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A spin-lattice relaxation study of dissolved cyclohexyl polycarbonate

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A dilute-solution spin-lattice relaxation time study was performed on a bisphenol polycarbonate related to the polycarbonate of bisphenol A except the two methyl, isopropylidene unit is replaced by a cyclohexyl group. ^{13}C spin-lattice relaxation times were measured at three Larmor frequencies: 50.3, 75.4, 125.7 MHz. The motion of cyclohexyl ring is seen to be isotropic on the spin-lattice relaxation time scale even though cyclohexyl rings undergo slow conformational change. Cyclohexyl ring relaxation is caused by segmental motion and was well interpreted in terms of the Hall–Helfand correlation function. The apparent activation energies for cooperative and individual bond transitions were 17 and 22 kJ mol^{-1}, while the corresponding Arrhenius prefactors were 15×10^{-13} and 5×10^{-13} s. This cyclohexyl polycarbonate differs from many other polycarbonates in that the two phenylene groups are inequivalent, one being axial and the other equatorial relative to the cyclohexyl ring. This difference could be clearly seen in the low temperature ^{13}C spectrum at a Larmor frequency of 125.7 MHz. In addition to segmental motion, it was found the equatorial phenyl ring underwent anisotropic internal rotation which could be described by the Woessner model, while the axial phenyl ring underwent restricted rotational diffusion which could be described by the Gronski model. Since full anisotropic rotation was observed in bisphenol A polycarbonate and restricted anisotropic rotational diffusion was observed in norbornyl polycarbonate, a clear picture of the effects of substitution in the isopropylidene units on local dynamics is developing. Copyright © 1996 Elsevier Science Ltd.

(Keywords: n.m.r.; polycarbonate; dynamics)

INTRODUCTION

A series of dilute-solution spin-lattice relaxation studies have been made on the polycarbonate of bisphenol A (BPA) and related structural analogues[1–5]. The present attempt is not only an extension of the earlier studies with yet another structural derivative, namely one where the isopropylidine unit is substituted with a cyclohexyl ring, but attracted our attention because this particular substitution altered the low temperature mechanical response[6] which is atypical of a substitution on the isopropylidene unit[7]. Usually substitution on the phenylene units is observed to shift the low temperature loss peak to higher temperature while, on the other hand, even when a norbornyl group is substituted onto the isopropylidene unit the low temperature response is largely unaffected.

To complicate further the consideration of local dynamics, simplistic conformational considerations would lead one to expect the two phenylene rings to be inequivalent since the cyclohexyl group essentially sits above one of the two rings. A similar inequivalency is present in the norbornyl polycarbonate. However, in this case, conformational exchange within the cyclohexyl ring offers the possibility of interchanging the two inequivalent phenylene rings. Conformational interchange within cyclohexyl groups can also occur in the solid state and is potentially a source of mechanical relaxation as well[8,9].

High resolution line shape spectra and spin-lattice relaxation measurements can be expected to define the respective rates and amplitudes of motion. Conformational interchange within cyclohexyl groups is a classical case for line shape collapse so the acquisition of spectra as a function of temperature is likely to define the presence and rate of this process. Motional processes that produce line shape collapse are unlikely sources of spin-lattice relaxation in the same temperature range in dissolved polymers because segmental motion and internal rotation of phenylene groups are usually very close to the frequency scale of Larmor precession[1–5] and will therefore be the dominant contributors to spin-lattice processes. Segmental motion is conveniently described by the Hall–Helfand correlation function[10] and internal rotation[11] of substituent groups is easily combined with this description of segmental motion[1–5]. In polycarbonates where phenylene group rotation is slow, relaxation arising from librational motion is often present and is the dominant contributor to spin-lattice relaxation. This motion has been interpreted with Gronski's formulation for restricted rotation[12,13].

