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Spin Relaxation and Local Motion in Four Structurally Related Dissolved Polycarbonates

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ABSTRACT: Carbon-13, proton, and fluorine-19 spin–lattice relaxation times are reported for 10 wt % solutions of four structural variations of the polycarbonate of bisphenol A. In the case of proton and fluorine-19 relaxation, measurements as a function of static field strength are included. The spin relaxation data is interpreted in terms of three local motions likely in these polymers. All three motions are in the nanosecond region but there are significant differences. The first of the three, segmental motion, is relatively comparable among the four polycarbonates while the other two, methyl and phenyl group rotation, are strongly affected by the structural modifications. Of the three dilute-solution motions, the presence of facile phenyl group rotation correlates with good impact resistance in the bulk, glassy polymer. Relationships between the time scale of solution motions and the temperature of relaxation in the glassy polymers are also presented. These relationships reflect the importance of intramolecular potentials to relaxation in both solution and the bulk material.

Introduction

A recent spin relaxation study[1] of the polycarbonate of bisphenol A in solution is expanded to three other structural derivatives to compare the local motions among the four polymers. The motivation for the first study and this extension is an examination of the relationships between dynamic processes and impact resistance. The structural changes among the four polycarbonates alter dilute-solution dynamics, bulk dynamics, and bulk properties. The first part of this paper contains a characterization of dilute-solution dynamics based on spin relaxation data. For this, a large body of spin relaxation data is developed and interpreted in terms of three motions likely in polycarbonates.[1,2] The motions are segmental fluctuations, phenyl group rotation, and methyl group rotation. The selective effects of structural changes on local dynamics relative to the three motions can then be considered. After this, relationships can be drawn among solution motions, bulk relaxations, and impact resistance. For bulk relaxations, the approach taken is to relate the time scale of a particular local motion in solution to the temperature of the corresponding sub-T_g relaxation.

Experimental Section

Three high molecular weight structural derivatives of poly[2,2-propanediylbis(4-hydroxyphenyl) carbonate] were kindly supplied by General Electric and Eastman Kodak. The structures of the basic repeat unit and the three derivative repeat units along with abbreviations are shown in Figure 1.

For spin relaxation measurements, 10 wt % solutions of the three derivatives in $CDCl_3$ were prepared in 10-mm NMR tubes. The samples were then subjected to five freeze–pump–thaw cycles and sealed.

The spectrometer used is a variable-field multinuclear pulse Fourier transform Bruker SXP 20-100. Carbon-13 spin–lattice relaxation times were measured at 22.63 MHz with simultaneous proton noise decoupling. Pulse Fourier transform fluorine-19 and proton spin–lattice relaxation times were determined at two different Larmor frequencies corresponding to field strengths 0.7 and 2.1 T. The fluorine-19 measurements were made at 84.6 and 28.2 MHz while the proton measurements were made at 90 and 20 or 30 MHz. All spin–lattice relaxation times were observed with a standard 180–τ–90 pulse sequence. The temperature was regulated to ±1 °C with a Bruker B-ST 100/700 which was calibrated against a thermocouple placed in a sample tube as well as the usual chemical NMR temperature standards.

Results

The decay of all the carbon-13, fluorine-19, and proton magnetizations for all samples at all temperatures followed a simple exponential dependence on delay time, τ. The spin–lattice relaxation time T_1 is easily calculated from a linear least-squares fit of the data in the form

$$\ln (A_\infty - A_\tau) = \ln 2A_\infty - 1/T_1 \qquad (1)$$

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Table I
Spin-Lattice Relaxation Times of BPA[a]

	Ph ^{1}H T_1				Ph ^{13}C T_1		Me ^{13}C T_1		Me ^{1}H T_1			
	90 MHz		20 MHz		22 MHz		22 MHz		90 MHz		20 MHz	
T, °C	exptl	sim	exptl	sim	exptl	sim	exptl	sim	exptl	sim	exptl	sim
−10	599	610	307	301	376	376	65	64	64	73	57	51
0	639	640	377	377	508	508	93	91	77	94	72	71
10	716	684	442	459	567	566	109	109	98	107	91	86
20	805	859	524	497	676	676	139	134	111	135	109	99
40	924	929	631	621	992	992	236	236	189	201	157	155
60	1237	1225	847	848	1410	1410	306	306	246	259	208	201

[a] All relaxation times are in ms.

