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(25) Note Added in Proof: We now appreciate that $B_1/(B_1 + 2B_2)$ measures the *number fraction* of donors in the interpenetration zone. If one assumes a uniform acceptor concentration in this domain and accounts for the dilution of acceptors upon mixing, the *volume fraction* of mixing is equal to $B_1/(B_1 + B_2)$. This topic is discussed in more detail in: Zhao, C.-L.; Wang, Y.; Hruska, Z.; Winnik, M. A.; Croucher, M. D. *Macromolecules*, in press.

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Main-Chain Reorientation in Polycarbonates

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ABSTRACT: The amplitudes of main-chain reorientations have been determined by dipolar rotational spin-echo ^{13}C NMR for bisphenol A polycarbonate, for the phenoxy resin made from bisphenol A and formaldehyde, and for the phenoxy resin made from bisphenol A and epichlorohydrin. All three polymers display prominent low-temperature mechanical-loss peaks, and all three polymers have main-chain rings undergoing rapid 180° flips at room temperature. The present results show that the amplitude of the main-chain rotational reorientation at the isopropylidene position for bisphenol A polycarbonate, and the isopropylidene and carbonate positions for the other two polymers, is less than 20° (root-mean-square). Small-amplitude motion at the carbonate position in bisphenol A polycarbonate has been observed before in measurements of carbonyl carbon chemical-shift tensors. Similar small-amplitude motion at the carbonate position has also been inferred from measurements of the volumes of activation for the ring-flip processes in bisphenol A polycarbonate and the phenoxy resin made from bisphenol A and epichlorohydrin. The combination of all of these results leads to the conclusion that the same kind of small-amplitude lattice reorganization controls ring flips for all three of these polycarbonates.

Introduction

The hydrostatic pressure dependence of the ring-flip process in polycarbonate (PC) and in the phenoxy resin made from bisphenol A and epichlorohydrin (PK) has been discussed recently in terms of the densification of chain packing in the glassy state.[1] In this description, steric interactions between *several* chains in the lattice are assumed ultimately to control the ring flips. This model of the ring-flip process in polycarbonates differs significantly from the defect-diffusion model proposed by Jones.[2] In the defect-diffusion model, the dominant physics is contained in the rotational reorientation of conformational defects within a *single* chain. Defects are assumed to diffuse up and down the long axis of the chain, with rings flipping as defects pass. Variations in the rate of defect diffusion result from variations in the local mean-field viscosity of the lattice. The defect-diffusion model has been used to interpret both NMR line shapes[3] and the results of mechanical loss experiments[4] and also has been invoked as a possible explanation for polycarbonate's aging, and its viscoelastic, and thermodynamic behavior.[5]

In this paper we report the results of ^{1}H-^{13}C dipolar rotational spin-echo experiments on PC, on PK, and on the phenoxy resin formed from bisphenol A and formaldehyde (FPC). These polymers differ in the carbonate, or carbonate-like, main-chain linkages connecting aromatic moieties. The carbonate linkages for the three polymers are as follows: PC, $-OC(=O)O-$; PK, $-OCH_2CH(-OH)CH_2O-$; and FPC, $-OCH_2O-$. Despite differences in the carbonate linkages, all three polymers display similar low-temperature mechanical-loss peaks[1] and all three polymers have rings undergoing rapid 180° flips at room temperature. The present NMR experiments are designed to measure the amplitudes of main-chain motions of the isopropylidene units in PC and PK and the carbonate-like units in FPC and PK. The results of these experiments indicate only small-amplitude main-chain motion at both isopropylidene and carbonate sites.

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.[6] Half-gram samples were spun in a double-bearing rotor[7] at 1859 or 930 Hz. The long-term stability of the spinning speed was ±1 Hz.

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[8] 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.[9] 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 so that strong dipolar echoes formed. A 16-point Fourier trans-

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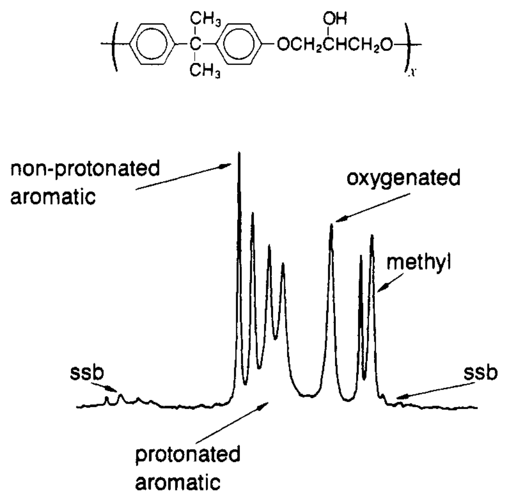