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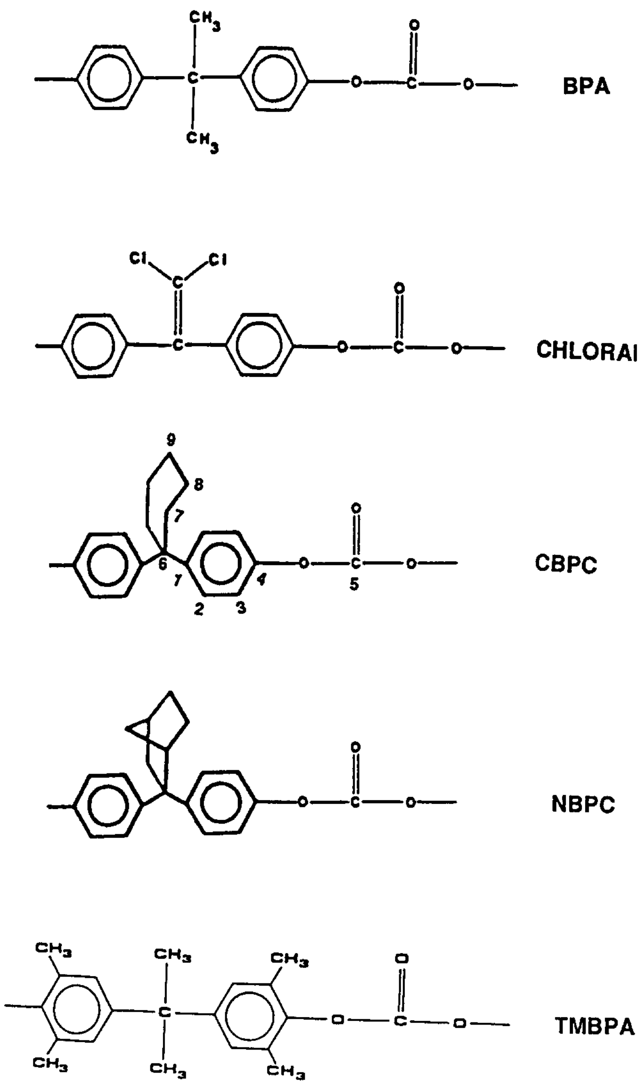

Figure 1 Repeat unit structures of the related polycarbonates

Molecular modeling calculations have long been used to understand conformational dynamics in polycarbonates[14] and are applied to this system to further the understanding of barriers to motion and the structure corresponding to the conformational minima.

EXPERIMENTAL

High molecular weight samples of cyclohexyl BPA (CBPC) were kindly supplied by General Electric. The CBPC samples were dissolved to 10 wt% in perdeuterio-1,1,2,2-tetrachloroethane, subjected to five freeze–pump–thaw cycles, and flame-sealed. CBPC samples dissolved in dichlorofluoromethane were also prepared in order to facilitate further lower temperature measurements.

Three spectrometers were used in this experiment: Bruker AC 200, Varian Unity 500, both at Clark University, and Bruker AC 300 at Holy Cross College. The ^{13}C spin-lattice relaxation times were measured by a $180° - \tau - 90°$ pulse sequence with proton broad band decoupling. Temperature calibrations were carried out for each probe. The chemical shift *versus* temperature method was employed and the standard calibration samples were ethylene glycol for high temperature and methanol for low temperature.

The experimental error in reported T_1 values was about 10% which includes errors arising from sample preparation, pulse widths, and fitting the return of the magnetization to equilibrium.

Conformational energies and rotational barriers are computed using the BIOSYM molecular mechanics/molecular dynamics program DISCOVER, and in particular the PCFF 2.1 (1 October 1993) forcefield released with version 2.96 of DISCOVER in 1995. It is noted that all barriers computed with the earlier version of the CVFF force-field are considerably smaller than the ones reported here, reflecting a too-small value of the torsional energy parameter for the aromatic carbon/aliphatic carbon ($C_p - C$) potential term.

RESULTS

The structures of the CBPC, and the related polycarbonates (abbreviated BPA, CHLORAL, TMBPA and NBPC) are presented in *Figure 1*. The ^{13}Carbon T_1 measurements were carried out for the CBPC in perdeuterio-1,1,2,2-tetrachloroethane at temperatures from −35° to 120°C. From the CBPC T_1 experimental data, it was found the magnetization of the protonated phenyl carbons and cyclohexyl carbons 8 and 9 followed

Table 1 Comparison between experimental and fitted ^{13}C T_1 data (ms) for cyclohexyl carbons 8 and 9 at various temperatures

	50.3 MHz			75.4 MHz			125.7 MHz	
T(K)	Expt	Fitting	T(K)	Expt	Fitting	T(K)	Expt	Fitting
296.6	83.5	87.1	249.8	171	171	263	255	296
312.2	101	96.3	260.3	122	146	273	251	253
322.2	94.5	105	271.8	132	132	283	215	229
332.3	106	116	284.6	108	126	293	208	215
342.4	113	129	296.4	113	124	303	205	207
352.4	129	144	307.4	111	127	313	201	205
362.5	154	162	319.3	131	134	323	194	207
372.6	165	183	330.7	136	144	343	218	222
382.6	163	207	353.1	154	174			
			364.6	166	194			
			376.5	194	218			
			388.1	217	246			

Table 2 Comparison ^{13}C T_1 values (ms) of the protonated phenyl carbons for CBPC with that for BPA and NBPC

	BPA	NBPC	CBPC			
T (°C)	62.9 MHz	62.9 MHz	T (°C)	50.3 MHz	T (°C)	75.4 MHz
−20	143	179	−19.1	162	−23.4	204
0	198	157	2.2	203	−1.4	202
20	278	164	23.4	204	22.6	251
40	436	185	39	232	46.1	340
60	657	221	59.1	307	57.5	392
80	933	287	79.2	456	79.9	532
100	1320	356	99.4	588	103.3	677
120	1943	470	119.5	735	114.9	759

a simple exponential dependence on delay time τ. The spin lattice relaxation time T_1 was easily calculated from the standard linear least squares form.

