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Local Molecular Motions in Glassy and Dissolved Polycarbonates

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ABSTRACT: The spin relaxation and dynamical mechanical data on the phenyl and methyl group rotation in bisphenol A polycarbonates are analyzed in the framework of the coupling model of relaxation, taking into consideration the presence of an inhomogeneous distribution of relaxation times in these local motions suggested by dipolar rotational spin-echo ^{13}C NMR of Schaefer and co-workers, pulsed deuteron NMR of Spiess, and carbon-13 chemical shift anisotropy line shapes of Jones et al. It is important to have a model that can relate quantitatively the difference in the relaxation characteristics of these local motions in both glassy and dilute solution polycarbonates. Preferably, the model should also relate theoretical calculations of backbone conformation states in these glassy polymers to the activation energy and preexponential factor obtained from spin relaxation and dynamic mechanical measurements. A model based on the coupling model generalized to include an inhomogeneous distribution of "primitive" relaxation times is shown to be able to explain and correlate the known facts.

Introduction

Recently the study of secondary relaxations due to local molecular motions in polycarbonates of bisphenol A (BPA) has intensified.[1-12] Of particular interest is the phenylene ring related motion which shows up prominently in dynamic mechanical measurements[1,6,9] of the glassy state. This secondary relaxation is strongly correlated with the high-impact strength of BPA polycarbonate.[1] Hence there is interest in the relation between bulk mechanical properties and the facile phenylene ring motions in the glass. The local molecular motions in glassy polycarbonates have been probed by a number of different techniques including dielectric relaxation,[13] dynamic mechanical measurements,[1,9] carbon-13 line-width studies,[2] ^{13}C spin-lattice relaxation,[3] dipolar rotational spin-echo ^{13}C NMR,[4,5] proton NMR relaxation,[6] pulsed deuteron NMR line-shape analysis,[10,12] and carbon-13 chemical shift anisotropy line-shape analysis.[8,11] The results of these diversely different measurements indicate large departure from exponential relaxation behavior with the possibility of either a broad distribution of relaxation times or an inherently nonexponential decay. The temperature dependence of the effective relaxation time τ^* is Arrhenius

$$\tau^* = \tau_\infty^* \exp(E_a^*/RT) \qquad (1)$$

where E_a^* and τ_∞^* have been determined to be 48-50 kJ/mol and 1.06×10^{-16} s, respectively.[6,8,11]

The same motions have been studied also in dilute solutions of polycarbonates by NMR spin-lattice relaxations.[14-18] Several structurally related polycarbonates of bisphenol A have been investigated. These include the poly [2,2-bis(4-hydroxyphenyl)propanecarbonate], abbreviated as BPA, and several structural derivatives of it. This solution spin relaxation study provides insight into the local motions of the phenylene group and the methyl group. The time scales and the activation energies of the phenylene motion in BPA and chloral are very different in the dilute solution and in the bulk of the same glassy polymer. The dilute solution activation energy of phenyl motion is 13 ± 5 kJ/mol for BPA and 15 ± 5 kJ/mol for chloral from one study using $CDCl_3$ as solvent.[14] In a later study using $C_2D_2Cl_4$ as the solvent the activation energies increase to 21 kJ/mol for BPA and 17 kJ/mol for chloral[15] (see Table I). We follow the suggestion of ref 15 that the increase in the activation energies by about 5 kJ/mol is consistent with the nature of the solvent change because $C_2D_2Cl_4$ is more viscous than the $CDCl_3$ used before. The relationships between these quantities in solution and in bulk that characterize the rate of local motion are intriguing and need to be addressed.

Table I
E_a and τ_∞ for Phenyl and Methyl Group Rotations in Two Structurally Related *Dissolved* Polycarbonates[a]

	phenyl		methyl	
structure	E_a, kJ/mol	$10^{13}\tau_\infty$, s	E_a, kJ/mol	$10^{13}\tau_\infty$, s
BPA	13 ± 5[c]	6.2	22 ± 5	0.15
			19[b]	0.69
chloral	15 ± 5	7.1	[d]	[d]

[a] From O'Gara et al.[14] [b] From ref 12 in bulk polycarbonate. [c] This should be compared with the SCF-MO calcn. of Bendler[6,20] of 13.8 kJ/mol. [d] Not applicable.

