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Molecular Motion in Polycarbonate and Modified Polycarbonates

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ABSTRACT: The special character of the molecular motion in the solid state has often been suggested as an explanation for the high impact strength of glassy polycarbonate. Consistent with this notion, the radio-frequency-field dependence of the magic-angle $T_{1\rho}$(C) of the protonated main-chain carbons of polycarbonate shows the presence of a broad distribution of high-frequency motions at room temperature, a situation unique in glassy polymers so far examined. Magic-angle $T_{1\rho}$(C) relaxation has also been used to measure molecular motion in the solid state of polycarbonates modified by an antiplasticizer, annealing, or structural substitutions. A general correlation can be established between microscopic motion in these modified polycarbonates and the impact strength of thin films. However, the correlation fails for thicker specimens, due to complications arising from a ductile-brittle transition.

The fast ^{13}C $T_{1\rho}$ relaxation (at about 30 kHz) of quenched bisphenol-A polycarbonate glass at room temperature has been established as spin-lattice in character by comparison with experimentally and theoretically determined slow spin-spin cross-polarization transfer rates between protons in the local dipolar field and carbons in the applied radio-frequency field.[1-3] This means that the observed protonated aromatic-carbon $T_{1\rho}$ relaxation characterizes mid-kilohertz main-chain motions in polycarbonate. Such motions presumably involve cooperative torsional oscillations of phenyl groups within conformations locked into the glass by interchain steric interactions.[3] These microscopic chain motions of polycarbonate have been linked previously in an empirical way to macroscopic mechanical properties such as impact strength or toughness.[3] In this paper we examine this connection in greater detail and, in particular, test its extension from polycarbonate to thermal, physical, and chemical modifications of polycarbonate.

Experiments

Carbon-13 cross-polarization NMR experiments were performed at 15.1 MHz with a spectrometer employing time-shared external ^{19}F field-frequency stabilization, routed quadrature detection,[4] spin-temperature alternation,[5] solid-state class A transmitters, and a double-tuned single-coil probe.[6] Magic-angle spinning results were obtained by using a Beams-Andrew design rotor[7] (0.7-cm^3 sample volume) and a spinning speed of 2.1 kHz. (A few experiments were performed with spinning speeds at 1.0 and 2.6 kHz.) Spinning samples occupied approximately two-thirds of the volume of the coil. The spectrometer was equipped with a software-controlled digital pulse programmer, which permitted automatic variation of pulse parameters coordinated with interleaved block-averaged data acquisition to counteract any drifts during prolonged $T_{1\rho}$(C) relaxation measurements. In these $T_{1\rho}$(C) experiments, following a matched spin-lock Hartmann-Hahn generation of a carbon polarization,[8] the proton radio-frequency field was turned off abruptly. After a 50-μs delay, measurement of the initial rate of decay (evaluated between 0.050 and 1.000 ms) of the total carbon magnetization held in its rotating field yielded $\langle T_{1\rho}(\mathrm{C})\rangle$, the average carbon spin-lock lifetime. Relaxation data were collected for carbon rotating frame times of up to 12 ms. Only spinning samples were examined.

Polycarbonate (General Electric Lexan 101) was examined by NMR in the form of compression-molded 0.4-mm-thick films, 3-mm-thick disks, and 9-mm-diameter cylindrical plugs 10 mm in length. The molding and annealing conditions used in the preparation of these samples from pellets dried overnight under vacuum at 120 °C are summarized in Table I. Experiments on a precipitated polycarbonate powder (Lexan 145-111) were also performed.

Polycarbonate containing 10% (by weight) antiplasticizer was prepared by adding Aroclor 1254 to a solution of polymer which was then used to cast a film. The film was powdered, dried, and subsequently molded in the same way as entry 12, Table I. Aroclor 1254 is a former commercial product of Monsanto Co. and consists of partially chlorinated biphenyls which form a liquid with a T_g of -24 °C.

Norbornyl polycarbonate was obtained from Dr. D. J. Massa (Eastman Kodak Co., Rochester, NY) and tetrachloro polycarbonate from Dr. Don LeGrand (General Electric Co., Schenectady, NY). Structural formulas for these chemically modified polycarbonates are shown in Table II. Samples of both polymers were molded at 275 °C with other conditions the same as for entries 10 and 16 of Table I. The former were used for impact tests and the latter for NMR measurements.

