Chain Packing in Ethoxyphenyl−Polycarbonate by $^{13}C\{^2H\}$ REDOR

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ABSTRACT: Rotational-echo double-resonance $^{13}C\{^2H\}$ NMR has been used to characterize the chain packing in a $^{13}C,^2H$-labeled ethoxyphenyl-substituted bisphenol A polycarbonate. Approximately 36% of the repeat units are locally ordered, and between 85% and 95% of carbonate linkages are trans. The local order in interchain packing is correlated with the local order of intrachain conformations of the carbonate linkages.

Introduction

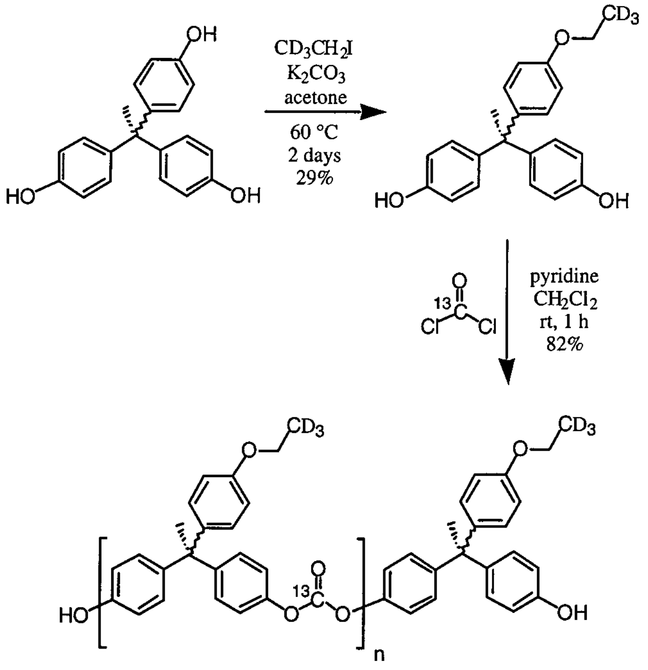
Rotation about the C−O single bonds of the carbonate linkage of polycarbonates results in main-chain kinks and bends. This conformational heterogeneity is thought to be responsible for introducing randomness in the chain packing of polycarbonate in the glassy state.[1] Conformational heterogeneity is, in fact, reflected in the relatively broad lines typically observed for polycarbonates in magic-angle spinning ^{13}C NMR experiments.[2] The widths of these resonance lines scale with magnetic field and are generally attributed to the presence of a distribution of isotropic shifts.[3] In support of this notion, measurements[4,5] and detailed quantum mechanical calculations[6] show that the isotropic chemical shifts in proteins are highly sensitive to local torsional angles and, consequently, the secondary structure. Thus, the ^{13}C chemical shift is now being used as a direct and effective measure of protein structure in solution[7] and in the solid state.[8]

The problem in learning anything about the local structure in polycarbonate glasses from chemical shifts is in detecting individual isotropic shifts in the presence of a broad distribution of shifts. In this paper, we show that the *interchain* packing in ethoxyphenyl−polycarbonate is locally ordered. Furthermore, we connect this order with the local *intrachain* conformation by correlating the chemical shifts with through-space interchain distances. We use the through-space dipolar coupling between the ^2H label on one chain and a ^{13}C label on another as the selection mechanism to detect a conformationally dependent chemical shift.

Experimental Section

Synthesis. The synthesis of the ethoxyphenyl-substituted bisphenol A polycarbonate (ethoxyphenyl−polycarbonate) involved the two-step procedure shown in Scheme 1. The ^2H-containing ethoxy group was introduced onto one of the three phenol functionalities of 1,1,1-tris(4′-hydroxyphenyl)ethane (Aldrich) by reaction with 2,2,2-d_3-ethyl iodide (Isotec) to give the diphenolic monomer unit. Polymerization was then achieved by condensation with ^{13}C-labeled phosgene (Isotec, 99% ^{13}C, as a 1.1 M solution in benzene).

Scheme 1



a. 1,1-Bis(4′-hydroxyphenyl)-1-(4′-(2,2,2-d_3-ethoxy)phenyl)ethane. In a Schlenk tube under nitrogen 1,1,1-tris(4′-hydroxyphenyl)ethane (6.98 g, 22.7 mmol), 2,2,2-d_3-ethyl iodide (1.86 mL, 3.63 g, 22.8 mmol), and potassium carbonate (4.08 g, 29.6 mmol) were added to dry acetone (50 mL). The mixture was brought to 60 °C, sealed, and allowed to react for 2 days. The residue was dissolved in ether, extracted with 10% $HCl_{(aq)}$, and washed with aqueous sodium bicarbonate. The organic layer was isolated and dried over $MgSO_4$. The ether was evaporated, and the resulting yellow crude was purified by flash column chromatography (silica gel, using a gradient solvent system as eluent: hexane:CH_2Cl_2, 10:90 until the triethoxy-substituted byproduct eluted, CH_2Cl_2 until diethoxy-substituted byproduct eluted, and finally ether:CH_2Cl_2, 10:90 until the desired monoethoxy-substituted product eluted) to yield 2.23 g (29.2%) as a colorless solid. ^1H NMR (acetone-d_6): δ 2.02 (s, 3H, $-C\boldsymbol{H}_3$), 3.92 (br s, 2H, $-OC\boldsymbol{H}_2-$), 6.72 and 6.89 (ABq, 8H, $-Ar\boldsymbol{H}-OH$, $J = 9.0$ Hz), 6.75 and 6.96 (ABq, 4H, $-Ar\boldsymbol{H}-OEt$, $J = 9.0$ Hz), 8.23 ppm (s, 2H, $-O\boldsymbol{H}$). ^{13}C NMR (acetone-d_6): δ 17.00, 31.15, 51.04, 63.51, 114.02, 115.05, 130.07, 130.14, 141.39, 142.45, 155.71, 157.52 ppm.

