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Spin Relaxation and Local Motion in Dissolved Polycarbonate

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ABSTRACT: Carbon-13 and field-dependent proton spin–lattice relaxation times were measured as a function of temperature and molecular weight for 10 wt % solutions of polycarbonate in $CDCl_3$. The spin–lattice relaxation times are interpreted in terms of segmental motion characterized by the sharp cutoff model of Jones and Stockmayer, phenyl group rotation, and methyl group rotation. Correlation times for all of the three local motions are very similar, from −10 to +60 °C, leading to the conclusion that these three local motions are coupled or synchronous. Correlation times range from about 0.35 ns at −10 °C to 0.05 ns at +60 °C. The temperature dependences of the motions differ slightly with phenyl group rotation, having the lowest apparent activation energy of 13 kJ. This low value is reasonable in view of a semiempirical calculation by Tonelli, and the apparent activation energies of segmental motion and methyl group rotation have more typical values of 19 and 22 kJ, respectively. Facile phenyl group rotation occurs in another engineering plastic, poly(2,6-dimethyl-1,4-phenylene oxide), but in this latter polymer the phenyl group rotation is not close in time scale to the other motions.

The polycarbonate of bisphenol A is the object of considerable interest because of the technologically important properties of the bulk material and the apparent relationship of these properties to local chain dynamics. While many informative dynamic studies of polycarbonates have been presented,[1-10] a nuclear spin relaxation investigation of dissolved polycarbonate is undertaken now to capitalize on the detailed information available on local motions at several positions within a repeat unit. To obtain a fairly complete dynamic description, an extensive series of carbon-13 and proton spin–lattice relaxation time experiments, the latter at two field strengths, is conducted. In addition, an interpretation based on a mathematical model for motions likely in this polymer is employed, since in the judgment of the authors this best serves the goal of elucidating local motions. The current work on dissolved polycarbonate is compared with a number of dynamic studies on solid polycarbonates, and there is a strong similarity between the interpretation in the bulk[1,5-9] and in solution. Also the bisphenol A polycarbonate is one of a number[11] of engineering plastics with aromatic groups in the backbone scheduled for comparative dynamic characterization based on nuclear spin relaxation and already considered in a series of semiempirical calculations.[12,13]

Experimental Section

A 20-g sample of Lexan 145 ($[\eta] \simeq 0.5$) was fractionated from a methylene chloride solution, using methanol. A total of 12 fractions was collected, and viscosity average molecular weights were calculated from the intrinsic viscosity of each fraction, according to the equation[14]

$$[\eta] = 1.2 \times 10^{-4} M_v^{0.82} \qquad (1)$$

Fractions range in viscosity average molecular weight, M_v, from 4.5×10^4 to 3.7×10^3.

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

The spectrometer used was 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, and field stability was maintained by an internal deuterium lock. Pulse Fourier transform proton measurements were made at 20 and 90 MHz. Both carbon and proton 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 methyl carbon and the two protonated phenyl carbon magnetizations all display a simple exponential dependence on delay time, τ, in the 180–τ–90 experiment. Therefore, T_1, the spin–lattice relaxation time, was calculated from a linear least-squares fit of the data in the form

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

The two protonated phenyl carbon magnetizations always had the same T_1 value within experimental error so that henceforth only one phenyl carbon magnetization, which is the average of the two observed values, will be discussed.

The methyl proton magnetization and one phenyl proton magnetization resulting from all eight phenyl protons produced the only two resolvable proton signals at 20 and 90 MHz. Again the data appear to follow eq 2 quite well with no indication of a nonexponential character to the return to equilibrium. This simple behavior is quite different from the strongly nonexponential behavior observed for the return of the proton magnetizations to equilibrium in solutions of poly(2,6-dimethyl-1,4-phenylene oxide).[11,15] In the present case, the exponential return to equilibrium is taken to indicate an absence of significant cross-relaxation and cross-correlation. Cross-relaxation is likely to be negligible since dipolar interactions among phenyl protons and dipolar interactions among methyl protons are much larger than dipolar interactions between phenyl

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Table I
Carbon-13 and Proton Spin–Lattice Relaxation Times[a] as a Function of Molecular Weight at 40 °C

mol wt × 10^3	Ph proton T_1 (90 MHz), ms	Me proton T_1 (90 MHz), ms	protonated Ph C T_1, ms	Me C T_1, ms
3.7	986	164	984	234
6.8	1018	177	922	192
20	923	215	952	212
25	925	164	1032	253
45	934	173	1012	215

[a] Experimental error is ±10%.

protons and methyl protons. The absence of cross-correlation is reasonable since the dynamic analysis leads to a rapid correlation time for isotropic segmental motions rather than domination of relaxation by an anisotropic internal rotation.