Impact strengths of thin films were measured with an instrumented dart impact tester.[9] A film sample, typically 25-mm square and 0.4-mm thick, was clamped over a 22-mm-diameter hole and punctured by a 6.4-mm-diameter hemispherical dart at a rate of 3.6 m/s. A quartz-crystal transducer mounted beneath the dart sensed the force during the impact. An integration of the digitized force-time response of the polymer yielded the multiaxial energy-to-fail. A near-linear relation between thickness and failure energy was observed for polycarbonate films from 0.1 to 0.5 mm.

Results

The magic-angle cross-polarization ^{13}C NMR spectrum of polycarbonate consists of five lines (Figure 1, top). These have been identified[3] from left to right, in order of increasing magnetic field, as a combination line arising from the carboxyl and nonprotonated aromatic carbons, two lines due to the protonated aromatic carbons, the aliphatic quaternary carbon line, and the methyl carbon line, respectively. The component of each of these lines which relaxes first in a $T_{1\rho}$(C) experiment appears motionally broadened (Figure 1, difference spectra), even in experiments with H_1's as large as 60 kHz.

The spectrum of polycarbonate blended with 10% Aroclor 1254 is naturally quite similar to that of polycarbonate. A few minor lines due to the Aroclor are resolved, particularly after longer hold times in $T_{1\rho}$(C) experiments (Figure 2). The spectrum of norbornyl polycarbonate is also similar to that of polycarbonate but with the methyl carbon line replaced by a complicated high-field pattern arising from the aliphatic carbons of the norbornyl ring. The spectrum of tetrachloro polycarbonate has only a single protonated aromatic carbon line while the high-field part of the spectrum is the same as that of polycarbonate. Examples of the spectra of both norbornyl and tetrachloro polycarbonates have been presented elsewhere.[10]

The full $T_{1\rho}$(C) relaxation curve (at 28 kHz) of the protonated aromatic carbons of quenched polycarbonate is nonlinear (Figure 3, upper plot, lower curve). This curve is an average of data collected in four consecutive experiments, each one generating a complete $T_{1\rho}$(C) curve in a

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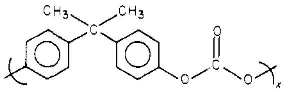
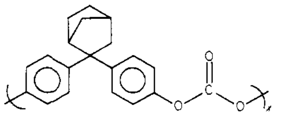
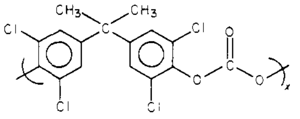
Table I
Polycarbonate Sample Preparations

sample no.	sample geometry	molding press, psi	molding temp, °C	mold cooling program	annealing temp, °C	annealing time, days
1	3-mm-thick disk	10 000	220	ice-water quench	125	0
2						0.1
3						1
4						2
5						3
6						10
7						20
8	3-mm-thick disk	10 000	220	ice-water quench	140	1
9	3-mm-thick disk	10 000	220	air cooled under pressure		
10	0.4-mm-thick film	10 000	220	ice-water quench	140	0
11						1
12	9-mm-diam plug	10 000	220	air cooled under pressure		
13		50 000				
14		100 000				
15	9-mm-diam plug	100 000	220	ice-water cooled		
16	9-mm-diam plug	100 000	225	air cooled under pressure		
17			250			
18			270			

Table II
Structural Formulas for Various Polycarbonates

polymer	structure
polycarbonate	
norbornyl polycarbonate	
tetrachloro polycarbonate	

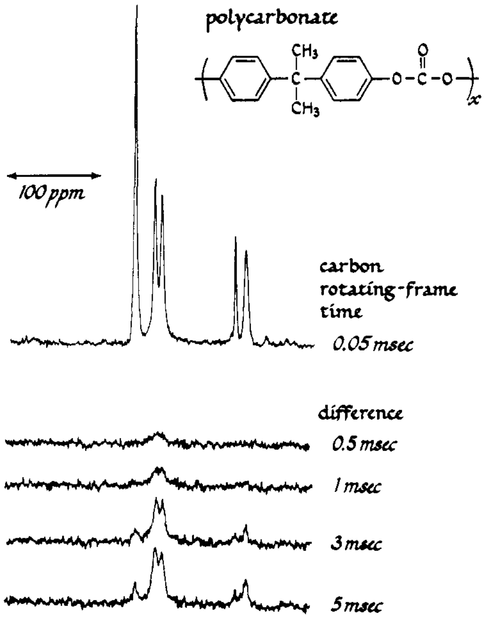


Figure 1. Magic-angle cross-polarization 15.1-MHz ^{13}C NMR spectra of polycarbonate (sample I, Table I) in a $T_{1\rho}$(C) experiment with H_1(C) = 28 kHz. The top spectrum was obtained by using a carbon rotating frame hold time of 0.05 ms after removal of the proton radio-frequency field. The bottom four spectra are differences between the top spectrum and the spectra obtained for correspondingly longer times in the carbon rotating frame.