Theoretical calculations of the phenylene ring motion in BPA and chloral polycarbonates have been undertaken by Tonelli[18] and by Bendler.[6,20] The extensive calculations of the latter support the findings of the former that phenylene ring motion occurs quite easily and the calculated value of the activation energy of pseudorotation about the carbonate unit is about 10 kJ/mol. The calculated cis-trans isomerization involving the 7-6-4-5 motion given by MNDO and ab intitio (Gaussian) methods[6] retains the spatial orientation of the C_1C_4 phenylene axis and causes phenylene rotational motion. On the basis of this result, Jones[21] has gone further to propose the exchange of a cis-trans (or trans-cis) conformation of the carbonate with a trans-trans conformation of a neighboring carbonate. This exchange is produced by rotation about one of the CO bonds in each of the two carbonate groups. As rotation about the CO bond occurs, the phenylene group attached to the other side of the same carbonate group flips about its C_1C_4 axis. The calculated value 10 kJ/mol of the activation energy[6,20] is in good agreement with the experimental value from dilute solution studies but is much smaller than 50 kJ/mol obtained for glassy bulk BPA polycarbonate.[1-13] The large difference of the activation energies between MNDO theoretical calculations and experimental data of bulk BPA is another problem that has to be resolved in polycarbonates.

A few years ago, in a collaborative effort with others,[6] we tried to interpret some of the experimental aspects including those described above that were available to us in 1982 with a molecular model of phenylene ring mot-

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ion[19,20] and a model of relaxation.[22] This relaxation model was then called the CSM model and is now more generally known as the coupling model[23] through its applications to a number of other problems in polymer physics.[23-27] The coupling model considers a primitive relaxation mode such as the cis-trans isomerization and its associated phenylene group motion and its coupling to other molecular units in addition to the conventional heat bath. The heat bath normally identified with molecular vibrations enables the phenylene ring to relax through its motion associated with the cis/trans isomerization.[6] At times short compared with a time ω_c^{-1} characteristic of the nature of the coupling, cooperativity of other molecular units in response to the relaxation associated with the phenylene group rotation has not yet started. The primitive mode interacts with the heat bath alone and relaxation proceeds with a rate

$$W_0 = \omega_\infty \exp(-E_a/RT) \tag{2}$$

which will be referred to as the primitive rate $W_0 \equiv 1/\tau_0$. In eq 2, ω_∞ is the "attempt frequency" of the cis-trans isomerization and E_a is the activation energy determined by the molecular potentials and can be identified with any acceptable Hartree-Fock theoretical calculations. In the glass, at longer times $t > \omega_c^{-1}$, coupling of the relaxing process with the other molecular units has to be considered. The coupling can be viewed as additional constraints on the motion in phase space of the cis-trans isomerization, and hence it slows down the relaxation process and reduces the primitive rate W_0. Physical models[23] have been constructed to show that the reduced relaxation rate for $\omega_c t > 1$ is time dependent, having the form of $W(t) \equiv W_0 f(t)$ with $f(t) = (\omega_c t)^{-n}$ where $0 < n < 1$. The actual value of the coupling parameter n is proportional to both the strength of the interaction of the phenylene ring with the other molecular units and the degree of complexity of the surrounding.

Both the strength of molecular interaction and the degree of complexity is much larger in the glassy bulk polymer than in the dissolved polymer at low concentration. In the limit of dilute solution, the degree of complexity due to polymer molecular crowding and interactions is severly reduced, and we expect n to be nearly zero. In other words the infinite dilution limit corresponds to an isolated chain in a simple surrounding consisting of the solvent which can be considered as the heat bath contributing a friction factor for the polymer motion. The relaxation rate is not slowed down at any time from its primitive relaxation rate W'_0 in the solvent. The normalized relaxation function is the familiar exponential $\exp(-W'_0 t)$.

Returning to bulk polymer, the discussion on the relaxation rate can be summarized by a time-dependent relaxation rate:

$$W(t) = \begin{matrix} W_0 & \omega_c t < 1 \\ W_0(\omega_c t)^{-n} & \omega_c t > 1 \end{matrix} \tag{3}$$

