

# Molecular Motions in Bisphenol A Polycarbonates as Measured by Pulsed NMR Techniques. I. Homopolymers and Copolymers

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## Synopsis

Molecular motions in homopolymers and copolymers based on bisphenol A polycarbonate (BAP) were investigated over a wide temperature range by means of two pulsed nuclear magnetic resonance methods: the spin-lattice relaxation time  $T_1$  and the spin-lattice relaxation time in rotating frame,  $T_{1\rho}$ . Nuclear magnetic relaxation measurements of bisphenol A polycarbonate indicated the existence of four transitions in the solid amorphous state. This included the glass transition  $T_\alpha$ , two transitions associated with localized motions of the main chain,  $T_\beta$  and  $T_\gamma$ , and a transition due to side-group motion,  $T_\delta$ . The results offer new evidence for the transition  $T_\beta$ , which is ascribed to localized segmental motions of the polycarbonate chain. The physical properties of the polymer (high impact strength and a large fractional free volume in the glassy state) can be explained by the presence of the two secondary transitions  $T_\beta$  and  $T_\gamma$ , which are both associated with main-chain motions. The presence of the bulky bromine on a bisphenol A unit of a polymer chain in a position ortho to the carbonate groups restricts all motions of the main chain, thus increasing  $T_\alpha$ ,  $T_\beta$ , and  $T_\gamma$ . As a result of an increase in the secondary transition temperatures, impact strength is reduced at least 20-fold as compared with the unsubstituted material. The results for tetrabromobisphenol A polycarbonate and copolymers of bisphenol A with tetrabromobisphenol A and bisphenol A with tetrachlorobisphenol A polycarbonate confirm the idea that the impact strength of the polymer is related to the secondary transitions ( $T < T_g$ ) arising from the main-chain motions. Copolymers of bisphenol A polycarbonate with tetrabromobisphenol A polycarbonate showed a single glass transition temperature whose value lay between those of the homopolymers. The results indicated multiple secondary transitions which corresponded to the transitions of the homopolymers with magnitudes proportional to the comonomer content.

## INTRODUCTION

When the properties of polymers are measured as a function of temperature, changes are noted at specific temperatures which are associated with transitions between modes of internal motion possible for the macromolecule. This subject has been reviewed by Boyer<sup>1-4</sup> and others.<sup>5,6</sup> The application of pulsed NMR techniques appeared promising<sup>7</sup> as a means of

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studying these transitions. Uses of nuclear magnetic resonance methods in general have been reviewed.<sup>8-11</sup> For the measurement of relaxation times, the pulsed techniques are used whereby the decaying signal following a radio-frequency pulse or the free induction decay under resonance conditions is observed. The pulsed technique has been used previously,<sup>12,13,14</sup> but publications related to polymers have been scarce.

There are three relaxation times measurable by nuclear magnetic resonance;  $T_1$ , spin-lattice relaxation;  $T_2$ , spin-spin relaxation; and  $T_{1\rho}$ , spin-lattice relaxation time in rotating frame. The relationship of  $T_{1\rho}$  to molecular motions has been discussed by Ailion and Slichter.<sup>14</sup> Measurements of  $T_1$  with particular emphasis on its temperature dependence have been made.<sup>11,15</sup> Natural rubber shows a sharper minimum<sup>15</sup> than expected from theory, a fact that was explained by a cooperative character of molecular motions in that polymer. Also observed<sup>11</sup> are broader minima for various polymers attributable to a broader distribution of the correlation frequencies in those polymers. An interesting compilation of the temperature dependence of correlation frequencies, including those obtained by nuclear magnetic resonance studies, is available.<sup>5</sup> The present study extends the earlier one<sup>7</sup> by including a wider range of polymers and by introduction of  $T_{1\rho}$  measurements as well as  $T_1$  data.

## EXPERIMENTAL

### Materials and Preparations

**Polycarbonate.** Bisphenol A polycarbonate (BAP), General Electric Lexan 140-111,  $\bar{M}_w$  30,000.

**Poly(dimethylsiloxane)** (PDMS). General Electric Silicone Fluid S-96, nominal viscosity 20 centistokes.

**Tetrabromobisphenol A Polycarbonate** (4BrBAP). Powder from General Electric Co.,  $\bar{M}_w$  92,500.

**Tetrachlorobisphenol A/Bisphenol A Copolymer** (4ClBAP/BAP). 65 wt-% tetrachlorobisphenol A/35 wt-% bisphenol A copolymer DL 444. General Electric Co.

**Tetrabromobisphenol A/Bisphenol A Copolymers** (4BrBAP/BAP). General Electric Co. 35 wt-% tetrabromobisphenol A/65 wt-% bisphenol A copolymer 105A-111 and 8 wt-% tetrabromobisphenol A/92 wt-% bisphenol A copolymer 2014-111.