Table II
Spin-Lattice Relaxation Times of Chloral[a]

	Ph ^{1}H T_1				Ph ^{13}C T_1	
	90 MHz		30 MHz		22 MHz	
T, °C	exptl	sim	exptl	sim	exptl	sim
−10	734	778	379	364	206	206
0	772	803	434	428	323	323
10	797	832	481	490	368	368
20	871	875	572	569	454	454
40	1005	965	685	709	590	591
60	1186	1157	777	792	766	766

[a] Relaxation times are in ms.

Many but not all of the observable relaxation times are useful sources of information. For BPA, chloral, and Cl_2F_4 there are two protonated phenyl carbon-13 signals which have the same T_1's within about ±15% so only one value for the phenyl carbon T_1 is reported. The Cl_4 polycarbonate has only one protonated phenyl carbon which is reported in the same manner. The carbon-13 methyl relaxation is useful in BPA and Cl_4 but not in Cl_2F_4 without simultaneous fluorine-19 decoupling. Obviously no methyl group relaxation can be reported for chloral since it does not contain a methyl group. Carbon-13 relaxation of unprotonated carbons is not reported since it is less informative.

Phenyl proton relaxation is an important indicator of segmental motion in BPA, chloral, and Cl_2F_4 but not in Cl_4. In the first three cases, the principal proton–proton interaction is between the two adjacent phenyl protons and parallel to the axis of rotation of the rigid phenyl group.[1] In the case of Cl_4, the principal interaction of the phenyl proton is with methyl protons and is not readily interpreted so values are not reported. In BPA and chloral the eight protons produce only one signal at all field strengths used but the phenyl protons of Cl_2F_4 show an AB quartet at 90 MHz. The components of the quartet have T_1's differing by about 25% but only an average value is reported and interpreted.

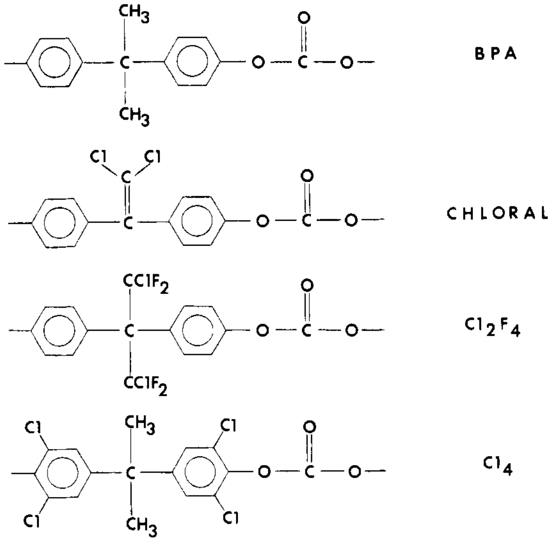

Figure 1. The four polycarbonate repeat unit structures and abbreviations.

The proton or fluorine relaxation of the methyl group is an important indicator of segmental motion and methyl group rotation in BPA, Cl_4, and also Cl_2F_4, taking the $CClF_2$ entity as a substituted methyl group. Thus all of these times are reported.

No measurements were made as a function of molecular weight since an examination of the molecular weight dependence of relaxation in BPA showed no effect even down to the relatively low molecular weight of 3.7×10^3. Though some nuclear Overhauser enhancements were measured, they are not reported since they are within experimental error of the full value. In such a case, they contain little dynamic information.

In summary, the carbon-13, fluorine-19, and proton T_1's are reported for the three structural derivatives of BPA in Tables II–IV while those of BPA are also included in Table I for comparison purposes though they have been reported before.[1]

Table III
Spin-Lattice Relaxation Times of Cl_2F_4[a]

	Ph ^{1}H T_1				Ph ^{13}C T_1		Me ^{19}F T_1			
	90 MHz		30 MHz		22 MHz		84.6 MHz		28.2 MHz	
T, °C	exptl	sim	exptl	sim	exptl	sim	exptl	sim	exptl	sim
−10	541	592	253	252	87	88	245	247	127	127
0	559	594	290	290	104	104	260	257	153	154
10	605	606	334	334	125	124	285	273	176	182
20	642	635	381	401	137	146	317	300	203	222
40	773	822	510	469	192	188	383	387	257	280
60	931	888	629	592	258	254	424	441	327	356

[a] All relaxation times are in ms.

Table IV
Spin-Lattice Relaxation Times of Cl_4[a]

T, °C	$Me^{13}C$ T_1 22 MHz exptl	sim	Me ^1H T_1 90 MHz exptl	sim	30 MHz exptl	sim	Ph ^{13}C T_1 exptl	sim
−10	43	40	54	54	31	34	78	77
0	50	49	65	61	39	41	90	89
10	63	56	61	67	44	46	104	103
20	91	83	74	84	60	64	140	131
40	129	118	109	120	87	83	182	175
60	161	165	159	159	102	102	243	243

[a] All relaxation times are in ms.