The correlation function $Q(t)$ for the phenylene group motion associated with the cis-trans isomerization relaxation obeys the rate equation

$$\mathrm{d}Q/\mathrm{d}t = -W(t)Q \tag{4}$$

If $Q(t)$ is rewritten as $Q(0)\phi(t)$ where $\phi(t)$ is the normalized relaxation function, then solution of eq 4 with $W(t)$ given by eq 3 gives

$$\phi(t) = \exp[-t/\tau_0] \quad \text{for } \omega_c t < 1 \tag{5}$$

$$\phi(t) = \exp[-(t/\tau^*)^{1-n}] \quad \text{for } \omega_c t > 1 \tag{6}$$

where

$$\tau^* = [(1-n)\omega_c^{\,n}\tau_0]^{1/(1-n)} \tag{7}$$

Here $\tau_0 \equiv W_0^{-1}$. Furthermore, the solution has the dominance property[23] that if $\omega_c\tau_0 \gg 1$ the Kohlrausch-Williams-Watts (KWW) function in eq 6 dominates the relaxation in the sense that it describes almost the entire relaxation of $\phi(t)$ from the unrelaxed value of unity to the relaxed value of zero. Under the reverse condition of $\omega_c\tau_0 \ll 1$, the exponential function in eq 5 dominates the relaxation instead. We shall see a posteriori that ω_c is of the order of 10^{11} s^{-1} for phenylene group relaxation in bulk glassy BPA and chloral polycarbonates. All experiments on phenylene group relaxation performed in bulk polycarbonates are under the condition $\omega_c\tau_0 \gg 1$, and the KWW function therefore dominates.

Equations 5-7 represent the *simplest version* of the coupling model.[22] All phenylene rings in the glass are assumed to have the *same* primitive rate W_0 given by eq 2. There is no absolute guarantee for the validity of this assumption although for many other relaxations in many complex systems, the presence of short-range order often validates this assumption. For example the coupling model has been previously applied to polymer melts[24-26] where the terminal Rouse mode of the chain replaces the phenylene group motion. If the system is monodisperse, all chains have the same molecular weight and hence the same primitive Rouse rate W_0. Equations 5-7 are immediately applicable to monodisperse polymer melts as evidenced by the success of several applications.[23-26] On the other hand, a polydisperse system with significant molecular weight distribution will have, at the outset, a distribution $\hat{g}(W_0)$ of primitive relaxation rates W_0 or, equivalently, a distribution $g(\tau_0)$ of relaxation times τ_0. Each W_{0i} of the distribution will be modified according to eq 3. The resultant relaxation function is a weighted sum over τ_{0i}. For simplicity in notation, we shall drop the subscript zero for the primitive relaxation times τ_{0i} and employ an integral instead of a discrete sum over the relaxation times. Then the three relations of eq 5-7 become

$$\phi(t) = \int_{-\infty}^{\infty} \mathrm{d}(\log\tau)\, g(\log\tau) e^{-t/\tau} \quad \text{for } \omega_c t < 1 \tag{5$'$}$$

$$\phi(t) = \int_{-\infty}^{\infty} \mathrm{d}(\log\tau)\, g(\log\tau) e^{-(t/\tau^*)^{1-n}} \quad \text{for } \omega_c t > 1 \tag{6$'$}$$

where τ^* in eq 6$'$ is obtained from the relation

$$\tau^* = [(1-n)\omega_c^{\,n}\tau]^{1/(1-n)} \tag{7$'$}$$

Equations 5$'$-7$'$ together with the dominance property[23] represent the *inhomogeneous distribution version* of the coupling model. It has retained the effects due to coupling on relaxation even in the more complicated situation of the presence of an inhomogeneous distribution of primitive relaxation times. If, in the phenylene ring motion problem of glassy bulk BPA polycarbonate, there is residual randomness (see Discussion) that gives rise to an inhomogeneous distribution of primitive W_0 or τ_0, then eq 5$'$-7$'$ are the appropriate ones to be used. The analysis presented below indicates that n is in the range 0.70-0.74 for phenylene ring motion. In contrast, the methyl group motions are not coupled to mechanical deformations and do not contribute to dynamic mechanical loss so that by inference the coupling parameter $n \simeq 0$ for methyl motions.

A previous application[6] of the coupling model to this problem had adopted the simple homogeneous distribution version (eq 5-7). At the time of writing that paper,[6] evidence for the presence or absence of an inhomogeneous distribution of phenylene group relaxation times was not entirely clear.[28] However, the presence of an inhomogeneous distribution of correlation times of phenylene ring motion was established afterwards by several groups[5-12] which we shall return to discuss. The use of the simple version[6] is also motivated by the desire for economy of concepts and parameters invoked to understand several physical phenomena associated with phenylene group motion. It was marginally successful in accounting for the experimental observations in solution and in bulk BPA and chloral and relating them to theoretical calculations of activation energy barriers. However, we noticed[6] even then that the theoretical predictions on the temperature dependences of the dynamical loss modulus and spin–lattice relaxation times T_1 and $T_{1\rho}$, and the frequency dependences of the dielectric loss ϵ'' obtainable from eq 6 never give completely satisfactory agreement with experimental data for *any* Kohlrausch exponent $1 - n$. A compromise choice of $n = 0.80$ in ref 6 was chosen to achieve reasonable fits to the shapes of G'' vs $1/T$ and T_1 or $T_{1\rho}$ vs $1/T$ curves together with an acceptable prediction for the relation between the activation energies of phenylene group motion in solution and in bulk. The relation follows from eq 7 with τ^* and τ_0 given by eq 1 and 2, respectively, and relates E_a^* to E_a by