**Specimens** were prepared by molding the powders or pellets into rods 7 mm in diameter and 2 cm long, followed by quenching rapidly. The specimens were annealed for one day at appropriate temperatures to relieve stresses and to remove traces of crystallinity.<sup>16</sup>

### Nuclear Magnetic Resonance Measurements

A Bruker SXP 4-60 (B-KR322S) pulse NMR spectrometer with variable frequency range between 4 and 62 MHz<sup>17</sup> was used for the measurements of the relaxation times. The Tektronix TR564B storage oscilloscope was

used for signal registration. A Hewlett-Packard electronic counter 52 12A was used to measure the exact pulse durations in rotating frame measurements. Measurements were made at a frequency of 30 MHz. In some cases, the sample was measured at different resonant frequencies ranging from 15 to 60 MHz. The rotating frame data were taken with an  $H_1$  (radio-frequency field) of about 30 gauss. The  $90^\circ$  pulse was of 2  $\mu$ sec duration, and the apparatus "dead" time ( $t_d$ ) following a pulse was about 3 to 4  $\mu$ sec. Temperature control of the sample was accomplished by using a quartz Dewar insert (Bruker, B-KR 300 Z11) in conjunction with the variable-temperature control unit (Bruker, B-ST 100/700).<sup>18</sup> The heat exchanger for temperatures below 300°K was eliminated and the liquid nitrogen was evaporated directly into the system as coolant. To increase the circulation in the Dewar insert, the sample holder tube was perforated and the gas flow reversed. Approximately 300 l./hr of coolant, evaporated liquid nitrogen or compressed air (for temperatures above 300°K), was used. The temperature uncertainty was  $\pm 0.3^\circ$ K.

The spin-lattice relaxation time  $T_1$  was measured using the  $n\pi/2$ ,  $\pi/2$ , or saturation sequence method. The relaxation in rotating frame  $T_{1\rho}$  was measured similarly. A strong radio-frequency pulse was applied to the sample; and after a time equivalent to a  $\pi/2$  pulse, a  $90^\circ$  phase shift was introduced into  $H_1$ .  $T_{1\rho}$  was determined from the height of the induction decay as a function of time which gives a linear logarithmic plot for pure polymers and copolymers. The two relaxation times  $T_1$  and  $T_{1\rho}$  were thus measures of the rates of change of magnetization along the fields  $H_0$  (external magnetic field) and  $H_1$ , respectively. The amplitude of the former was of the order of kilogauss corresponding to measurements in the radio-frequency region for protons. The latter, on the other hand, was varied from 3 to 30 gauss depending on the power of the radio-frequency transmitter available. The precision of  $T_1$  and  $T_{1\rho}$  measurements was  $\pm 3\%$ .

The NMR correlation frequencies ( $\nu_c$ ) for molecular motions were calculated by assigning molecular motions for the polymers examined and checking the results with other methods of measurements on the same or related polymers. The correlation between various experimental methods was accomplished by use of "transition" ( $\log \nu_c$  vs.  $1/T$ ) maps.<sup>5</sup> Observation of broad  $T_1$  and  $T_{1\rho}$  minima in the experimental curves indicated the presence of a distribution of correlation frequencies. Thus,  $\nu_c$  represents the center of the distribution for the observed motion. The materials studied were bis phenol A polycarbonate whose transitions have been investigated using various methods.<sup>5,7,16,20,21</sup> By selecting the basic material (polycarbonate) which shows a positive relation between mechanical properties and molecular motions,<sup>3</sup> analysis of the data was extended to the relationship between transitions and impact strength in heterogeneous polymer systems (part II, this issue).

The transitions observed in pure homopolymers were designated  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ , where  $\alpha$  indicates the glass transition temperature;  $\beta$ , the first transition when the temperature is lowered to  $T < T_g$ ; and so on, to the

transition observed at the lowest temperature within the experimental range.

### Impact Strength and Flexural Modulus

These were measured with an Izod impact tester according to ASTM test method D-256 (Method A) and an Instron Universal Testing Instrument following ASTM Procedure D-695, respectively.

## RESULTS AND DISCUSSION

The masses of data generated were summarized by plotting the temperature dependence of the values of  $T_1$  and  $T_{1\rho}$ , rather than by attempting to record individual measurements under all experimental conditions. The temperature range was usually 100° to 500°K.

### Bisphenol A Polycarbonate (BAP)

Figure 1 shows the plots for NMR relaxation times for bisphenol A polycarbonate at 33 MHz. Table I summarizes the relaxation results in terms of correlation frequencies, assigned motions, and activation energies deduced either from  $T_1$  and  $T_{1\rho}$  minima or from the transition map.<sup>5</sup> All data correlated well with dielectric, mechanical, and wide-line NMR results on the temperature-frequency plot. The  $T_1$  results agreed with the earlier data obtained at 18 MHz.<sup>7</sup> The main  $T_1$  minimum occurred at