little more than 2 h (Table III). These experiments were performed on a stack of four 3-mm-thick disks which never

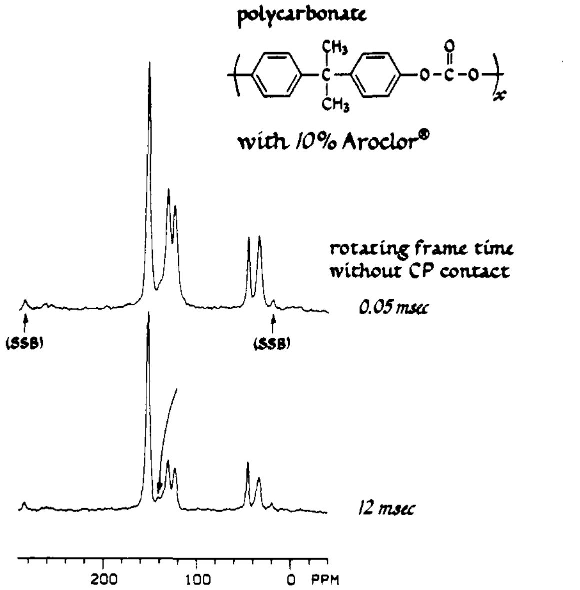


Figure 2. Magic-angle cross-polarization 15.1-MHz ^{13}C NMR spectra of polycarbonate blended with 10% (by weight) of an Aroclor antiplasticizer in a $T_{1\rho}$(C) experiment with H_1(C) = 28 kHz. Spinning sidebands at 2.1 kHz are just visible. One of the slowly relaxing Aroclor lines is resolved (arrow, bottom spectrum) after 12 ms in the carbon rotating frame. More digital filtering has been used on these spectra than on those of Figure 1.

Table III
$T_{1\rho}$(C) (28 kHz) Relaxation Data for the Protonated Aromatic Carbon Region of Polycarbonate and Polycarbonate-Aroclor (T = 26 °C) Spinning at the Magic Angle at 2.1 kHz

	polycarbonate		polycarbonate-Aroclor	
t, ms	$S(t)/S_0$	σ[a]	$S(t)/S_0$	σ[a]
0.050	1.000		1.000	
0.200	0.980	0.006	0.981	0.006
0.400	0.954	0.001	0.955	0.003
0.600	0.926	0.004	0.932	0.004
0.800	0.898	0.005	0.901	0.008
1.000	0.865	0.010	0.881	0.004
2.000	0.782	0.006	0.794	0.010
3.000	0.711	0.008	0.732	0.006
5.000	0.601	0.006	0.631	0.005
8.000	0.474	0.008	0.527	0.008
12.000	0.371	0.006	0.424	0.010

[a] Standard deviation for four consecutive independent experiments.

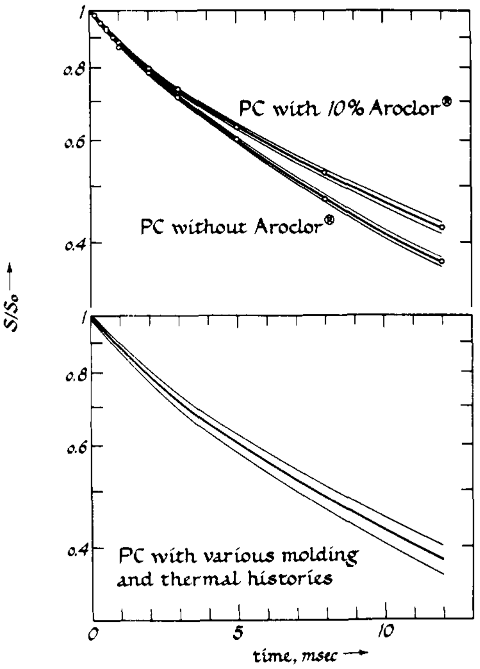


Figure 3. (Top) The 2.1-kHz magic-angle $T_{1\rho}$(C) relaxation (H_1(C) = 28 kHz) of the protonated aromatic carbon region of polycarbonate (sample 8, Table I) and of polycarbonate blended with 10% (by weight) of Aroclor 1254. Numerical values for the experimental data (open circles) are presented in Table III. The heavy solid line is the average of four complete consecutive $T_{1\rho}$(C) experiments, the standard deviation of which is indicated by the lighter solid line. (Bottom) The 2.1-kHz magic-angle $T_{1\rho}$(C) relaxation (H_1(C) = 28 kHz) of the protonated aromatic carbons of polycarbonate. The heavy solid line is the average of experiments performed on all the compression-molded samples of Table I, Lexan 101 pellets, and Lexan 111-145 powder. The standard deviation is indicated by the lighter solid line.

had been previously under high-speed spinning conditions. No differences between the four individual relaxation curves were obvious. Experiments with spinning speeds at 1.0 and 2.6 kHz gave similar results.