Interpretation

The standard relationships between T_1's and spectral densities, J, are employed. For carbon-13, the appropriate expressions are[3]

$$1/T_1 = W_0 + 2W_{1C} + W_2$$

$$W_0 = \sum_j \gamma_C^2 \gamma_H^2 \hbar^2 J_1(\omega_0)/20r_j^6$$

$$W_{1C} = \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 J_1(\omega_C)/40r_j^6 \qquad (2)$$

$$W_2 = \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 J_2(\omega_2)/10r_j^6$$

$$\omega_0 = \omega_H - \omega_C \qquad \omega_2 = \omega_H + \omega_C$$

For protons, the comparable expression is[4]

$$1/T_1 = \sum_j {}^9\!/_8 \gamma^4 \hbar r_j^{-6} [{}^2\!/_{15} J_1(\omega_H) + {}^8\!/_{15} J_2(2\omega_H)] \qquad (3)$$

and the equation for fluorine-19 is analogous. For all three nuclei, intramolecular relaxation is considered to be the dominant contribution to relaxation since the solutions are relatively dilute. Cross relaxation between methyl protons and phenyl protons is also not considered to be of major importance since the two types of protons are fairly well separated from each other relative to the separation among those of the same type. Similarly, the separation between phenyl protons and the fluorine-19 in Cl_2F_4 is fairly large relative to the separation among phenyl protons or among ClF_2 fluorines.

The internuclear distances used in consideration of intramolecular relaxation are the following. The CH distance for phenyl carbons is taken as 1.09 Å and the CH distance for methyl carbons is taken as 1.10 Å. The distance between the 2 and 3 phenyl proton is set at 2.41 Å,[1] and the distance between two protons within a methyl group is set at 1.77 Å. Lastly, the FF distance in the $CClF_2$ group is taken to be 2.15 Å.[5]

The expressions to be employed for the spectral density are those given by Jones and Stockmayer[2] which allow for the inclusion of the three motions of interest. A description of segmental motion is derived from the action of three bond jumps on a tetrahedral lattice with a sharp cutoff of coupling. The time scale of segmental motion is characterized by either the harmonic-average correlation time τ_h or the simple-average correlation time τ_a, and the breadth of the distribution of correlation times is characterized by the parameter m or the quantity $2m - 1$. The number of coupled bonds is m and the length of the segment in bonds which is coupled to the central bonds of the segment is $2m - 1$. Since some recent theoretical considerations call into question the presence of crankshaft-type motions,[6-8] one could also view this description of segmental motion as a form which has been successful in accounting for spin relaxation in a number of cases.[9] In addition to segmental motion, methyl group rotation and phenyl group rotation

Table V
Correlation Times and Number of Coupled Bonds

T, °C	segmental τ_h, ns BPA	chloral	Cl_2F_4	Cl_4	phenyl τ_{ip}, ns BPA	chloral	Cl_2F_4	Cl_4	methyl τ_{im}, ns BPA	Cl_2F_4	Cl_4	m BPA	chloral	Cl_2F_4	Cl_4
−10	0.37	0.23	0.54	0.68	0.24	0.86	4.0	4.0	0.36	5.0	0.62	3	5	3	3
0	0.29	0.18	0.43	0.52	0.17	0.43	2.7	3.5	0.21	3.5	0.48	3	5	3	3
10	0.23	0.15	0.35	0.43	0.16	0.39	2.1	2.8	0.18	2.8	0.42	3	5	3	3
20	0.14	0.125	0.28	0.31	0.14	0.30	1.8	2.2	0.15	2.2	0.27	5	5	3	3
40	0.11	0.097	0.16	0.19	0.087	0.22	1.5	1.5	0.05	1.6	0.17	5	5	5	5
60	0.059	0.065	0.12	0.12	0.065	0.18	1.0	1.0	0.046	1.3	0.10	7	7	5	7

