All our arguments until now pertain to *long flexible* polyions (i.e., polymers with negligible inherent stiffness in the uncharged state). In order to extend the discussion to *long stiff* polyions as well, we now consider a polymer of contour length L and *nonelectrostatic* persistence length L_p, bearing N charges a distance a from each other. In the uncharged state and for $L \gg L_p$ this polymer may be represented by an equivalent Gaussian chain, of $\tilde{N} = L/2L_p$ Kuhn statistical segments of length $\tilde{a} = 2L_p$. Equation 3 becomes then

$$\langle S^2 \rangle_0 = (\tfrac{1}{6}\tilde{a})L \tag{16}$$

The charge density parameter ξ remains the same as before, and the parameter describing solvent screening $\chi^* = \kappa^* a$ becomes $\tilde{\chi}^* = \kappa^* \tilde{a} = 2\kappa^* L_p$. Reasoning in the same fashion as above leads us to an asymptotic relation of the same formal structure as eq 13, namely

$$\alpha_s = \tilde{f}(\xi,\chi^*)\tilde{N}^{\tilde{g}(\xi,\tilde{\chi}^*)} \tag{17}$$

However, the statements following eq 8 and 9 must be modified. For $\xi > 1$, we still expect that the expansion becomes independent (or very weakly dependent) of ξ but the salt dependence is governed by $\tilde{\chi}_c = \kappa 2L_p$ instead of $\chi_c = \kappa\lambda$. In other words, the salt-dependence curve of highly charged polyions of the same length is not universal anymore but depends on their elastic properties through L_p.

Futhermore, the functions of $\tilde{f}$ and $\tilde{g}$ will be different from f and g since now the Kuhn segments themselves and not merely their joints are charged. As mentioned above, this local stiffening effect has already been discussed in the theories of Odijk and Houwaart[9] and Fixman and Skolnick,[10] of course, within the limitations of the Flory approach, which always predicts $\tilde{g}$ = constant.

We hope that the findings presented herein demonstrate the necessity of a complete reconsideration of the polyion expansion problem both from the theoretical and from the experimental side and may serve as starting points for future quantitative work.

Acknowledgment. This work was completed while D.S. was visiting The Weizmann Institute of Science. Thanks is due Professors J. Schlessinger, A. Silberberg, and S. Lifson for their warm hospitality and many stimulating discussions. We also express our thanks to Professors Manning, Odijk, Fixman, and Bailey for sending us preprints of their work and the Deutsche Forschungsgemeinschaft and EMBO for financial assistance of D.S. through research grants.

References and Notes

(1) Richmond, P. *J.* Phys. *A* **1973**, *6*, L109.
(2) Bailey, J. M. *Macromolecules* **1977**, *10*, 725.
(3) Edwards, S. F. *Proc. Phys. Soc. London* **1965**, *85*, 613.
(4) de Gennes, P. G. *Rep. Prog. Phys.* **1969**, *32*, 187.
(5) Reiss, H. *J. Chem. Phys.* **1967**, *47*, 186.
(6) Yamakawa, H. *J. Chem. Phys.* **1968**, *48*, 3845.
(7) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(8) Yamakawa, H. *J. Chem. Phys.* **1971**, *54*, 2484.
(9) Odijk, T.; Houwaart, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 627.
(10) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863.
(11) Throughout this work we discuss only the effects of electrostatic forces. Furthermore, we prefer to characterize the expansion by means of the radius of gyration $R_G = \langle S^2 \rangle^{1/2}$ and α_s, instead of using the end-to-end distance $\langle R^2 \rangle^{1/2}$ or α_R because the former quantities are the ones directly determined by light scattering techniques.
(12) Manning, G. *J. Chem. Phys.* **1969**, *51*, 924, 934, 3249.
(13) Soumpasis, D. *J. Chem. Phys.* **1978**, *69*, 3190.
(14) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(15) Stockmayer, W. H. *J. Polym. Sci.* **1955**, *15*, 595.
(16) Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978**, *68*, 4878.
(17) Domb, C. *Adv. Chem. Phys.* **1969**, *15*, 229.
(18) Wall, F. T.; Erpenbeck, J. J. *J. Chem. Phys.* **1959**, *30*, 634, 637.
(19) Alexandrowitz, Z.; Accad, Y. *J. Chem. Phys.* **1971**, *54*, 5338.
(20) de Gennes, P. G. *Phys. Lett. A* **1972**, *38A*, 339.
(21) le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(22) Smith, N. C.; Flemming, R. J. *J. Phys. A* **1975**, *8*, 938.
(23) Flemming, R. J. *J. Phys. A* **1979**, *12*, 2157.
(24) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys.* (*Paris*) **1978**, *39*, 77.
(25) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(26) For a theoretical discussion of the threshold for asymptotic behavior see ref 22.
(27) Orofino, T. A.; Flory, P. J. *J. Phys. Chem.* **1959**, *63*, 283.
(28) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(29) Fisher, L. W.; Sochor, A. R.; Tan, J. S. *Macromolecules* **1977**, *10*, 949.
(30) Raziel, A.; Eisenberg, H. *Isr. J. Chem.* **1973**, *11*, 183.
(31) Tan, J. S.; Gasper, S. P. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *12*, 1785.
(32) Stejskal, J.; Beneŝ, M. J.; Kratochvil, P.; Pêska, J. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1803.
(33) Tan, J. S.; Gasper, S. P. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1705.
(34) The question of Θ conditions for polyelectrolytes will be discussed extensively in a future publication.
(35) Scruggs, R. L.; Ross, P. D. *Biopolymers* **1964**, *2*, 593.

Molecular Structure Effects on the Dynamic Mechanical Spectra of Polycarbonates

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ABSTRACT: The dynamic mechanical spectra of molecularly modified derivatives of poly[2,2-bis(4-hydroxyphenyl)propane carbonate] are measured. The modifications consist of substitutions for the carbonyl, the isopropylidene, and the aromatic protons with various other groups. These measurements have enabled us to deduce the nature of the secondary relaxations. The low-temperature γ relaxation is associated with the motion of the monomer unit as a whole. The intermediate β relaxation is probably due to packing defects in the glassy state. Other details of the spectra are discussed.

Introduction

The mechanical properties of solid poly[2,2-bis(4-hydroxyphenyl)propane carbonate] (BPA-PC) have been the subject of numerous investigations not only because of its well-known toughness but also because it exhibits virtually all the known mechanical behavior of all glassy polymers in different combinations of time and temperature conditions. For a comprehensive review of the various

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mechanical properties of BPA-PC, the interested reader is referred to a paper by Kambour and Robertson.[1]

The time scale and temperature dependence of the mechanical properties indicate that they are related to the viscoelastic properties of the material. Many of the investigations into the mechanical properties of BPA-PC have been phenomenological as well as on the continuum level. Some, however, attempt to relate molecular structure and motions to relaxation properties. These are the dynamic mechanical, dielectric, and NMR studies.[2] In a few cases these results have led to intriguing correlations with macroscopic mechanical properties. For example, the temperature dependence of plane strain fracture energy and the loss tangent have been shown to have a good correlation.[3,4] The temperature and strain rate dependence of the yield stress are also well described by assuming an Arrhenius-type relationship using the activation energy of the relaxations.[5-8] The physical basis of these correlations is poorly understood, partly because the nature of the molecular motions responsible for the relaxation is itself not well understood. The salient features of some of the dynamical (mechanical, dielectric, and NMR) studies will be summarized in approximate chronological order below.