Figure 1. The 15.1-MHz cross-polarization, magic-angle spinning ^{13}C NMR spectrum of the phenoxy resin PK. The spinning speed was 1859 Hz.

form of the 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.[10]

Materials. The PC used in these experiments was commercial Lexan pellets manufactured by General Electric. The FPC was an experimental material generously supplied by Dr. Elizabeth Williams (General Electric Co., Schenectady, NY). Low-molecular-weight material in this sample was removed by fractionation in chloroform. The PK was a former commercial product of Union Carbide designated as PKHH resin.[11] Thin sheets of each polymer were melt pressed above T_g and annealed by slow cooling to room temperature in the press. The NMR samples consisted of stacks of thin disks. Crystalline 4,4′-isopropylidenediphenol (bisphenol A or BPA) was obtained from Aldrich Chemical Co. (Milwaukee, WI).

Results

The ^{13}C NMR spectra of PK (Figure 1) is similar to that of FPC which has been discussed in detail elsewhere.[10] For both polymers, the oxygenated-carbon resonances are well resolved from aromatic and isopropylidene carbon resonances.

Dipolar rotational spin-echo ^{13}C NMR spectra of both PC and PK were obtained as a function of the duration of a carbon spin lock (with proton decoupling turned off) preceding dipolar evolution. Because of fast spin-lattice relaxation in PC,[12] a 10-ms spin-lock period with $H_1(C) = 50$ kHz is sufficient to reduce each of the two protonated aromatic carbon lines at 120 ppm to about one-fourth the integrated intensity of the combination nonprotonated aromatic and carbonyl carbon line at 150 ppm (Figure 2, bottom left). Four carbons contribute to each of the former and five carbons to the latter.[12] In general, the ^{13}C NMR spectrum of PC is free from severe spectral overlaps. Thus, the methyl carbon line at 25 ppm is well resolved even with magic-angle spinning at 930 Hz (Figure 2, right).

The intensities of the dipolar echoes following 16 MREV-8 cycles are about 60% for the protonated aromatic carbons of PC and about 30% after 32 MREV-8 cycles (Figure 2). Plots of echo intensities against time evolution were symmetrical about their centers. Dipolar rotational sideband intensities for the protonated aromatic and methyl carbon resonances of PC and PK are presented in Table I as function of the length of the carbon spin lock preceding dipolar evolution. Only the aromatic carbon dipolar pattern of PK changes significantly with the duration of the carbon spin lock. Dipolar patterns for the methyl carbons of PC and PK differ slightly from that of crystalline bisphenol A (BPA); the latter pattern is compared to calculated methyl carbon patterns in Table II.

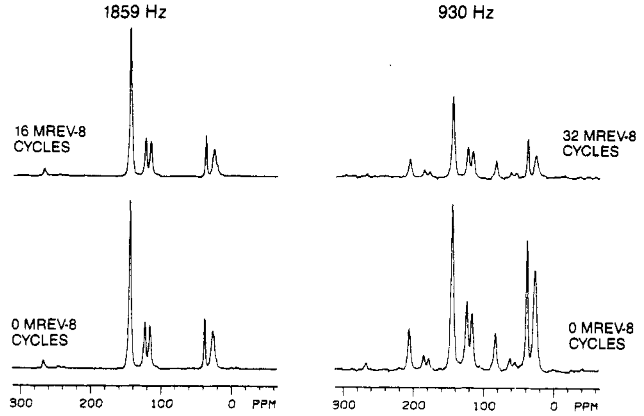

Figure 2. Dipolar rotational spin-echo 15.1-MHz ^{13}C NMR spectra of annealed polycarbonate at room temperature as a function of the number of semiwindowless MREV-8 cycles used during ^{1}H–^{13}C dipolar evolution. A 2-ms proton–carbon cross-polarization transfer and a 10-ms, 50-kHz carbon spin lock (without proton decoupling) preceded the dipolar evolution. Spinning at 1859 Hz (left) was used for determining aromatic carbon dipolar patterns and at 930 Hz (right) for methyl carbon patterns. Each spectrum in the time evolution was the accumulation of 10 000 scans.