b. $^2H,^{13}C$-Labeled Ethoxyphenyl-Substituted Bisphenol A Polycarbonate. 1,1-Bis(4′-hydroxyphenyl)-1-(4′-(2,2,2-d_3-ethoxy)phenyl)ethane (1.30 g, 3.91 mmol) was dissolved in

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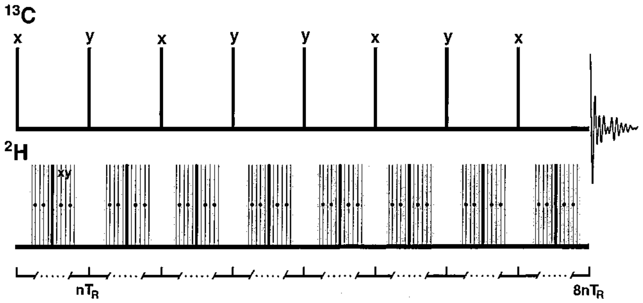

Figure 1. REDOR pulse sequence in which the total number of ^{13}C π pulses is fixed at 8. The total number of ^{2}H dephasing π pulses is $8(2n - 1)$, where nT_r is the dipolar evolution time between carbon pulses and $n = 1, 2, 3, ...$

degassed CH_2Cl_2 (20 mL). Pyridine (0.95 mL, 12 mmol) was added to the solution and allowed to stir for 0.5 h. Carbon-13-labeled phosgene (3.8 mL, 1.1 M in benzene, 4.2 mmol) was added to the solution and allowed to stir for 0.5 h. Subsequent additions of ^{13}C-labeled phosgene (2×0.50 mL additions) were made at 30 min intervals, while polymer growth was monitored by GPC (based on calibration with polystyrene standards). Once the polymer had reached the desired molecular weight, CH_2Cl_2 was added to the reaction mixture and then extracted with 10% $HCl_{(aq)}$ solution followed by 5% aqueous sodium bicarbonate solution. The organic layer was isolated, dried over $MgSO_4$, and concentrated in vacuo. The resulting viscous liquid was dissolved in THF and precipitated into methanol to yield 1.17 g (82.0%) as a white powder. M_w = 130 000, M_n = 57 000 g/mol from GPC based on polystyrene standards. T_g(DSC) = 172 °C. ^1H NMR (THF-d_8): δ 2.16 (br s, 3H, $-C\boldsymbol{H}_3$), 3.96 (br s, 2H, $-OC\boldsymbol{H}_2-$), 6.79 and 7.00 (ABq, 4H, $-Ar\boldsymbol{H}-OEt$, $J = 9.0$ Hz), 7.15 and 7.19 ppm (ABq, 8H, $-Ar\boldsymbol{H}-OCO-$, $J = 9.0$ Hz). ^{13}C NMR (THF-d_8): 52.19, 62.98, 114.28, 114.50, 120.88, 141.02, 148.02, 150.25, 151.76, 152.88, 158.26 ppm.

REDOR NMR. REDOR ^{13}C NMR spectra were acquired from a 150 mg sample of $^{13}C,^{2}H$-labeled ethoxyphenyl−polycarbonate at ambient temperature using a Chemagnetics CMX-300 spectrometer operating at 75.453 MHz for carbon and a three-frequency transmission-line probe. REDOR experiments are always done in two parts: once with dephasing pulses and once without.[9] Both parts have the identical number of refocusing pulses. The differences in ^{13}C signal intensities in the two parts of REDOR experiments performed on a ^{13}C- and ^{2}H-labeled material are directly related to the corresponding distances between ^{13}C and ^{2}H labels. The REDOR pulse sequence that was used for double-labeled ethoxyphenyl−polycarbonate had a fixed total of eight ^{13}C π pulses for all dipolar evolution times (Figure 1). XY8 and XY4 phase cycling were used for the ^{13}C and ^{2}H π pulses, respectively.[10] All the ^{13}C π pulses were at the completion of rotor cycles, with the first pulse immediately following the $^{1}H \rightarrow {}^{13}C$ cross-polarization transfer. (The transfer is not shown in the pulse sequence.) The advantage of this scheme is the elimination of an additional two-rotor-cycle Hahn-echo period to avoid the coincidence of the start of data acquisition with a ^{13}C π pulse. This may be desirable in slow-spinning experiments. The disadvantage is the insertion of a ^{13}C phase transient resulting from the rapid switching from cross-polarization to refocusing modes. Other experimental conditions included a 2 ms, 50 kHz matched $^{1}H-^{13}C$ cross-polarization contact, 75 and 80 kHz B_1 fields for the ^{13}C and ^{2}H π pulses, respectively, and 60 kHz proton decoupling. Increasing the decoupling field to 100 kHz did not change the observed line shapes. The B_1 fields used were large compared to spin−spin, shift, and quadrupolar interactions. All ^{2}H and ^{13}C homonuclear couplings were weak and their effects removed by magic-angle spinning.