Illers and Breuer[9] first studied the dynamic mechanical behavior of BPA-PC with a torsion pendulum at 1 Hz. They observed three relaxation peaks at +155, +80, and -97 °C, which we shall label as α, β, and γ, respectively. The very prominent α relaxation is undoubtedly due to the large-scale segmental motion possible during the glass-rubber transition. The small and broad β relaxation is attributed by them to orientational stress in the specimen.[9,10] Annealing at 100 °C, they found that the loss tangent decreased approximately logarithmically with time.[9] As for the γ relaxation, without attributing it to the motion of any specific molecular group, they concluded that its existence at such a low temperature is the reason for the toughness of BPA-PC.[9] Later Reding et al.,[11] Nielsen,[12] and Tomikawa and Fujimoto[13] attributed the γ relaxation to motion of the carbonate group. These interpretations are perhaps influenced by the dielectric work of Muller and Huff[14] and Krum and Muller.[15] Reding et al.[11] also attributed the β-relaxation to motion of the phenyl group, while Tomikawa and Fujimoto[13] attributed it to chain motion in weak intermolecular potentials. Bussink and Heijboer,[16] however, assigned the γ relaxation to "small molecular movement around the COO-link". This appears to mean that the motion does not involve the carbonate group itself, in direct contradiction to previous investigations. All the above interpretations appear to have been based on considerations of the molecular structure as well as of the strongly dipolar nature of the carbonate group. With the exception of Bussink and Heijboer,[16] the investigators appear to have agreed that the carbonate group motion was responsible for the γ relaxation. Yet it is difficult to understand how the motion of such a small group—in terms of volume, moment of inertia, and possible amplitude—could be responsible for the remarkable ductility of BPA-PC.

The broad-line NMR and dielectric studies of Matsuoka and Ishida[17] shed new light on the subject. They concluded that the inception of restricted motion of the phenylene group coincides with the restricted motion of the carbonate group. Thus, according to these workers, the γ relaxation is due both to the carbonate group and to the phenylene group. This interpretation is supported by recent ultrasonic work by Phillips et al.[18] This is an important conclusion, for the high chain mobility can now conceivably be related to the macroscopic ductility. In further studies of BPA-PC and related polymers by broad-line NMR Garfield[19] concluded that the methyl group rotation is cooperative with the restricted and cooperative motion of the phenylene and carbonate groups. These views are supported by Massa and co-workers.[20,24]

LeGrand[22] investigated the ductile-brittle transition in the notched Izod impact behavior of BPA-PC and LeGrand and Erhardt[23] studied further its dynamic mechanical behavior. Noting that the γ peak is very broad, they concluded that it is probably due to the superposition of three separate peaks at -150, -100, and -50 °C. They ascribed the -150 °C peak to methyl group mobility, the -100 °C peak to motion of the carbonate unit, and the -50 °C peak to motion of the phenylene carbonate unit. They also found that the loss tangent in the 120-150 °C region generally decreased slightly with annealing and thought that it was related to the phenomenon of embrittlement due to annealing.[22,24-26] They further hypothesized that the embrittlement phenomena was associated with changes in molecular structure and in molecular volume. However, they also thought that residual orientation caused the β peak in some of their specimens. It should be noted that the thermal mechanical history of the specimens used in the above investigations are all different and that the change of the loss tangent (β) noted by Illers and Breuer was found at a lower temperature.

Difficulties still remain, however, in the concept of the ability of the carbonate unit to undergo independent motion. Consideration of a space-filling molecular model reveals that, even allowing for minor distortions of bond angles, the motion of the carbonate relative to the phenylene groups, though possible, is somewhat hindered. This steric hindrance is such that the carbonate group is probably constrained to move along with, and not independent of, the motion of the neighboring phenylene groups. Thus, the motion of the phenyl unit has to be the determining factor in the γ relaxation. We shall present new data in this paper to support this argument.

The nature of the phenylene group motion also needs to be clarified. In principle, each of the phenylene rings can undergo rotational or torsional motion about the oxygen-phenyl-carbon axis.[43] The two phenyl rings, together with the isopropylidene and the carbonate groups, can also move as a unit; i.e., the entire monomer unit can undergo a torsional motion. That the two phenyl rings and the isopropylidene group move as a unit has been proposed by Lunn and Yannas from IR dichroism measurements,[27] Davenport and Manuel in broad-line NMR measurements,[28] and Schaefer et al. in solid NMR with magic angle spinning.[29] To account for the dielectric activity, it is logical to propose that the carbonate group moves along with the motion of the bisphenol. The difference in energetics, as well as the amount of mobility these various proposed motions represent, is enormous. As mentioned previously, the fractional volume and moment of inertia of the carbonate unit is small compared to that of the monomer unit. Motion of the phenylene groups about the oxygen-phenyl-carbon axis involves a larger fractional volume and moment of inertia but is primarily intramolecular in nature. Motion of the entire monomer unit, however, involves a substantially larger moment of inertia and is primarily intermolecular in nature. Since the deformation of a polymer necessarily involves large-scale motion of the molecules, the more extensive the intermolecular relaxational motion, the more importantly it contributes to the overall mobility. It is therefore of crucial importance for us to be able to distinguish among the proposed motions.

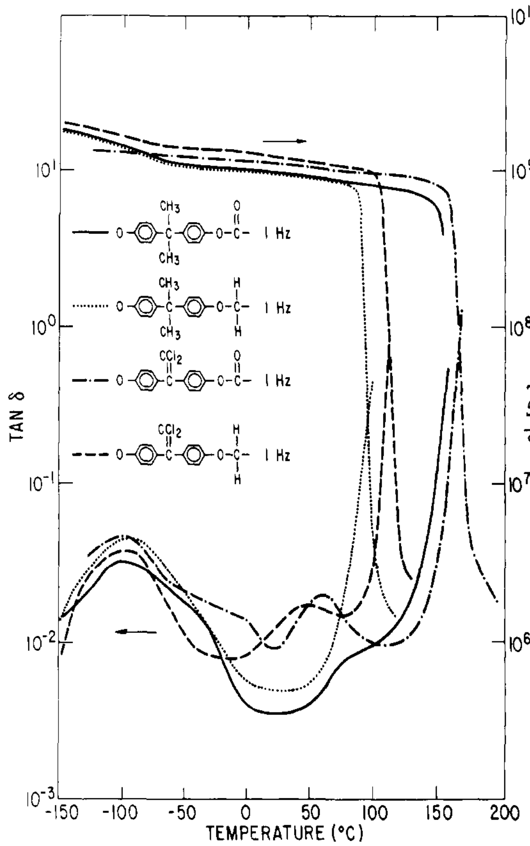


Figure 1. Dynamic mechanical spectra in torsion showing the effects of substituting the carbonyl.

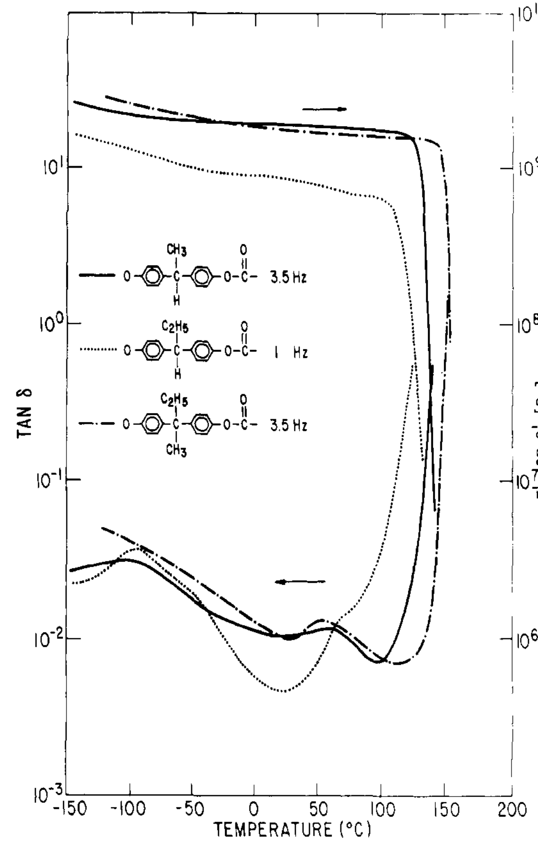


Figure 2. Dynamic mechanical spectra showing the effects of substituting the isopropylidene. Tensile data for poly[1,1-bis(4-hydroxyphenyl)ethane carbonate] and poly[2,2-bis(4-hydroxyphenyl)butane carbonate] are from Tomikawa and Fujimoto.[13]

Early[11,30] and more recent efforts[13,16,19,21] in the determination of the effects of structural modifications to the isopropylidene and aromatic portions of the polycarbonate have provided some clues, and the current work is intended to further augment the data base from which interpretations can be made. In particular, substitutions have been made for the carbonate, the isopropylidene, and on the aromatic groups to varying degrees in order to determine their effects upon the mechanical relaxation spectra. The changes seen are rationalized in terms of motions participated in by the modified segments, and the evidence developed to date toward determination of the extent of cooperativity is discussed. The effects on T_g of the modifications are also discussed.

