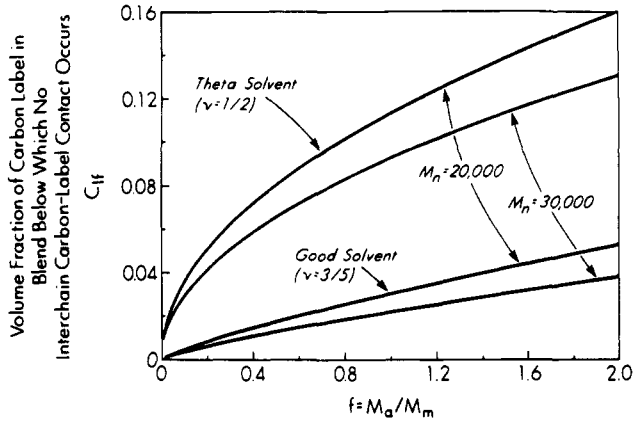

Figure 4. Calculated volume fraction of ^{13}C-labeled effective rigid units in a sphere of radius defined by the root-mean-square end-to-end distance of the ^{13}C-labeled coil as a function of the ratio of the molecular weight of the chain's effective rigid unit to that of the chain's monomer repeat unit.

radius is

$$c_C = N/R_F^3 = a^{-3}N^{(1-3\nu)} \quad (6)$$

and is zero outside of this sphere.[13] Thus, the volume fraction, C_{lf}, of ^{13}C-labeled effective rigid units in the sphere containing a ^{13}C-labeled coil is

$$C_{lf} = N^{(1-3\nu)} \quad (7)$$

This volume fraction is plotted in Figure 4 as a function of the effective rigid-unit-to-monomer ratio, f. We see that for an f of about 1, a mixture of ^{13}C-labeled chains and ^2H-labeled chains (precipitated from a solution of concentration greater than c^*) will have all the ^{13}C-labeled chains completely surrounded by ^2H-labeled chains if the ^{13}C isotopic concentration is less than about 8%. In general, Figures 3 and 4 specify the conditions necessary to make a precipitated homogeneous blend of two kinds of labeled polycarbonates. The polymer concentration in solution is defined by Figure 3, and the relative isotopic concentrations are defined by Figure 4.

REDOR of Polycarbonate Mixtures. At 75 MHz, the carbonyl carbon resonance in the ^{13}C NMR spectrum of a precipitated mixture of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [3,3′,5,5′-*ring*-d_4,*methyl*-d_6]polycarbonate is partially resolved (Figure 5, top). The spectrum of the blend of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [*methyl*-d_6]polycarbonate (not shown) is indistinguishable from

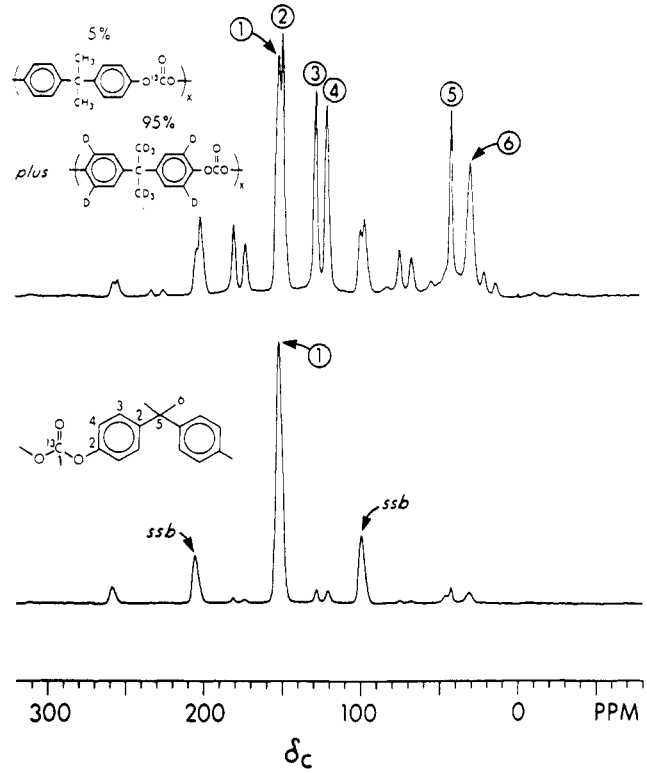

Figure 5. 75-MHz cross-polarization, magic-angle spinning ^{13}C NMR spectra of a homogeneous mixture of 5% [*carbonyl*-^{13}C]-polycarbonate and 95% [3,3′,5,5′-*ring*-d_4,*methyl*-d_6]polycarbonate (top) and of [*carbonyl*-^{13}C]polycarbonate homopolymer (bottom). First spinning sidebands of the carbonyl carbon peak are identified as "ssb".