$$E_a^* = E_a/(1 - n) \tag{8}$$

We expect $n \simeq 0$ in dilute solution and, from eq 8, E_a^* then reduces to E_a. Hence the observed activation energy in dilute solution[14] of 13–15 kJ/mol can approximately be identified with the primitive E_a as obtained by MNDO calculations.[6,19,20] Applying eq 8 again to phenylene group relaxation in the bulk requires the observed activation energy of 50 kJ/mol to be the same as $13/(1 - n)$ or $15/(1 - n)$ kJ/mol, and thus $n = 0.74$ or $n = 0.70$, respectively. The $n = 0.80$ was a compromise choice because the experimental G'' vs $1/T$ peaks and T_1 ($T_{1\rho}$) vs $1/T$ minima are appreciably broader than that predicted from eq 6 with values of $n = 0.70$ or $n = 0.74$. In fact for $n = 0.80$, the predicted G'' peak is still narrower than the experimental data as evidenced from Figure 5 in ref 6. Improvement to this situation was not sought in this[6] and other[8] earlier works because this simple version of the coupling model could already explain semiquantitatively a number of outstanding features of the experimental data. Moreover, there was not enough experimental evidence at that time to indicate which direction an improvement of the theory should be made. Certainly introduction of an inhomogeneous distribution in primitive τ_0 will broaden the predicted G'' peaks and the T_1 and $T_{1\rho}$ minima. This additional element allows the coupling parameter n to be reduced to 0.70 or 0.74 to achieve a better agreement with eq 8 and yet manages to produce an even better fit to the shapes of G'' and ϵ'' peaks and T_1 and $T_{1\rho}$ minima than with $n = 0.80$. This was not carried out in ref 6 and 8 because, at the time of writing these works, experimental evidence for an inhomogeneous distribution was not yet clear.

In 1983, dipolar rotational spin–echo ^{13}C NMR experimental results of bulk polycarbonate were reported by Schaefer and co-workers[4] indicating site heterogeneity. This work was followed by an extensive study[5] that included several other polycarbonates (chloral, formal, norbornyl, and tetrachloro) with essentially the same conclusions of frequency heterogeneity of ring motion. Motional trends in BPA, chloral, and Cl_4 polycarbonates were established also. Later, pulsed deuteron NMR work of Spiess and co-workers[10,12] and analysis of carbon-13 chemical shift anisotropy line shapes by Jones and co-workers[11] have also suggested the presence of an inhomogeneous distribution. These developments have influenced us to incorporate this aspect into the coupling model analysis in the present work and reevaluate our understanding and interpretation of local motions in polycarbonate.

Coupling Model Including Inhomogeneous Distribution

The foundation of the coupling model with the presence of an inhomogeneous distribution of primitive τ's has been discussed in the Introduction. The results are summarized in eq 5′–7′. The integration over a distribution of τ in eq 6′ will, in general, cause $\phi(t)$ to deviate from the Kohlrausch form of eq 6. In the present case the distribution function g is not known a priori. For this reason we proceed by first considering eq 7′ and its implication on data taken in solution[14,15] and bulk.[1-13] In dilute solution we can expect the absence of an inhomogeneous distribution and the vanishing of the value of the coupling parameter n. This is because for local motions, whatever the cause of the inhomogeneous distribution of relaxation times in the glass, it does not persist in dilute solution. Also, in dilute solution separations of the chains have drastically reduced the coupling of the relaxing phenylene group with the surrounding molecular units of other chains. When $n = 0$, eq 7 reduces to the identity $\tau^* = \tau_0$. The spin relaxation measurements of local motions in dilute solutions provide information about the primitive τ_0. Corresponding to eq 2 we write