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

Not all of the observable relaxation times were independent useful sources of the information. For CBPC, the two protonated phenyl carbons had the same T_1's and the two cyclohexyl carbons 8 and 9 also had the same T_1's within the experimental error range. Only averaged T_1 values of phenyl and cyclohexyl carbons are reported in this paper. The experimental spin-lattice relaxation times for cyclohexyl and phenyl carbons are presented in *Tables 1* and *2*.

The low temperature ^{13}C spectrum were obtained from −10° to −110°C for the CBPC in dichlorofluoromethane. The expanded spectra of the protonated phenylene carbons are presented in *Figure 2*.

INTERPRETATION

The interpretation begins with an analysis of segmental motion. Spin-lattice relaxation of the cyclohexyl moiety appears to be only influenced by isotropic segmental motion because rapid internal motion would likely make T_1 values for cyclohexyl carbons 8 and 9 different and no difference is observed. Also, the variable temperature ^{13}C spectra show that the chair-to-chair conversion is slow on the T_1 timescale. Starting with the standard relationships between T_1 and spectral densities J the expression for ^{13}C is[2]

$$\begin{aligned}\frac{1}{T_1} = {} & \sum_j \gamma_C{}^2\gamma_H{}^2\hbar^2 J_1(\omega_0)/20r_j{}^6 \\ & + 2\sum_j 3\gamma_C{}^2\gamma_H{}^2\hbar^2 J_1(\omega_c)/40r_j{}^6 \\ & + \sum_j 3\gamma_C{}^2\gamma_H{}^2\hbar^2 J_2(\omega_2)/10r_j{}^6 \qquad (2)\end{aligned}$$

where $\omega_0 = \omega_H - \omega_C$ and $\omega_2 = \omega_H + \omega_C$.

The internuclear distances employed are 1.08 Å for cyclohexyl C-H and 1.073 Å for the phenyl C-H. The Hall–Helfand[3,6] expression for the spectral density for segmental motion is

