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Local Chain Dynamics in Poly(ester carbonate)s

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ABSTRACT: Magic-angle spinning $^{13}C\{^1H\}$ recoupling NMR experiments have been performed on two series of poly(ester carbonate) block copolymers. The first series is based on bisphenol A blocks (B) and the second on tetramethylbisphenol A blocks (T). Three types of saturated-ring ester linkers were used, two of which contained bicyclic rings. The dynamic mechanical γ transitions of the B-series copolymers (but not the T-series copolymers) were shifted to higher temperatures. None of the ester linkers altered significantly the motional averaging at 300 K of $^1H-^{13}C$ dipolar couplings within either the B or T aromatic rings from the averaging observed for the corresponding polycarbonate homopolymers. All the B rings flip faster than 10 kHz at 300 K in the poly(ester carbonate)s, just as they do in polycarbonate itself, and none of the T rings flip, either in tetramethyl polycarbonate homopolymer or in the T-based poly(ester carbonate)s.

Introduction

Measurements of craze stresses and yield stengths performed on poly(ester carbonate)s with 1,4-cyclohexylene linkages have been interpreted by assuming that the conformational transition of the cyclohexylene rings in the copolymer enhances local main-chain mobility.[1] Impact strength also increases with increasing ester content. Presumably, ester mobility distributes strain over a larger molecular volume, thereby helping to collapse nanovoids that are the precursors of stable craze nuclei.[1] In this paper we report the results of dipolar rotational spin echo[2] (DRSE) ^{13}C NMR and dynamic mechanical spectroscopy (DMS) experiments performed on the poly(ester carbonate) block copolymers. The block lengths in the poly(ester carbonate)s varied from three to nine units and were based on either bisphenol A or tetramethyl ring-substituted bisphenol A. These blocks were linked by three types of esters, two of which contained a bulky bicyclic saturated ring system. Our strategy in this work is to use DMS to identify the presence of sub-T_g motions essential for macroscopic relaxation and NMR to infer details of the microscopic nature of this relaxation.

We have adopted an unconventional approach to the NMR characterization of polycarbonate main-chain dynamics. The approach is based on the time scale established by the 10 kHz scaled $^{13}C-^1H$ dipolar interaction. Ring flips, for example, are simply categorized as either faster or slower than 10 kHz at 300 K. In the former situation, we say that the rings flip and, in the latter situation, that they do not flip. We believe such a simplistic classification can lead to useful insights because the property of the ring-flip process that is most important is its structural component: the chain packing that acts as a switch or gate to enable or disable the flip of a substituted or unsubstituted ring. Thus, in the past few years, we have examined[3−5] a series of structurally different polycarbonate copolymers and blends in an attempt to characterize general features of the gate. We believe that this effort is a first step toward gaining an understanding of the chain-packing structural framework of polycarbonates and that, without this understanding, the details of motion (flip rates, librational amplitudes, distributions of correlation times) cannot be connected to macroscopic properties.

Experiments

The synthesis of alternating block copoly(ester carbonate)s has been described before.[6] The resulting materials are designated B_xC, B_xH, T_xC, and T_xO, where B stands for bisphenol A, T for tetramethyl bisphenol A, C for 1,4-cyclohexylene, H for 1,4-bicycloheptylene, and O for 1,4-bicyclooctylene, and x represents the number of carbonate repeat units within each block. The molecular weights of the copolymers were in the 30 kDa range with polydispersity indices of about 2.5. DMS analysis[7] was performed on these materials as a function of temperature at 1 Hz. ^{13}C NMR spectra were obtained at room temperature at 15.1 MHz. ^{13}C dipolar line shapes were characterized by DRSE with dipolar evolution over one rotor cycle and magic-angle spinning at 1859 Hz.[5,8] Concurent DRSE experiments were performed on sodium 1,4-cyclohexylene dicarboxylate used as a standard for saturated ring motion.

Results

Glass transition temperatures were a modest function of ester content, increasing, for example, by 5−10 °C as x decreased from 9 to 3 in both B_xC and T_xC series (Tables 1 and 2). Results from dynamic mechanical spectroscopy were dependent on ester content for B_xC. The γ transition of polycarbonate was shifted from −100 to about −65 °C for B_3C, with proportionally lesser amounts for B_5C (Figure 1) through B_9C (not shown). The broad, featureless tan δ response of tetramethylpolycarbonate[4] centered at about +40 °C was not altered noticeably for the copolymers (data not shown).