Experiment

The resolved shear modulus and the loss factor tan δ, as a function of temperature, were measured with a Rheometrics mechanical spectrometer operating in the oscillating forced torsion mode at 0.1, 1, and 10 Hz. The operation of the spectrometer is described by Davis and Macosko.[31] The phase shift of the spectrometer's transducers and associated electronics was determined at each of the test frequencies by testing bars of stainless steel. At 1 Hz and less, no corrections were needed, as the residual shift was less than 0.5×10^{-3} rad, lower than the resolution obtainable with the polymer samples. At 10 Hz, the phase shift correction was about 14×10^{-3} rad. Typical data scatter with a 1.6-mm-thick polymer bar was about $\pm 1 \times 10^{-3}$ rad when averaged over 10 cycles. The spectrometer was set in all cases to produce a peak strain amplitude of 0.20%. The temperature range scanned was from −160 °C to about T_g plus 5 °C. Measurements were made at nominally 5 °C intervals, and 5 min was allowed at each temperature before the final readings were taken. Temperature stability of the sample chamber is estimated to be about ±0.2 °C after an initial brief overshoot of about 2 °C.

Sample Preparation. The samples examined in this work were kindly supplied by Dr. V. Mark of the Lexan Products Department, General Electric Co., Mt. Vernon, Ind., and by Drs. A. S. Hay and J. R. Campbell and Mr. G. R. Loucks of this laboratory. The intrinsic viscosities of these materials are generally in the range between 0.4 and 0.6 dL/g in methylene chloride.

The glass-to-rubber transition for each of the polycarbonates tested on the spectrometer was determined by differential scanning calorimetry at a rate of 20 °C min^{-1}. The instrument used was a Perkin-Elmer DSC-II. The point of inception of the heat capacity change at the second scan was taken as T_g.

All materials were received in the form of powdery or mildly fibrous precipitate. After drying, compression molding was used to form bars with dimensions 1.6 × 12.7 × 64 mm. The drying was done at 110 °C under vacuum for at least 48 h. To facilitate handling, cold pressing of the powders was done after 24 h of drying.

The cold-pressed bars were placed in a steel frame jacketed by chromed brass ferrotype plates and 3-mm-thick steel plates. The entire cold assembly was then placed in the hydraulic press and preheated in all cases to about T_g plus 70 °C. Two minutes under light pressure (approximately 100 bar) was sufficient for thorough melting and was followed by 0.5 min at high pressure (approximately 700 bar) to form the sample and ensure knitting. The mold assembly would then be transferred to another press where the platens were cooled by circulating cold water. Time for cooling under pressure to below T_g was about 2 min. No annealing was performed on the sample before determining their mechanical spectra. Examination between crossed polarizers revealed very little birefringence in the plane of the specimens.

Results and Discussion

The results of this experiment, together with some related results found in the literature, are presented in Figures 1–8. For ease in comparing these results, the temperatures of the relaxation peaks and the activation

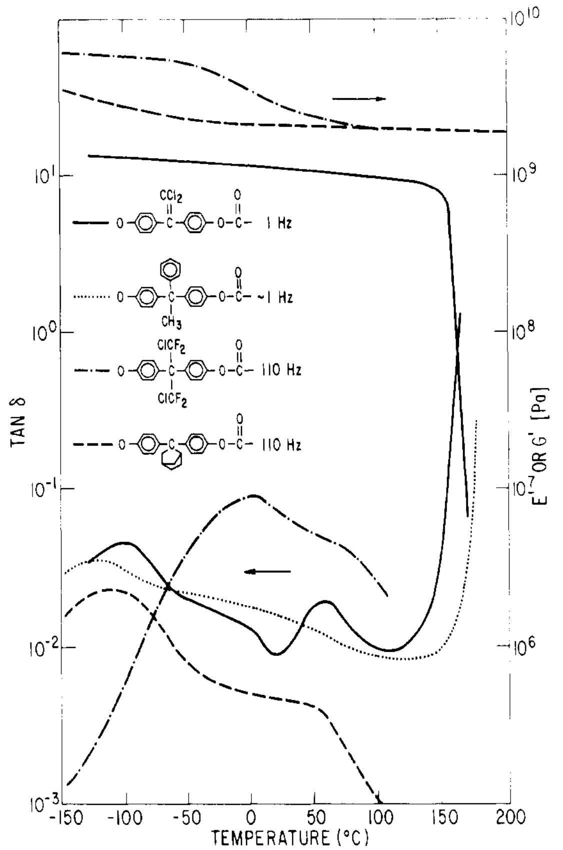
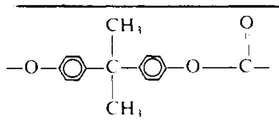
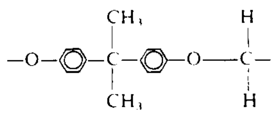
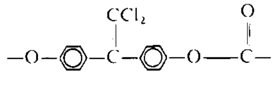
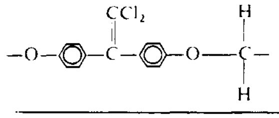


Figure 3. Dynamic mechanical spectra showing the effects of substituting the isopropylidene by more rigid groups. Torsional data for poly[(bisphenol of acetophenone) carbonate] are from Reding et al.[11] Tensile data for poly[2,2-bis(4-hydroxyphenyl)-1,3-dichloro-1,1,3,3-tetrafluoropropane carbonate] and for poly[(bisphenol of norbornane) carbonate] are from Massa and Rusanowsky.[21]

Table I

EFFECTS OF SUBSTITUTING THE CARBONYL GROUP BY A METHYLENE GROUP.
The activation energy shown is for the γ relaxation.

Structure	T_α °C	$T\beta$ °C	$T\gamma$ °C	Ea(γ) Kcal/Mole	Ref.
	150[a]	80[a]	-100[a]	13	1
	90[a]		- 95[a]	13	1
	164[a]	50[a]	-100[a]	13	1
	108[a]	45[a]	-100[a]	13	1

References:
1 This work

Notes:
a. Torsional measurement at 1 Hz

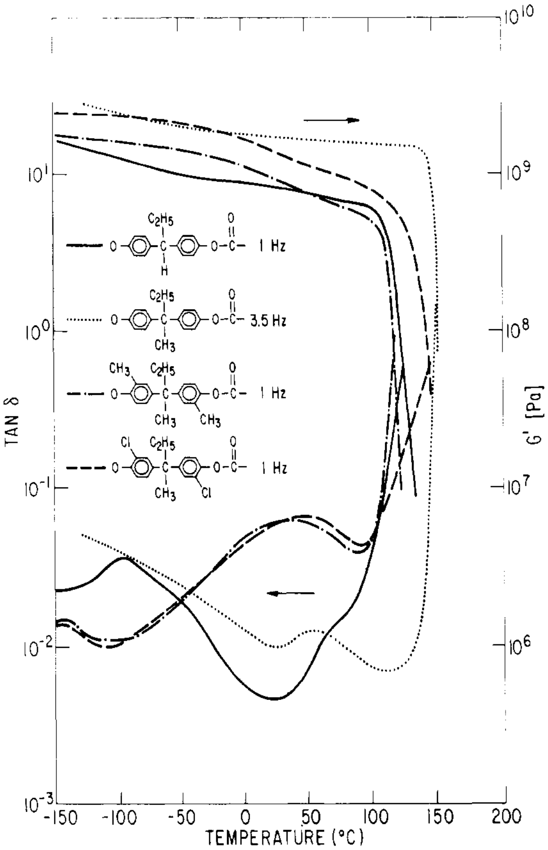


Figure 4. Dynamic mechanical spectra showing the effects of symmetric disubstitution on phenyl rings. Tensile data for poly[2,2-bis(4-hydroxyphenyl)butane carbonate] are from Tomikawa and Fujimoto.[13]

energies, where available, are summarized in Tables I–III. In the present work, three principal forms of substitution have been employed in the examination process. First, a change from polycarbonate to polyformal is effected, with the relevant materials being listed in Table I. Table II deals principally with the effects of substitutions for the isopropylidene center group of the bisphenol. Table III lists the materials for which substitution for one to four of the aromatic protons have been made.