$$J(\omega) = 2\{[(\tau_0^{-1})(\tau_0^{-1} + 2\tau_1^{-1}) - \omega^2]^2$$

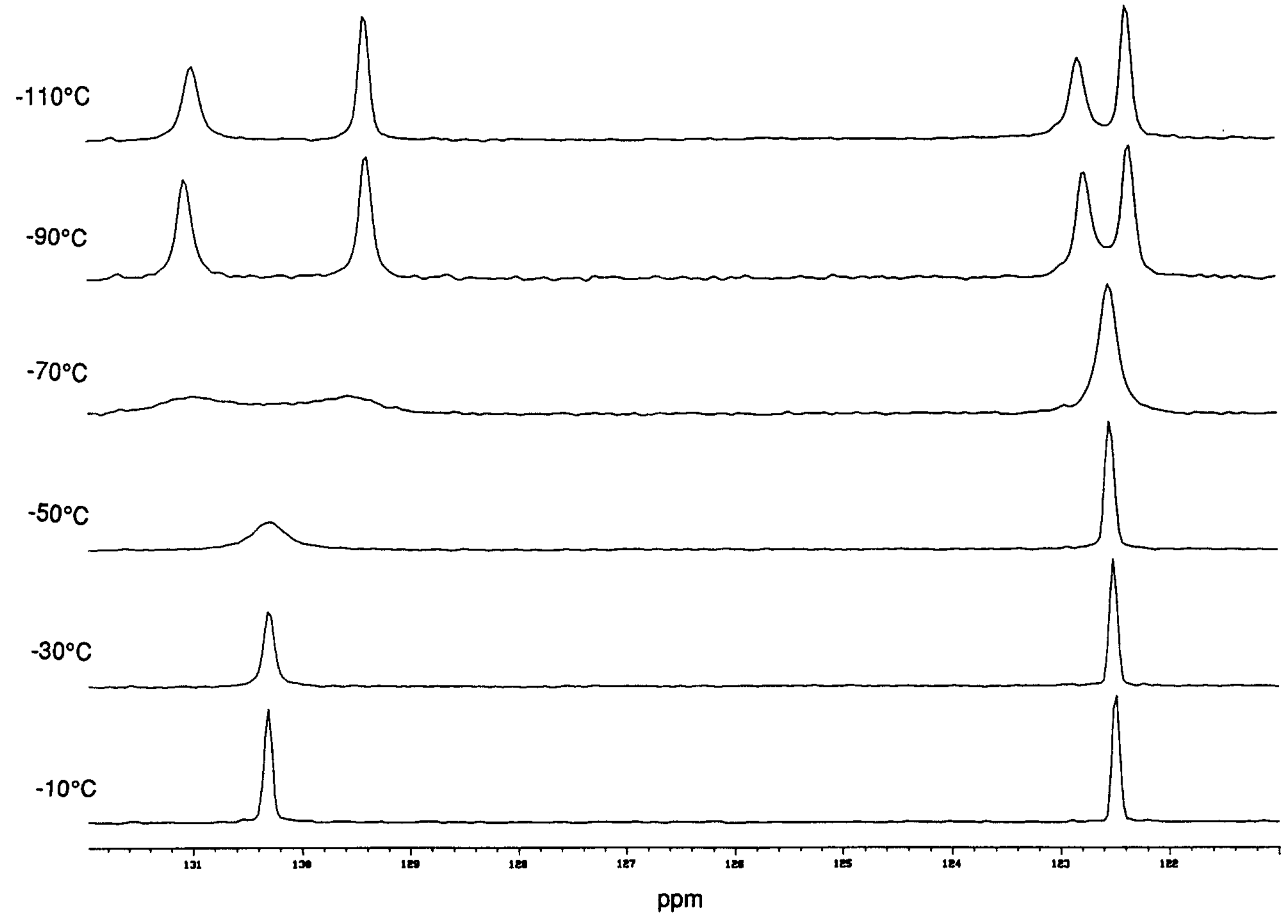

Figure 2 The protonated phenylene carbon region of the ^{13}C n.m.r. spectrum of CBPC in dichlorofluoromethane

$$
\begin{aligned}
&+ [2(\tau_0^{-1} + \tau_1^{-1})\omega]^2\}^{-1/4} \\
&\times \cos[1/2 \arctan\{2(\tau_0^{-1} + \tau_1^{-1}) \\
&\times\omega/[(\tau_0^{-1})(\tau_0^{-1} + 2\tau_1^{-1}) - \omega^2]\}] \qquad (3)
\end{aligned}
$$

The correlation time for single-bond conformational transition is τ_0 and the correlation time for cooperative or correlated conformational transitions is τ_1. At each temperature τ_0 and τ_1 are chosen to simulate the averaged ^{13}C T_1 values of cyclohexyl carbons 8 and 9 at three different frequencies. The values of τ_0 and τ_1 as a function of temperature can be summarized by an apparent activation energy and Arrhenius prefactor. The activation energies for cooperative and single-bond transitions are 17 and 22 kJ mol^{-1}, respectively, and the prefactors are 15×10^{-13} and 5×10^{-13} s, respectively. The comparison of the experimental and fitted T_1 data for cyclohexyl carbon 8 and 9 at three different magnetic fields are presented in *Table 1*. The root mean square deviation between experimental values and the fit is less than the 10% experimental error.

Next we turned our attention to the motion of the phenylene group. The phenylene groups are assumed to undergo the same segmental motion as the cyclohexyl ring since they are both in the backbone. In addition, the phenylene group can also rotate or librate about the C_1C_4 axis as observed in other polycarbonates. If one compared the T_1 data of protonated phenyl carbons of CBPC with that of BPA and NBPC as shown in *Table 2*, it was found that when the temperature was over 20°C the T_1 data for the CBPC were in between that of BPA and NBPC; so the phenyl groups of CBPC could be seen to be qualitatively reflecting less motional freedom than BPA, but more motional freedom than NBPC. Similar to the NBPC[5], the T_1 minimum of the protonated phenyl carbons of CBPC occurs almost at the same temperature range as that of the cyclohexyl carbons. This indicates that there is only modest additional freedom of the phenyl group relative to the cyclohexyl ring. First the Woessner model for free rotation and the Gronski model for libration were individually used to try to fit the experimental phenyl T_1 data as was done with the other polycarbonates.

The spectral density equations for the model combining the segmental motion with phenyl group rotation about the C_1C_4 axis can be written as

$$
J(\omega) = AJ_a(\tau_0, \tau_1, \omega) + BJ_b(\tau_{bo}, \tau_1, \omega) + CJ_c(\tau_{co}, \tau_1, \omega) \qquad (4)
$$

where $A = (3\cos^2\Delta - 1)^2/4$
$B = 3(\sin^2 2\Delta)/4$
$C = 3(\sin^4\Delta)/4$