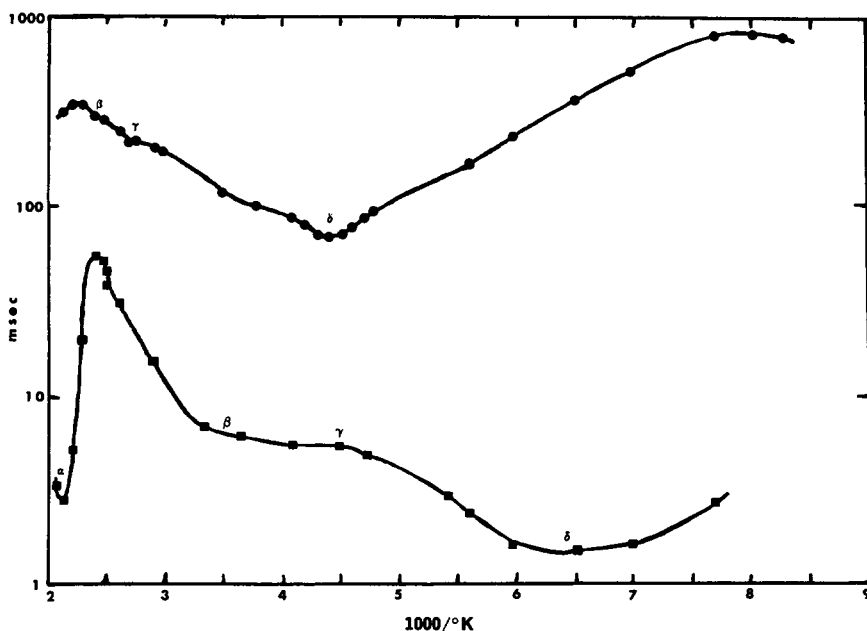


Fig. 1. Temperature dependence of the NMR relaxation times for bisphenol A polycarbonate: (●)  $T_1$ ; (■)  $T_{1\rho}$ .

TABLE I  
NMR Relaxation Results for Polycarbonate

	$\log \nu_c$	$T_\alpha$	$T_\beta$	$T_\gamma$	$T_\delta$
$T_1$ minimum	7.6	—	~417°K	~370°K	~230°K
$T_{1\rho}$ minimum	5.1	470°K	~285°K	~220°K	~156°K
$\Delta E$	—	—	14° kcal/mole	6 kcal/mole	5 kcal/mole
Type of motion	—	general main-chain motions	localized segmental motions	restricted reorientation of phenyl and carbonate group	CH <sub>3</sub> group rotation

$\sim 230^\circ\text{K}$ . This minimum was assigned to methyl group reorientation. At  $\sim 156^\circ\text{K}$ , the corresponding  $T_{1\rho}$  minimum was observed. An activation energy of 5 kcal/mole was deduced from these two minima. At  $470^\circ\text{K}$ , another  $T_{1\rho}$  minimum was observed indicating the onset of general chain backbone motions which were associated with the glass transition. At temperatures below the glass transition, another  $T_{1\rho}$  "minimum" was observed between  $220^\circ$  and  $290^\circ\text{K}$ . McCall and Falcone<sup>21</sup> reported the same minimum in their determination of  $T_{1\rho}$  but observed no effects on values of  $T_1$ . The present data indicated the presence of the corresponding weak minima in the  $T_1$ -temperature plot, one at  $\sim 417^\circ\text{K}$  and the other at  $\sim 370^\circ\text{K}$ .

The measurements for  $T_1$  for polycarbonate at different frequencies confirmed these results. Figure 2 shows the  $T_1$  data at six different frequencies between 18 and 60 MHz. At resonant frequencies above 23 MHz, the two minima became sufficiently separated to be detected. The activation energies deduced for the two motions were 14 and 6 kcal/mole, respectively. The minima at the lower temperature correlated well with the dielectric and broad-line NMR results of Matsuoka and Ishida.<sup>16</sup> This motion was ascribed to restricted motion of the main chain which involved both phenyl