The observed molecular weight dependence of the carbon-13 and proton T_1's is displayed in Table I, while the observed temperature dependence of these relaxation parameters for the average of two high molecular weight samples (20×10^4 and 25×10^4) is displayed in Table II. Each reported T_1 is an average of two to four separate determinations, and a precision typically better than ±10% is indicated by the repetitive determinations. No systematic errors larger than 10% are likely either, so ±10% is given as the error estimate.

Interpretation

The standard relationships between T_1's and the spectral densities, J's, are employed. For carbon-13, the appropriate expressions are[16]

$$\begin{aligned} 1/T_1 &= W_0 + 2W_{1C} + W_2 \\ W_0 &= \sum_j \gamma_C^2 \gamma_H^2 \hbar^2 J_0(\omega_0)/20r_j^6 \\ W_{1C} &= \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 J_1(\omega_C)/40r_j^6 \\ W_2 &= \sum_j 3\gamma_C^2 \gamma_H^2 \hbar^2 J_2(\omega_2)/10r_j^6 \\ \omega_0 &= \omega_H - \omega_C; \quad \omega_2 = \omega_H + \omega_C \end{aligned} \tag{3}$$

For proton, the analogous expression is[17]

$$1/T_1 = \sum_j (9/8)\gamma^4 \hbar^2 r_j^{-6}(J_1(\omega_H) + J_2(2\omega_H)) \tag{4}$$

The relevant internuclear distances, r's, and angles are shown in Figure 1. All of the distances except the 2.41 Å between adjacent phenyl protons are typical of those commonly employed. The 2.41 Å is shorter than the distance in benzene, for instance, because a value of 62° was employed for the angle between the C–H vector and virtual bond axis of the phenyl group as shown in Figure 1. The choice of 62° instead of 60° is not based on independent experimental data since no determination of C–H bond angles in polycarbonate appears to be available, but this choice was required to interpret the proton spin–lattice relaxation times. At −10 °C and 90 MHz, the T_1 minimum is being approached, and the minimum value is shorter than values calculated with distances larger than about 2.41 Å. This calculation is not model dependent in the sense that a distribution of exponential correlation times raises T_1 above the value calculated for a single exponential correlation time, and the only apparent way to account for the short T_1 observed is to assume a distance somewhat shorter than would be calculated from perfect hexagonal geometry. Inclusion of other proton–proton distances besides this nearest neighbor interaction was found to be too small to account for the discrepancy. A distortion of 2° does not seem unreasonable in view of the bulky end groups on the phenyl ring, but no independent verification of this distortion was found. It could be argued that the minimum in T_1 can be used for a structure determination, but only an upper limit to the value is produced since a model involving a broader distribution of correlation times relative to a narrow distribution or a single correlation time would result in shorter estimates. Essentially, the maximum distance of 2.41 Å consistent with the two −10 °C values of the phenyl proton T_1 at 90 and 20 MHz was employed for the rest of the interpretation, and this distance can be considered simply as an effective internuclear separation including contributions both from small changes in hexagonal geometry and from other minor internuclear interactions.

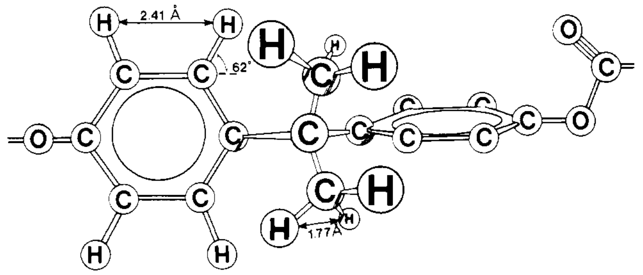

Figure 1. Polycarbonate repeat unit. The values of pertinent geometric quantities are included, but for clarity the hydrogens attached to the second phenyl ring are not shown.

Usually the main aspect of interpretation is associated with the form of the spectral densities which depends upon the description of chain motion. This is indeed the most important component of this work, and a dynamic model applied to several other polymers will be utilized here.[18,19] Three types of motion will be considered in this model as sources of relaxation through modulation of the dipole–dipole interaction.