Typical cross-polarization magic-angle spinning ^{13}C NMR spectra are shown in Figure 2, along with a few key line assignments.[9] The protonated aromatic ring-

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Table 1. Dipolar Sideband Intensities for Six Alternating Block Copoly(ester carbonate)s and Polycarbonate (B_x)

			n_2/n_1	
carbonate block	ester linker	T_g[a] [°C]	aromatic-ring CH (120 ppm)	aliphatic-ring CH_2 (30 ppm)[b]
B_3	C	172	0.39	0.76
B_3	H	156	0.44	0.74
B_5	C	161	0.39	0.76
B_5	H	152	0.43	0.76
B_7	C	159	0.42	0.69
B_9	C	158	0.40	0.71
B_x		150	0.42	

[a] By DSC at a rate of 10 °C/min. [b] Methyl-carbon contribution removed by difference.

Table 2. Dipolar Sideband Intensities for Five Alternating Block Copoly(ester carbonate)s and Tetramethylpolycarbonate (T_x)

			n_2/n_1		
carbonate block	ester linker	T_g[a] [°C]	aromatic-ring CH (120 ppm)	aromatic-ring CH_3 (15 ppm)	aliphatic-ring CH_2 (30 ppm)[b,c]
T_3	C	206	1.20	0.45	0.63
T_3	O	210	1.16	0.51	0.59
T_5	C	198	1.24	0.47	0.71
T_7	C	199	1.24	0.45	0.69
T_9	C	196	1.30	0.46	0.63
T_x	C	200	1.20	0.45	

[a] By DSC at a rate of 10 °C/min. [b] Methyl-carbon contribution removed by difference. [c] Experimental value for sodium 1,4-cyclohexylene dicarboxylate is 0.73; rigid-lattice calculated value is 0.74 (see ref 8).

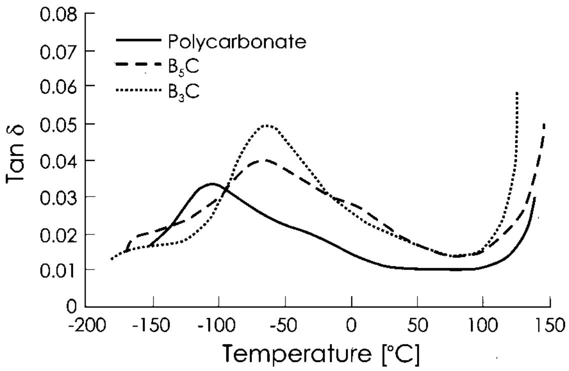

Figure 1. Dynamic mechanical spectra at 1 Hz of polycarbonate (solid line), B_3C poly(ester carbonate) (dotted line), and B_5C poly(ester carbonate) (dashed line).

carbon peak at 120 ppm (Figure 2, top) is often used to monitor ring motion[2-5] in B units by DRSE. The aliphatic ring methylene-carbon peak for the ester linkers appears at 30 ppm (Figure 2, middle), which is also the Larmor frequency for the isopropylidene methyl carbon of the B and T units (Figure 2, top). Motion of the aliphatic ring of the ester unit can be extracted by difference, using the scaled DRSE spectra of B_x or T_x homopolymers as a reference to estimate the contribution to the 30 ppm n_2/n_1 by the methyl carbons. For B_3C, for example, the scale factor is 1.5 to account for the six methyl carbons of the three isopropylidenes and the four methylene carbons of the single saturated ring. We found that, in general, the larger *x*, the more difficult the differencing.