$$\tau_0 = \tau_\infty \exp(E_a/RT) \tag{9}$$

We summarize the results obtained by O'Gara et al.[14] in dissolved BPA and chloral polycarbonates for phenyl and methyl group rotations in Table I. The modeling of the phenylene group motion in dissolved BPA and chloral polycarbonates as slow, complete anisotropic rotation about the C_1C_4 axis in this early study[14] with one carbon-13 frequency is confirmed by measurements at two Larmor frequencies.[15] However, the same conclusion for a diring-substituted Cl_4 polycarbonate and possibly isopropylidene-group-substituted ClF_2 polycarbonate have been amended.[16-18] Phenylene ring rotation in these two derivatives is better described in terms of restricted rotational diffusion. Actually earlier studies[5,7-12] of molecular motions in bulk polycarbonate and its derivative have reached the conclusion that the free ring rotation is changed to a restricted rotation. The restricted rotation is an extensive π-flip in bulk BPA and chloral polycarbonates. For substituted polycarbonates, Schaefer et al. have found even earlier that the amplitude of the restricted rotation is reduced for norbornylpolycarbonate and much reduced for tetrachloropolycarbonate.[5]

Relaxation maps have been constructed[6,11] showing that proton spin relaxation, NMR line-shape collapse, dielectric loss, and dynamic mechanical loss can all be related in time. The estimates of the ring frequencies above 60 kHz and probably above 300 kHz at room temperature are consistent with the relaxation map. Thus, we are led to the conclusion that although restricted rotation (π-flip) of the ring may be part of a more extensive segmental-like motion responsible for mechanical loss, the ring frequency is the same as that of its parent motion.

The coupling parameter n for the phenylene group motion in the glassy bulk of a particular polycarbonate can now be obtained via eq 8, where E_a^* is taken from the relaxation map made up of dynamical mechanical,[1] spin–lattice relaxation,[5,6,8] and other measurements[7-13] and E_a from dilute solution studies[14,15] summarized in Table I. The results are entered into Table II together with τ_∞^*

Table II
E_a^*, τ_∞^*, and n for Phenyl and Methyl Group Motions in Two Structurally Related *Bulk* Glassy Polycarbonates

	T_γ[e] at 1 Hz	phenyl E_a^*, kJ/mol	phenyl τ_∞^*, s	phenyl n[c]	phenyl ω_c,[d] s^{-1}	methyl E_a^*, kJ/mol	methyl τ_∞^*, s	methyl n
BPA	−100	50 ± 8	4×10^{-17}[a] 1×10^{-16}[b]	0.74	3.4×10^{11} 4.6×10^{11}	19 ± 1[f]	0.7×10^{-13}	0
chloral	−100	50 ± 8	3.4×10^{-16}	0.70	3.0×10^{11}	[g]	[g]	

[a] From relaxation map: log f_{max} vs $1000/T$ plot.[5,8] [b] From CSA line-shape analysis.[11] [c] Obtained from relation $E_a/E_a^* = 1 - n$ with E_a given by Table I. [d] Deduced from eq 7′. [e] From ref 1. [f] From ref 12. [g] Not applicable.

deduced also from experimental data of the bulk.[1,6,8] By inspection of Tables I and II, we can see that BPA and chloral have rather similar variables that characterize the dynamics of the phenylene group motion both in solution and in the bulk. In solution E_a and τ_∞ are quite comparable, and this similarity continues to hold in the bulk for the corresponding variables E_a^* and τ_∞^*. The coupling parameter n is approximately 0.7 and about the same for both. The magnitude of τ_∞ is reasonable for a physical molecular motion such as that involving the phenylene group. The same cannot be said about τ_∞^*. Its order of magnitude of 10^{-16} s is unphysical and an explanation is needed. One explanation follows from eq 7′ which gives rise to two relations: eq 8 and

$$\tau_\infty^* = [(1 - n)\omega_c^{\,n}\tau_\infty]^{1/(1-n)} \qquad (10)$$

For a choice of $\omega_c \simeq 4 \times 10^{11}$ s^{-1}, $n = 0.74$, and $\tau_\infty = 6.2 \times 10^{-13}$ s, taken from Table I, the right-hand side of relation 10 gives correctly the size of τ_∞^*. This procedure of obtaining n and ω_c is repeated for chloral. The results in Table II show that the magnitude of ω_c^{-1} is physically reasonable for the onset of slowing down of phenylene ring relaxation. Also listed in Table II is T_γ, the temperature of the dynamic mechanical relaxation peak attributed to phenylene group motion at 1 Hz. The temperature T_γ characterizes the mobility of the phenylene motion.