The overall relaxation of polycarbonate blended with 10% (by weight) Aroclor 1254 is somewhat slower than ordinary polycarbonate, with differences most clear for longer carbon rotating frame spin-lock times (Figure 3, upper plot, upper curve; Table III). Initial and final slopes of $T_{1\rho}$(C) curves (as a function of the applied carbon H_1) for polycarbonate and polycarbonate plus Aroclor, as well as for norbornyl polycarbonate, and tetrachloro polycarbonate, are presented in Table IV. The polycarbonate and polycarbonate–Aroclor protonated aromatic carbon $T_{1\rho}$ show a very minor dependence on H_1 (this is true for the methyl carbon $T_{1\rho}$ as well), while both the initial and final slopes of the norbornyl and tetrachloro polycarbonate protonated aromatic $T_{1\rho}$(C) relaxation curves are significantly H_1 dependent. Evaluating the initial slopes of $T_{1\rho}$(C) curves by least-squares straight-line fits to data over the first millisecond of relaxation results in more conservative values of $\langle T_{1\rho}(\mathrm{C})\rangle$ than reported earlier.[3]

The effects on the $T_{1\rho}$(C) relaxation of polycarbonate arising from molding and thermal annealing histories are quite complicated. For example, quenched polycarbonate disks annealed at 125 °C for 0 and 2 h and 1, 2, 3, 10, and 20 days, respectively, produced $T_{1\rho}$(C) curves in which the final $T_{1\rho}$(C)'s first increased from 15 to 20 ms with annealing and then decreased to 18 ms with further annealing (Table IV). These results were not random fluctuations due to experimental errors (see Table III). Rather, we suspect the $T_{1\rho}$(C) curves are reflecting changes in a broad distribution of relaxation times, different components of which are changing in opposite directions. The net result is a decay curve which, given the present level of precision, defies a straightforward deconvolution and characterization. Instead, we have averaged the results of some 20 separate $T_{1\rho}$(C) experiments on different samples (Table I plus polycarbonate pellets and powders) and present only the average and standard deviation (Figure 3, bottom). None of the molding or annealing conditions listed in Table I produced dramatically large effects; that is, all the decay curves fall within a reasonably narrow band.

Table IV

$T_{1\rho}$(C) Relaxation Parameters for Protonated Aromatic Carbons of Polycarbonate and Modified Polycarbonates (T = 26 °C) Spinning at the Magic Angle at 2.1 kHz

polymer[a]	H_1(C), kHz	$\langle T_{1\rho}(\mathrm{C})\rangle$,[b] ms	$T_{1\rho}{}^{\mathrm{f}}$(C),[c] ms
polycarbonate (sample 15, Table I)	20	5.2	12
	28	6.6	15
	37	7.4	17
	44	8.2	19
	60	8.6	26
polycarbonate + 10% Aroclor 1254	20	5.0	11
	28	7.4	18
	37	8.3	22
	44	8.1	24
	60	10.5	31
norbornyl polycarbonate	28	3.9	11
	44	7.0	29
tetrachloro polycarbonate	28	40	45
	44	130	130

[a] All samples were 9-mm-diameter plugs. [b] Least-squares straight-line fit to relaxation data collected from t = 0.050 to t = 1.000 ms after turnoff of the proton H_1. [c] Least-squares straight-line fit to relaxation data collected from t = 5 to t = 12 ms after turnoff of the proton H_1; the superscript f denotes a nominal final slope.

For all of the $T_{1\rho}$(C) experiments described above, the protonated aromatic carbon magnetization was measured by the sum of the peak heights of the doublet centered about δ_{C} 130 (Figure 2). Since this doublet is not resolved to the base line and since a significant fraction of the intensity of the doublet is contained in its broad base, using areas to measure signal intensity would have been practical only by difference spectra, such as those in Figure 1. This, in turn, would have required spending half of the total data acquisition period characterizing the 50-μs spectrum so that difference spectra were not unduly noisy. Such a procedure would have resulted in accurate initial slopes, but at the expense of poorer characterization of the full $T_{1\rho}$(C) curve. Since we feared that stresses in the solid samples under tension due to the magic-angle spinning might eventually affect relaxation properties (depending on sample preparation, annealing, etc.), arbitrarily long data acquisition times were not available. We therefore decided upon the use of peak heights as the most reliable, least subjective measure of signal intensity, fully realizing that this would result in an overestimate of $\langle T_{1\rho}(\mathrm{C})\rangle$. For example, when areas are used, $\langle T_{1\rho}(\mathrm{C})\rangle$ of sample 15 of Table I is about 4.5 ms at 28 kHz, compared to 6.6 ms when peak heights are used (Table IV).

