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Local Chain Dynamics in Poly(fluorocarbonate)s

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ABSTRACT: Magic-angle spinning $^{13}C\{^1H\}$ and $^{13}C\{^{19}F\}$ recoupling NMR experiments have been performed on two polycarbonates with fluoro substituents on every fourth ring in the main chain. The results of these experiments show that the fluoro-substituted rings do not undergo 180° ring flips faster than 10 kHz at 300 K. Most if not all of the unsubstituted rings are flipping. The fluoro substitutions also affect global chain dynamics in the poly(fluorocarbonate) glasses as revealed by shifts and broadening of the dynamic mechanical γ transitions.

Introduction

An important goal in the design of glassy engineering plastics is the creation of low-cost materials with high ductility, a high glass transition temperature, chemical resistance, and a low physical aging rate. Polycarbonate has some but not all of these desirable qualities. Naturally, designing improvements in polycarbonate would be aided by an understanding of the microscopic origin of its macroscopic properties; that is, an understanding of how the chains in polycarbonate are packed both locally and globally and how this packing results in motions on different length and time scales.

Currently there are two approaches to the description of chain packing in polycarbonate: one starts from the notion that the chain packing is homogeneous, or random, like that in a nearly isotropic melt or rubber, but with some local ordering superimposed.[1−3] The other description starts from the notion that the chain packing in polycarbonate is crystalline-like, but with very small ordered domains, consisting of only a few repeat units of a few proximate chains.[4,5] These domains are themselves imperfect, vary in size, and are randomly packed with respect to one another in a globally disorganized matrix. Both descriptions are in agreement with the fact that there is no long-range order in a polycarbonate glass.[6,7] A more realistic model of chain packing in polycarbonate probably lies somewhere between these two extremes, but a consensus on exactly where has not yet emerged.

The dominant large-amplitude motion for the main chain in polycarbonate is a 180° ring flip.[8−11] NMR monitors ring flips by the collapse of a quadrupolar line shape[8] (100 kHz), a dipolar line shape[9] (10 kHz), a chemical-shift line shape[10] (10 kHz), or polarization exchange (10 Hz−1 kHz).[11] The flipping ring spends half its time on one side and half its time on the other side and almost no time in between, just like a burger in a frying pan. The relevant spatial coordinate for this mechanically active two-site flip is not the ring C_2 axis, but a generalized coordinate that depends on the positions of the other main chains and side chains that gate the ring motion on and off. Ring flips are not ubiquitous in polymers but require just the right mix of tightness and flexibility for the gate. If chain packing is too tight, as in the highly regular arrays of parallel chains[12] in crystalline poly(ethylene terephthalate), the rings do not flip.[13] On the other hand, even when the packing is looser, if it is also inflexible, as occurs for the jumbled side chains of polystyrene, the rings still do not flip.[14] Thus, the characterization of 180° ring flips in polycarbonate defines not only a time scale for cooperative main-chain motion but also the placement of the gating apparatus, a structural parameter.

Chain dynamics in polycarbonate block copolymers have been examined recently[15] by a combination of dynamic mechanical spectroscopy (DMS) and dipolar rotational spin echo[9] (DRSE) ^{13}C NMR. The results of these experiments have shown that the modest structural perturbation of ring methyl-group substitution is sufficient to shift the γ transition to higher temperatures by 100 K or more and block 180° ring flips (faster than 10 kHz at 300 K) not only for the methyl-substituted rings but also for some of their unsubstituted neighbors.[16] In this paper we examine the surprisingly large effects on chain dynamics of an even more subtle ring substitution: the replacement of just one or two hydrogens by one or two fluorines of every fourth ring in the polycarbonate main chain. In a companion paper[17] that immediately follows, we will contrast the sizable effects of ring substitution on polycarbonate chain dynamics with the less pronounced effects of structural changes at the linkages between repeat units.