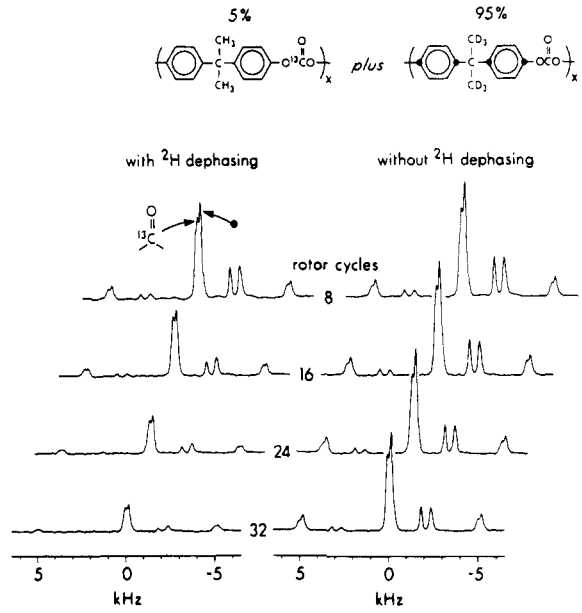

Figure 6. 75-MHz REDOR ^{13}C NMR spectra of a homogeneous mixture of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [*methyl*-D_6] polycarbonate as a function of the number of rotor cycles of evolution of carbon magnetization with (left) and without (right) ^2H dephasing π pulses. The spectra were obtained using the pulse sequence of Figure 1.

that in Figure 5. All of the aromatic carbon peaks of the latter blend are dephased by ^2H REDOR π pulses (Figure 6), including the carbonyl carbon peak, 80% of which arises from the labeled carbonate carbons of chains having no ^2H substitution. The absence of a plateau at 0.26 in the REDOR dephasing shown in Figure 7 indicates dipolar coupling of the carbonyl carbons to distant deuterons. The REDOR dephasing of the carbonyl carbons of the

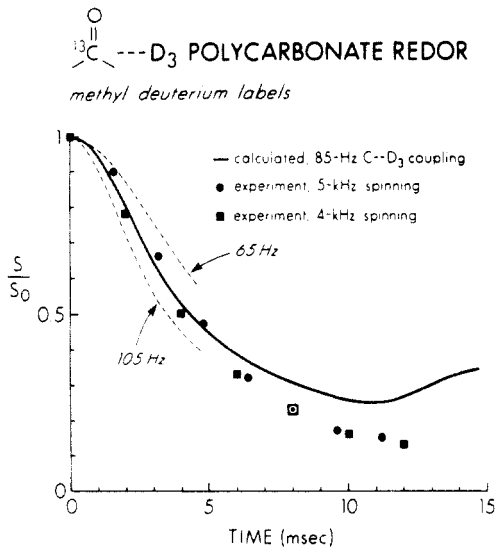

Figure 7. REDOR dephasing for the carbonate carbon of a homogenous mixture of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [*methyl*-d_6]polycarbonate. The total dephasing time is nT_R, where n = 8, 16, 24, ... and T_R is the rotor period (circles, T_R = 200 μs; squares, T_R = 250 μs). The calculated dephasing (solid line) assumed an 85-Hz dipolar coupling to a single CD_3 group.

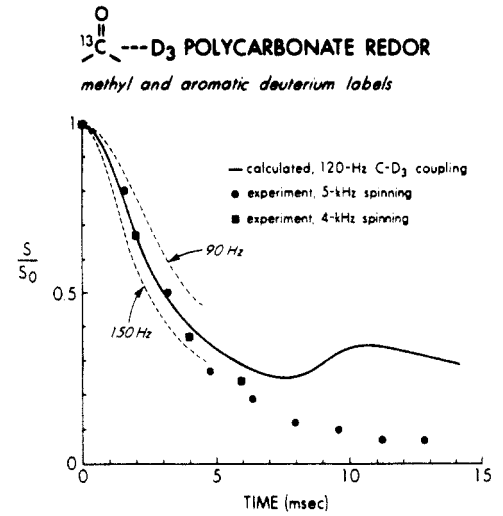

Figure 8. REDOR dephasing for the carbonate carbon of a homogeneous mixture of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [3,3′,5,5′-*ring*-d_4,*methyl*-d_6]polycarbonate. The total dephasing time is nT_R, where n = 8, 16, 24, ... and T_R is the rotor period (circles, T_R = 200 μs; squares, T_R = 250 μs). The calculated dephasing (solid line) assumed a 120-Hz dipolar coupling to a single CD_3 group.