After the coupling parameter $n = 0.74$ for BPA has been determined by eq 7′ via its corollary eq 8, we proceed to include an inhomogeneous distribution $g(\log \tau)$ of the primitive τ's as required by the findings of NMR works.[10-12] With the relaxation function $\phi(t)$ given by eq 6′ and 7′ and parameters n and ω_c for BPA taken from Table II, $\phi(t)$ is determined for any distribution in $g(\log \tau)$ at a fixed temperature T. From $\phi(t)$ we can determine a loss modulus $G''(\omega,T)$ by the relation

$$G''(\omega,T) = \Delta G \int_0^\infty \sin \omega t \phi(t)\, dt \qquad (11)$$

After $G''(\omega)$ is calculated for different temperatures in the range of interest, the dynamic loss modulus at any fixed frequency $f \equiv \omega/2\pi$ is obtained from $G''(\omega,T)$ by fixing the frequency. In practice we assume g to be a log Gaussian distribution function as suggested by Schmidt et al.[10] Equations 6′ and 7′ were therefore evaluated with the normalized $g(\log \tau)$ of the form

$$g(\log \tau) = (1/\Delta \sqrt{\pi}) \exp[-(\log \tau - \log \tau_0)^2/\Delta^2] \qquad (12)$$

The maximum of g occurs at $\log \tau_0$, with τ_0 given by eq 9 and parameters from Table I. The width Δ of the log-Gaussian is adjusted until a best fit of the shape of the calculated $G''(\omega,T)$ to measurements is obtained. The constant ΔG in eq 11 was adjusted to obtain the correct height of the loss peak. The value of ΔG is 1.6×10^9 Pa for BPA. Examples of the fits for BPA and chloral at 1 Hz are shown in Figures 1 and 2. The width Δ of the log Gaussian required is 0.87 decade for BPA and also 0.87 decade for chloral. As discussed earlier, the presence of this distribution is consistent with a value of the coupling parameter in the range $n = 0.70$–0.74. This is lower than the compromise choice of $n = 0.80$ used in our earlier work[6] where the inhomogeneous distribution was not used. The predicted primitive activation energies E_a via eq 8 are now in better agreement with the measured values. It would

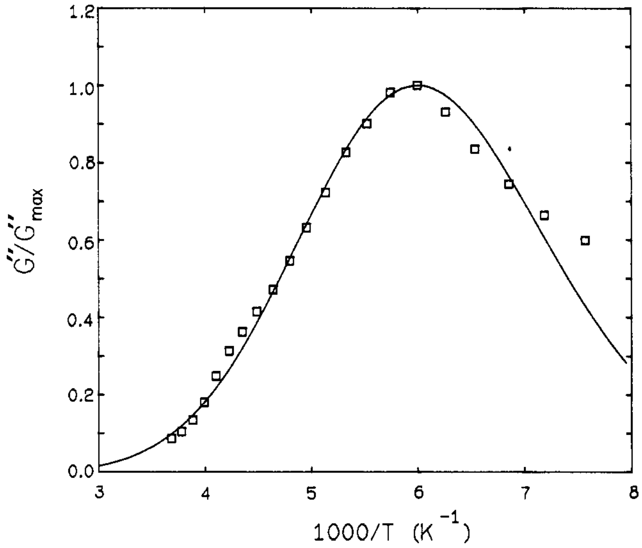

Figure 1. Normalized loss modulus of BPA polycarbonate at 1 Hz plotted versus inverse temperature. Data points are from ref 1. Solid line is calculation by the coupling model with the inclusion of an inhomogeneous log–Gaussian distribution of primitive relaxation times τ. The width of the log–Gaussian distribution is $\Delta = 0.87$. The parameters used are $n = 0.74$, $E_a = 13$ kJ/mol, and $\tau_\infty = 6.2 \times 10^{13}$ s (see Tables I and II).

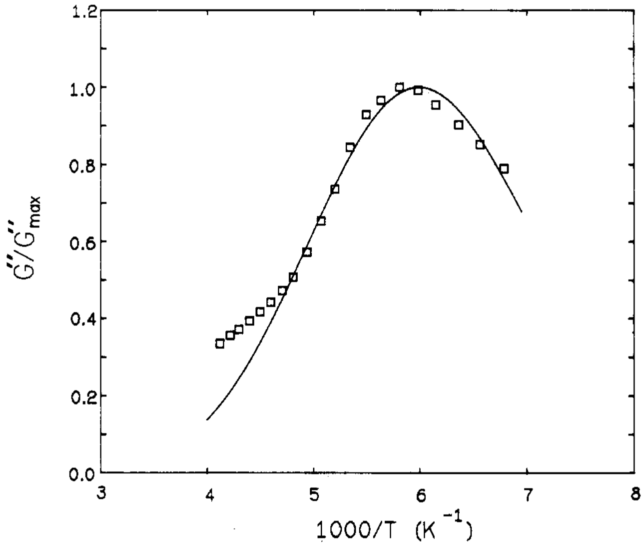

Figure 2. Normalized loss modulus of chloral plotted versus inverse temperature. Data points are from ref 1. Solid line is calculation by the coupling model with the inclusion of an inhomogeneous log Gaussian distribution of primitive relaxation times τ. The width of the distribution is $\Delta = 0.87$. The parameters used are $n = 0.70$, $E_a = 15$ kJ/mol, and $\tau_\infty = 7.1 \times 10^{13}$ s (see Tables I and II).