Table VI
Apparent Activation Energies

polymer	segmental τ_a, kJ	phenyl τ_{irp}, kJ	methyl τ_{irm}, kJ
BPA	11	13	22
chloral	10	15	
Cl_2F_4	11	13	14
Cl_4	11	15	19

are added as independent local motions. Methyl group rotation is described as jumps among three minima at ϕ and $\phi \pm 120°$ with a correlation time τ_{irm} while phenyl group rotation is described as stochastic diffusion with a correlation time τ_{irp}. The composite spectral density expression is[2,9]

$$J_i(\omega_i) = 2\sum_{k=1}^{s} G_k \; \frac{A\tau_{k0}}{1+\omega_i^2\tau_{k0}^2} + \frac{B\tau_{bk0}}{1+\omega_i^2\tau_{bk0}^2} + \frac{C\tau_{ck0}}{1+\omega_i^2\tau_{ck0}^2}$$

$$\tau_{k0}^{-1} = \tau_0^{-1} + \tau_k^{-1}$$

$$\tau_k^{-1} = W\lambda_k \qquad s = (m+1)/2$$

$$\lambda_k = 4\sin^2[(2k-1)\pi/2(m+1)]$$

$$G_k = 1/s + (2/s)\sum_{q=1}^{s-1}\exp(-\gamma q)\cos[(2k-1)\pi q/2s] \qquad (4)$$

$$\gamma = \ln 9$$

$$A = (3\cos^2\Delta - 1)^2/4$$

$$B = 3(\sin^2 2\Delta)/4$$

$$C = 3(\sin^4\Delta)/4$$

For stochastic diffusion

$$\tau_{bk0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + \tau_{ir}^{-1}$$

$$\tau_{ck0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + (\tau_{ir}/4)^{-1}$$

For a threefold jump

$$\tau_{bk0}^{-1} = \tau_{ck0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + \tau_{ir}^{-1}$$

The procedure for determining τ_h, τ_{irm}, and τ_{irp} from the data using eq 2–4 has been given before for the interpretation of BPA.[1] Briefly, τ_h and $2m - 1$ are set from the phenyl proton data at two field strengths since the dominant dipole–dipole interaction for these protons is reoriented only by segmental motion. The phenyl group rotation correlation time is determined from the phenyl carbon relaxation since the relevant dipole–dipole interaction here is reoriented by both segmental motion and phenyl group rotation. The description of segmental motion determined from the phenyl proton data is retained, leaving only τ_{irp} to adjust to account for the phenyl carbon T_1. The correlation time for methyl group rotation is determined from the methyl carbon T_1 in a similar fashion. The methyl proton data at two field strengths is not needed to set any model parameters but values for these T_1's can be calculated from the model as a check. The simulated results are compared with the experimental results in Table I, and the correlation times producing the simulation are given in Table V.

For the polycarbonate chloral, an exactly analogous procedure is followed except there is no methyl group involved. The simulated T_1's are compared with the experimental data in Table II, and the correlation times producing the simulation are given in Table V.

The situation is almost the same for the Cl_2F_4 polycarbonate. The only difference is that τ_{irm} is determined by the field-dependent fluorine T_1's. Actually both phenyl group rotation and methyl group rotation are so slow relative to segmental motion that the correlation times τ_{irp} and τ_{irm} have fairly large uncertainties. Indeed, both the phenyl proton data and the $CClF_2$ fluorine data are used to set τ_h and $2m - 1$, with τ_{irm} being only a minor contributor to the calculation of the fluorine T_1's. Simulated and experimental T_1's are compared in Table III, and the associated model parameters are displayed in Table V.

For Cl_4, the interpretation must proceed a little differently. No useful phenyl proton data are available to help determine τ_h and $2m - 1$. Therefore, τ_h, $2m - 1$, and τ_{irm} are all deduced from the field-dependent methyl proton data and the methyl carbon data. Then the segmental motion parameters τ_h and $2m - 1$ are assumed to be valid for the segmental contribution to phenyl carbon relaxation, leaving only τ_{irp} to be adjusted to account for the phenyl carbon T_1. This interpretation rests on a less secure basis though our experience with the other polycarbonates leads us to believe it is substantially correct. Experimental and simulated T_1's are compared in Table IV with the correlation time for the simulation presented in Table V.

From the correlation times in Table V, one can calculate apparent activation energies. Actually the average value of the correlation time for segmental motion τ_a is used for this calculation instead of the harmonic correlation time τ_h though the two are simply related.[2] A summary of the apparent activation energies is given in Table VI, with the similarity between the values for a given motion fairly apparent since the uncertainty is about ±5 kJ.