The dipolar patterns of the oxygenated carbons in FPC and PK are generally similar to one another (Table III), even though the latter are superpositions of patterns from two methylene carbons and one methine carbon. Both patterns are broad[13] and close to that expected for a lattice undergoing only small-amplitude rotational reorientations.[10] On the basis of the relative intensities of the centerband and first two dipolar sidebands, the PK experimental pattern (Figure 3, top left) is matched reasonably well by assuming each ^{1}H–^{13}C internuclear vector undergoes rapid, isotropic reorientation through a 12.5° (rms) solid angle.[10]

Discussion

Amplitudes of Main-Chain Motions. On the basis of measurements of chemical shift tensors, all of the rings of PC and FPC[10] and about half of the rings of PK[1] have been shown to undergo large-amplitude motions including 180° flips at room temperature.[14] Nevertheless, the nonaromatic carbons of these polymers undergo only small-amplitude motions. The oxygenated carbons of PK and FPC, for example, have dipolar patterns consistent with root-mean-square angular displacements of about 15° (Figure 3 and Table III). The methyl carbon dipolar patterns of both PC and PK (Table I) similarly indicate root-mean-square angular excursions of about 10° (Table II). Since the oxygenated carbon and methyl carbon ^{1}H–^{13}C dipolar interactions are direct measures of the amplitudes of main-chain motions in PC and PK, these results are only consistent with small-amplitude rotational reorganization of the lattice.

The absence of large-amplitude motions of the carbonate link in PC has been inferred by Henrichs et al., based on the observation of a sizeable carbonyl carbon chemical shift anisotropy which is independent of temperature.[16] Translating the results of the chemical-shift experiments into an amplitude for main-chain rotational reorientation is complicated by the unavailability of a rigid-lattice value for the PC carbonyl carbon, chemical-shift anisotropy. Nevertheless, by assuming an anisotropy equal

Table I
Dipolar Rotational Sideband Intensities[a] for PC and PK

polymer	carbon	$T_{1\rho}(C)$[b] spin-lock, ms	fractn of starting magnetizatn	sideband number 0	1	2	3	4	5	6
PC	protonated aromatic	0	1.00	0.252	0.216	0.109	0.038	0.010	0	0
		10	0.48	0.247	0.213	0.110	0.037	0.013	0	0
PC	methyl	0	1.00	0.204	0.196	0.115	0.046	0.026	0.012	0.003
		10	0.72	0.198	0.206	0.112	0.039	0.026	0.011	0.007
		20	0.60	0.188	0.219	0.117	0.039	0.020	0.010	0
PK	protonated aromatic	0	1.00	0.205	0.185	0.124	0.051	0.025	0.006	0.005
		5	0.44	0.181	0.171	0.151	0.058	0.017	0.005	0.008
PK	methyl	0	1.00	0.203	0.195	0.115	0.044	0.026	0.013	0.007
		10	0.64	0.209	0.203	0.104	0.059	0.028	0	0
		20	0.41	0.222	0.226	0.106	0.033	0.001	0.009	0.014

[a] Semiwindowless MREV-8 multiple-phase decoupling. Theoretical scale factor is 0.54. Magic-angle spinning was at 1859 Hz for aromatic carbons and 930 Hz for methyl carbons. [b] $H_1(C) = 50$ kHz.

Table II
Methyl Carbon Dipolar Sideband Intensities[a] for Crystalline Bisphenol A

experiment or motional model	sideband number 0	1	2	3	4	5	6
BPA	0.194	0.195	0.129	0.052	0.025	0.009	0
simulation[b] ($\theta_{rms} = 0$)	0.186	0.187	0.105	0.041	0.034	0.014	0.009
simulation[b,c] ($\theta_{rms} = 5°$)	0.191	0.188	0.104	0.041	0.033	0.014	0.009
simulation[b,c] ($\theta_{rms} = 10°$)	0.203	0.190	0.101	0.041	0.032	0.013	0.009
simulation[b,c] ($\theta_{rms} = 15°$)	0.227	0.193	0.095	0.040	0.028	0.011	0.008

[a] Semiwindowless MREV-8 multiple-pulse decoupling. Theoretical scale factor is 0.54. Magic-angle spinning was at 930 Hz. [b] Effective scale factor is 0.39. [c] Average C–H internuclear vector is assumed to undergo random, isotropic reorientation on the surface of a sphere through a solid angle, θ. (See ref 10 for details.)

to the largest carbonyl carbon anisotropy in the literature, Henrichs and co-workers were able to place an upper limit of 40° on the main-chain rotational reorientation in PC. This upper bound is consistent with the direct observation of 15° main-chain motion for FPC and PK (Table III, rows 1 and 5) and supports the assertion that small-amplitude lattice reorganization controls ring flips in the same way for all three polycarbonates.