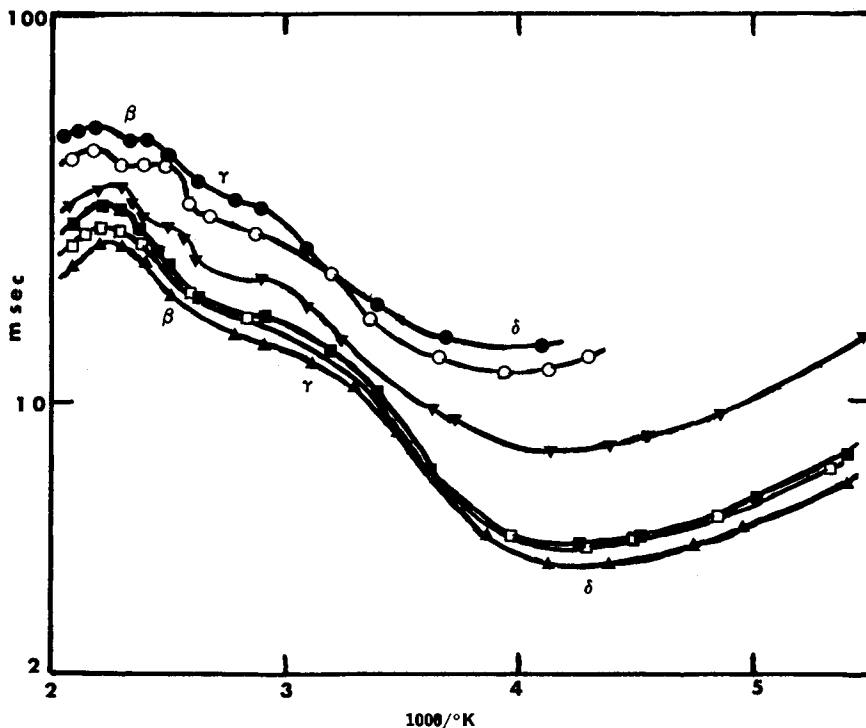


Fig. 2. Temperature dependence of the relaxation time  $T_1$  for bisphenol A polycarbonate at various frequencies: (●) 60 MHz; (○) 40 MHz; (▼) 30 MHz; (■) 23 MHz; (○) 20.6 MHz; (□) 18 MHz.

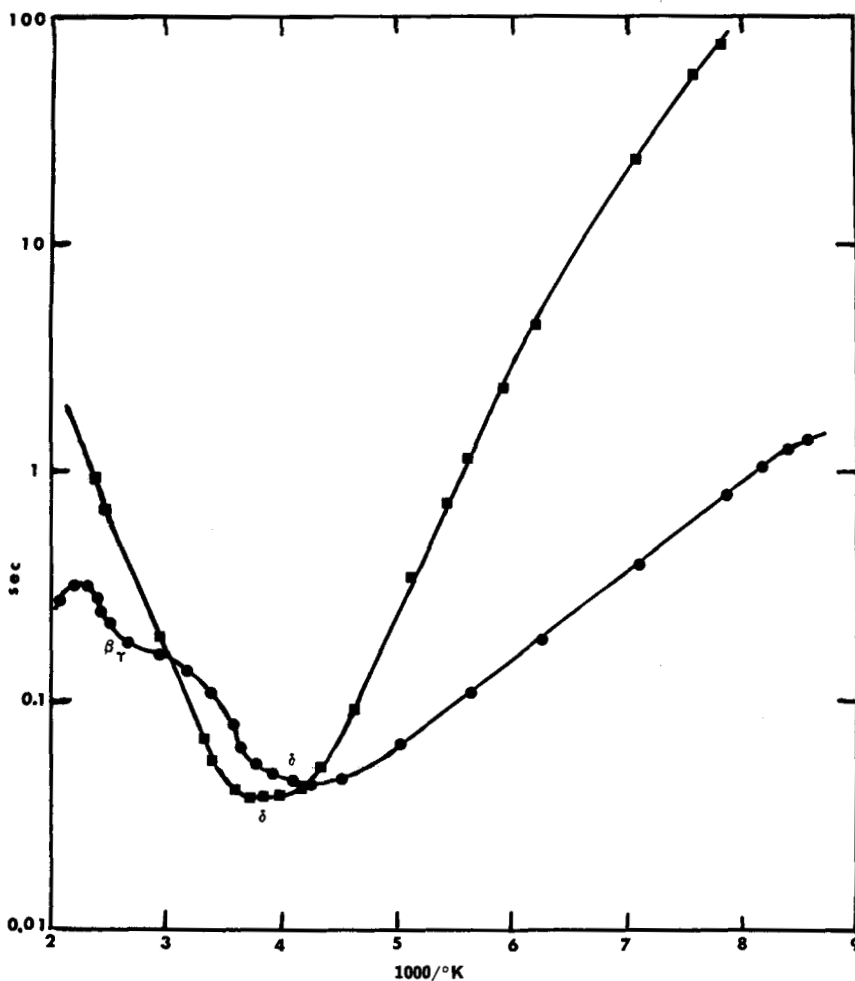


Fig. 3. Temperature dependence of the relaxation time  $T_1$  for bisphenol A (■) and bisphenol A polycarbonate (●) at 20.6 MHz.

groups as seen by the NMR relaxations in the above results and wide-line NMR measurements,<sup>16,22,23</sup> and the carbonate group in the polycarbonate chain as seen by dielectric<sup>16</sup> and mechanical<sup>24</sup> relaxation measurements. The  $T_1$  minimum at the higher temperature correlated well with isolated dielectric measurements on the transition map for polycarbonate,<sup>5</sup> and it was ascribed to localized segmental motion of the chain. The most recent IR-spectroscopic evidence for motions of the polycarbonate chain backbone below  $T_g$ <sup>25</sup> supports this assignment.

The temperature dependence of  $T_1$  for bisphenol A polycarbonate and bisphenol A at 20.6 MHz are compared in Figure 3. The results indicated that all the observed transitions in polycarbonate, except one ( $T_\delta$ ), were connected with the motions of the macromolecular chain. The  $T_\delta$  transi-

tion which was associated with the rotation of side methyl group in polycarbonate was the only transition observed for bisphenol A. The distribution of nonequivalent  $\text{CH}_3$  groups in a polymer chain of bisphenol A polycarbonate corresponding to a distribution of correlation times, as well as activation energies for this motion, was seen as an apparently lower intramethyl dipolar relaxation rate<sup>7</sup> (higher  $T_1$  value) and broader minimum compared to the  $T_1$  minimum for bisphenol A molecules.