Experiments

The strategy for the synthesis of strictly alternating block copolymers of polycarbonate was used[16] with one of the bisphenol A monomers fluorine substituted. Locations of the fluorines in the polymers designated as [F]polycarbonate and [F_2]polycarbonate are shown in Figure 1. The molecular weights of the polymers were in the 20 kDa range with polydispersity index of about 2.5. DMS analysis[19] was performed on these materials as a function of temperature at 1 Hz. ^{13}C NMR spectra of the poly(fluorocarbonate)s were obtained both at 15.1 MHz using a 12-in. resistive magnet and at 50.3 MHz using an 89 mm bore superconducting solenoid. Details of the spectrometers have been described previously.[14]

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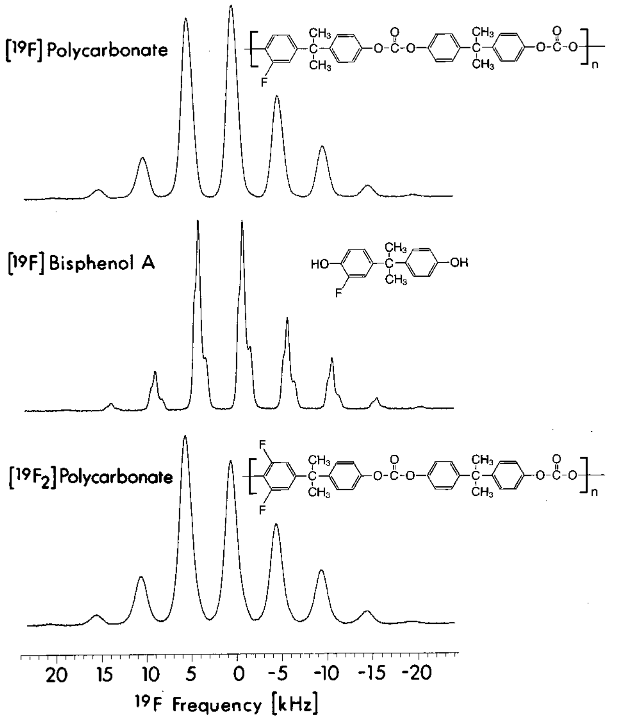

Figure 1. The 188 MHz ^{19}F NMR spectra of [F]polycarbonate (top), the singly fluoro-substituted bisphenol A monomer (middle), and [F$_2$]polycarbonate (bottom). Magic-angle spinning was at 5 kHz.

^{13}C$-$^{1}H dipolar line shapes were characterized by DRSE at 15.1 MHz with dipolar evolution over one rotor cycle and magic-angle spinning at 1859 Hz.[20] This spinning speed is fast compared to the width of the chemical shift tensors at 15.1 MHz but slow compared to the multiple-pulse scaled ^{13}C$-$^{1}H dipolar interactions for protonated carbons of 11.3 kHz. This is a good combination to generate a broad spinning sideband pattern in the dipolar dimension with no complications because of spinning sidebands in the chemical-shift dimension. Rapid free rotation of the rings would collapse essentially all the dipolar intensity into the centerband because the C$-$H internuclear vector is almost at the magic angle relative to the ring C_2 axis. Free rotation would be particularly easy to detect but has not been observed for any polycarbonate near 300 K. Because the second spinning sideband is near the maximum of a rigid-lattice dipolar Pake powder pattern under the conditions of these experiments, the ratio of intensities of the second to first dipolar sidebands (n_2/n_1) is a sensitive measure of averaging of the ^{13}C$-$^{1}H dipolar coupling by ring flips.[9,14,21] The n_2/n_1 ratio is of the order of 3/2 if there are no flips and 1/2 if all the rings flip.[13,14]

A ring flip is the only large-amplitude motion in polycarbonate faster than 10 kHz at 300 K. Variations in the ring-flip frequency between 30 kHz and 3 MHz arise because of variations in local packing.[9,22] A shift of ring-flip frequencies in poly(fluorocarbonate)s or poly(ester carbonate)s to higher values than those in polycarbonate will not affect the n_2/n_1 ratio, whereas a shift to lower frequencies will increase the ratio.