For a twofold jump

$$
\tau_{bo}^{-1} = \tau_0^{-1} + \tau_{irp}^{-1}
$$

$$
\tau_{co}^{-1} = \tau_0^{-1}
$$

For stochastic diffusion

$$
\tau_{bo}^{-1} = \tau_0^{-1} + \tau_{irp}^{-1}
$$

$$
\tau_{co}^{-1} = \tau_0^{-1} + (\tau_{irp}/4)^{-1}
$$

The form of the J_a, J_b, and J_c was the same as in equation (3) with τ_0 replaced by τ_0, τ_{bo}, and τ_{co}, respectively. The correlation time for internal rotation of the phenyl group is τ_{irp}. The combination of stochastic diffusion for the internal rotation about the C_1C_4 axis with segmental motion using parameters set from the cyclohexyl ring motion can fit the phenyl data for all three frequencies at higher temperatures but not as well at lower temperatures. The activation energy for phenyl rotation was 22 kJ mol^{-1} and the corresponding prefactor was 4.5×10^{-13} s. The combination of a twofold jump for the internal motion about the C_1C_4 axis with segmental motion failed to fit the experimental data.

Another interpretation can be considered for the phenylene carbons using the restricted rotation model in addition to segmental motion determined by the cyclohexyl ring T_1 simulation. A restricted anisotropic rotational diffusion model developed by Gronski[12,13] had been combined with the Hall–Helfand segmental motion correlation function. The composite spectral density can be written as

$$
\begin{aligned}
J(\omega) = &\left\{ A + \frac{B}{\ell^2}[(1-\cos\ell)^2 + \sin^2\ell] \right. \\
&\left. + \frac{C}{4\ell^2}[(1-\cos 2\ell)^2 + \sin^2 2\ell] \right\} J^{01}(\omega) \\
&+ \frac{B}{2}\sum_{n=1}^{\infty}\left[\left(\frac{1-\cos(\ell-n\pi)}{\ell-n\pi} + \frac{1-\cos(\ell+n\pi)}{\ell+n\pi}\right)^2\right. \\
&\left. + \left(\frac{\sin(\ell-n\pi)}{\ell-n\pi} + \frac{\sin(\ell+n\pi)}{\ell+n\pi}\right)^2\right] \mathrm{J}_{\mathrm{n}}^{\lambda}(\omega) \\
&+ \frac{C}{2}\sum_{n=1}^{\infty}\left[\left(\frac{1-\cos(2\ell-n\pi)}{2\ell-n\pi} + \frac{1-\cos(2\ell+n\pi)}{2\ell+n\pi}\right)^2\right. \\
&\left. + \left(\frac{\sin(2\ell-n\pi)}{2\ell-n\pi} + \frac{\sin(2\ell+n\pi)}{2\ell+n\pi}\right)^2\right] J_n^{\lambda}(\omega) \qquad (5)
\end{aligned}
$$

where

$$
\begin{aligned}
J^{01}(\omega) = &\, 2\{[\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega^2]^2 + [2\tau_{01}^{-1}\omega]^2\}^{-1/4} \\
&\times \cos\left[\frac{1}{2}\tan^{-1}\frac{2\tau_{01}^{-1}\omega}{\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega^2}\right]
\end{aligned}
$$

and

$$
\begin{aligned}
J_n^{\lambda}(\omega) = &\, 2\{[(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \tau_1^{-1} + \lambda_n) - \omega^2]^2 \\
&+ [2(\tau_{01}^{-1} + \lambda_{\mathrm{n}})\omega]^2\}^{-1/4} \\
&\times \cos\left[\frac{1}{2}\tan^{-1}\frac{2(\tau_{01}^{-1} + \lambda_n)\omega}{(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \lambda_n) - \omega^2}\right]
\end{aligned}
$$

with

$$
\tau_{01}^{-1} = \tau_0^{-1} + \tau_1^{-1}
$$

$$
\lambda_n = (n\pi/I)^2 D_{ir}
$$

where D_{ir} is the diffusion constant for restricted diffusion and I is the angular amplitude of the restricted diffusion. Here restricted anisotropic rotational diffusion is characterized by two parameters in lieu of the correlation times, D_{ir} and I. If the restricted rotation was a harmonic well, I should be proportional to $T^{1/2}$ and D should be proportional to T.