### Tetrabromobisphenol A Polycarbonate

The relaxation data for tetrabromobisphenol A polycarbonate are compared with data for bisphenol A polycarbonate in Figure 4. Table II summarizes the transitions observed. The substitution of the protons with bromine on the phenyl groups ortho to the carbonate link of the polycarbonate resulted in a shift (by approximately  $90^\circ\text{K}$ ) of the  $T_\delta$  toward lower temperatures. A very shallow  $T_1$  minimum was observed at approximately  $140^\circ\text{K}$ . The relaxation time for this motion, which was associated

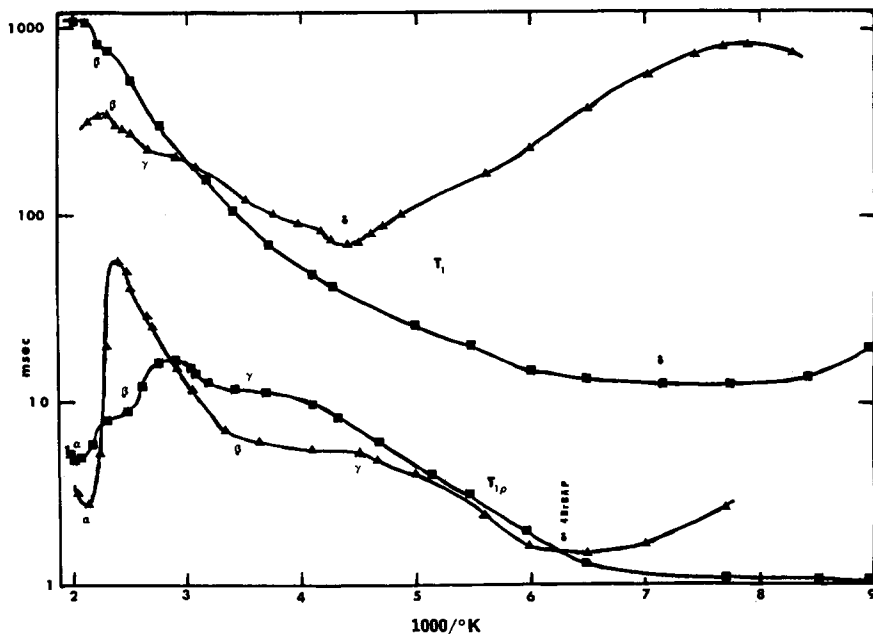


Fig. 4. Temperature dependence of NMR relaxation times for bisphenol A polycarbonate ( $\Delta$ ) and tetrabromobisphenol A polycarbonate ( $\blacksquare$ ).

TABLE II  
NMR Relaxation Results for Tetrabromobisphenol A Polycarbonates

	$\log \nu_c$	$T_\alpha$	$T_\beta$	$T_\gamma$	$T_\delta$
$T_1$ minimum	7.6	—	$\sim 455^\circ\text{K}$	—	$\sim 140^\circ\text{K}$
$T_{1p}$ minimum	5.1	$487^\circ\text{K}$	$\sim 410^\circ\text{K}$	$\sim 280^\circ\text{K}$	—



with methyl group reorientation, decreased from 70 to 13 msec. The high-temperature side of the minimum had a slope which gave an approximate  $\Delta E$  value of 1.2 kcal/mole for this motion.

Both motional minima associated with main chain motions were shifted toward higher temperatures. The  $T_\gamma$  transition ascribed to restricted rotation of phenyl and carbonate groups of the main polymer chain increased by  $\sim 40^\circ\text{K}$  in relation to  $T_1$  for bisphenol A polycarbonate. The  $T_{1p}$  minimum for this motion was observed at  $280^\circ\text{K}$ . The corresponding  $T_1$  minimum was hidden on the high-temperature side of the minimum for methyl group reorientation and was not observed. Similarly, the  $T_\beta$  transition increased by  $38^\circ\text{K}$  relative to bisphenol A polycarbonate at an experimental frequency of 30 MHz. A weak  $T_1$  minimum for this transition was observed at  $455^\circ\text{K}$ . The corresponding  $T_{1p}$  minimum was found at  $410^\circ\text{K}$ .