^{13}C$-$^{19}F dipolar line shapes were characterized by rotational-echo double resonance[23] (REDOR) at 50.3 MHz with dipolar evolution over eight rotor cycles and magic-angle spinning at 6250 Hz.[22] In the REDOR experiment, a single ^{13}C refocusing pulse was used, and the positions of the ^{19}F dephasing pulses were varied symmetrically within each rotor period.[23] The ^{13}C magnetization was observed with 90 kHz proton decoupling and 70 kHz fluorine decoupling. REDOR dephasing in the presence of motion was calculated using the methods first developed for $-$CF$_3$ groups.[24,25]

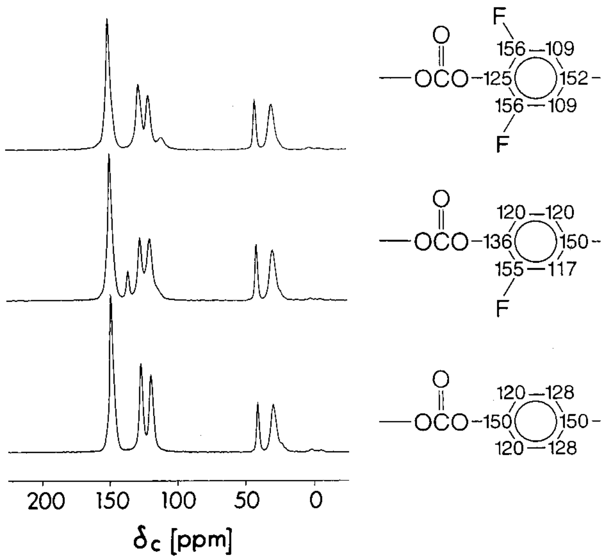

Figure 2. The 50.3 MHz cross-polarization magic-angle spinning ^{13}C NMR of [F$_2$]polycarbonate (top), [F]polycarbonate (middle), and polycarbonate (bottom). Magic-angle spinning was at 6250 Hz. Aromatic-carbon line assignments are based on the results of ^{19}F$\rightarrow$^{13}C coherence-transfer experiments (see ref 26).

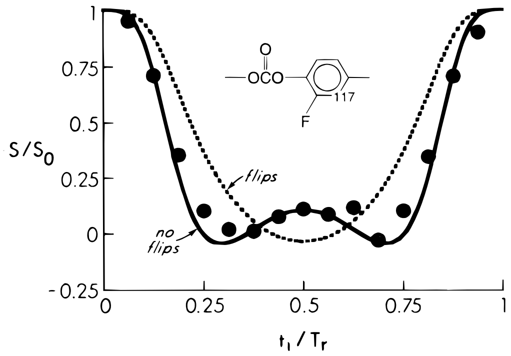

Figure 3. The 50.3 MHz ^{13}C{^{19}F} REDOR dephasing (S/S_0, solid circles) for the 117 ppm peak of [F]polycarbonate after eight rotor periods of dipolar evolution with magic-angle spinning at 6250 Hz. The position of the symmetrically placed ^{19}F dephasing π pulses within the rotor period is indicated by t_1. The dephasing calculated assuming ring flips faster than 10 kHz at 300 K is shown by the dotted line and that assuming static rings by the solid line.

Results

The ^{19}F NMR spectra of the poly(fluorocarbonate)s have shift-tensor, spinning-sideband intensities comparable to those of the rigid crystalline monomer (Figure 1). This result shows unambiguously the absence of motional averaging by large-amplitude ring motions.[21] That is, the fluoro-substituted rings are blocked from undergoing ring flips at 300 K at a rate comparable to the 20 kHz frequency range of the ^{19}F chemical shift tensor.

Aromatic-ring line assignments for the 50.3 MHz ^{13}C NMR spectra of polycarbonate and the poly(fluorocarbonate)s are shown in Figure 2. The assignments were aided by analysis of ^{19}F$\rightarrow$^{13}C coherence transfers.[26] Because the line widths arise from a distribution of isotropic chemical shifts,[19] spectra at 50.3 MHz are not significantly better resolved than those at 15.1 MHz (cf. Figure 5). The fact that the fluoro-substituted rings do not flip is confirmed by the two-bond ^{13}C{^{19}F} REDOR results for [F]polycarbonate (Figure 3) and [F$_2$]-