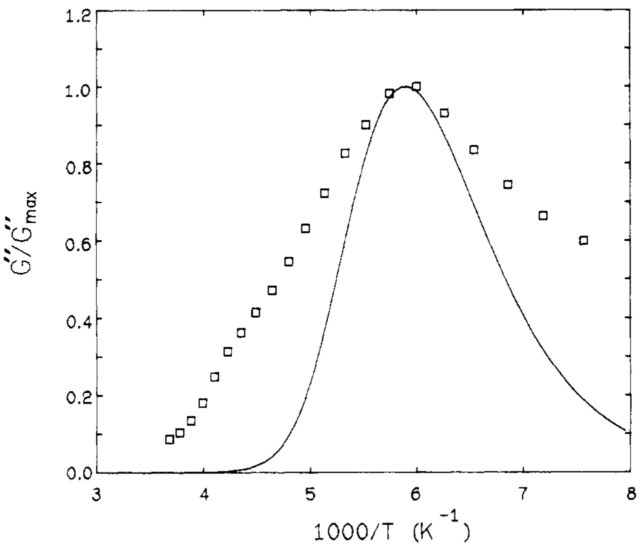

Figure 3. Solid line represents the loss modulus of BPA polycarbonates obtained from the coupling model *without* the inclusion of a distribution of primitive relaxation times. Parameters of the coupling model (other than Δ) are the same as those used in Figure 1. The large discrepancy between calculation and experimental data (squares) provide additional evidence for the presence of an inhomogeneous distribution of the primitive τ's.

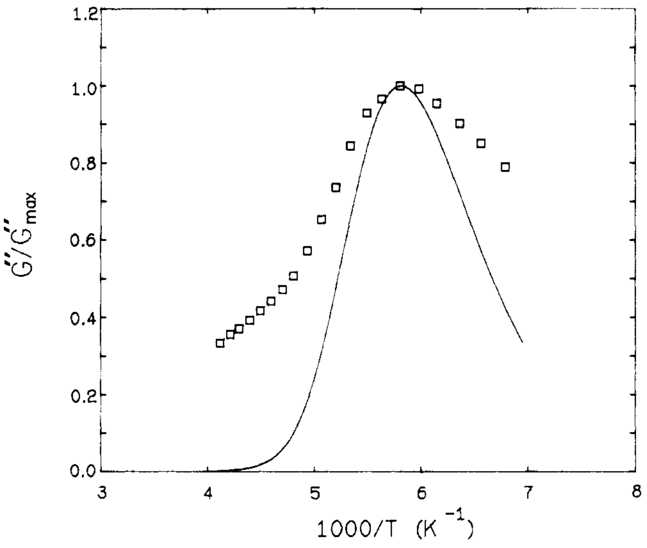

Figure 4. Similar to Figure 3 but for chloral polycarbonate.

be valuable to go a step further and relate the value of $\Delta = 0.87$ deduced from the present coupling model analysis directly to the carbon and deuteron line-shape data.[9-12] This requires further analysis that is beyond the scope of this paper. Figures 3 and 4 present the predictions according to eq 6 and 7 without an inhomogeneous distribution of the primitive τ, for the same n and ω_c values. The G'' predicted in this manner is much narrower than the actual data. This lends support to the presence of an inhomogeneous distribution in τ_0, consistent with NMR data. The coupling model, generalized to include an inhomogeneous distribution in the primitive τ_0's, has improved the understanding of the rather broad and non-Kohlrausch nature of the dynamical loss modulus data. At the same time, the model gives an even better correlation between phenylene ring relaxation data in dilute solution with those in the glassy bulk (Tables I and II). It is worth recalling other successes of the coupling model which is still retained in this analysis using the inhomogeneous distribution version of the coupling model. These include the good agreements obtained[6] for (1) the predicted amount of the motionally modulated second moment of 2.0×10^{-2} mT^2 and experimental value of $(1.5 \pm 0.4) \times 10^{-2}$ mT^2, (2) the predicted temperature dependence of the second moment and experimental data, and (3) the deduced primitive activation energy E_a and the cis–trans isomerization barrier energy obtained by theoretical calculations.[6,19,20]