The first of these motions is simple overall rotatory diffusion with a correlation time τ_0 which is calculated from[11]

Table II
Experimental[a] and Simulated Proton and Carbon-13 Spin–Lattice Relaxation Times

	Ph proton T_1 (90 MHz), ms		Ph proton T_1 (20 MHz), ms		protonated Ph ^{13}C T_1, ms		Me ^{13}C T_1, ms		Me proton T_1 (20 MHz), ms		Me proton T_1 (90 MHz), ms	
T, °C	expt	sim	expt	sim	expt	sim	expt	sim	expt	sim	expt	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] Experimental error is ±10%.

$$\tau_0' = 2M[\eta]\eta_0/3RT \qquad (5)$$

and

$$\ln (\tau_0/\tau_0') = k'[\eta]c$$

Thus this motion is entered into the model as known, calculated from the molecular weight M, the intrinsic viscosity $[\eta]$, the Huggins constant k', the solvent viscosity η_0, the concentration c, and the temperature T. Actually, $[\eta]$ is calculated according to eq 1, and a value of $k' = 0.29$ is used.[20]

The next motion considered is segmental or backbone rearrangements involving only a few repeat units. Here the "sharp cutoff" model of Jones and Stockmayer[19,21] will be employed which is based on the occurrence of the three-bond jump on a tetrahedral lattice. This description of segmental motion is not strictly applicable to polycarbonate since the virtual bonds, two phenyl groups and a carbonate group, are not equivalent, and the angles for a tetrahedral lattice are only roughly approximated. On the other hand, the correlation function based on the occurrence of a three-bond jump on a tetrahedral lattice is equivalent to defect diffusion in one dimension[18,19] and very similar to the correlation function based on a different crankshaft motion, a two-bond jump.[21,22] For both of these reasons, the three-bond jump correlation functions may be suitable though not strictly correct for many polymers where segmental motions are associated with either the diffusion of a favorable conformation for rearrangement or crankshaft type motions. The two model parameters in this discussion of segmental motion are first the correlation time τ_h, which is equal to the inverse of twice the three-bond jump rate, and second m, which is the number of coupled bonds in a segment.[18,19] The parameter for the number of coupled bonds essentially controls the breadth of the distribution of exponential correlation times composing the total segmental correlation function, with a larger number of bonds corresponding to a broader distribution.

A second type of local motion considered in the interpretation is anisotropic substituent-group rotation.[18,23] Both the methyl and phenyl groups might rotate about their respective symmetry axes, and the barrier to phenyl group rotation has been predicted to be rather low.[13] Two different descriptions are reasonable for both methyl and phenyl rotation, but in each case only one of the two descriptions could account for the data. For methyl group rotation, jumps among three minima[23] at ϕ and $\phi \pm 120°$ could account for the data, while a stochastic diffusion picture[23] is inconsistent with the observations. For phenyl group rotation, the situation is reversed with a stochastic diffusion description[23] accounting for the data better than the other reasonable alternative, jumps between two minima[24] at ϕ and $\phi + 180°$. No a priori reasoning allowed a selection between the various rotational descriptions, though as mentioned, the barrier to phenyl group rotation was predicted to be low. The combined spectral density equations actually utilized, including overall rotatory diffusion, segmental motion, and anisotropic rotations, are given below.[18,19,24]

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

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

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

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

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

$$\gamma = \ln 9$$

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

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

$$C = 3(\sin^4 \Delta)/4 \qquad (6)$$

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 rate of occurrence of the three-bond jump is w, and this is usually summarized by the correlation time $\tau_h^{-1} = (2w)$, where τ_h is also the harmonic average of the τ_k's. The angle between the internuclear interaction and the axis of rotation[23,24] Δ is fixed according to Figure 1, while the correlation time for an internal rotation is given the symbol τ_{ir}. Also the number of coupled bonds m is usually reported in terms of a segment length which equals $2m - 1$ since alternate bonds are coupled by the three-bond jump.

Even with eq 3, 4, and 6 in hand, it is not obvious how to determine the parameters characterizing the local motions for the proton and carbon-13 spin-lattice relaxation times. Before the pathway employed here is traced out, the parameters to be fixed are τ_h and $2m - 1$ for the segmental motion, τ_{irp} for phenyl group rotation, and τ_{irm} for methyl group rotation. The data base includes the methyl and protonated phenyl carbon-13 relaxation times and the phenyl and methyl proton relaxation times at 20 and 90 MHz, all as a function of temperature. An inspection of the data in Table I indicates no discernible trend in any of the T_1's as a function of molecular weight over the range studied. Therefore there is no information to be gained by considering the molecular weight dependence in this system, and all attention will be focused on interpreting the data in Table II which were taken on two rather high molecular weight fractions. The interpretation produced by considering the data in Table II must be consistent with little or no molecular weight dependence on the spin-lattice relaxation times between 3.7×10^3 and 4.5×10^4, and eq 5 is used to estimate this contribution.