Calculations. Chemical shielding calculations for the carbonyl carbon of Ar−O−C(=O)−O−Ar were performed using the Gaussian 98 program[11] on Silicon Graphics (SGI, Mountain View, CA) Origin-2000 and Hewlett-Packard (HP, Palo Alto, CA) Exemplar clusters at the National Center for Supercomputing Applications, located in Urbana, IL. All shieldings were calculated at the Hartree−Fock (HF) level of theory using the uniform basis set 6-311++G(2d,2p). The structure of Ar−O−C(=O)−O−Ar was constructed by using standard bond lengths and angles (Cerius 2, Molecular Simulations Inc., San Diego, CA), and the planes of the Ar groups were set perpendicular to the plane of the carbonate group. The chemical shielding was then calculated as a function of the rotation of one of the Ar groups about the proximate C(=O)−O main-chain bond, while the other Ar group was held fixed.

Results and Discussion

Total Dephasing and Interchain Separation. ^{13}C-{^{2}H} REDOR NMR spectra of [carbonyl-^{13}C, $-OCH_2$-CD_3]ethoxyphenyl−polycarbonate are shown in Figure 2 as a function of dipolar evolution time under slow-spinning conditions. The dephased-echo spectra (S) are dominated by the carbonyl carbon peak (147 ppm) and its associated spinning sidebands. The relatively narrow quaternary carbon peak is also an easily recognized feature of the spectra at 47 ppm. Signals from protonated carbons appear as minor peaks and shoulders; these disappear with increasing evolution time because of short T_2's. The main-chain, nonprotonated aromatic carbons have chemical shifts similar to that of the carbonyl carbon and therefore contribute to the intensity of the 147 ppm peak.[2] However, these contributions are minor. From the spectra of [$-OCH_2CD_3$]ethoxyphenyl−polycarbonate (not shown), the natural abundance ^{13}C contributions at 147 ppm were estimated to be at most 5% of the labeled carbonyl carbon intensity for short evolution times and less for longer evolution times. All of the other natural abundance ^{13}C resonances are shifted from the carbonyl and quaternary carbon peak positions.[12]

The total REDOR dephasing ($\Delta S/S_0$, where $\Delta S = S_0 - S$, and S and S_0 are the integrated echo intensities of the sum of centerband and all sidebands, with and without ^{2}H dephasing pulses, respectively) is shown in Figure 3 for the carbonyl and quaternary carbon peaks (symbols). Values of $\Delta S/S_0$ varied between repeated experiments by less than ±1% for the carbonyl carbon and ±3% for the quaternary carbon. The dephasing for the carbonyl carbon exceeds the dephasing for the quaternary carbon for all values of the dipolar evolution time.

The lower solid and dotted lines in Figure 3 represent the expected *intramolecular* dephasing for the carbonyl and quaternary carbons, respectively, in an all-trans chain conformation. Once the chain geometry is specified, REDOR calculations with multiple dephasing centers is unambiguous and straightforward.[13,14] Based on a model for the most likely conformation of a trans chain,[15] the calculations were performed for the carbonyl carbon assuming two $-CD_3$ neighbors, each 10 Å distant.[15] The quaternary carbon was assumed to have a nearest-neighbor $-CD_3$ group 7 Å away in the same repeat unit and two next-nearest $-CD_3$ groups 13 Å distant, in neighboring repeat units. The $-CD_3$ group was treated as a pseudo spin-3 nucleus located on the methyl group C_3 axis in the plane of the three deuterons.[12] The short 7 Å distance to the nearest-neighbor $-CD_3$ ensured that the dephasing of the quaternary carbon peak exceeded that of the carbonyl carbon peak (Figure 3, bottom).