blend of 5% [*carbonyl*-^{13}C]polycarbonate and 95% [3,3′,5,5′-*ring*-d_4,methyl-d_6]polycarbonate (Figure 8), which arises from both ring and methyl deuterium labels, is only slightly faster than that shown in Figure 7 for dephasing by methyl deuterium labels only. The complete dephasing shown in Figures 7 and 8 is an experimental demonstration of the microscopic homogeneity of the mixing of ^{13}C- and ^{2}H-labeled chains. The incomplete dephasing which would result from heterogeneous mixing could be used in future NMR studies of the fundamental chain parameters of eqs 3–7.

Discussion

Zinc Acetate. The ^{13}C–^{2}H dipolar coupling in the absence of methyl rotation is 477 Hz, corresponding to the geometry-independent, two-bond, 2.13-Å internuclear distance in zinc acetate.[17] The angle β between the internuclear C–D vector and the C_3 axis of rotation is 29°.

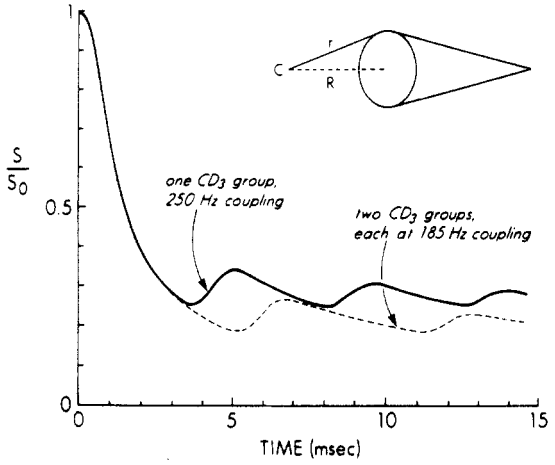

Figure 9. Calculated REDOR dephasing for ^{13}C- - -CD_3 dipolar coupling for one CD_3 group (R = 2.15 Å, r = 2.38 Å; solid line) and two collinear CD_3 groups (R = 2.50 Å, r = 2.70 Å; dotted line).

Thus, in the presence of fast rotation, the dipolar coupling is scaled by $P_2(\cos\beta)$, resulting in an effective coupling of 310 Hz. The two-bond, 250-Hz C–D_3 dipolar coupling used to fit the REDOR results of Figure 2 is about 20% less than the 310-Hz value calculated by assuming no motion other than fast rotation about the methyl C_3 axis and 1.48-Å C–C and 1.10-Å C–D bond lengths. This reduction is comparable to those observed for C–H and N–H dipolar couplings in dipolar-rotational spin-echo experiments.[18] Such reductions have been attributed to a combination of ultrahigh-frequency librational motion of the entire molecule within the crystalline lattice and bond-specific internal torsional and vibrational motions.[19] The librational motions affect all dipolar couplings within the molecule, and the resulting averaging has been cited in the approximately 6% reductions of ^{13}C–^{15}N dipolar coupling commonly observed for nominally rigid, crystalline amino acids.[20] Calculations have suggested that vibrational motions may only account for about a 5% reduction of C–H and N–H dipolar couplings[21] but the exact amount depends on details of the anharmonicity of the motion and may be larger than 5%.

The absence of a spinning-speed dependence for the dephasing in Figure 2 means that there is no significant reduction of ^{13}C–^{2}H coupling by spinning-dependent residual ^{2}H–^{2}H dipolar interactions.

Polycarbonate. The similar initial dephasings of the carbonyl carbon magnetization for the two polycarbonate mixtures indicate that the ^{13}C–^{2}H dipolar coupling is dominated by methyl deuterons. The aromatic deuterons appear to make no more than a 20% contribution to the dephasing (Figure 8). In addition, the experimental uncertainty in the initial dephasing is well within a ±20% bracket (Figures 7 and 8). An uncertainty of 20% in REDOR dephasing means an uncertainty of only 6% in the corresponding internuclear distance determination.