Turning to the data in Table II, first the segmental motion will be characterized from the 20 and 90 MHz phenyl proton relaxation times. Note that the predominant dipolar interaction for the phenyl protons is between two phenyl protons on the same side of the phenyl ring, and the angle between the direction of the interaction and the axis of phenyl group rotation is zero. Therefore in the dynamic model to be used, the phenyl proton relaxation times are independent of internal rotations. Minor dipolar interactions across the ring and between phenyl and methyl protons can be estimated from the repeat unit structure to contribute about 10% or less to T_1. Thus τ_h and $2m - 1$ are chosen to account for the phenyl proton T_1 at 20 and 90 MHz at a given temperature.

Next the parameter τ_{irp} can be determined for a given temperature by adjusting it to account for the protonated phenyl carbon-13 T_1's while holding τ_h and $2m - 1$ at the values determined from the phenyl proton data. Since the angle between the C-H bond for these carbons and the axis of phenyl group rotation is 62°, there is significant dependence of the carbon-13 T_1's on τ_{irp} in addition to the

Table III
Correlation Times and Segment Lengths

T, °C	τ_h, ns	$2m - 1$	τ_{irp}, ns	τ_{irm}, ns
−10	0.37	5	0.24	0.36
0	0.29	5	0.17	0.21
10	0.23	5	0.16	0.18
20	0.140	9	0.14	0.15
40	0.110	9	0.087	0.050
60	0.059	13	0.065	0.046

dependence on τ_h and $2m - 1$.

In a similar fashion, τ_{irm} can be determined by adjusting it to account for the methyl carbon-13 T_1's at one temperature, again holding τ_h and $2m - 1$ at the values fixed by the phenyl proton T_1's.

Lastly, one can now check the values of τ_{irm}, τ_h, and $2m - 1$ by comparing a calculated value for the methyl proton T_1's at 20 and 90 MHz. Actually, in Table II all the carbon-13 and proton T_1's simulated in this manner are compared with experimental values, and the correlation times and segment lengths for each temperature are shown in Table III. It is worth noting that except for 3 of the 36 T_1's the simulated values are within 10% of the experimental values or within experimental error. There are some systematic differences between the simulated methyl proton T_1's and the measured values. However, since the correlation times are set primarily by the first four columns of data in Table II and then are essentially used to predict the last two columns, it is not too surprising that the larger and more systematic differences occur in the latter columns. Nonetheless, the differences are generally still within experimental error. Several of the parameters, namely τ_h, τ_{irm}, and $2m - 1$, are overdetermined, while the values of τ_{irp} rest solely on the protonated phenyl carbon-13 spin–lattice relaxation times. The combined uncertainty in correlation times stemming from experimental error and the sensitivity of the simulation process is about 30%. Also, since the determination of τ_{irp} and τ_{irm} rests upon the choice of τ_h and $2m - 1$, τ_{irp} and τ_{irm} have cumulative uncertainties.

One can calculate apparent activation energies for segmental motion, methyl group rotation, and phenyl group rotation from the temperature dependence of τ_h, τ_{irm}, and τ_{irp}, respectively. Plots of log $(1/\tau)$ vs. $1/T$ were fit by linear least squares, and the correlation coefficient was typically 0.98. The apparent activation energy for segmental motion was 19 kJ, for methyl rotation 22 kJ, and for phenyl group rotation 13 kJ, and the uncertainty in all of these values is about 5 kJ.

Discussion

The most obvious aspect of the interpretation apparent by inspecting Table III is that all three correlation times for the three distinct motions are very nearly equal at each temperature. Without doubt the combined uncertainties stemming from experimental error and the employment of necessarily simple dynamic models allow for the possibility that all three motions have the same correlation time and indeed are coupled or cooperative motions. The interpretational model assumes that internal rotations are independent from the segmental motion, but the analysis of the data leads to apparent cooperativity. Heatley and Begum[25] have argued for dynamic cooperativity or interdependence in several polymers when segmental correlation times and methyl group rotational correlation times parallel each other as a function of temperature, even though the data were not analyzed with a model initially allowing for cooperativity or coupling of the different motions. In at least one of these polymers, concentration changes separated the time scales of the two motions, showing them not to be coupled under all circumstances. In the present case, apparent cooperativity between three distinct motions in solution is apparently without precedent, though comparison with solid state dynamic studies of polycarbonate indicates a striking analogy.