Nomenclature of the Peaks. As mentioned in the Introduction, BPA-PC exhibits three dynamic mechanical relaxation peaks at 1 Hz from −150 to +150 °C. In order of descending temperature, these peaks are labeled α, β, and γ, respectively. The α peak is due to the large-scale motion at T_g, and in the structurally modified polycarbonates all T_g's will likewise be labeled α. The γ peak is related to motions of the phenylene rings, as we will endeavor to prove later. To facilitate comparison, in the structurally modified polycarbonates the peaks thought to be due to phenylene group motion will be labeled γ, irrespective of whether or not an intermediate β peak exists. As is shown by the results, β peaks do not exist for all the polymers investigated, and when they do, they do not necessarily represent the same motion. These aspects will be more thoroughly examined in a later section. For the polycarbonates where one of the center methyl groups has been substituted by C_2H_5 an additional low-temperature peak, which we shall label δ, also exists. The nature of this δ peak will also be discussed.

Substitution for the Carbonyl. Replacement of the carbonyl by a methylene unit, and the effect this has on the mechanical relaxation behavior, is demonstrated here for two polymers. Figure 1 shows the spectra for BPA-PC and its polyformal counterpart, as well as the chloral derivatives. Table I summarizes the salient points.

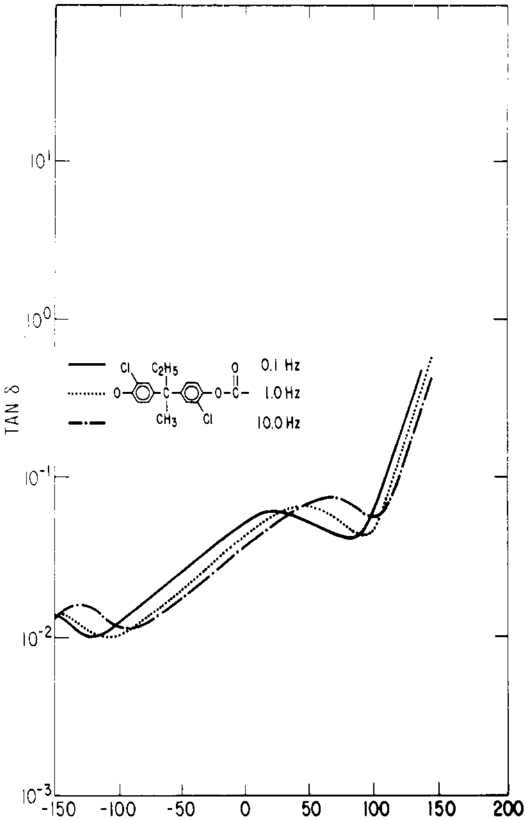


Figure 5. Dynamic mechanical spectra at three frequencies showing the γ and the δ relaxations of poly[2,2-bis(3-chloro-4-hydroxyphenyl)butane carbonate].

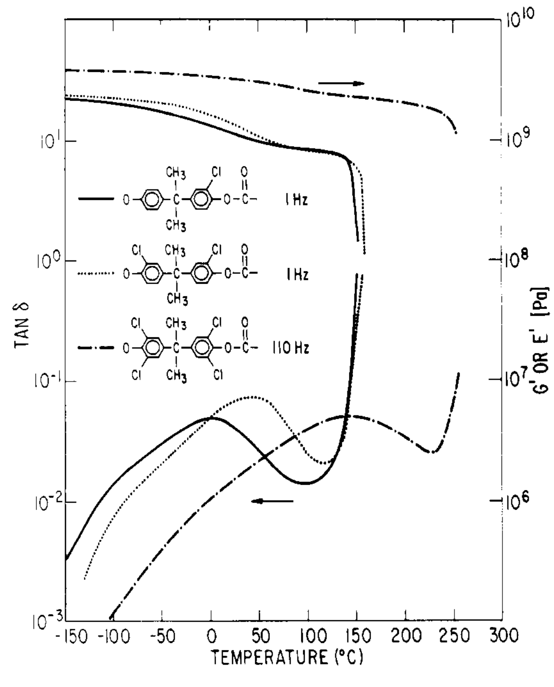


Figure 6. Dynamic mechanical spectra showing the effects of increasing chloro substitution on the phenyl groups. Tensile data for poly[2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane carbonate] are from Massa and Rusanowsky.[21]

It is readily apparent that one effect of the substitution has been the lowering of T_g by about 60 °C. It may be reasonably supposed that the removal of the polar carbonyl group has resulted in some lessening of the intermolecular interactions.

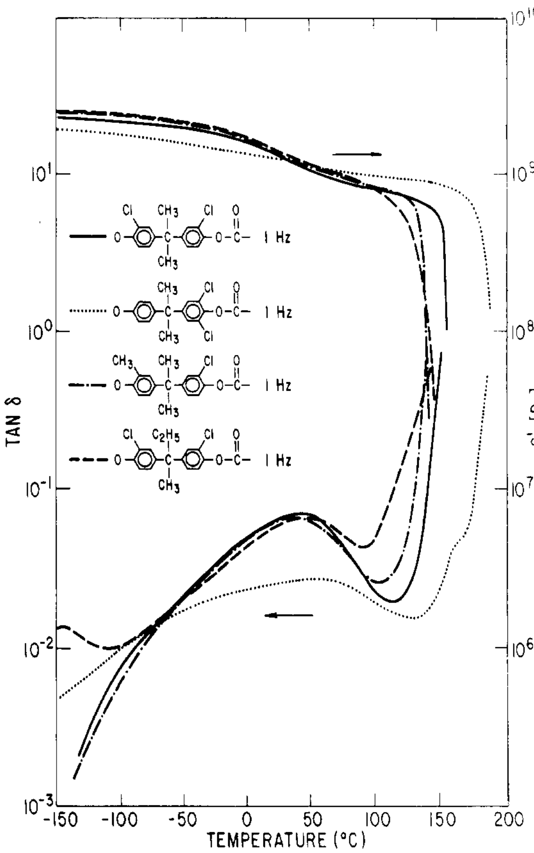


Figure 7. Dynamic mechanical spectra showing the effects of substitution of two aromatic protons.

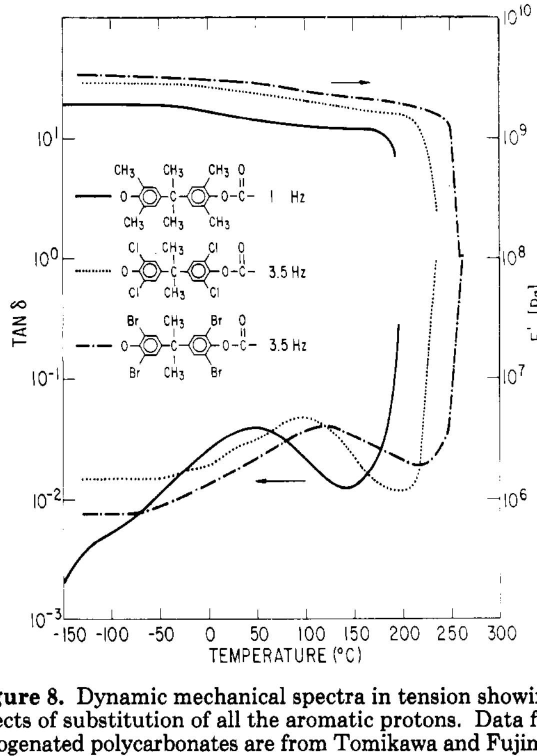
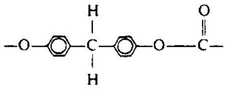
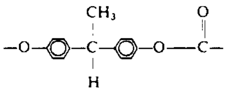
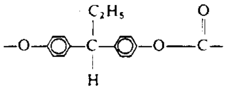
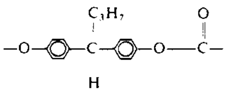
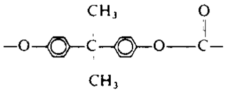
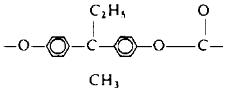
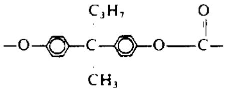