A set of DRSE spectra for T_3C is shown in Figure 3. The aromatic methyl-carbon peak of the T blocks is fully resolved (15 ppm). Even though the protonated aromatic-carbon peak is not resolved, an approximate dipolar pattern for this carbon can be obtained from the Fourier transform of the peak shoulder at δ_C 120 (Figure 3, left arrow) as a function of the 16 time-domain points of the dipolar evolution dimension. Dipolar sideband intensity ratios obtained from Fourier analysis of the DRSE spectra of B-based poly(ester carbonate)s are presented in Table 1 and those for T-based poly(ester carbonate)s in Table 2. The accuracy of the aromatic-carbon n_2/n_1 ratios is estimated as ±0.02, and that of the aliphatic-

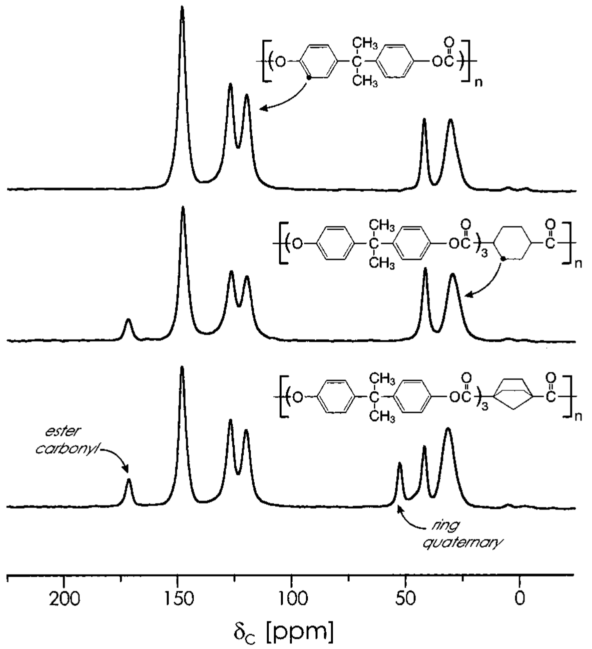

Figure 2. Cross-polarization magic-angle spinning 15.1 MHz ^{13}C NMR spectra of polycarbonate (top), B_3C poly(ester carbonate) (middle), and B_3H poly(ester carbonate) (bottom). The peaks at 30 and 40 ppm of the poly(ester carbonate) spectra are combination lines. The peak at 30 ppm arises from contributions due to the methyl carbons in B units and the methylene carbons in C units; the peak at 40 ppm arises from contributions from quaternary carbons in B units and methine carbons in C units. Magic-angle spinning was at 1859 Hz.

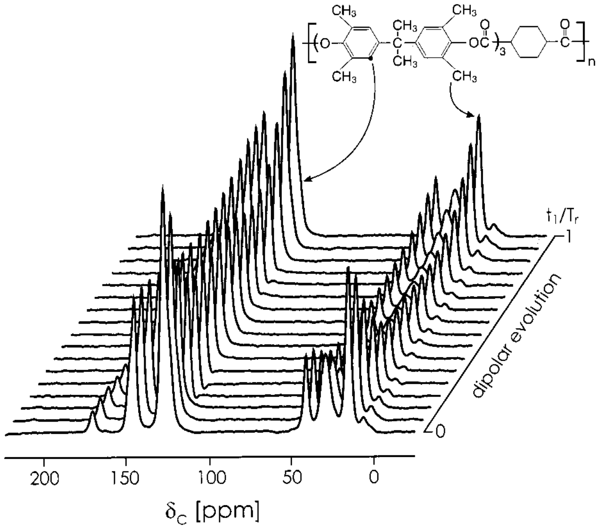

Figure 3. Dipolar rotational spin echo 15.1 MHz ^{13}C NMR spectra of T_3C poly(ester carbonate) as a function of $^1H-^{13}C$ dipolar evolution time during which proton−proton interactions were suppressed by muliple-pulse decoupling. The dipolar evolution times (t_1) varied from zero to one rotor period (T_r). Magic-angle spinning was at 1859 Hz. Chemical shifts were measured in ppm from external tetramethylsilane.

carbon ratios as ±0.04, the lesser accuracy due to the required differencing.