In more than 100 REDOR experiments on $^{13}C,^{2}H$-labeled ethoxyphenyl−polycarbonate with different evo-

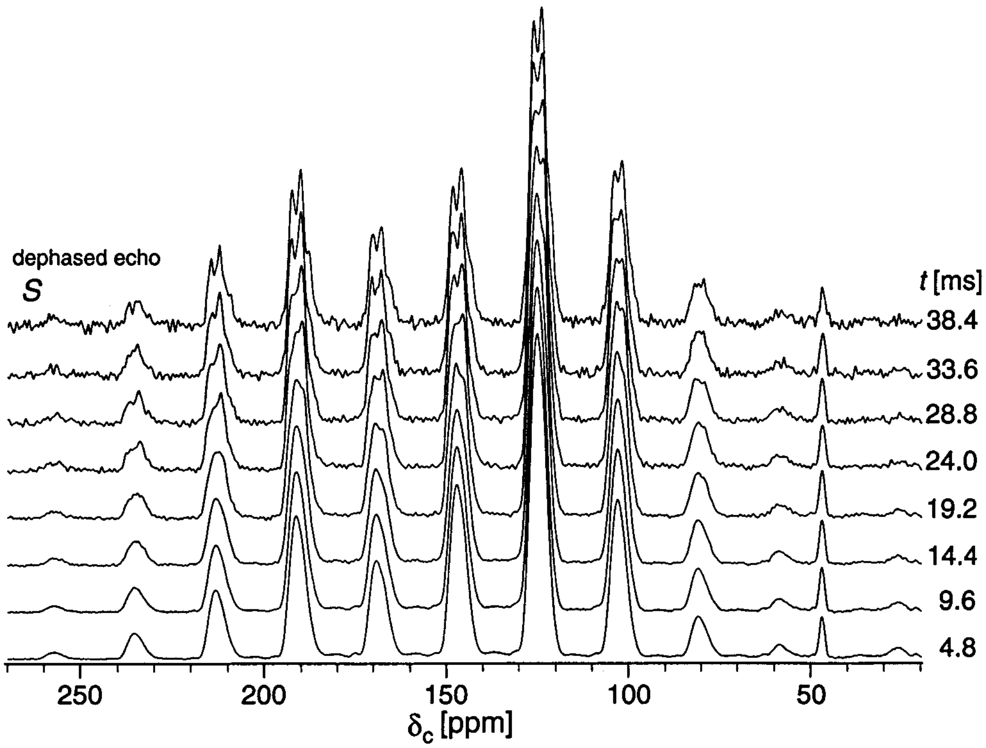

Figure 2. Dephased-echo (S) REDOR ^{13}C NMR spectra of [carbonyl-^{13}C,$-OCH_2CD_3$]ethoxyphenyl−polycarbonate as a function of the total dipolar evolution time, t. The spectra have been scaled for equal maximum peak heights; absolute integrated intensities are established using Figure 3. Each spectrum was the result of the accumulation of 8192 scans. Magic-angle spinning was at 1667 Hz.

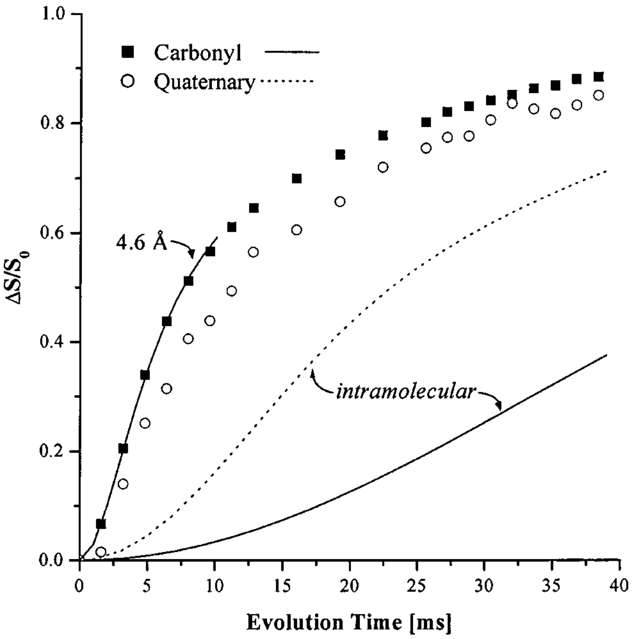

Figure 3. Total REDOR dephasing ($\Delta S/S_0$, where $\Delta S = S_0 - S$, and S and S_0 are the integrated echo intensities of the sum of centerband and all sidebands, with and without ^2H dephasing pulses, respectively) for the carbonyl carbons (solid squares) and quaternary carbons (open circles) of double-labeled ethoxyphenyl−polycarbonate. Magic-angle spinning was at 5 kHz. The solid line matching the initial carbonyl carbon data is the calculated dephasing assuming a narrow Gaussian distribution of nearest-neighbor distances centered at 4.6 Å. The lower dotted and solid lines represent the calculated intramolecular dephasing for the quaternary and carbonyl carbons, respectively.

lution times, magic-angle spinning rates, and sequence-repetition periods, performed on samples that had undergone a variety of $T < T_g$ annealing protocols, the dephasing of the carbonyl carbon peak exceeded that of the quaternary carbon peak. There were no exceptions. Because the calculated intramolecular dephasing has the reverse ranking, the total dephasing for the carbonyl carbon must be dominated by interchain dipolar couplings arising from interchain $^{13}C-^{2}H$ distances substantially less than 7 Å.