Figure 8. Dynamic mechanical spectra in tension showing the effects of substitution of all the aromatic protons. Data for the halogenated polycarbonates are from Tomikawa and Fujimoto.[13] Data for poly[2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane carbonate] are from Yee and Maxwell.[39]

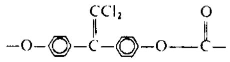
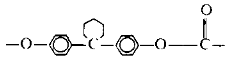
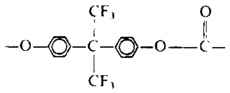
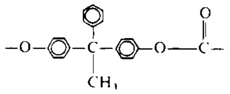
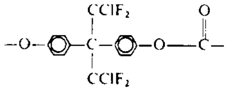
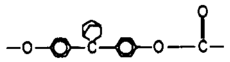
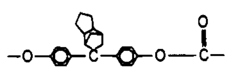
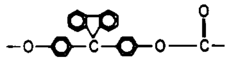
Of greater relevance to the problem at hand, however, is the behavior of the γ dispersions after the methylene substitution is made. In neither case has there been a significant change in the temperature at which the γ loss

Table II

Part 1
EFFECTS OF SUBSTITUTING THE ISOPROPYLIDENE GROUP BY MORE FLEXIBLE GROUPS

Structure	T_g °C	T β °C	T γ °C	Ea(γ) Kcal/Mole	T δ °C	Ref.
	147^d					II
	130^d	70^b	-100^b			II, VII
	128^d	75^a	-95^a		-150^a	I
	123^d					II
	150^a	80^a	-100^a	13		I
	134^b	60^b	-100^b			VII
	130^a		-100^b			II, VII

Part 2
EFFECTS OF SUBSTITUTING THE ISOPROPYLIDENE GROUP BY MORE RIGID OR BULKY GROUPS.
The activation energy shown is for the γ relaxation.

Structure	T_g °C	T β °C	T γ °C	Ea(γ) Kcal/Mole	T δ °C	Ref.
	157^a	60^a	-100^a	13		I
	171^d					II
	176^i		-100^f			III
	180^a		-120^a			IV
	184^i		5^f	17		V
	232^i		-108^f	11.5		III
	247^i	115^f	-110^f	12.3		III
	275^i	200^e	-100^e			VI

References:
- I. This work
- II. Schnell(30)
- III. Massa and Rusanowsky(21)
- IV. Reding, et al.(11)
- V. Massa and Flick(20)
- VI. Kambour, et al.(38)
- VII. Tomikawa and Fujimoto(13)

Notes:
- a. Torsional measurement at 1 Hz
- b. Tensile measurement at 35 Hz
- d. Dilatometric measurement
- e. Tensile measurement at 110 Hz
- f. Tensile measurement at 11 Hz
- i. Thermal analysis

maximum occurs or in the activation energy associated with this process (see Table I). It is readily apparent, therefore, that the γ dispersion cannot be due to the reorientation of the carbonate group independently of the rest of the monomer unit, as is sometimes suggested. The methylene protons are even more sterically hindered by the four aromatic protons than the oxygen in the carbonyl is. If the γ dispersion is due to the reorientation of the formal group, it should be shifted to a higher temperature. The lack of any change indicates that the carbonate or the formal units cannot be the determining factor in the γ dispersion. On the other hand, if the γ motion is due to the phenylene units, then the formal or the carbonate units are constrained to move along with it, although not necessarily with the same amplitude of reorientation. Thus, some relative motion of the methylene or the carbonyl units with respect to the phenylene units is still possible.

Substitution for the Isopropylidene Unit. Table II presents the results of this work and some examples from the literature where the center isopropylidene unit has been substituted. Part 1 includes the polycarbonates with flexible center groups; Part 2 presents those where stiffer and/or bulkier groups have replaced the methyls of the isopropylidene unit. The data from this work as well as some from the literature are presented in Figures 1–3.

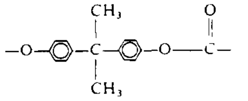
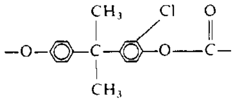
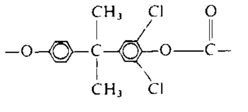
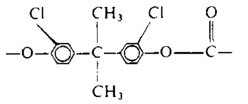
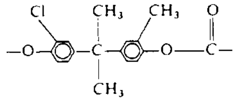
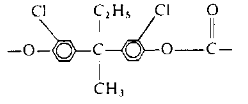
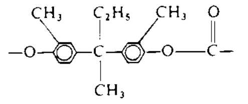
The most obvious effect of the substitutions for the isopropylidene is the change produced in the temperature at which the T_g transition takes place. Substitution by long flexible groups lowers T_g and can easily be rationalized. The incorporation of the highly flexible hydrocarbon chains on the molecule has the effect of increasing the number of degrees of freedom of the molecule. This enhances the chain mobility such that conformational rearrangements are possible to a lower temperature. The concept of the glass transition as an isoviscous state[32] is useful here. The effect is enhanced by increasing the length of the side chain.

The incorporation of the bulky but rigid groups has the effect of raising the T_g. During conformational rearrangements these groups interfere with other segments, thus decreasing the chain mobility such that the glass transition occurs at a higher temperature. Here again the concept of the glass transition as an isoviscous state is useful. The greater the rigidity of the substitutted center group, the more pronounced is the increase seen in T_g, as can be seen in the data in Table II. Additionally, there

Table III

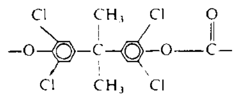
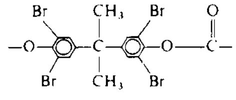
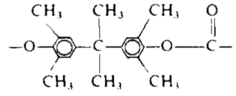
Part 1

EFFECTS OF SUBSTITUTING THE AROMATIC PROTONS BY METHYL OR HALOGEN GROUPS. The activation energy shown is the γ relaxation.

Structure	T_g °C	T β °C	T γ °C	Ea (γ) Kcal/Mole	T δ °C	Ref.
	150^a	80^a	-100^a	13		I
	146^a		5^a	24		I
	186^a	160^a	50 (broad)	(apprx. 17)		I
	146^a		40^a	27		I
	138^a		39^a	21		I
	142^a		50	21	-145	I
	119^a		32	19	-140	I

Part 2

EFFECTS OF SUBSTITUTING THE AROMATIC PROTONS BY METHYL OR HALOGEN GROUPS. The activation energy shown is for the γ relaxation.

Structure	T_g °C	T β °C	T γ °C	Ea(γ) Kcal/Mole	T δ °C	Ref.
	220^a		75^a			II
	225^b		95^b			III
	230^i		112^f	22		IV
	250^b		120^b			III
	203^g		50^g	19		V

References:
- I. This work
- II. Reding, et al.(11)
- III. Tomikawa and Fujimoto(13)
- IV. Massa and Rusanowsky(21)
- V. Yee and Maxwell(39)

Notes:
- a. Torsional measurement at 1 Hz
- b. Tensile measurement at 3.5 Hz
- f. Tensile measurement at 11 Hz
- g. Tensile measurement at 1 Hz
- i. Thermal analysis measurement

may be a contribution due to the polarity of the substituted groups, similar to the effect produced by having a carbonyl rather than a methylene in the backbone, with a concomitant increase in the interchain forces. The 1,1-cyclohexylidene bisphenol polycarbonate has a lower T_g than the acetophenone polycarbonate because the cyclohexyl group has the greater flexibility and hence is less able to impede the relative motions of neighboring molecules. In similar fashion, substitution by the highly rigid norbornane group results in a still higher T_g.