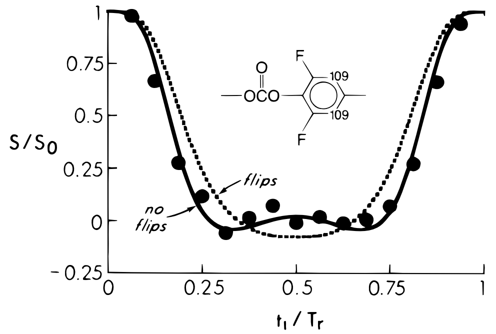

Figure 4. The 50.3 MHz $^{13}C\{^{19}F\}$ REDOR dephasing (S/S_0, solid circles) for the 109 ppm peak of [F$_2$]polycarbonate after eight rotor periods of dipolar evolution with magic-angle spinning at 6250 Hz. The position of the symmetrically placed ^{19}F dephasing π pulses within the rotor period is indicated by t_1. The dephasing calculated assuming ring flips faster than 10 kHz at 300 K is shown by the dotted line, and that assuming static rings by the solid line.

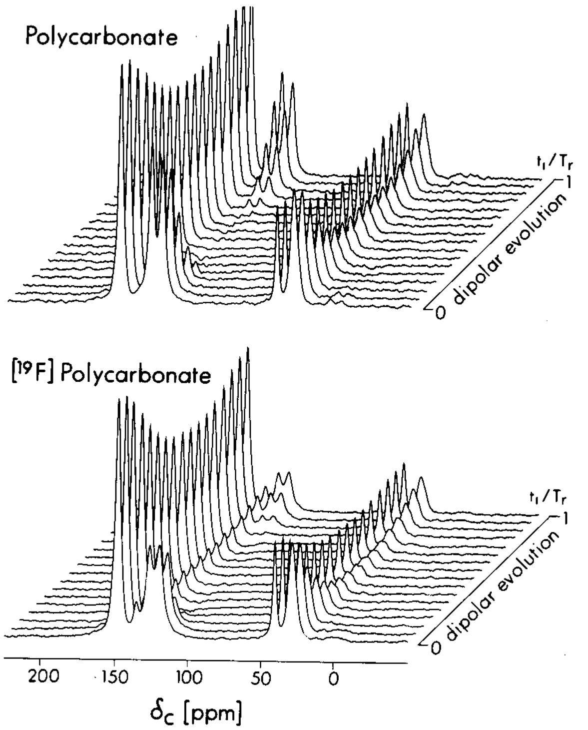

Figure 5. Dipolar rotational spin echo 15.1 MHz ^{13}C NMR spectra of polycarbonate (top) and [F]polycarbonate (bottom) as a function of $^1H-^{13}C$ dipolar evolution time during which proton−proton interactions were suppressed by muliple-pulse decoupling. Chemical shifts were measured in ppm from external tetramethylsilane. The dipolar evolution times vary from zero to one rotor period. Magic-angle spinning was at 1859 Hz.

polycarbonate (Figure 4), as well as by the one-bond $^{19}F-^{13}C$ dipolar couplings reported earlier.[26]

Even though all the fluoro-substituted rings are blocked from undergoing ring flips, virtually all of the non-fluoro-substituted rings flip. This result is established by DRSE experiments on the protonated aromatic-carbon peak at 128 ppm (Figure 5). This peak arises exclusively from non-fluoro-substituted rings.[21] In polycarbonate the ratio of second-to-first dipolar sideband intensities (n_2/n_1) is 0.46 (slightly higher than the ratio for the protonated aromatic-carbon peak at 120 ppm[15,16]), and in crystalline dimethoxybenzene the ratio is 1.35 ± 0.02. There are no fast ring flips in dimethoxybenzene.[9] Thus, if all the unsubstituted rings were blocked from flipping in the poly(fluorocarbonate)s, the n_2/n_1 ratio would be 1.35; if half were blocked, 0.91; and if one-fourth were blocked, 0.68. The observed ratio for [F]polycarbonate is 0.54, which indicates that at most only 9% of neighboring rings are blocked. The increased ratio relative to that in polycarbonate could be the result of inhibited main-chain motions which also contribute to motional averaging.