Matched spin-lock cross-polarization transfer times,[3,8] T_{IS}(SL), at 28 kHz, for the protonated aromatic carbons of quenched polycarbonate, annealed polycarbonate, norbornyl polycarbonate, polycarbonate–Aroclor, and tetrachloro polycarbonate were 91, 90, 71, 68, and 45 μs, respectively. These values described the apparent first-order kinetics of the polarization transfer during the first 40 μs following carbon–proton contact. Since the ^{1}H–^{1}H dipolar interactions of the aromatic protons of all the

Table V
Thin-Film Instrumented Dart Impact Strengths

sample	failure energy,[a,b] mJ
quenched polycarbonate	810
annealed polycarbonate[c]	540
polycarbonate + 10% Aroclor 1254[d]	340
tetrachloro polycarbonate	27
norbornyl polycarbonate	27
poly(2,6-dimethylphenylene oxide)[e]	610
polysulfone[f]	430
polystyrene[g]	14

[a] Film thicknesses between 0.08 and 0.4 mm were used, depending on toughness; failure energies reported are normalized to 0.4-mm thickness. [b] Estimated accuracy ±10%. [c] Annealed at 140 °C for 20 h. [d] Film thickness 0.08 mm. [e] Supplied by Aldrich Chemical Co.; no additives; molded as entry 10, Table I, at 285 °C. [f] Supplied by Union Carbide Corp.; molded as entry 10, Table I, at 250 °C. [g] Supplied by Monsanto Co.; molded as entry 10, Table I, at 225 °C.

polycarbonates are about the same, $T_{IS}^{\dagger}(SL)$'s (where the dagger indicates that the dependence of the matched spin-lock cross-polarization transfer rate on ^1H–^1H interactions has been removed[3]) are proportional to the corresponding $T_{IS}(SL)$'s.

Impact strengths determined by the instrumented dart test for thin films of polycarbonate and modified polycarbonates, along with values for thin films of some common engineering plastics for comparison, are presented in Table V. Unlike the situation for thick samples,[11] prolonged annealing has little effect on the toughness of thin films of polycarbonate. Larger effects on toughness result from modifications of polycarbonate by addition of Aroclor antiplasticizer or by various structural substitutions.

Discussion

The $T_{1\rho}(C)$ relaxation curve of the protonated aromatic carbons of polycarbonate has only a weak dependence on $H_1(C)$. The initial slope changes by less than a factor of 2, and the final slopes a little more than a factor of 2, for a change of $H_1(C)$ from 20 to 60 kHz (Table IV). This weak dependence means that the broad distribution of cooperative main-chain phenyl-group torsional motions responsible for the pronounced nonlinear $T_{1\rho}(C)$ relaxation must be composed largely of components whose correlation frequencies are of the order of 10^5 Hz (or higher) at room temperature. Distributions of lower frequency motions would have a stronger $H_1(C)$ dependence than is observed.[12] Of the 30 or so glassy polymers we have examined by ^{13}C NMR, this kind of relaxation behavior is unique to polycarbonate. On the basis of the theory of Cheung and Yaris,[2] the amplitude of these high-frequency motions must involve angular excursions of at least 10°.

The fact that the high impact strength of polycarbonate is also unique among glassy polymers prompts an attempt at a correlation between $T_{1\rho}(C)$ relaxation and mechanical toughness. At first glance, such a correlation may seem implausible since the shear component of the impact strength is known to involve nonlinear plastic deformation and flow.[13] We rationalize, however, that the motions characterized by an NMR experiment, performed on a material only slightly deformed by stresses induced by 2-kHz spinning, are nevertheless related to the motional and flow behavior of the same material undergoing large-scale deformations.[14]

This connection can be made in the same spirit that infrared measurements of vibrational frequencies of a diatomic molecule can be related to the bond strength of the molecule. That is, we accept that vibrational motion near the bottom of an anharmonic potential well still reflects the anharmonicity and hence the limiting or long-range behavior of the potential. Similarly, we claim that the restricted local main-chain motions resulting in the $T_{1\rho}(C)$ relaxation must reflect the same interchain cooperativity ultimately responsible for plastic flow.