It is instructive to contrast the effects of norbornyl, chloral, and tetrafluorodichloro substitution on the central carbon on the γ relaxation (Figure 3). The γ peaks of the two former polymers are at roughly the same temperature as the unsubstituted BPA-PC, whereas that of the latter is shifted up by nearly 100 °C. It is reasonable to suppose that the origins of the γ relaxations of the BPA, the norbornyl, and the chloral polycarbonates are the same. In that case, the γ relaxation cannot be due only to the motion of the methyl group substitutions because the norbornyl and the chloral groups clearly cannot rotate with respect to the central carbon they are attached to, unlike the methyl groups of BPA. That leaves motions of the phenyl groups as the principal cause of the γ relaxation (without precluding the motion of the other groups along with these motions). That this is the case is shown unambiguously when the effects of substitutions on the phenyl rings are considered in the next section. However, the phenyl rings in BPA-PC have two possible modes of action, viz., rotation with respect to the axis joining the 1,4-phenyl positions, and motion of the two rings and the central group as a unit. Both types of possible motions find support in NMR relaxation studies. Phenyl ring rotation or oscillation was first suggested by Garfield in line-narrowing studies in the solid state,[19] then by Jones and co-workers in dilute-solution work,[40] and most recently by Inglefield et al. in chloral polycarbonate in the solid state.[41] The latter work is unambiguous and most convincing. Motion of the two rings and the central group as a unit was first suggested by Davenport and Manuel in line-narrowing studies on BPA-PC,[28] and supported by Schaefer and co-workers[29] in high-resolution NMR studies on the solid. While clear evidence of ring rotation is provided by the study by Inglefield et al. on chloral polycarbonate, such a motion is much more difficult in the norbornyl polycarbonate. Examination of a framework molecular model of this polymer reveals strong steric hindrances to ring rotation between the 2,6-aromatic protons and some of the protons on the norbornyl group oriented toward the rings. Some highly synchronous wagging and contortion of the norbornyl group would be required to accommodate the ring rotation. Examination of a model for the chloral polycarbonate reveals that a similar motion is much less restricted. Yet both their mechanical γ peaks are at the same location and have similar activation energies. The high-resolution NMR spectra of the BPA and the norbornyl polycarbonates are also rather similar.[29] The double bond renders any rotational motion of the chloral unit highly unlikely, and at the same time imparts a partial double-bond character to the bonds joining the phenylene rings to the central carbon. Evidence that such a partial double-bond character exists is provided by UV spectra of the characteristic phenylene ring absorption in the 250-nm region. The absorption peak in the chloral is shifted to longer wavelengths and exhibits a significantly higher extinction coefficient.[37] Further evidence that the rotation of the phenylene rings might be more difficult in the chloral than in the BPA polycarbonate is found in the solution NMR work by Jones and co-workers,[40] who found that phenylene ring rotation relaxation time is about a factor of 2 longer in the chloral than in the BPA polycarbonate. If the γ dispersion is due to the primarily rotational motion of the phenylene groups about the oxygen–phenyl–carbon axis, i.e., relative motion with respect to the central carbon, the above conditions should increase the activation energy; but the data do not support this hypothesis.

These considerations and others described in this paper prompt us to assign the mechanical γ relaxation to the motion of the rings and the central group as a unit. This assignment, though in apparent contradiction to the interpretations of some other workers, does not necessarily exclude other modes of motion, notably phenyl ring rotation. This point will be considered in greater detail in the Discussion.

We now consider the case of the tetrafluorodichloro polycarbonate (F_4Cl_2-PC). The γ relaxation of this polymer is shifted to a significantly higher temperature[20] relative to others in Figure 3. This shift might be taken as evidence that the very bulky halide groups are hindering the rotation of the phenyl rings. The supposition that the halide groups provide stronger steric hindrance to ring rotation is undoubtedly true; but then the same might be said of the norbornyl groups considered above, where, in contrast, the γ peak is not shifted. Thus, the rise in γ relaxation temperature in F_4Cl_2-PC is perhaps not due to the increased steric hindrance to ring rotation, but some other factor. The halide groups are bulky and highly polar. What effect these two factors might have on the ground-state orientation of the various moieties and on the overall conformation is difficult to conjecture without detailed calculations. No crystallographic information is available on this material. No definitive explanation of the differing behavior of this polymer is possible at this point. It may be that the γ motion here requires a higher degree of cooperativity than in the other cases considered here.

Before concluding the subject of the effects of center-group substitution, it should be noted that a dispersion, termed δ, is observed for the polycarbonates tested containing a 2,2-butylidene or a 1,1-propylidene center group, near −150 °C (see Figures 4 and 5). Clear evidence for its existence is shown in Figure 5. This dispersion is not found in polycarbonates with shorter or more rigid center groups and is not noticeably affected by ring substitution. The activation energies where measurable are, at about 7–8 kcal/mol, in the range one would expect for rotation of the pendant ethyl group, and to that motion we ascribe it.

Substitution on the Phenyl Rings. Table III is a compilation of the available relevant data on ring-substituted polycarbonates. The data are presented in Figures 4–8.

One interesting result in the contrast that can be seen is the effect on T_g of mono- and disubstitution. The presence of one or two monosubstituted (symmetric and asymmetric) rings has little effect on T_g. One or two disubstituted rings, however, produce a pronounced rise in T_g. Consideration of the segmental symmetry is useful in explaining this behavior. Monosubstitution leads to an asymmetric segment which can result in less efficient packing and hence more free volume than would be the case for the symmetrically substituted or unsubstituted molecule. As symmetry is restored, the steric effects of the bulky substituted groups apparently begin to assert themselves. The increase in T_g seen when going from one to two disubstitutions can be seen as due probably to the increased moment of inertia and the increase in the number of sterically hindering groups.

With the addition of the ring-substituted data, the motions associated with the γ dispersion begin to be more clearly defined. The participation of the phenyl rings can be suggested unequivocally. The addition of one chlorine raises T_γ by 100 °C and doubles the activation energy of the barrier to the motion. Further chlorine addition continues to raise the temperature of the dispersion. This can also be seen in the cases of methyl substitutions studied.

It is reasonable to suppose that the effect is due to the increased moment of inertia of the rings produced as the substitutions are made. If the effects of two substitutions are examined, it becomes apparent that the type and location of the substituent are relatively unimportant, especially in contrast with the effects due to the degree of substitution. The temperatures of maximum dispersion and the activation energies associated with them do not differ significantly.

While the motion of the phenyl rings can be suggested unequivocally as the principal cause of the γ relaxation, the question of whether it is the independent rotation of the phenyl rings or the motion of the monomer unit as a whole still needs to be addressed. For this purpose it is useful to examine the effects of chloro substitutions on the rings, particularly the contrasting effects of asymmetric mono- and dichloro substitutions. The γ peak for the monochloro-substituted BPA-PC (Figure 6), at 5 °C, about 100 °C higher than the γ peak in unsubstituted BPA-PC, has about the same shape as the other symmetrically substituted PC's in the same figure. There is no question as to whether or not this is a single peak. If the phenyl rings move independently one would expect to see two peaks: one at about −95 °C for the unsubstituted phenyl ring, and one at about 45 °C for the single substitution at the 2-position (see the symetrically substituted tetrachloro-BPA-PC). Clearly there is no evidence that the peak we see at 5 °C is a superposition of two peaks at −95 and at +45 °C. We would be tempted, based on this evidence, to conclude that the two rings must move in concert. Unfortunately, the data for the asymmetrically substituted dichloro-BPA-PC (Figure 7) render such a conclusion somewhat tenuous. Again for the 2,6-disubstituted phenyl we expect a peak at about 80 °C (see Table III, Part 2, for tetrachloro-BPA-PC), and for the unsubstituted ring a peak at −95 °C if the rings move independently. The data show a broad peak centered at around 50 °C, with a slight shoulder between −100 and 0 °C. It should be pointed out that since tan δ is plotted on a logarithmic scale, as is customarily done, the size of the shoulder appears larger than its true magnitude. Nevertheless, the width of the peak, in comparison with that of all other polymers studied here, suggests that it may consist of more than one component. This in turn implies that if the peak is still due to phenyl ring motion then the two types of rings might not be moving in concert. It should be noted here that this suggested asynchronous motion of the two rings is contrary to the finding of most of the recent studies.[19,28,29,40] A possible cause for this unique behavior may be that the asymmetric substitution of bulky polar groups changes the solid structure and the long-range interactions. That such may be the case is evidenced by the unusually high T_g of this polymer in comparison with the other disubstituted polycarbonates (Figure 7).