We determine average interchain distances from the observed carbonyl carbon dephasing for short evolution times.[15] This dephasing is governed by the single, nearest-neighbor $-CD_3$ group, for which we estimate an average *interchain* $^{2}H-^{13}C$ distance of 4.3−4.6 Å. The lower estimate is based on total dephasing (sum of sidebands and centerband, not shown) obtained with magic-angle spinning at 1667 Hz and an assumption of a single distance (no distribution). The upper estimate is based on total dephasing with spinning at 5000 Hz (Figure 3, top, solid line) and a Gaussian distribution of $^{13}C-CD_3$ distances for the nearest neighbor centered at 4.6 Å with a full width at half-height of 1 Å. While there is not much difference between the two estimates, the low-speed spinning result is probably the more accurate because fewer (imperfect) dephasing pulses were used.

The relative $^{13}C\{^{2}H\}$ total dephasing of the carbonyl and quaternary carbon peaks proves that the packing in this polycarbonate is not random. If the chain packing were truly random, then the dephasing from interchain $^{13}C-^{2}H$ dipolar couplings would be the same for both quaternary and carbonyl carbons. With equal interchain dephasing for quaternary and carbonyl carbons and, as discussed above, a larger intrachain dephasing for the quaternary carbon, greater total dephasing would be expected for the quaternary carbon than for the carbonyl carbon at all dipolar evolution times. Because the

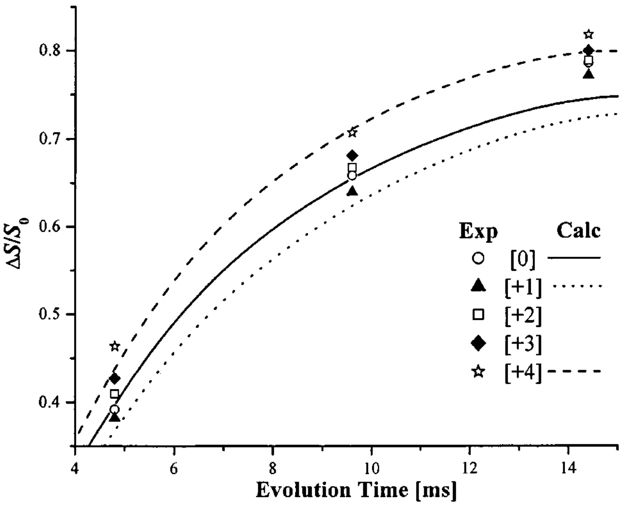

Figure 4. REDOR dephasing ($\Delta S/S_0$) for the centerband and low-field spinning sidebands (magic-angle spinning at 1667 Hz) of the carbonyl carbon resonance of the ethoxyphenyl−polycarbonate of Figure 2 as a function of the dipolar evolution time (symbols). The lines represent calculated values based on $f = 0.36$, $\alpha_D = 60°$, $\beta_D = 70°$, and a ^{13}C−^{2}H distance of 4.3 Å. The calculated +2 and +3 rankings are also in agreement with the data but have been omitted for clarity.

opposite ranking is observed, the interchain ^{13}C−^{2}H couplings must be greater and the ^{13}C−^{2}H distances less for the carbonyl carbon than those for the quaternary carbon, which means that the packing is not random.

Sideband Dephasing and Local Orientation. Orientation information in REDOR is contained in the relative dephasing rates of the spinning sidebands.[14,16] The dephasing of the carbonyl carbon spinning sidebands in a ^{13}C{^{2}H} REDOR experiment in which the ^{13}C label is on one chain and the ^{2}H label on another depends on the orientation of the ^{13}C−^{2}H internuclear vector with respect to the carbonyl carbon chemical shift tensor. If chain packing were truly random, then all the sidebands and the centerband would dephase at the same rate. For ethoxyphenyl−polycarbonate the low-field carbonyl carbon sidebands and centerband dephase at different rates (Figure 4, symbols), whereas the high-field sidebands dephase at the same rate (not shown), within experimental error. The intensity of the dephased sidebands of ethoxyphenyl−polycarbonate can be written as[16]

$$I_N = \int R_D[\Omega;\, \alpha_D, \beta_D, \lambda_D]\; G_N[\Omega;\, \delta_{CS}, \eta_{CS}]\; d\Omega \quad (1)$$

where $G_N[\Omega]$ is the distribution of powder orientations contained in sideband N generated by magic-angle sample spinning at ω_R, and $R_D[\Omega]$ is the orientational dependent REDOR dephasing of a single crystal. Powder angles are given by Ω, shift tensor anisotropy and asymmetry by δ and η, respectively, and orientation of the dipolar tensor relative to the shift tensor by α_D (azimuthal) and β_D (polar); λ_D is the REDOR evolution parameter, which equals the product of the evolution time and dipolar coupling. Approximating the −CD$_3$ group as a pseudo spin-3 nucleus,[12] we find that $R_D[\Omega]$ is given by