We have proposed before a correlation between impact strength (as measured by a conventional notched Izod test) and microscopic molecular motion for nominally homogeneous glassy homopolymers at room temperature.[3] Microscopic motion is measured by a ratio of $\langle T_{IS}^{\dagger}(SL)\rangle$ to $\langle T_{1\rho}(C)\rangle$, where the brackets indicate an average over the entire sample. The ratio of these two numbers gives a rough indication of the shape of the spectral density distribution describing main-chain motions. For polymers such as polycarbonate, poly(phenylene oxide), and polysulfone, this ratio is large, indicating a distribution of motions with a significant density in the same mid-kHz range as the high-frequency Fourier components of a typical mechanical impact. We suggest that the interchain steric interactions within these polymers are such that their cooperative main-chain motions are fast enough to lead to plastic flow, thereby distributing the energy of the impact without stress concentrations, crack formation, and brittle failure. For polymers such as polystyrene the ratio of relaxation parameters is smaller, suggesting a relatively greater concentration of main-chain motions at lower frequencies and hence less resistance to a high-speed impact.

In fact, the impact strengths of polycarbonate and polysulfone are greater than that of polystyrene, regardless of whether they are measured by an Izod test or by a thin-film dart test (Table V). Similar correlations with other glassy polymers can also be made.[3] Thus, the existence of some sort of connection between microscopic motion and macroscopic properties is at least qualitatively reasonable. We now examine the generality of this connection to various modifications of polycarbonate known to alter its physical properties.

1. Thermal History. Neither the $\langle T_{1\rho}(C)\rangle$ nor the impact strength of *thin films* of polycarbonate changes significantly with prolonged annealing (Figure 3 and Table V). Changes in the former are no more than 10–20%, and in the latter less than about 50%. (We did not observe the somewhat larger changes in $T_{1\rho}(C)$'s with annealing reported earlier for polycarbonate rods.[3]) In addition, we see no dependence of $\langle T_{1\rho}(C)\rangle$ on sample thickness. Yet it is well-known that the impact strengths of thicker pieces of polycarbonate are drastically affected both by the thickness of the sample and by annealing.[11,15] For example, we have observed that the notched Izod impact strength of an annealed 3-mm-thick bar of polycarbonate is almost an order of magnitude less than that of a quenched sample.

The effects of thickness and annealing on the impact strength of polycarbonate can both be understood within the framework of a ductile–brittle transition. The failure mechanism for materials that deform plastically depends on the thickness. In thin specimens deformation can occur by shear processes at nearly constant volume because of lateral contraction. In thicker specimens, where bulk constraints inhibit lateral contraction, the deformation boundary conditions change from plane stress to plane strain, and a transition from ductile to brittle failure takes place.[16] Similarly, annealing tends to embrittle plastic materials by increasing the chain packing density, inhibiting flow, and inducing a transition from shear yielding to crazing as the predominant mode of failure.[17] Therefore, the ductile–brittle transition in polycarbonate is likely determined by the combined effects of geometrical constraints and thermal history. Mills[18] has observed such an interplay between thickness and annealing and interpreted the results of impact experiments in much this same manner.

We observe that annealing has an observable but complicated effect on the average microscopic chain motion in polycarbonate (Figure 3, bottom). As stated earlier, we suspect that the $T_{1\rho}$(C) curves are reflecting changes in a broad distribution of relaxation times, some of which correspond to motional modes important in the initiation of shear processes. The modest level of these motional changes is consistent with the observed minor decrease in the multiaxial failure energy of thin films with annealing (Table V). In such thin films, annealing does inhibit flow processes (and reduce the impact strength) but not to the extent necessary to cause a ductile–brittle transition.

Naturally a geometric dependence of impact strength emphasizes a limitation on any attempt at a correlation between impact strength and NMR characterizations of microscopic molecular motion. Namely, an NMR parameter will only correlate with the shear or flow component of the failure process.[3] The volume or dilational component of failure involves macroscopic crack propagation. This component is therefore sensitive to sample thickness, internal flaws, inclusions, surface scratches, solvent etching, etc., all of which have negligible effects on the average microscopic chain motion. Thus, $\langle T_{1\rho}(\mathrm{C})\rangle$ specifies an inherent molecular toughness which is the same as the observed impact strength only as long as the failure mode does not change.