The preponderance of evidence produced thus far by dynamic mechanical studies appears to favor the thesis that the motion of the monomer unit as a whole is the origin of the *mechanical* γ relaxation, while some evidence exists to support the other thesis that the rotation or oscillation of the phenyl rings is the origin. Both theses find support in NMR studies. The question of whether or not dynamic mechanical and NMR studies necessarily probe the same molecular motions (and therefore can be used to support each other) will be discussed in the final section.

The β Relaxation. As defined above, the β relaxation is that which occurs at temperatures intermediate to the α and γ relaxations. We have briefly alluded to two types of β relaxations. The first type can be traced to certain motions of various moieties in the molecule or even to the less specific cooperative or local mode motions.[1] To distinguish the first type from the second type we use the following operational definition: it cannot be substantially eliminated upon annealing at a temperature lower than but close to T_g. The second type, on the contrary, can be systematically reduced in amplitude upon annealing. This aspect of annealing has been thoroughly discussed by Struik.[33] The second type of relaxation probably has as its origin defects in packing upon rapid quenching from the melt state, as has been discussed by Goldstein.[34] Annealing has the effect of reducing the population of defects, as attested to by the concomitant increase in the bulk density; hence its influence on the relaxation amplitude. The results from this work, as well as those from the literature, demonstrate that the β relaxation cannot always be detected. This is generally the case where the γ relaxation occurs at temperatures close to the α relaxation, say, within 100 °C of each other. The width of these two relaxations are such that detection of the usually low-amplitude β relaxation is all but impossible. One could go to very low frequencies, say, 0.001 Hz, and hope that this would shift the γ relaxation to a substantially lower temperature and, thereby, reveal the β relaxation. But then, if the β relaxation is of the second type which is sensitive to physical aging, which is quite likely, the time scale of the experiment might be so long, i.e., of the order of 10^4 s, that the β relaxation would be annealed out before its detection. In those cases where the γ relaxation is at substantially lower temperature than the α relaxation, say 150 °C or more, a β relaxation is always detected, with the possible exception of the polyformal of the chloral-substituted BPA (see Figure 1). Even here, the possible existence of a β relaxation cannot be entirely ruled out since the α relaxation is relatively close to the γ relaxation. Furthermore, if a β relaxation exists, its peak is close to room temperature, and storage at this temperature might have reduced its amplitude.

Our operational definition of the two types of β relaxations has already suggested ways to investigate the origin of those which are detected in this work. This, however, was not done. It will be the subject of a future effort. However, in view of our interpretations of the γ relaxation as the motion of entire monomer units, the existence of β motions of the first type of higher activation energy than the γ relaxation is quite unlikely. This suggests that the β relaxations we have detected are all of the second type. This interpretation finds support in the data from the dynamic mechanical studies by Illers and Breuer,[9,10] Golden et al.,[24] LeGrand and Erhardt,[23] and Allen et al.[25] and, more recently, in the dielectric study by Watts and Perry.[35]

Final Discussion and Conclusions

The results presented here as well as those from literature sources have allowed us to draw certain tentative conclusions as to the effect of structural variations on the dynamic mechanical spectra of polycarbonates and the nature of the relaxations. The conclusions have been arrived at largely without having to resort to NMR information. It is commonly assumed that the various dynamical techniques probe the same molecular motions in different time scales but yield identical information. Indeed, use is often made of relaxation maps where relaxation peaks at different temperatures and frequencies are plotted with data originating from various techniques.[2] It is perhaps relevant to discuss the issue of whether or not in every case NMR and DMS are necessarily probing the same motions. Only by doing so can it be decided as to whether or not NMR results should be included as relevant material in arriving at conclusions. For this purpose some recent NMR studies on polycarbonate will be very briefly discussed here. It is not the purpose of this paper to discuss the merits of the various NMR techniques and interpretations. The aim is to contrast the results between DMS and NMR studies and among the various NMR studies.

Inglefield et al.[41] studied the NMR spectra of chloral polycarbonate in the solid state, and Davenport and Manuel[28] studied, using similar techniques and apparently in the same time scale, BPA-PC, also in the solid state. The resultant second-moment spectra are very similar in shape but are shifted by approximately 100 °C in temperature. In contrast, the dynamic mechanical spectra for these two materials are very similar in the γ-relaxation region. The fact that the two groups of NMR workers have come to very different conclusions is irrelevant here. The significant question is why, if NMR and DMS techniques are probing identical molecular motions, the NMR results should be different while the DMS results are the same. A similar question arises in comparing the solution NMR results from Jones and co-workers[40] with solid DMS results by Massa and Flick[20] on F_4Cl_2 and Cl_4 polycarbonate. The solution NMR results indicate nearly identical correlation times and activation energies for phenyl group motions in the two polymers. Yet the mechanical γ relaxations by DMS differ by over 100 °C and about 5 kcal in activation energies. The temperature difference is obviously sufficiently large to be significant. A possible answer to this contradiction may be that the molecular motions are significantly altered in going from the solution to the solid state. Such an explanation would, however, contradict the notion that the γ motion is largely intramolecular. Again, comparing the results from Inglefield et al.[41] and Jones and co-workers[40] and this work on chloral polycarbonate, the apparent activation energy for the proposed phenyl motion is approximately 4 kcal in solution, approximately 5 kcal in the solid (NMR), and 13 kcal by DMS. While the NMR workers caution against placing too much significance on the numerical value of the activation energy, the difference of over a factor of 2 between the two types of results is perhaps worthy of contemplation. Finally, some recent preliminary investigations by Jones and co-workers[42] on BPA-polyformal indicate that the substitution of the carbonyl group by the methylene group has resulted in a completely different NMR spectrum; yet the DMS results presented here are identical in the γ relaxation region. The conclusion that can be drawn from these comparisons is quite clear: NMR and DMS techniques do not necessarily probe the same molecular motions even after the proper frequency differences have been taken into account.

The reason the two dynamical techniques do not necessarily probe the same molecular motions is considered here. There are perhaps two important aspects to the description of molecular motions in the solid: kinematics and dynamics. In kinematics one finds out what molecular motions are impossible. In dynamics one finds out the specific nature of a given motion, e.g., whether a motion is over an energy barrier (aperiodic) or oscillating in a potential well (periodic), and the rate at which such motions take place. It is clear that the range of motions is large, from the small oscillations of, say, methyl groups in an intramolecular potential to long-range cooperative motions involving multiple monomer units. This range of motions would require different dynamical techniques to probe. Thus, in NMR relaxation experiments the magnetization correlation function $C_M(t)$ is found:

$$C_M(t) = \langle M(t)M(0)\rangle$$

Similarly in DMS the strain correlation function $C_\epsilon(t)$ is found:

$$C_\epsilon(t) = \langle \epsilon(t)\epsilon(0)\rangle$$

It is clear that there is no a priori way of knowing if $C_M(t)$ and $C_\epsilon(t)$ are identical. In fact, one would expect that they are different, owing to two factors: first, NMR probes short-range interactions, whereas, DMS can probe long-range effects; second, DMS causes a relative displacement of the molecular segments, thus distorting some potentials, whereas, NMR is coupled to the spin of nuclei, with a negligible effect on the molecular motions themselves. Thus, in principle, NMR and DMS as well as other dynamical and scattering techniques complement each other in providing kinematic and dynamic information. In practice, however, an accurate description of molecular motions depends on the existence of theories dealing with the coupling between the probes and the molecular motions. In NMR this theory is somewhat better developed, although far from being entirely satisfactory. In DMS there is no theory at all, and, therefore, the bulk of DMS work is phenomenological, and only in rare cases are the assignments of molecular motions well substantiated. Yet there is no reason to insist that NMR and DMS must agree completely, owing to the foregoing discussion on $C_M(t)$ and $C_\epsilon(t)$. DMS, in spite of the lack of a theoretical foundation, has certain unique advantages: it measures motions under deformational stresses, and it is, therefore, more closely relatable to mechanical properties, the chief impetus of this and many other investigations. It also measures motions with long-range coupling which are of special importance to mechanical properties.