We attribute the initial dephasing of the carbonyl carbon magnetization to a *single* CD_3 group. A random distribution of C–D distances (with variations in distances of the order of a factor of 2) would leave about half of the carbonyl carbons with no strong C–D couplings and only slow dephasing. But a slowly dephasing population of carbonyl carbons is not observed. The experimental carbonyl carbon dephasing is matched to the calculated dephasing by assuming a *single* dipolar coupling of 85 Hz. A pair of CD_3 groups identically distant from the carbonyl carbon would produce the same initial dephasing with a weaker dipolar coupling (Figure 9), but such an arrange-

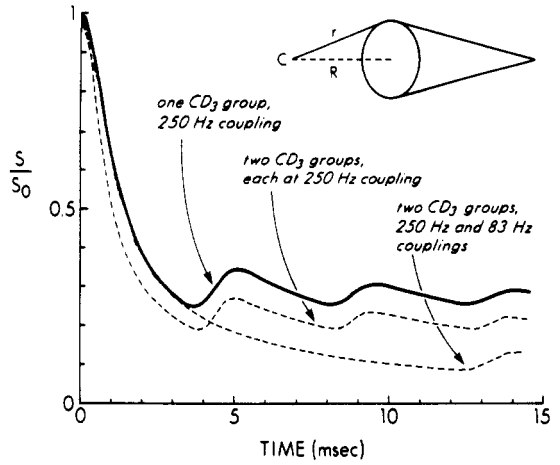

Figure 10. Calculated REDOR dephasing for ^{13}C- - -CD_3 dipolar coupling for one CD_3 group (R = 2.15 Å, r = 2.38 Å; top, solid line) and two collinear CD_3 groups having equal carbon–deuterium dipolar couplings (R = 2.15 Å, r = 2.38 Å; middle, dotted line) and unequal carbon–deuterium dipolar couplings (R_1 = 2.15 Å, r_1 = 2.38 Å, R_2 = 3.50 Å, r_2 = 3.64 Å; bottom, dotted line).

ment is physically implausible. To preserve the approximate orthogonality of tightly packed rings on adjacent chains, the isopropylidene of one chain must be tilted with respect to the carbonate of the nearest-neighbor chain so that one of the methyls is closer to the carbonate than the other.[5] Two methyl groups with significantly different couplings result in an initial dephasing that is dominated by the closer CD_3 group (Figure 10).

A ^{13}C- - -CD_3 dipolar coupling of 85 Hz accounts for the initial dephasing of Figure 5 in terms of a single methyl group undergoing no motion except fast rotation about the methyl C_3 axis. As described above for zinc acetate, ignoring small-amplitude motional averaging results in about a 5% overestimate of a distance from an observed dipolar coupling. If we assume that the carbonyl carbon lies on the C_3 axis of the closest CD_3 group, then the distance from the carbonyl carbons to the base of the rotational cone is 3.4 Å. This is the closest possible approach, and one which would allow neighboring intermolecular rings to be close to orthogonal. If the carbonyl carbon–deuteron (d_3) internuclear vector is perpendicular to the C_3 axis, then the estimated separation from the carbonyl carbon to the center of the base of the CD_3 rotational cone increases to 4.2 Å. The average value is 3.8 Å. Additional experiments to determine other intermolecular, internuclear distances in polycarbonate are in progress and should allow refinements in the interpretation of the CD_3 geometrical factors and an assessment of the extent of small-amplitude motional averaging of the carbonate- - -CD_3 coupling. For the present, we cite the nearest-neighbor, carbonate- - -CD_3, intermolecular distance as 3.8 ± 0.4 Å.

The crystal structure of low molecular weight polycarbonate analogues places the carbonate group in proximity to the isopropylidene group and the 2,2′,4,4′ ring positions, not the 3,3′,5,5′ positions,[5] consistent with the results of Figure 6. Even though the long-range order of crystalline model compounds is irrelevant to the structure of polycarbonate itself, crystal and glass necessarily have similarities on a 5-Å scale. This fact is substantiated by the initial dephasing rate of Figure 5 which shows no slowly changing component. In other words, all carbonates are near a methyl and the distribution of intermolecular carbonte–isopropylidene distances in the glass is therefore narrow.

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