The  $T_{1p}$  minimum associated with the glass transition ( $T_\alpha$ ) was observed at  $487^\circ\text{K}$ , which is  $17^\circ\text{K}$  higher than the corresponding transition for bisphenol A polycarbonate. The lack of mechanical and dielectric data prevents correlation of these results on a transition map.<sup>5</sup> The mechanical measurements<sup>26,27</sup> for tetrachlorobisphenol A polycarbonate showed a shift from  $180^\circ\text{K}$  to  $348^\circ\text{K}$  for the  $T_\beta$  transition and from  $445^\circ\text{K}$  to  $493^\circ\text{K}$  for the  $T_\alpha$  transition. Since the tetrachlorobisphenol A polycarbonate showed a higher  $T_\beta$  than tetrabromobisphenol A polycarbonate, the above data are in good agreement with the experimental results. The presence of a bulky bromine on the bisphenol A unit of a polymer chain in a position ortho to carbonate groups restricts all the motions of the main chain, thus increasing the glass transition ( $T_\alpha$ ) temperature as well as the  $T_\beta$  and  $T_\gamma$  transition temperatures.

The immobilized motions of the main chain, particularly those of the phenyl group, caused an increase in motional freedom for the methyl groups due to reduced interference from the adjacent phenyl groups. The interference between the chains was reduced due to steric hindrance and the polarity of the bromine substituent. As a result, the  $T_\beta$  transition decreased. This is inconsistent with wide-line NMR measurements<sup>23</sup> for tetrachlorobisphenol A polycarbonate in which the methyl group motion remained unaffected by the presence of halogen.<sup>28,29</sup> The alternative interpretation of the observed temperature decrease of the  $T_1$  minima is that the methyl group rotation occurred via quantum mechanical tunnelling. This phenomenon has been observed in polymers, and it was suggested that the mechanism of such a motion involves a periodic rotation.<sup>28,29</sup> The value for the activation energy is in agreement with the reported value.

### Tetrabromobisphenol A/Bisphenol A Copolymers

The relaxation data for two copolymers of different compositions are summarized in Figure 5. The observed minima are listed in Table III. The glass transition temperature ( $T_\alpha$ ) depended on the compositions of copolymers, as expected for homogeneous random copolymers.<sup>1</sup> The  $T_\beta$

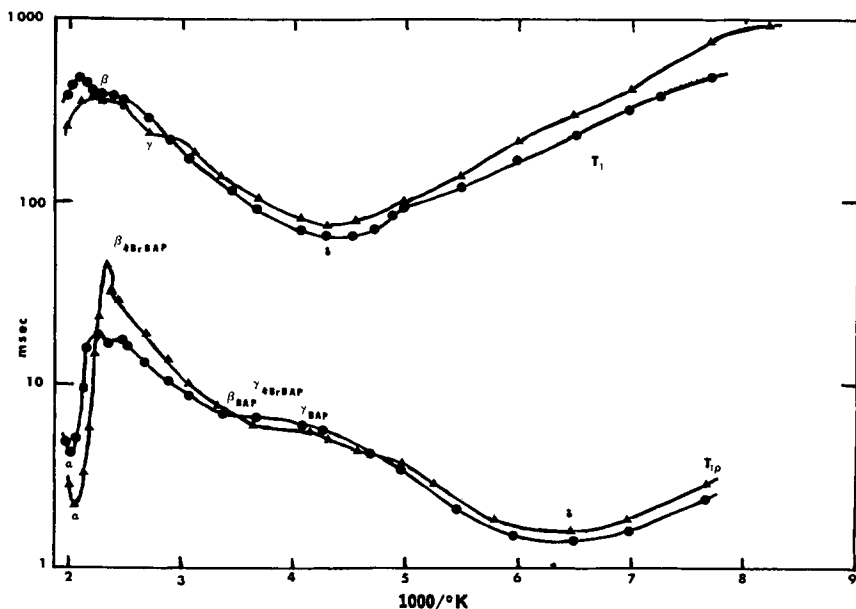


Fig. 5. Temperature dependence of NMR relaxation times for bisphenol A/tetrabromobisphenol A copolymers for different compositions: (●) 35 wt-% tetrabromobisphenol A copolymer; bisphenol A/65% bisphenol A copolymer; (▲) 8 wt-% tetrabromobisphenol A/92 wt-% bisphenol A copolymer.

transition due to side group motion remained unchanged with copolymer composition, and it was approximately the same as the  $T_g$  for bisphenol A polycarbonate. The results also indicated that the localized motions of the main chain in both copolymers studied retained the motional characteristics of the constituent homopolymers so that beta and gamma transitions each suggest two distinct transition temperatures,  $T_{\beta\text{BAP}}$ ,  $T_{\beta\text{4BrBAP}}$  and  $T_{\gamma\text{BAP}}$ ,  $T_{\gamma\text{4BrBAP}}$ , corresponding to the bisphenol A polycarbonate and tetrabromobisphenol A polycarbonate homopolymers. Since both transitions involve small segments of the chain of one or two monomer units, these results are easily understood. Although there is an indication of the corresponding motional minima in the  $T_1$  data, they were not sufficiently separated to be determined.

Inspection of relaxation curves for bisphenol A polycarbonate and tetrabromobisphenol A homopolymer is Figure 4, in comparison with relaxation curves for copolymer with 35 wt-% tetrabromobisphenol A, showed that the values of the relaxation times at motional minima reflected the copolymer composition. This effect was most evident in a  $T_{1p}$  plot for the  $\beta$ -transition because of the large differences between the relaxation times for the two homopolymers at  $T_\beta$ .