$$\begin{aligned} R_D[\Omega;\, \alpha_D, \beta_D, \lambda_D] = (7 + 12\cos[2\Theta_D[\Omega;\, \alpha_D, \beta_D, \lambda_D]] +{}& \\ 6\cos[4\Theta_D[\Omega;\, \alpha_D, \beta_D, \lambda_D]] +{}& \\ 2\cos[6\Theta_D[\Omega;\, \alpha_D, \beta_D, \lambda_D]])/27 \quad & (2) \end{aligned}$$

where Θ_D is the phase accumulated from dipolar evolution.[14,16] The dephasing for the first 5 ms is dominated by the single, nearest-neighbor −CD$_3$. The ^{2}H−^{13}C average distance for this nearest neighbor is 4.3 Å, based on the total dephasing measurements described above. If we assume that only a fraction, f, of the ^{13}C−^{2}H dipolar vectors have the same orientation relative to the carbonyl carbon shift tensor, and the remainder, $1 - f$, are isotropically oriented, then

$$I_N^{\text{observe}} = (1 - f) I_N^{\text{isotropic}} + f\, I_N \quad (3)$$

The best fit to the observed dephasing rates for short evolution times (Figure 4, solid and dotted lines) is obtained for $f = 0.36$ and orientation angles $\alpha_D = 60°$ and $\beta_D = 70°$ (Figure 5). This means that 36% of the ethoxyphenyl−polycarbonate repeat units have a specific orientation relative to a neighboring chain. This value pertains to orientation and not to other measures of local order such as interchain packing proximities. Thus, even though only 36% of all methyl groups have a specific orientation relative to the carbonyl carbon in the nearest-neighbor chain, nearly all of the methyl groups are about 4.3 Å from their nearest-neighbor carbonyl carbon (as determined by the total dephasing).

A chain-pair packing model is presented in ref 15. This model has the simplest type of local order consistent with the REDOR orientation results. A segment of a typical chain pair[17] is shown in Figure 5 (right). Naturally, the presence of long, locally parallel chain segments does not require the presence of long, straight cylinders of chains. A pair of chains making turns and bends in tandem remains locally parallel (see Figure 10 in ref 15). The average chain length over which the parallelism persists in either ethoxyphenyl−polycarbonate or linear phenol−polycarbonate[15] is not yet known.

Conformational Defects. For long evolution times, the carbonyl carbon peaks of the dephased-echo spectra are partially resolved, showing a dip at 147 ppm and a shoulder at 144 ppm (Figure 2, top). An expanded view of the centerband region for the spectrum after 38.4 ms of dipolar evolution is shown in Figure 6. This region is due to carbonyl ^{13}C labels because, as mentioned above, the integrated intensity of the dephased-echo (S) for [−OCH$_2$CD$_3$]ethoxyphenyl−polycarbonate (no ^{13}C label) was smaller by a factor of 15 than that of the dephased echo for [carbonyl-^{13}C,−OCH$_2$CD$_3$]ethoxyphenyl−polycarbonate. In addition, when the former was subtracted from the latter, no significant change in line shape was observed. The dephased-echo S spectrum of Figure 6 depends strongly on those ^{13}C's that are the farthest removed from coupling to −CD$_3$ groups. Such carbons are likely to be in defect conformations in which tight chain packing is impeded by steric repulsions. Thus, we tentatively assign the prominent high-field shoulder of the carbonyl carbon peak (144 ppm) to carbonyl carbons in cis defect conformations.

The 145−150 ppm low-field region of the spectrum is generally assigned to carbonate carbons in trans conformations.[2,3] The center of this region (147 ppm) has a chemical shift that matches the shift observed for the carbonyl carbon ^{13}C{^{2}H} ΔS arising from a mixture of 5% [carbonyl-^{13}C]polycarbonate and 95% [methyl-d_6]-polycarbonate after a short dipolar evolution time.[12] This shift also matches the shift position of the carbonyl carbon ^{13}C{^{2}H} ΔS peak for [carbonyl-^{13}C, −OD]phenol−polycarbonate.[15] The center of the 147 ppm region