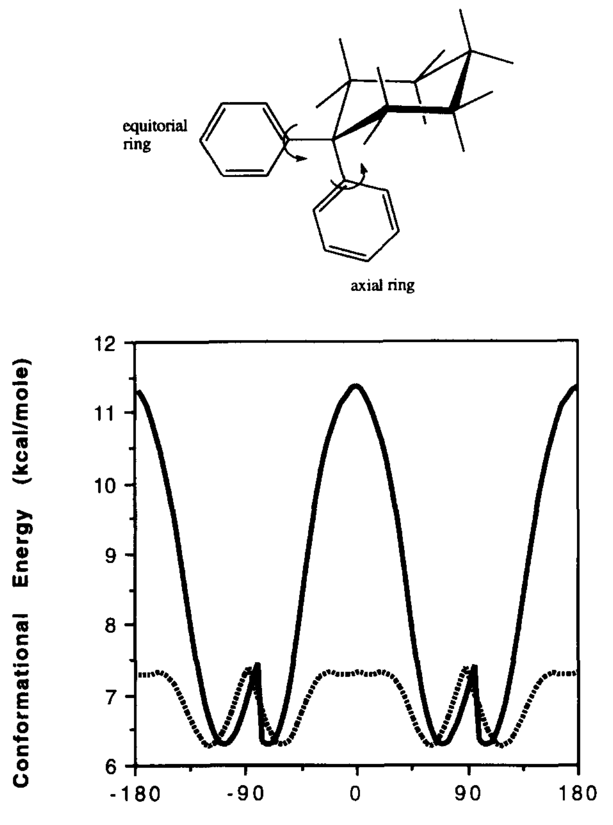

Figure 3 Potential energy diagram of the barriers to rotation in 1,1-diphenyl cyclohexane. The solid line represents the axial aromatic ring and the dotted line the equatorial ring

The fit of the phenyl T_1 data of CBPC yielded,

$$D = (18.63 \times 10^7)T - 1.1 \times 10^9$$

$$I = 24.1\ T^{1/2} - 300$$

where T was in Kelvin. In terms of angular width, I increases from 65.5° at −43°C to 177.8° at +120°C. Almost the same quality of fit was obtained as was obtained using the internal rotational model and the low temperature problems still exist.

Actually the two phenylene rings of CBPC may not be equivalent as is indicated by consideration of a space filling model (subsequently verified by modeling calculations) and this could be the source of the fitting difficulties. The phenylene ring in the equatorial position is likely to be less restricted than the one in axial position because the cyclohexyl group lies over the axial phenylene group. Thus it is reasonable to assume the rings have two different mobilities which cannot be independently observed at the temperature of the T_1 measurements because of slow exchange.

To check this point, low temperature ^{13}C line shape measurements were made to look for phenylene ring inequivalencies at temperatures below the range of the T_1 measurements. The CBPC sample was dissolved in dichlorofluoromethane because of the low freezing point of −146°C. ^{13}C spectra were acquired at a Larmor frequency of 125.7 MHz from −10° to −110°C and these spectra are presented in *Figure 2*. It can be clearly seen that the phenylene carbons 2 and 3 each split into two peaks at −90° and −70°C, respectively. As the temperature decreases to −90°C, the cyclohexyl chair–chair inversion becomes slow on the n.m.r. chemical shift time-scale so that the equatorial and axial phenylene carbons can now be distinguished. The now resolved axial phenylene carbons show additional broadening relative to the equatorial carbons as the temperature decreases. This is indicative of restricted motion of the axial phenylene ring relative to the equatorial.

To further confirm this interpretation calculations were made on the barriers to rotation in 1,1-diphenyl cyclohexane. *Figure 3* shows the barriers to rotation of the equatorial aromatic ring and the axial aromatic ring as a function of dihedral angle. The location of the energy maxima and minima are very similar to those calculated for diphenyl propane except the size of the barriers has changed and the two rings are inequivalent. The equatorial ring barrier is seen to be considerably lower than the axial ring barrier.

Given this knowledge of ring inequivalency, a successful fit is produced by treating the equatorial ring with the Woessner model for rotation and axial ring with the Gronski model for libration. Because of conformation exchange within the cyclohexyl group, the axial and equatorial rings are interchanged on a time scale slow with respect to spin-lattice relaxation but fast with respect to line shape collapse so only a single T_1 is determined for each protonated carbon. The single T_1 value is then a simple average of the two types of local motion according to the equation

$$1/T_1 = 0.5/T_1^G + 0.5/T_1^W$$

where T_1^W is the spin-lattice relaxation time for the equatorial ring undergoing rotation and T_1^G is the spin-lattice relaxation time for the axial ring undergoing restricted diffusion or libration. The fit of the phenylene T_1 data of CBPC yields the following dynamic parameters for the axial ring

$$D = 1.0 \times 10^7 T - 1.75 \times 10^9$$

$$I = 18.7\ T^{1/2} - 215$$

The angular amplitude increases from 82.4° at −20°C to 155.7° at 120°C. The activation energy for phenylene rotation for the equatorial ring is 19.4 kJ mol^{-1} and the corresponding prefactor is 3.0×10^{-13} s. A comparison of the ^{13}C T_1 data fitted by the combined description is compared with the experimental T_1 data in *Table 3*. Very good fitting results were obtained even at low temperature.