The especially high impact strength of some quenched polycarbonate sheets as thick as 3–5 mm reflects a resistance to a change in failure mode which we feel is related to its exceptionally broad distribution of high-frequency main-chain motions. Nevertheless, to the extent that only the impact strengths of end-use thickness, annealed or partially annealed, glassy polymers are of interest, we conclude that the $T_{1\rho}$(C) characterization of molecular motion by itself is not a useful, predictive parameter. A similar conclusion has been reached regarding the use of dielectric relaxation measurements of molecular motions. Watts and Perry[19] saw no substantial difference in the β processes of quenched and annealed polycarbonate, implying that a change in the local motions cannot completely explain the observed ductile–brittle transition.

2. Antiplasticizers. Aroclor 1254 produces a two- to threefold reduction in the impact strength of thin films or polycarbonate (Table V) *without* altering the molecular motion of the polymer. That is, $\langle T_{1\rho}(\mathrm{C})\rangle$ of the protonated aromatic carbons of polycarbonate–Aroclor is different from that of polycarbonate by only some 10% (Table III and IV). In fact, the $T_{1\rho}$(C) relaxation of the polycarbonate–Aroclor system is similar to that of a two-phase system, consisting of an unperturbed polymer mixed with an Aroclor diluent, the latter acting as an immobilized and slow relaxer (Figure 2). This result is consistent with the findings of Petrie et al.,[20] who concluded from dielectric and mechanical measurements of various polycarbonate–Aroclor mixtures that (a) embrittlement does not require suppression of low-temperature secondary loss peaks (i.e., motion) and (b) the extent of embrittlement of an antiplasticized polymer should be thought of in terms of the dynamics of both components, polymer and diluent. We suspect an immobilized antiplasticizing diluent may act in the same way as an inclusion or internal flaw and so promote a change in the mode of failure from ductile to brittle. This would explain why embrittlement of polycarbonate by an antiplasticizer is more dramatic for thicker samples.[21] Such a change, as discussed above for thermally annealed materials, would not be reflected in microscopic molecular motion of the polymer and so would not correlate with $\langle T_{1\rho}(\mathrm{C})\rangle$.

Even in the absence of a change in the failure mode of the polymer, there is no reason to expect the effect of an immobilized foreign heterogeneity on the cooperativity of main-chain motion to be equivalent to that of a normal local packing irregularity in a nominally homogeneous glass. Thus, the impact strength of a heterogeneous two-component system need not be described by the usual single average $T_{1\rho}$(C). Unfortunately, in examining a variety of two-component systems (including copolymers), we have found no simple alternate prescription for predicting impact strength based on sums of individual $\langle T_{1\rho}(\mathrm{C})\rangle$'s.

3. Structural Substitutions. Chlorinated polycarbonates have in the past been described as internally antiplasticized.[21] Certainly the impact strength of thin films of tetrachloro polycarbonate is greatly reduced relative to that of polycarbonate (Table V). However, we feel the character of this embrittlement is quite different from that induced by external Aroclor diluents. The chloro substitution has drastically reduced the main-chain motion of the polymer itself, as indicated by an increased $\langle T_{1\rho}(\mathrm{C})\rangle$ (Table IV). In addition, a strong H_1(C) dependence of the tetrachloro polycarbonate $\langle T_{1\rho}(\mathrm{C})\rangle$ shows polycarbonate's broad distribution of high-frequency motion has been eliminated. Thus, the embrittlement of tetrachloro polycarbonate is likely due to an inability of the polymer main chains to respond to the high-frequency stress components of the impact and initiate significant plastic flow.

The H_1(C) dependence of the protonated aromatic carbon $\langle T_{1\rho}(\mathrm{C})\rangle$ of norbornyl polycarbonate (Table IV) indicates that structural substitution of the bulky fused-ring system for the *gem*-dimethyl group has also reduced the broad distribution of high-frequency motions of polycarbonate, but not nearly to the same degree as the chloro substitution. This result and the similarity of the H_1 dependence of the protonated aromatic and methyl carbon $T_{1\rho}$(C)'s in polycarbonate are consistent with the idea that a basic motional unit in polycarbonate consists of two phenyls fairly rigidly coupled through the *gem*-dimethyl group and more loosely coupled to other motional units in the same and other chains by the carbonate group.[3] The reduction in motion for norbornyl polycarbonate is also much less than that resulting from the asymmetric kink in the rigidified main-chain of *o*,*p*-bisphenol-A polycarbonate.[1] Apparently, adding to the bulk of a main-chain motional unit is less important than inserting restrictions about the flexible carbonate linkage. Thus, motions having frequency components reduced from, say, 100 kHz to about 30 kHz could account for the short $\langle T_{1\rho}(\mathrm{C})\rangle$ of norbornyl polycarbonate.