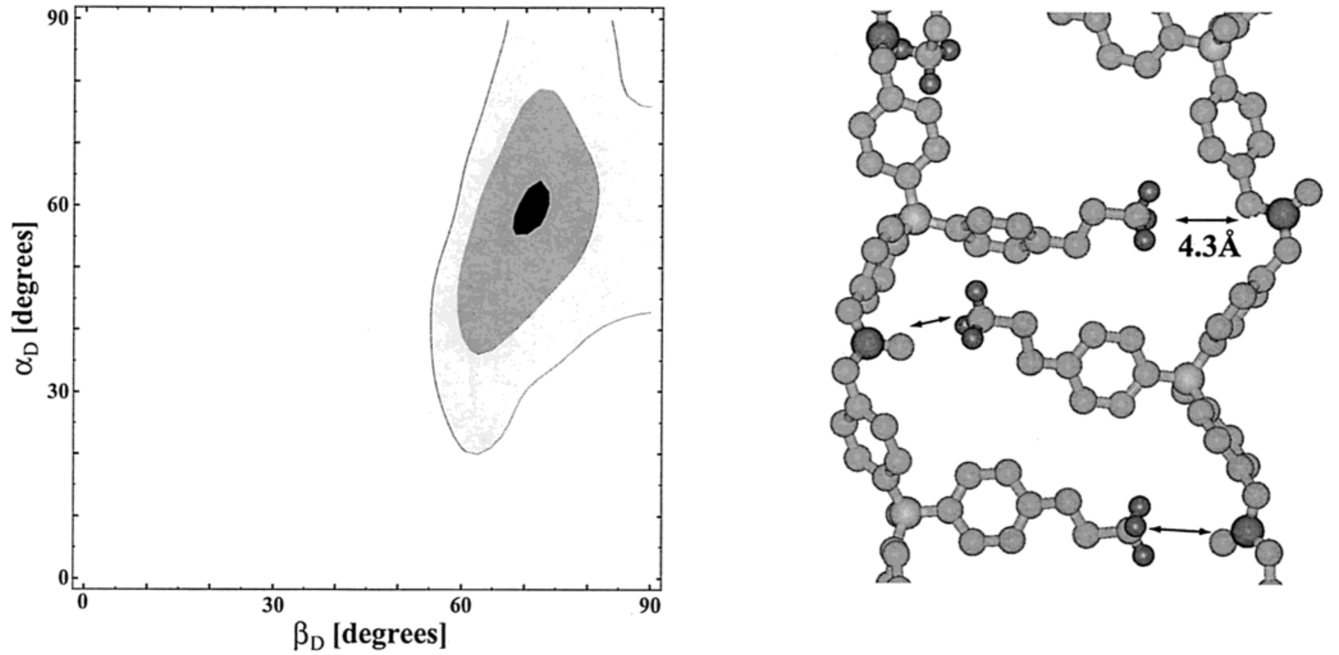

Figure 5. (left) Best-fit contour plot of the error function χ^2 (see eq 5 of ref 15) for the orientation of the $^2H-^{13}C=O$ vector and the carbonyl carbon chemical shift tensor for the data shown in Figure 4. Each contour represents a 50% increase in χ^2. (right) Proximity of the $-OCH_2CD_3$ and carbonate groups of two locally parallel chains.

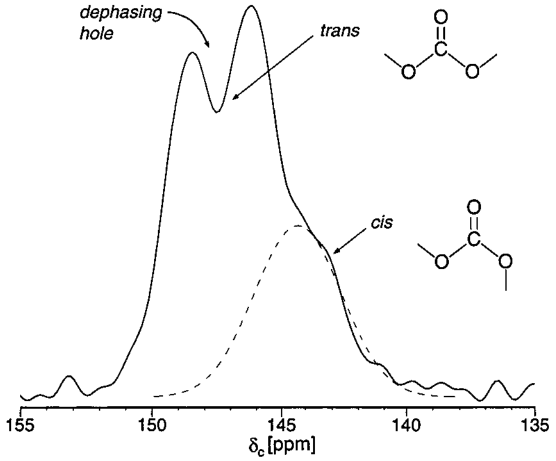

Figure 6. Expanded view of the centerband region of the spectrum of Figure 2 (38.4 ms of total evolution time). All of the major observed peaks between 140 and 155 ppm are due to the carbonyl ^{13}C label. Deconvolution permits an estimate of the intensity of the high-field shoulder (dotted line) as 40% of the total.

has reduced intensity. We believe that this part of the spectrum arises from carbonyl carbons in local conformations that permit the tightest packing; that is, from carbonyl carbons in locally parallel all-trans conformations. The signal intensity has been reduced because it has been dephased by strong interchain $^2H-^{13}C$ dipolar coupling resulting from proximity of a labeled carbonyl carbon and a $-CD_3$ group.

To quantify the fractions of cis (144 ppm) and trans (147 ppm) conformations, we assumed that there were two types of ^{13}C carbonyl labels. One type is in tightly packed chains and associated with complete dephasing at 38.4 ms as a result of both intra- and intermolecular $^{13}C-^2H$ couplings ($\Delta S/S_0 = 0.98$). The second type is in such poorly packed chains that only intrachain couplings cause dephasing ($\Delta S/S_0 \approx 0.35$, Figure 3, bottom, solid line). With this assumption, and using the experimental value of $\Delta S/S_0 = 0.89$ at 38.4 ms, we estimate that approximately 15% of the polymer is poorly packed, presumably because of kinked cis conformational defects.

We can also quantify the concentration of cis conformations directly from deconvolution of S and S_0 spectra. The broad cis peak (dotted line) represents about 40% of the total area of the spectrum of Figure 6 and therefore at least 6% of the total conformational population. This is a lower-limit estimate based on the total intensities of Figure 3 and the assumption that there is no interchain dephasing in the pooly packed regions. An upper-limit estimate of 14% was made using a similar deconvolution (same peak positions and widths), but of the S_0 spectrum obtained after only 4.8 ms of evolution. This estimate is consistent with the 15% value for poorly packed chains based on total dephasing. Thus, we conclude that the cis defect concentration is between approximately 5% and 15% or, equivalently, that between 85% and 95% of all carbonate linkages are trans. These relative fractions did not change following annealing ($T < T_g$) for 1 week at $T = 135$ °C.