DISCUSSION

CBPC undergoes isotropic segmental motion that can be very well described by the Hall–Helfand correlation function. Even though the cyclohexyl ring undergoes conformational interchange, this motion is too slow to contribute to T_1. According to the Hall–Helfand model, two subclasses of segmental motion are observed. First, there are conformational changes produced by rotation about an single backbone bond and this process is described by an exponential correlation time, τ_0. The second process is a correlated motion where a second rotation about a backbone bond is observed to follow the first rotation closely in time. The second rotation

Table 3 Comparison of ^{13}C T_1 data (ms) of the protonated phenylene carbons of CBPC with that fitted by the inequivalent ring model

	50.3 MHz			75.4 MHz			125.7 MHz	
T (K)	Expt	Fitting	T (K)	Expt	Fitting	T (K)	Expt	Fitting
243.5	156	143	238.7	213	229	243	396	410
254.1	162	147	249.8	204	212	263	316	345
264.7	164	160	260.3	201	212	273	327	343
275.4	203	178	271.8	202	226	283	344	355
286.0	181	202	284.6	228	252	293	339	378
296.6	204	230	295.8	251	283	303	375	410
312.2	232	280	307.4	304	322	313	399	448
322.2	291	316	319.3	340	368	323	446	494
332.3	307	356	330.7	392	418	343	515	601
342.4	418	399	336.6	433	445			
352.4	456	444	353.1	532	529			
362.5	476	492	364.6	578	593			
372.6	588	544	376.5	677	663			
382.6	749	599	388.1	759	736			
392.7	735	659						

Table 4 Comparison of the segmental motion fitting parameters τ_1 and τ_0 (ns) for BPA, TMBPA, NBPC, CBPC and CHLORAL

	BPA		TMBPA		NBPC		CBPC		CHLORAL	
T (°C)	τ_1	τ_0	τ_1	τ_0	τ_1	τ_0	τ_1	τ_0	τ_1	τ_0
−20	1.88	25.0	5.0	300.0	5.41	265.6	4.85	17.42	1.80	30.0
0	1.32	18.8	2.5	110.0	2.35	93.4	2.68	8.10	1.63	11.1
20	0.68	16.6	1.4	35.0	1.14	37.9	1.61	4.18	0.93	6.8
40	0.58	15.8	0.6	15.3	0.61	17.3	1.03	2.35	0.63	4.7
60	0.24	6.3	0.37	6.4	0.35	8.64	0.70	1.41	0.37	3.0
80	0.18	3.1	0.23	3.1	0.21	4.67	0.49	0.90	0.26	2.1
100	0.11	2.5	0.17	1.8	0.14	2.70	0.36	0.60	0.18	1.5
120	0.09	2.0	0.12	1.1	0.093	1.65	0.27	0.42	0.13	1.2
E_a (kJ mol^{-1})	19	16	23	34	24	30	17	22	17	18
$\tau_\infty \times 10^{14}$ (s)	28	1603	10.8	3.3	6	17	150	50	94	409

Table 5 Comparison of the diffusion constant D_{ir} and angular amplitude I determined by the Gronski model for TMBPA, NBPC and by the inequivalent ring model for CBPC

	TMBPA		NBPC		CBPA	
T (°C)	$D_{ir} \times 10^{-8}$ (s^{-1})	I (deg)	$D_{ir} \times 10^{-8}$ (s^{-1})	I (deg)	$D_{ir} \times 10^{-8}$ (s^{-1})	I (deg)
−20	11.0	73.0	8.50	79.3	7.80	82.4
0	13.0	77.0	10.16	89.6	9.80	94.0
20	14.1	80.5	11.82	99.5	11.8	105.1
40	15.2	83.4	13.48	109.2	13.8	115.8
60	16.1	86.2	15.14	118.5	15.8	126.2
80	17.2	88.5	16.80	127.5	17.8	136.3
100	18.2	90.5	18.46	136.3	19.8	146.2
120	19.3	92.5	20.12	144.9	21.8	155.7

compensates for distortion of the backbone produced by the first conformational event. This process is characterized by a correlation time τ_1. In the computer simulations of the polyethylene, the most rapid and therefore dominant segmental motion was the single bond transition[10]. In the analysis of more complicated repeat units such as the polycarbonates, the correlated motion always appears more rapid and therefore dominant[1–5]. This seems plausible since a translation or rotation of chain ends would seem to be more difficult if the repeat units were very large, though it is difficult to know whether one should interpret the outcomes of the

Table 6 Comparison of the internal rotation correlation time τ_{irp} (ns) determined by stochastic diffusion for BPA and CHLORAL and by the inequivalent ring model for CBPC

T (°C)	BPA	CHLORAL	CBPC
−20	1.95	2.12	3.03
0	0.850	1.07	1.55
20	0.510	0.685	0.862
40	0.225	0.406	0.518
60	0.170	0.259	0.331
80	0.096	0.180	0.222
100	0.075	0.140	0.156
120	0.046	0.098	0.114
E_a (kJ mol^{-1})	22	18	19.4
$\tau_\infty \times 10^{14}$ (s)	6	40	30

Hall–Helfand correlation function to this level of detail.