Heterogeneity of Main-Chain Motions. The nonlinearity of $T_{1\rho}(C)$ and $T_1(C)$ plots reported before[1,12,15] is a direct measure of site-to-site variations of motion in the glassy lattice.[12] However, a long methyl carbon $T_{1\rho}(C)$ can be associated with a relatively large-amplitude slower motion as well as a small-amplitude faster motion. This combination blurs the resolution of a variable, carbon spin lock for selection for amplitude heterogeneity in polycarbonates. As a result, while the methyl carbon dipolar patterns for both PC and PK (Table I) are reduced slightly from that observed for crystalline bisphenol A (Table II), indicating the averaging of 100-kHz regime main-chain reorientational motion,[10] there are only minor differences observed for methyl carbon dipolar patterns for the short and long $T_{1\rho}(C)$ populations of the two polymers.

The pronounced difference observed in the dipolar patterns of the protonated aromatic carbons of PK with short and long $T_{1\rho}(C)$s (dipolar sideband n_2/n_1 ratios of 0.67 and 0.89, respectively, Table I) arises from the fact that only about half the rings in PK undergo flips. The ring-flip population has more motion, a shorter $T_{1\rho}(C)$, a narrower dipolar pattern, and a smaller n_2/n_1 ratio. All the rings in PC both flip and wiggle, and there are no significant differences in the observed dipolar patterns for aromatic carbons with short or long $T_{1\rho}(C)$s.

Defect-Diffusion Model of the Ring-Flip Process. The defect-diffusion model proposed by Jones for ring flips in PC assumes 120° angular reorientations of the carbonate unit linking phenyl rings at the ring-flip defect sites.[2] Defect concentrations of only 1% are likely. The defect is presumed to move within a single chain by successive steps such as (1) → (2) → (3):

(1) ...–trans–*cis*–trans–trans–trans–trans–trans...

(2) ...–trans–trans–*cis*–trans–trans–trans–trans...

(3) ...–trans–trans–trans–*cis*–trans–trans–trans...

The cis and trans designations indicate the conformational geometry of the aromatic rings around a linking carbonate moiety. As the carbonate reorients from trans to cis, one of the two rings in a PC repeat unit makes a flip.[2] As the defect moves on, the repeat unit involved in the first rearrangement now undergoes a cis to trans conversion, and both carbonate and aromatic ring are returned to their original orientations. A time average over the period during which the NMR free induction decay is obtained would therefore result in spectra for both ring and carbonate carbons reflecting primarily the trans conformation. This occurs because defect diffusion is rapid, and the total time for any site spent in the cis conformation is too small to have a significant effect.

However, ^{2}D and ^{13}C NMR observations[10,14] indicate rapid flipping for all rings. We can account for this averaging, if we make the additional assumption that in the cis state, the rings can undergo additional flips. (This assumption is not part of the original Jones model.[2]) Then on returning to the trans conformation, the ring will have equal probability to be in its original orientation or flipped 180° from its original orientation. The carbonate, on the other hand, will always be returned to its original orientation. Under these conditions, time averaging brings the predictions of the defect-diffusion model into agreement with the ^{2}D and ^{13}C NMR observations that all PC rings are indeed rapidly flipping at room temperature but that carbonate carbons show little average motion.[16]

Despite this agreement with the NMR data, the cis–trans defect-diffusion model has serious physical complications. Because there are only 1% defects, defect diffusion must be sufficiently rapid that all the rings in all the chains are undergoing ring flips at room temperature at an average rate of 500 kHz.[10,14] Moreover, because two cis defects cannot pass through one another in the same chain, each defect must disappear from the end of the chain to allow a defect of opposite orientation to form and travel down the chain. Otherwise, only half the rings of each chain will flip. If we assume that there are 100 repeat units on average per chain (with one cis defect