The reduction in impact strength of norbornyl polycarbonate is not reflected in a reduction of $\langle T_{\mathrm{IS}}^{\dagger}(\mathrm{SL})\rangle / \langle T_{1\rho}(\mathrm{C})\rangle$ relative to that of polycarbonate as measured at 28 kHz but would be in a ratio measured at, say, 60 kHz. The choice of 28 kHz had been based on the assumption that this H_1(C) was greater than the highest frequency describing main-chain motion.[3] The H_1(C) dependence of the polycarbonate $T_{1\rho}$(C) shows this assumption to be incorrect. Thus, the correlation between impact strength and $T_{1\rho}$(C) should actually be made at higher H_1's. In any event, for either H_1, the unusually small values of the norbornyl polycarbonate $\langle T_{1\rho}(C)\rangle$ (in comparisons with tetrachloro polycarbonate and other polymers with a similar $H_1(C)$ dependence) are not in line with its low impact strength. This demonstrates that the correlation between a single average $T_{1\rho}(C)$ value and impact strength is, in fact, not universal and that for some systems a more elaborate use of $T_{1\rho}(C)$ relaxation behavior may produce a better guide to deformation events on a molecular scale.

In summary, the extensive collection of relaxation data discussed in the previous three sections supports a general connection between the macroscopic physical property of toughness and microscopic molecular motion for polycarbonate and various modifications of polycarbonate but also defines a number of exceptions and qualifications (mostly dealing with sample geometry) which necessarily limit the utility of this connection in practical applications.

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Analysis of the Room-Temperature Molecular Motions of Poly(ethylene terephthalate)

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ABSTRACT: Carbon-13 rotating-frame relaxation parameters have been obtained from magic-angle high-resolution ^{13}C NMR spectra of various poly(ethylene terephthalates). Comparisons of $\langle T_{1\rho}(C)\rangle$'s and $\langle T_{IS}(ADRF)\rangle$'s show that $T_{1\rho}(C)$ relaxation is a spin–lattice process for the amorphous material and so can be used to characterize molecular motion in the low-to-mid-kilohertz frequency range. Annealing below T_g reduces the mid-kilohertz rotational segmental motions of the ethylene groups in poly(ethylene terephthalate). The transition from ductile to brittle mechanical failure observed with low-temperature annealing may result from the loss of these cooperative components of main-chain motion. By contrast, either the amplitude of the mid-kilohertz phenyl motions increases or the frequency decreases during this period, consistent with the notion that precrystalline organization leads to coplanarity of the phenyl rings, an increase in the carbonyl–phenyl dihedral angle, and a reduction of the barrier to internal phenyl-group rotation. Annealing above T_g allows conformations at the ethylene linkages to change from gauche to trans. On the basis of a resolution of the ethylene-carbon resonance into contributions from gauche and trans conformations, a reduction in molecular motion is observed for ethylene groups with gauche conformations in the amorphous region after annealing above T_g, while the dynamic behavior of the trans-ethylene conformations in the amorphous region becomes indistinguishable from that in the crystalline regions. The latter result suggests that some correlations involving the properties of annealed poly(ethylene terephthalate) should be based on gauche–trans ratio rather than weight fraction of crystallinity.

The analysis of molecular motion in polymers, particularly those motions responsible for mechanical properties, has historically relied on dielectric and mechanical measurements.[1,2] However, the assignment of low-temperature dielectric and mechanical loss peaks to specific molecular motions often requires extensive supplemental information from other measurements such as infrared, ^{1}H NMR, X-ray diffraction, and calorimetry. Even when reasonable assignments can be made, it is not always clear that the types of motions which occur at low temperatures are necessarily related to room-temperature molecular motions and mechanical properties.

We have shown previously that high-resolution carbon-13 NMR spectra can be obtained of solid glassy polymers[3] and that measurement of relaxation parameters for the resolved resonances allows an unambiguous assignment of molecular motion in the mid-kilohertz frequency range.[4–6] Furthermore, we have shown a correlation between these NMR relaxation parameters and the room-temperature impact strength for a variety of polymers.[7] We report here the results of an analysis of the molecular motions at 26 °C in poly(ethylene terephthalate) (PET) as derived from carbon-13 rotating-frame relaxation measurements. We report also the effects of annealing on those molecular motions and the relationship between microscopic molecular motions and the transition from ductile to brittle mechanical behavior resulting from the annealing.

Experiments

Poly(ethylene terephthalate) (Goodyear Tire and Rubber Co., lot no. VFR 1625A) was vacuum-oven dried, melt pressed at 270 °C, and quenched in ice water to form either 0.3- or 3.2-mm films. These are referred to hereafter as thin and thick films, respectively. The films were clear, free from visible voids and defects, and

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