The aromatic-ring CH n_2/n_1 values for the B_xC poly(ester carbonate)s are all near the polycarbonate value of 0.42 (Table 1), which means that all B rings are flipping faster than 10 kHz at 300 K.[2,5] The aliphatic-ring CH_2 n_2/n_1 for B_xC and B_xH is greater than the motionally averaged value of 0.64 resulting from chair−chair interconversions.[9] Of course, only wiggling motions and not chair−chair interconversions are possible for the H and O bicyclo ester linkers. (The chemical structure of the H linker is shown in Figure 2; the structure of the O linker is similar, except that both rings of the bicyclic system are six-membered.) Both C and O ester linkers are wiggling in T_xC, based on the aliphatic-ring CH_2 n_2/n_1 values, which are generally less than 0.7 (Table 2). None of the T rings are flipping because neither the aromatic-ring CH n_2/n_1 nor the aromatic-ring CH_3 n_2/n_1 ratios (Table 2) show signs of averaging by large-amplitude ring motion.[4,10]

Discussion

Insertion of sterically bulky C, H, and O rings into the poly(ester carbonate) main chains does not affect the local chain dynamics monitored by DRSE aromatic-carbon dipolar sideband intensity ratios (Tables 1 and 2). All the B rings flip in the poly(ester carbonate)s, just as they do in polycarbonate itself, and none of the T rings flip, either in tetramethyl polycarbonate homopolymer or in the T-based poly(ester carbonate)s. This is true even though the O rings are not rigidly packed but are wiggling, as inferred from the methylene-carbon aliphatic-ring n_2/n_1 ratios (Tables 1 and 2), which are less than that observed for sodium 1,4-cyclohexylene dicarboxylate and less than that calculated[8] for a rigid-lattice CH_2 group (Table 2). The C-ring wiggling may also include chair−chair conformational rearrangements.[9] Because aromatic-ring motions are not enhanced or suppressed, the saturated rings are not acting as either plasticizer or antiplasticizer diluents.[11,12] We conclude that the balance between tightness of chain packing and flexibility in chain motion that permits ring flips in polycarbonate persists in the B_xC poly(ester carbonate)s, although their mechanical relaxation (Figure 1) suggests that both packing and flexibility may have been altered.

The B_xC copolymers and polycarbonate are equally lossy at −90 °C with comparable tan δ relaxation, consistent with all the B-rings flipping faster than 10 kHz at 300 K, although it is certainly possible that the distribution of ring-flip frequencies varies from polymer to polymer.[13] The poly(ester carbonate)s have a significant sub-T_g transition near −50 °C (Figure 1), which is not present in polycarbonate. We believe that this relaxation peak may be connected to the improved impact strength for the B_xC poly(ester carbonate)s.[1] The location in space of C rings in the B_xC block copolymers is not known at present, but their placement might facilitate longer range (and hence larger volume) cooperative motions than those that occur in polycarbonate itself. For the T_xC poly(ester carbonate)s, the increase in flexibility afforded by cooperative C-ring motions[1,9] is not sufficient to overcome the tight packing due to the T-ring methyl groups. No new aromatic-ring motions are observed for any of the T_xC poly(ester carbonate)s.

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References and Notes

(1) Liu, J.; Yee, A. F. *Macromolecules* **2000**, *33*, 1338.
(2) Schaefer, J.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. *Macromolecules* **1984**, *17*, 1479.
(3) Klug, C. A.; Wu, J.; Xiao, C.; Yee, A. F.; Schaefer, J. *Macromolecules* **1997**, *30*, 6302.
(4) Goetz, J. M.; Wu, J.; Yee, A. F.; Schaefer, J. *Macromolecules* **1998**, *31*, 3016.
(5) Wu, J.; Xiao, C.; Yee, A. F.; Goetz, J. M.; Schaefer, J. *Macromolecules* **2000**, *33*, 6849.
(6) Xiao, C.; Yee, A. F. *Macromolecules* **1992**, *25*, 6800.
(7) Jho, J. Y.; Yee, A. F. *Macromolecules* **1991**, *24*, 1905.
(8) Garbow, J. R.; Schaefer, J. *Macromolecules* **1987**, *20*, 819.
(9) Chen, L. P.; Yee, A. F.; Goetz, J. M.; Schaefer, J. *Macromolecules* **1998**, *31*, 5371.
(10) Hansen, M. T.; Boeffel, C.; Spiess, H. W. *Colloid Polym. Sci.* **1993**, *271*, 446.
(11) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Colloid Polym. Sci.* **1987**, *265*, 815.
(12) Zhang, C.; Wang, P.; Jones, A. A.; Inglefield, P. T.; Kambour, R. P. *Macromolecules* **1991**, *24*, 338.
(13) Schmidt, C.; Kuh, K. J.; Spiess, H. W. *Prog. Colloid Polym. Sci.* **1985**, *71*, 71.

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