Both cis and trans shift assignments are supported by calculations of the isotropic shifts for carbonate carbonyl carbons (Table 1), which suggest a 4 ppm upfield shift for the cis carbonate conformation relative to the trans carbonate conformation. The widths of both cis and trans carbonate peaks for ethoxyphenyl–polycarbonate indicate that each is itself a distribution of isotropic shifts, possibly arising from the minor rotations about a main-chain C(=O)–O bond (see Table 1) that are part of main-chain bends or from conformational distortions resulting from sterically strained local packing. In addition, variations in the angle of the plane of the aromatic ring relative to that of the carbonate group can be expected,[17] and these will also lead to line broadening. (We calculated a 0.3 ppm shift for the shielding of the trans carbonate carbonyl peak for a 90° rotation of the plane of one of the rings about the Ar–O bond.)

Table 1. Calculated Chemical Shifts for the Carbonyl Carbon of Ar−O−C(=O)−O−Ar as a Function of the Rotation of One of the Ar Groups about the Proximate C(=O)−O Bond[a]

rotation angle [deg]	isotropic shift [ppm]	anisotropy [ppm]
0[b]	163.27	101.13
20	163.23	104.01
40	163.20	110.21
60	162.96	116.34
80	162.32	119.49
100	161.27	118.61
120	160.01	114.92
140	159.14	111.27
160	159.24	110.02
180[c]	159.42	109.93

[a] Computed chemical shifts are reported in ppm from TMS using the convention that high-frequency, low-field, paramagnetic or deshielded values are positive and were computed from the theoretical shieldings by taking the absolute shielding of TMS to be 186.43 ppm (Jameson, A. K.; Jameson, C. J. *Chem. Phys. Lett.* **1987**, *134*, 461). Although the absolute chemical shifts for these carbonyl groups are only expected to be accurate to ca. 20 ppm, the differences in shifts are expected to be accurate to about ±1 ppm. [b] Trans carbonate conformation. [c] Cis carbonate conformation.

Table 2. Orientational Parameters for Two Phenyl-Substituted Bisphenol A Polycarbonates

polycarbonate	α_D [deg][a]	β_D [deg][a]	f [b]
ethoxyphenyl[c]	60	70	0.36
phenol[d]	30	70	0.66

[a] Angles, α_D (azimuthal) and β_D (polar), specifing the orientation of the $^2H-^{13}C$ vector relative to the carbonyl carbon chemical shift tensor for [carbonyl-^{13}C,$-OCH_2CD_3$]ethoxyphenyl−polycarbonate and [carbonyl-^{13}C,−OD]phenol−polycarbonate. See Figure 6 of ref 15. [b] From eq 3. [c] This work. [d] From ref 15.

Comparison of Phenyl-Substituted Bisphenol A Polycarbonates. Both ethoxyphenyl−polycarbonate and phenol−polycarbonate have similar packing in which the $-CD_3$ group or phenolic deuteron of one chain is approximately 4.5 Å from the carbonyl carbon of another chain. For ethoxyphenyl−polycarbonate, the low-field sidebands dephase at different rates and the high-field sidebands dephase at the same rate, whereas for phenol−polycarbonate, the reverse is observed.[15] The reversal is a result of differences in the $R_D[\Omega]$ dephasing functions (eq 2) for a single deuteron compared to that for a $-CD_3$ group. Nevertheless, both phenyl-substituted polycarbonates have similar values for α_D and β_D (Table 2) and therefore similar local orientational order. The main difference in orientation between the two polymers is the larger value of α_D for ethoxyphenyl−polycarbonate. This difference may be the result of the relative sizes of the two side chains or possibly the effect of hydrogen bonding by the phenolic deuteron. The latter possibility may also contribute to the local order in phenol−polycarbonate, which is approximately 66%, compared to only 36% in ethoxyphenyl−polycarbonate (Table 2).

The local order demanded by the REDOR dephasing for both ethoxyphenyl−polycarbonate and phenol−polycarbonate preferentially places the ^2H labels of the ethoxy or phenol group of one chain proximate to the ^{13}C label of the carbonate of a neighboring chain (see Figure 5, right). Similar packing has been inferred from the results of relaxation[18] and homonuclear[19] and heteronuclear[20,21] recoupling experiments on bisphenol A polycarbonate and from the results of relaxation experiments on a variety of other linear polycarbonates.[22] The origin of this local order in glass-forming polycarbonates is not yet known analytically, but the similarities in properties between polycarbonates suggest that the basic geometry of the chains results in an entropically driven[23] condensed-phase match of the ethoxyphenyl (or phenol or isopropylidene) moiety of one chain and the carbonate of another.[15] In short, this seems to be the easiest way for two polycarbonate chains to fit together.

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