Taken by themselves, the results of each type of substitution made are suggestive but inadequate clues to the nature and extent of the cooperative motions involved in producing the γ dispersion. Viewed together, and taking into account the work of others in the literature, the picture begins to take on greater substance. The ring-substituted polycarbonates tell us that some sort of concerted motion of both phenyl rings is most probably taking place. This cannot happen, of course, without concurrent motion of some kind, i.e., of one of the groups between them, the isopropylidene or the carbonate. It has already been noted in comparison with the polyformals that the contribution of the carbonate to the mechanical loss is apparently small. This suggests that, while most likely the carbonate unit undergoes a reorientation, this motion is controlled by the larger motion of the phenylene rings. The notion of the motion of the isopropylidene unit might also appear appealing. After all, it might be reasonably supposed that if the center group undergoes motion, an increase in its mass or bulkiness might at least raise the temperature of the dispersion. This, however, does not seem the case. The following explanation is offered. The polymers investigated are all in the glassy state resulting from cooling from the melt state. In the melt state all rotational motions are allowed. The bulkier molecules have, therefore, reserved room necessary for their motion. This "reserved room" presumably persists into the glassy state, and if the γ motion is in the domain of available volume, little or no steric effect would be noticed. As the extent of motion occurring at γ is likely to be rather limited, this does not seem unreasonable. Furthermore, the general absence of effect on γ of substitution of more rigid groups on the central carbon suggests the lack of relative motion of the phenylene rings about it. This would have the effect of ensuring both the cooperativity of the phenyl group motion and the participation of the center group in it.

On the whole, therefore, it appears likely that the γ dispersion arises from motions involving the displacement of the entire monomer unit. The exceptions have already been noted. Cooperativity between adjacent monomer units along the chain and on neighboring chains becomes a necessary hypothesis. This hypothesis is made more plausible by the recent discovery that the γ dispersion has even stronger bulk relaxation than shear relaxation.[36] It should be emphasized that while a proposal has been offered to explain the mechanical γ relaxation, the motion of the phenyl groups about their rotational axes is not precluded. It may be that while a rapid ring rotation is going on, the entire monomer unit is also moving slowly.

We support the view that the inception of the γ dispersion together with its associated main-chain motion at low temperature is a prerequisite for a tough polymer. In the case of polycarbonate, it seems apparent that improved high-temperature performance, as reflected by T_g, is best obtained in a fashion that does not restrict the low-temperature motions. From the results reported here, it can be suggested that center-group substitutions will be of the greatest utility in achieving this goal.

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References and Notes

(1) Kambour, R. P.; Robertson, R. E. In "Polymer Science"; Jenkins, A. D., Ed.; North-Holland Publishing Co.: Amsterdam, 1972; p 687.
(2) McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: London, 1967; Chapter 13.
(3) Ravetti, R.; Gerberich, W. W.; Hutchinson, T. E. *J. Mater. Sci.* **1975**, *10*, 1441.
(4) (a) Gerberich, W. W.; Martin, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 897. (b) Martin, G. C.; Gerberich, W. W. *J. Mater. Sci.* **1976**, *11*, 231.
(5) (a) Bauwens-Crowet, C.; Bauwens, J. C.; Homes, G. *J. Polym. Sci., Part A-2* **1969**, *7*, 735. (b) Bauwens, J. C. *J. Mater. Sci.* **1972**, *7*, 577. (c) Bauwens-Crowet, C.; Oats, J. M.; Bauwens, J. C. *Ibid.* **1974**, *9*, 1197.
(6) Kastelic, J. R.; Baer, E. *J. Macromol. Sci., Phys.* **1973**, *B7*, 679.
(7) Neki, K.; Geil, P. H. *J. Macromol. Sci., Phys.* **1973**, *B8*, 295.
(8) Brady, T. E.; Yeh, G. S. Y. *J. Macromol. Sci., Phys.* **1974**, *B9*, 659.
(9) Illers, K. H.; Breuer, H. *Kolloid-Z.* **1961**, *176*, 110.
(10) Illers, K. H.; Breuer, H. *J. Colloid Sci.* **1963**, *18*, 1.
(11) Reding, F. P.; Faucher, J. A.; Whitman, R. D. *J. Polym. Sci.* **1961**, *54*, 556.
(12) Nielsen, L. E. In "Mechanical Properties of Polymers and Composites"; Marcel Dekker: New York, 1974; p 224.
(13) Tomikawa, M.; Fujimoto, N. *Kobunshi Kagaku* **1968**, *25*, 625.
(14) Muller, F. H.; Huff, K. *Kolloid-Z.* **1959**, *164*, 34.
(15) Krum, F.; Muller, F. H. *Kolloid-Z.* **1959**, *164*, 81.
(16) Bussink, J.; Heijboer, J. In "Physics of Non-Crystalline Solids"; Prins, J. A.; Ed.; North-Holland Publishing Co.: Amsterdam, 1965; p 388.
(17) Matsuoka, S.; Ishida, Y. *J. Polym. Sci., Part C* **1966**, *14*, 247.
(18) Phillips, D. W.; North, A. M.; Pethrick, R. A. *J. Polym. Sci.* **1977**, *21*, 1859.

Macromolecules 1981, *14*, 64–68

(19) Garfield, L. J. *J. Polym. Sci., Part C* **1970**, *No. 30*, 551.
(20) Massa, D. J.; Flick, J. R. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1973**, *14* (2), 1249.
(21) Massa, D. J.; Rusanowsky, P. P. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1976**, *17* (2), 184.
(22) LeGrand, D. G. *J. Appl. Polym. Sci.* **1969**, *13*, 2129.
(23) LeGrand, D. G.; Erhardt, P. F. *J. Appl. Polym. Sci.* **1969**, *13*, 1707.
(24) Golden, J. H.; Hammant, B. L.; Hazell, E. A. *J. Appl. Polym. Sci.* **1967**, *11*, 1571.
(25) Allen, G.; Morley, D. C. W.; Williams, T. *J. Mater. Sci.* **1973**, *8*, 1449.
(26) Ryan, J. T. *Polym. Eng. Sci.* **1978**, *18*, 264.
(27) Lunn, A. C.; Yannas, I. V. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 2189.
(28) Davenport, R. A.; Manuel, A. J. *Polymer* **1977**, *18*, 557.
(29) (a) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384. (b) Schaefer, J. In *Top. Carbon-13 NMR Spectrosc.* **1979**, *3*.
(30) Schnell, H. "Chemistry and Physics of Polycarbonates"; Interscience: New York, 1964.
(31) Davis, W. M.; Macosko, C. W. *Polym. Eng. Sci.* **1977**, *17*, 32.
(32) Lipatov, Y. *Adv. Polym. Sci.* **1978**, *26*, 63.
(33) Struik, L. C. E. "Physical Aging in Amorphous Polymers and Other Materials"; Elsevier: Amsterdam, 1978.
(34) Goldstein, M. In "Amorphous Materials"; Douglas, R. W., Ellis, B., Eds.; Wiley-Interscience: London, 1972; p 23.
(35) Watts, D. C.; Perry, E. P. *Polymer* **1978**, *19*, 248.
(36) Yee, A. F., unpublished results. Also see: Yee, A. F.; Takemori, M. T. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (1), 758. Yee, A. F. *Ibid.* **1980**, *21* (2), 29.
(37) Factor, A. General Electric Co., Research and Development Center, Chemical Laboratory, unpublished results.
(38) Kambour, R. P.; Faulkner, D.; Kampf, E. E.; Miller, S.; Niznik, G. E.; Shultz, A. R. *Adv. Chem. Ser.* **1976**, *No. 154*, 312.
(39) Yee, A. F.; Maxwell, M. A. *J. Macromol. Sci., Phys.* **1980**, *B17*, 543.
(40) (a) Jones, A. A.; Bisceglia, M. *Macromolecules* **1979**, *12*, 1136. (b) O'Gara, J. F.; Desjardins, S. G.; Jones, A. A. *Macromolecules* **1981**, *14*, 64.
(41) Inglefield, P. J. T.; Jones, A. A.; Lubianez, R. P.; O'Gara, J. F., paper accepted by *Macromolecules.*
(42) Jones, A. A., private communication.
(43) Tonelli, A. *Macromolecules* **1972**, *5*, 558.

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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