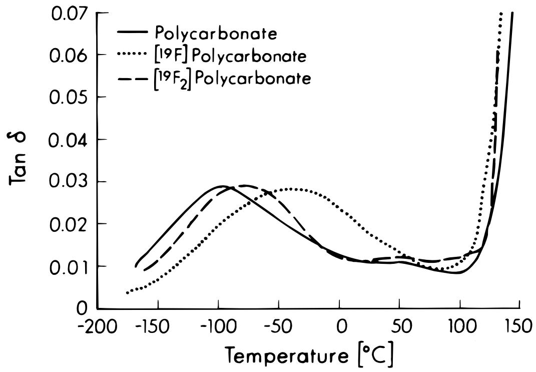

Figure 6. Dynamic mechanical spectra at 1 Hz of polycarbonate (solid line), [F]polycarbonate (dotted line), and [F$_2$]-polycarbonate (dashed line).

Despite the fact that the ring blocking is highly localized, the DMS γ transition in polycarbonate shifts to higher temperatures in the poly(fluorocarbonate)s. The γ transition shifts to −75 °C in [F$_2$]polycarbonate and −40 °C in [F]polycarbonate (Figure 6). Because the shift to higher temperature resulting from one fluorine substitution is greater than that resulting from two, the increase in mass of the substituted ring is not directly responsible for the shift. The general shape of the loss spectrum is unaffected by the fluoro substitution for [F$_2$]-polycarbonate but is broadened somewhat for [F]polycarbonate. The fluoro substitution has no significant effect on T_g.

Discussion

In this and in the following companion paper on poly(ester carbonate)s,[17] we will limit the discussion to generalities that are independent of the choice of a specific packing model of the glassy state for polycarbonates. We intend to revisit these results and expand the discussion when we have completed current REDOR, DRSE, and molecular modeling studies on new types of saturated-ring poly(ester carbonate)s, polycarbonate−poly(ethylene terephthalate) block copolymers, and linear and hyperbranched phenol-substituted polycarbonates.

The Bohr radius of an F atom is only about 0.3 Å greater than that of a proton, and a C−F bond length is less than 0.3 Å longer than a C−H bond.[27] Yet the simple substitution of F for H is sufficient to stop all of the fluoro-substituted rings of the poly(fluorocarbonate)s from flipping (faster than 10 kHz at 300 K). If such slight perturbations in structure are enough to turn the flips off, there must be an extremely delicate balance between tightness of chain packing and flexibility in chain motion responsible for gating the flips in the first place. The sensitivity of flips to ring substitution is in marked contrast to the insensitivity of flips to main-chain substitutions. Substantive structural perturbations including the insertion of both phenyl and chlorine substituents at the isopropylidene position[21] and bulky saturated rings at the carbonate position[17] of the polycarbonate main chain have little or no effect on the ring flips. It is therefore difficult to imagine how the isopropylidene and carbonate moieties can act as gates. We conclude that the polycarbonate ring flips are gated in the glass by a specific main-chain aromatic *ring*−*ring* interaction.[5]

We emphasize that ring flips are a property of chain packing in the glassy state because in solution, or in the melt, polycarbonate rings (even chlorine-substituted rings) are rotors on the time scale defined by the ^{13}C−^{1}H dipolar interaction. We emphasize that the gate is specific, not random, because all of the fluoro-substituted rings are blocked, not just an unfortuitously packed fraction of them. The gating ring−ring interaction is highly localized because most, if not all, of the non-fluoro-substituted nearest neighbors to the fluoro-substituted rings continue to flip. Thus, the speculations[27,28] that ring flips in polycarbonate result from an intrachain cooperative maneuver of both rings in a bisphenol A repeat unit are not supported.

The fluoro substitution has an effect on cooperative motion in the glass. Particularly for the asymmetrically substituted [F]polycarbonate, the low-frequency, high-temperature component of the DMS γ transition has been shifted and broadened (Figure 6). Perhaps the shift is simply the result of an increased barrier for the florinated-ring flip process or perhaps a new kind of mechanically active motion is present that necessarily involves long-range cooperativity. Experiments designed to monitor slow motions of the rings in the poly(fluorocarbonate)s are in progress.

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