Table III
Dipolar Rotational Sideband Intensities[a] for FPC and PK

expt or motional model	carbon	sideband number 0	1	2	3	4	5	6
FPC	CH_2	0.151	0.154	0.115	0.078	0.054	0.014	0.010
simulation[b] ($\theta_{rms} = 0°$)	CH_2	0.139	0.116	0.086	0.080	0.069	0.043	0.023
simulation[b] ($\theta_{rms} = 12.5°$)	CH_2	0.145	0.125	0.091	0.085	0.066	0.036	0.017
simulation[b] ($\theta_{rms} = 20°$)	CH_2	0.153	0.141	0.100	0.090	0.055	0.025	0.010
PK	OCH_2 plus OCH	0.158	0.139	0.122	0.077	0.048	0.026	0.010
simulation[b,c] ($\theta_{rms} = 0°$)	CH_2 plus CH	0.136	0.123	0.120	0.077	0.057	0.033	0.016
simulation[b,c] ($\theta_{rms} = 12.5°$)	CH_2 plus CH	0.142	0.136	0.120	0.077	0.053	0.027	0.012
simulation[b,c] ($\theta_{rms} = 20°$)	CH_2 plus CH	0.154	0.159	0.120	0.075	0.043	0.018	0.006

[a] Semiwindowless MREV-8 multiple-pulse decoupling. Theoretical scale factor is 0.54. Magic-angle spinning was at 1859 Hz. [b] Effective scale factor is 0.39. [c] The combination consists of two CH_2's and one CH.

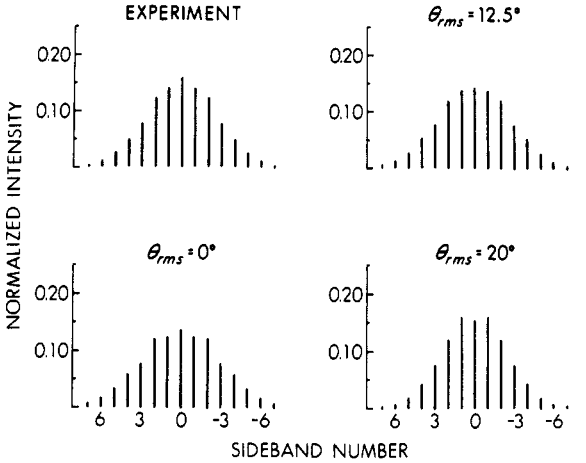

Figure 3. Experimental (top left) and theoretical dipolar sideband patterns for the oxygenated carbons of the phenoxy resin PK.

per chain) and that each repeat unit must be visited, say, 10 times in a ring-flip period by both cis–trans and trans–cis defects to achieve random motional averaging, then, because the motion is diffusive in nature, there must be some 10^6 diffusive steps in less than a microsecond. This corresponds to a jump frequency of 10^{12} Hz, which is comparable to bond vibrational frequencies. In fact, the observed mechanical-loss frequency (which measures the rate of lattice-volume reorganization) is comparable to the NMR-observed ring-flip rate, not orders of magnitude greater.[10] In addition, the activation volume for the ring-flip process in PC has been found to be less than 10% of the repeat-unit molar volume,[1] while a volume of activation for the ring-flip process of about 25% of the repeat-unit molar volume is expected for the defect-diffusion model.[2] We therefore believe that the cis–trans defect-diffusion model for the ring-flip process in polycarbonate involves a reorganization of the lattice which is both too fast and too large to be physically plausible.

Molecular Mechanisms of Motion in Polycarbonates. Identifying a single specific motion, of a single isolated chain, with a single mechanical-loss process in a glassy polymer, is an idea which has motivated a considerable body of work. Attempts have been made to correlate macroscopic mechanical properties with detailed calculations of single-chain motion in vacuo, as well as with experimental determinations of a variety of solution-state NMR relaxation parameters. Heterogeneity in glassy solid polymers has been taken into account in these correlations by invoking distributions in the frequencies of chain motion.

In general, it is true that any single motion of a chain can always be thought of as having frequency heterogeneity, simply by imagining variations in the coupling of the isolated chain to the mean-field surroundings. But in an isolated-chain model, the character of this motion can never change. Thus, a ring-flip process in a glass must remain a ring-flip process in the melt and a ring-flip process in solution. Only the rate of the flipping can increase from glass to melt to solution. However, experimentally we observe that while rings flip in polycarbonate glasses, the rings are only slightly hindered rotors in the melt and in solution.[17] In other words, the character of the dominant large-amplitude ring motion changes. Thus, an insightful model of polycarbonate should include more than one type of molecular motion and should describe the details of the physical interactions by which one type of motion is favored over another.

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Registry No. FPC, 25085-75-0; PKHH, 25068-38-6; PC (SRU), 24936-68-3; PC (copolymer), 25037-45-0; crystalline bisphenol A, 80-05-7.