Discussion

The effect of the structural modifications of the various polycarbonate repeat units can be readily ascertained from Table V. For example, segmental motion does not vary greatly among the four forms since the values of τ_h at a given temperature are within a factor of 2 of the τ_h for BPA. BPA and chloral are quite similar dynamically, with chloral displaying somewhat slower phenyl group rotation. The Cl_4 and Cl_2F_4 polycarbonates are significantly different from BPA and chloral. In both cases, phenyl group rotation slows dramatically. In Cl_4 the methyl group rotation slows a little relative to BPA, but in Cl_2F_4 the $CClF_2$ group rotation slows a great deal.

Among the four polycarbonates, BPA and chloral have good impact resistance while Cl_4 and Cl_2F_4 are brittle.[10] All four have similar segmental motion. One from each

Table VII
Solution Correlation Times Relative to BPA and Solid Relaxation Temperatures

	segmental		phenyl		methyl	
polymer	τ_a/τ_a(BPA)	T_g,[a] °C	τ_{irp}/τ_{irp}(BPA)	T_γ,[a] °C	τ_{irm}/τ_{irm}(BPA)	T_m,[b] °C
BPA	1	+147	1	−100	1	−100
chloral	1.0 ± 0.1	+157	2.7 ± 0.5	−100		
Cl_2F_4	1.6 ± 0.2	+184	15 ± 2	+5	20 ± 8	+57
Cl_4	1.8 ± 0.2	+255	17 ± 2	+95	2.3 ± 0.6	−100

[a] Reference 15. [b] Reference 18.

of the two categories has facile methyl group rotation, and one from each of the two categories has no methyl group or slow methyl group rotation. The only correlation between local dynamics and impact resistance is facile phenyl group rotation. BPA and chloral have mobile phenyl groups relative to Cl_4 and Cl_2F_4. Such a correlation between facile phenyl group motion and impact resistance has been suggested before,[11,12] but the relationship is restricted to phenyl group rotation or possibly oscillation and does not include segmental or methyl group motion.

Interesting comparisons between solution dynamics and relaxations observed in bulk glassy polymers can also be drawn. To accomplish this, a summary of the time scale of a given motion in solution is desirable. Since each type of motion has a somewhat similar apparent activation energy, we can normalize the time scale of a particular motion at one temperature relative to the time scale of the same motion in BPA. Thus to compare phenyl group rotations, we divide the correlation time for phenyl group rotation in each of the polymers at one temperature by the correlation time of phenyl group rotation in BPA at the same temperature. The calculation is repeated for all temperatures, and then an average ratio is calculated for the time scale of phenyl group rotation in one of the structural modifications by averaging over all temperatures. The process is repeated for methyl group rotation and segmental motion. The ratios averaged over all temperatures and the associated standard deviations are reported for all three motions in all four forms in Table VII.

Now these average relative time scales for a particular motion can be identified with the temperature of the associated relaxation in the glassy state[13] as shown in Table VII. The correlation time for segmental motion is identified with the glass transition. While there is little doubt about this identification, the increase of glass transition temperature with slower segmental motion in solution is reassuring.

Phenyl group rotation is identified with the broad low-temperature dynamic mechanical relaxation labeled T_γ by some investigators.[14,15] The nature of the motion corresponding to T_γ has been the subject of many reports[14-18] and several of these conclude T_γ involved motion of the phenyl group. However, different types of phenyl group motion have been proposed,[14-16] and a recent wide-line NMR study[17] on chloral definitely identified phenyl group rotation or oscillation as the principal low-temperature intramolecular motion. With this in mind, a good correlation is noted between T_γ and τ_{irp} with slow motion corresponding to a high T_γ.

The last motion to be identified between the solution and the glassy state is methyl group motion. Since methyl group rotation is not a strong contribution to dynamic mechanical loss, wide-line NMR[18] was relied upon to define T_{m}, the temperature of onset of methyl group rotation. Wide-line NMR data correspond to an experimental frequency of about 10^4 Hz while most of the dynamic mechanical studies involve a frequency in the 1–10-Hz range. This difference need not affect comparison between solution and the glassy state as long as wide-line NMR is used consistently for methyl group considerations and comparisons among methyl, phenyl, and segmental motions are avoided. Again there is a good correspondence between τ_{irm} and T_{m}.

Conclusion

Not only can a detailed solution spin relaxation study provide insight into motion in solution but the dynamic processes in solution correlate well with the same dynamic process in the bulk polymer. This implies that intramolecular potentials dominant in solution relaxation also play an important role in bulk relaxation. This relationship between motions in solution and the bulk and the importance of intramolecular effects lend pertinence to the study of dilute-solution relaxation and give hope to the utilization of intramolecular potentials in the interpretation of bulk relaxation processes.

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