#### Tetrachlorobisphenol A/Bisphenol A Copolymer

The relaxation data for 65 wt-% tetrachlorobisphenol A/bisphenol A copolymer (65% 4ClBAP/BAP) are given in Figure 6 and are compared

TABLE III  
NMR Relaxation Results for Tetrabromobisphenol A/Bisphenol A Copolymers (4BrBAP/BAP)

Copolymer	log $\nu_c$	$T_\alpha$	$T_\beta$		$T_\gamma$		$T_\delta$
			BAP	4BrBAP	BAP	4BrBAP	
35% 4BrBAP/BAP	$T_1$ min	—	—	435°K	—	—	~230°K
	$T_{1p}$ min	477°K	(~285°K)?	~410°K	~220°K	~(270°K)?	~155°K
	$T_1$ min	—	—	—	~370°K	—	~230°K
8% 4BrBAP/BAP	$T_{1p}$ min	470°K	(~285°K)?	~410°K	~220°K	(~270°K)?	~155°K
	$T_1$ min	—	~417°K	—	~370°K	—	~230°K
	$T_1$ min	470°K	~285°K	—	~220°K	—	~155°K
4BrBAP homopolymer	$T_1$ min	—	—	~455°K	—	—	~140°K
	$T_{1p}$ min	487°K	—	~410°K	—	~280°K	—

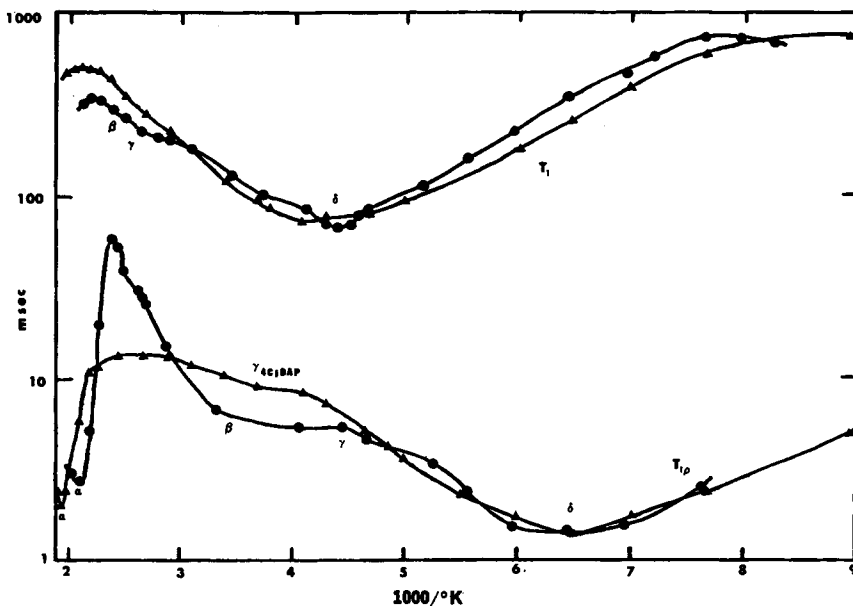


Fig. 6. Temperature dependence of NMR relaxation times for bisphenol A polycarbonate (●) and 65 wt-% tetrachlorobisphenol A/35 wt-% bisphenol A copolymer (▲).

with those for bisphenol A polycarbonate. The results were very similar to those for tetrabromobisphenol A copolymers and can be interpreted in the same way. The glass transition temperature was higher and in agreement with dilatometric measurements of the  $T_g$  for tetrachlorobisphenol A polycarbonate and tetrabromobisphenol A polycarbonate. Because of relatively high percentage of tetrachlorobisphenol A in the copolymer composition, the minima associated with the  $T_\beta$  and  $T_\gamma$  transitions in the  $T_1$  data were not effective enough to be observed. The  $T_{1p}$  plot showed less distinctive minima for the same transitions than the same plot for tetrabromobisphenol A copolymers. It was also difficult to decide whether the restricted motions of carbonate and phenyl group in all monomer units of the copolymer were shifted to higher temperature or if the rotations in the bisphenol A units ( $T_{\gamma\text{BAP}}$ ) were not effective enough at the higher 4ClBAP compositions of the copolymer to be observed. Note that the temperature of the  $\delta$ -transition is the same as that for bisphenol A polycarbonate (Table IV).

TABLE IV  
NMR Relaxation Data for 65% 4ClBAP/BAP

	log $\nu_c$	$T_\alpha$	$T_\beta$		$T_\gamma$		$T_\delta$
			4ClBAP	BAP	4ClBAP	BAP	
$T_1$ min	7.6	—	—	—	—	—	$\sim 240^\circ\text{K}$
$T_{1p}$ min	5.1	488°K	$\sim 400^\circ\text{K}$	—	( $\sim 270^\circ\text{K}$ )?	—	$\sim 155^\circ\text{K}$

## GENERAL DISCUSSION AND SUMMARY

Based on the transitions of bisphenol A polycarbonate and other constituent homopolymers, molecular motions in homogeneous polymer systems based on bisphenol A polycarbonate were studied over a wide temperature range. Using high ( $\sim 10^8$  Hz) and medium ( $\sim 10^5$  Hz) experimental frequencies, characteristic changes in all of the examined materials were observed. The interpretation of these effects is qualitative and given in terms of the component materials of the system.