The activation energies of correlated motion[1–4] are 19, 17, 17, 23 and 24 kJ mol^{-1} for BPA, CHLORAL, CBPC, TMBPA and NBPC, respectively. CBPC seems to fall into the expected range of values. Meanwhile, the activation energies of single bond conformational transitions are 16, 18, 22, 34 and 30 kJ mol^{-1} for BPA, CHLORAL, CBPC, TMBPA and NBPC, respectively. The glass transition temperatures[1–4,6] for BPA, CHLORAL, CBPC, TMBPA and NBPC are 147, 157, 185, 203 and 232°C, respectively. The glass transition would appear to be correlated with single bond conformational transitions[5] even though the trend is not perfectly consistent for the TMBPA and NBPC. The τ_1 and τ_0 values for different polycarbonates[3–5] are listed in *Table 4*.

We found for the restricted diffusion of the axial phenylene ring a diffusion constant and an angular amplitude very similar to that of NBPC (*Table 5*). It appears that the steric hindrance of the axial aromatic ring of CBPC by the cyclohexyl ring resembles that of the aromatic rings of NBPC by the norbornyl ring. Comparison of the internal rotation correlation time τ_{irp} determined by the Woessner model for BPA and CHLORAL with that for the equatorial ring of CBPC is presented in *Table 6*. It is found the equatorial phenylene ring internal rotation is quite similar to phenylene ring rotation in CHLORAL. This means the cyclohexyl steric hindrance to the axial aromatic ring is much larger than that to the equatorial one. The experimental value for the apparent activation energy for rotation of the equatorial ring is 19.4 kJ mol^{-1} while the calculated barrier is 14.6 kJ mol^{-1}. The larger experimental value includes the effects of the solvent viscosity and the difference is of an appropriate size.

If the two phenylene groups in CBPC are considered to be equivalent and are treated with either the Woessner internal rotation model of the Gronski libration model, not only is the fit worse but we found the resulting parameters were not comparable to those of the previous studies. The τ_{irp} obtained by the stochastic diffusion model for CBPC is then much larger than that for BPA and CHLORAL which in combination with the poor fit would normally lead us to apply the restricted diffusion model. It was found the diffusion constant, obtained by applying the Gronski model to both rings in an equivalent fashion, was much larger and angular amplitude was almost 180° at 120°C for CBPC. It indicated that if we considered both phenylene rings to undergo restricted anisotropic rotational diffusion, the rings diffused very quickly and at high temperature they almost underwent full rotation. If both rings are treated equivalently, it seems the motion is in between internal rotation and restricted rotational diffusion with neither giving a good fit or yielding dynamic parameters comparable to the earlier studies. On the other hand, if one ring is considered to librate and one to rotate, then the parameters appear close to the outcomes of earlier investigations and the fit is improved as shown in *Tables 3*, *5* and *6*.

The CBPC shows a low temperature or 'γ' mechanical loss peak[6] at a temperature of −22°C for a frequency of 110 Hz, which is much higher than that for BPA and NBPC which are almost the same: −72, −75°C, respectively. The γ transition is generally insensitive to several of the structural modifications. The insertion of the stiff, bulky norbornyl group in the NBPC chain has a minor effect on the γ transition despite a large increase in the glass transition temperature. However the cyclohexyl group in CBPC has a major effect on the γ transition. McHattie *et al.*[6] have studied the free volume of a series of polycarbonates and found CBPC is the only polymer in the series with a lower free volume than BPA. In NBPC, the motional restrictions caused by their substituent groups are offset by a comparable increase in free volume[6]. In other words, the isopropylidene unit of BPA has been replaced with a larger group, but the intermolecular spacing has also increased therefore leaving the γ transition essentially unchanged. In CBPC, because of the presence of conformational rearrangements of the cyclohexyl sidechain, this increase in chain spacing is not observed. Instead the polymer molecules are able to pack more efficiently, presumably because of the flexibility of the cyclohexyl unit. We found in our n.m.r. studies that the phenylene motion of BPA was totally different from that of NBPC and half of the phenyl ring of CBPC had the same motion as that in BPA and the other half the same as that in NBPC. This indicates that the intramolecular barriers to phenylene group rotation observed in solution are not the sole factor influencing the low temperature loss peak.

The solution results place CBPC in the context of the other polycarbonates in terms of intramolecular factors. Solid state studies of the motion of the phenylene rings and the cyclohexyl ring will be required for a more complete view of the dynamics in the glassy state.

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