A combination of dielectric relaxation,[6,8,9] wide-line NMR,[5–7] and dynamic mechanical techniques[1–4] indicates that some degree of motional freedom for the methyl group, phenyl group, and carbonate group simultaneously commences at about −100 °C. The observation of the onset of the three motions by different experimental techniques but at the same temperature plus measurements on polycarbonate of somewhat different repeat unit structure led to the deduction that the motions are cooperative.[1,5,6] Since the motions are cooperative in dilute solutions where chains are relatively isolated as well as in the glassy solid, this cooperative character is apparently an intramolecular property of the polycarbonate repeat unit. Further studies of concentrated solutions intermediate between the dilute solution and the solid will be examined in the future as will some polycarbonates of different structure. From our standpoint, it is reassuring to find the parallel between solid and solution relaxations. This indicates the value of pursuing solution relaxation studies where detailed interpretations are possible. For polycarbonate, both relative mobility and the cooperativity of the various local motions apparent in solution and in the solid may provide some insight into the unusual properties of the material, particularly impact resistance.

The other high impact resistant polymer well studied by NMR is poly(2,6-dimethyl-1,4-phenylene oxide).[11] In both of these polymers, the phenyl group in the backbone is very mobile. However, in the poly(phenylene oxide), the segmental motion, methyl group rotation, and phenyl group rotation are separated in time scale by orders of magnitude.[11] The polycarbonate is very different in this regard, and other examples of these classes of polymers will be studied to determine any significance to be associated with these differences.

One aspect of the interpretation which is not very satisfying is the temperature dependence of the extent of coupling among backbone bonds or equivalently the temperature dependence of the breadth of the distribution of correlation times. In most of the other systems over temperature ranges of 50 to 100 °C, the extent of coupling or breadth parameter as measured by $2m - 1$ is not usually temperature dependent,[19] although temperature-dependent breadth parameters from other models have been noted in some other polymers.[25,26] At this time, the physical significance of such behavior is not clear, and it may also be only an artifact of the interpretation. In particular, the somewhat uncertain choice of the distance between phenyl protons may affect the distribution parameter in polycarbonate since the distribution is first determined by fitting the phenyl proton spin–lattice relaxation times at 20 and 90 MHz. However, a consistent interpretation for the methyl carbon-13 relaxation times and the methyl proton relaxation times is also produced which rests heavily upon the description of segmental motion in addition to methyl group rotation. The temperature dependence of the breadth of the distribution is not a product of the use of the "sharp cutoff" model, and other descriptions of segmental motion involving distributions would show analogous trends.

Although the three motions are close in time scale, they have somewhat different activation energies, but again these energies are also almost within experimental error of one another. The activation energy for phenyl group rotation is the lowest at 13 kJ, and this is indeed a low value. The only comparable system is poly(2,6-dimethyl-1,4-phenylene oxide), which also has a low phenyl group rotation energy,[11] and both of these polymers were predicted to have low activation energies for this motion from a semiempirical calculation by Tonelli.[12,13] The other activation energies of 19 and 22 kJ for segmental motion and methyl group rotation respectively are typical of polymers[19] though again a little on the low side.

A sidelight to the present study concerns the use of only spin–lattice relaxation times and not carbon-13 nuclear Overhauser enhancements (abbreviated NOE). Actually, some NOE's were determined, but for this polymer in a 22 kG field the values are so close to a full enhancement that little dynamic information is obtained. Nearly full NOE's are consistent with the interpretation and the correlation times in Table III, but a wide range of correlation times approximately equal or shorter to these are also consistent with a full enhancement. In view of this, the proton field strength data are vital to the interpretation, especially since the proton T_1's changed appreciably as a function of the static field. With one modern variable field spectrometer, these proton measurements are relatively easy and can be made with much less instrumentation than field-dependent carbon-13 measurements. These latter studies are also extremely useful,[27,28] but unfortunately a spectrometer is required for each field strength.

One question not yet addressed is whether the methyl and phenyl groups are rotating or only oscillating. Several models are now available to describe substituent group oscillation,[29,30] but in addition to a parameter for time scale a second parameter enters for angular amplitude. At the present time, spin relaxation data cannot be used to decisively distinguish between rotation and fairly large amplitude oscillation[29] in solution, so only the simpler rotational descriptions are used here.

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