The NMR relaxation results for pure polycarbonate obtained from our experiments confirmed previously observed transitions ( $\alpha$ ,  $\gamma$ ,  $\delta$ ) and indicated another transition for the first time. This transition has been designated as a  $\beta$ -transition and has been ascribed to localized motion of the main chain. The unusual physical properties of polycarbonate can be discussed in view of these results. The high impact strength of the polymer was related to the low-temperature loss peak by Heijboer.<sup>24</sup> He also suggested that low-temperature transition ( $T < T_g$ ) would improve room-temperature impact strength of a glassy polymer if the transition arose from the motion in the backbone chain but not if a side group were involved. On the other hand, it was estimated that the secondary loss peak in polycarbonate (designated  $\gamma$ ), although very pronounced, absorbs only 20% of the applied energy.<sup>3</sup>

It was also found that polycarbonate has an unusually large fractional free volume in the glassy state, i.e., about 0.16 compared to an average of 0.11 for all polymers, values which in turn are proportional to impact strengths. Several investigators independently proposed that transitions lying below  $T_g$  generate extra free volume in the glassy state.<sup>3</sup> The presence of localized segmental motions ( $T_\beta$ ), in addition to restricted cooperative motions of phenyl and carbonate groups ( $T_\gamma$ ), explains the above findings. The  $\beta$ -transition is particularly significant because a relationship between motions of the chain segments and high impact strength of glassy polycarbonate was proposed recently.<sup>30</sup>

Measurements for tetrabromobisphenol A polycarbonate showed the expected effects. The presence of a bulky bromine restricted the motions of the main polymer chain and increased  $T_\alpha$ ,  $T_\beta$ , and  $T_\gamma$ . This resulted in increased tensile strength and modulus but impaired the toughness and impact properties of the material. Data on mechanical relaxation and physical properties<sup>26,27</sup> showed that tetrachlorobisphenol A polycarbonate has a similar behavior, except that the general segmental motions of the polymer chain were even more restricted, which was reflected in a high  $T_g$  (Table V).

The mobility of the side methyl group ( $T_\delta$ ) was either increased or unaffected by the halogen substitution. The results showed that this does not influence the impact properties of the material and confirms Heijboer's proposal that the secondary transitions which involve side group motions do not affect impact strength.<sup>24</sup>

TABLE V  
Data on Polycarbonates<sup>a</sup>

Polycarbonate from	Impact strength, cm · kg/cm <sup>3</sup>	Elong., %	Tensile strength, kg/cm <sup>2</sup>	T <sub>g</sub> , °C
Bisphenol A	900	180	820	149
Tetrachloro-bisphenol A	35	10	1154	180
Tetrachloro-bisphenol A	36	8	1112	157

<sup>a</sup> From Schnell.<sup>27</sup>

The copolymers of bisphenol A with tetrabromobisphenol A or tetrachlorobisphenol A polycarbonate showed a single glass transition temperature whose value lay between the values for the two homopolymers, the behavior expected for such systems. The NMR results also showed multiple secondary transitions which could be identified with the transitions of the corresponding homopolymers. The magnitude of these transitions was proportional to the comonomer. It was further found that copolymer composition had little or no effect on low temperature transitions associated with the side group motion.

The impact strength and flexural modulus data for these copolymers are given in Table VI. The data for bisphenol A polycarbonate and tetrabromobisphenol A polycarbonate homopolymers are also included. The results showed that even a low percentage of tetrabromobisphenol A in the copolymer impaired the impact strength of the material.

TABLE VI  
Impact Strength and Flexural Modulus Data for Bisphenol A Polycarbonate (BAP), Tetrabromobisphenol A polycarbonate (4BrBAP), and Their Copolymers of Different Composition

Material	Impact strength, ft-lb/in. of notch	Flexural modulus, psi × 10 <sup>3</sup>
4BrBAP	0.45	—
35 wt-% 4BrBAP/BAP	0.65	413
8 wt-% 4BrBAP/BAP	1.97	500
BAP	16.0	370

Supported by the National Research Council of Canada, the Department of University Affairs of the Province of Ontario, and the Defence Research Board of Canada. The receipt of Ontario Graduate Fellowships is acknowledged. Fruitful discussions were held with Professor J. P. Carver of the Department of Cell Biology, University of Toronto, who offered many suggestions and permitted the use of the NMR instrument. Professor M. M. Pintar, Department of Physics, University of Waterloo, supplied the facilities for initial experiments and made helpful suggestions.

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Received September 19, 1973

Revised November 26, 1973