Methyl Motion

The methyl group motion probed by spin–lattice relaxation in dilute solution by O'Gara et al.[14] has been seen in the bulk also by Schmidt et al.[10] The latter have proposed that the methyl rotation consists of threefold jumps about the C_3 axis. Their line-shape analysis in bulk BPA yields a mean activation energy of 18 kJ/mol for the methyl rotation. This should be compared with the dilute solution value of 22 ± 5 kJ/mol[14] and 21 kJ/mol[15] for BPA, 19 ± 5 kJ/mol,[14] and 20 kJ/mol[18] for Cl_4 BPA and 22.4 kJ/mol for TMBPA.[17] Within experimental errors the activation energy of methyl rotation is the same in dilute solution and in bulk. It follows from eq 8 that the coupling parameter n for methyl rotation in BPA is nearly zero. That is, the relaxation of the methyl group does not couple to its surroundings. This deduction obtained from the coupling model via eq 8 is consistent with the idea that methyl motions are not coupled to mechanical deformations and does not contribute to dynamic mechanical loss and dispersion.[1,9] Even the addition of the plasticized polychlorinated biphenyls, which slows drastically the phenyl group relaxation, has left the methyl relaxation time and its inhomogeneous distribution essentially unchanged.[9,10] The differences between phenylene and methyl groups in contribution to mechanical properties and the effect of a plasticizer should be correlated with the large value of the coupling parameter n for phenylene motion and a vanishing one for methyl motion. The correlation supports the pertinence of n in relating local molecular relaxation to mechanical properties.

The spin–lattice relaxation data[14] of O'Gara et al. on the methyl motion in BPA when analyzed by taking the activation energy to be 18 kJ/mol as given by Schmidt et al. (see Table I) gives the value of 0.7×10^{-13} s for τ_∞ in eq 9. This is close to the value of 1.05×10^{-13} s obtained by O'Gara et al. and the value of 1.5×10^{-13} s obtained by Ratto et al.[18] for τ_∞ of methyl motion in Cl_4. A connection of methyl relaxation in dilute solution to that in the bulk can be made. To demonstrate this, we calculate τ_0 at 163 K for BPA using $\tau_\infty = 0.7 \times 10^{-13}$ s and $E_a = 18$ kJ/mol by eq 9. The value is τ_0 (163 K) $= 7.6 \times 10^{-8}$ s. The corresponding frequency f_0 (163 K) $\equiv (2\pi\tau_0)^{-1}$ (163 K) is 2.1×10^6 Hz. This value obtained by extrapolation from *dilute solution* data is remarkably close to the peak of the log Gaussian distribution of correlation frequencies for the methyl group at 163 K deduced from pulsed deuteron NMR[10,12] in *bulk* BPA. This gives further support that methyl motion is uncoupled to its surrounding, its rate being the same in dilute solution and in bulk.

Discussion

In this work, we have taken into consideration the evidence from dipolar rotational spin-echo ^{13}C NMR,[4,5] pulsed deuteron NMR,[12] and ^{13}C solid-state NMR line-shape[11] studies for the existence of an inhomogeneous distribution of relaxation times for phenylene ring motion in bulk BPA polycarbonate. This feature is incorporated into the coupling model which by itself gives rise to an intrinsic nonexponential relaxation. The result is a superposition of intrinsically nonexponential Kohlrausch relaxation processes $\exp[-(t/\tau^*)^{1-n}]$. The superposition arises from an inhomogeneous distribution $g(\tau)$ of primitive relaxation times τ, where τ^* and τ are related by eq 7′. A distribution of the primitive relaxation times τ for the secondary relaxation such as the phenylene ring motion is not unexpected because of the presence of density fluctuation in a glassy polymer. If holes are used to describe density fluctuations, then the ultrasonic velocity and positronium annihilation data of Malhotra and Pethrick[29] have shown that the average hole has radius of 0.17 nm in polycarbonate. The small-angle X-ray scattering data on PMMA of Curro and Roe[30] have led to an estimate of (0.47 nm)^3 for the hole volume, consistent in the order of magnitude with that of polycarbonate. Most recent measurements in polystyrene photochromic and fluorescence techniques by Victor and Torkelson[31] have given the median of the local free volume in unannealed polystyrene to be (0.65 nm)^3, with over 90% larger than about (0.48 nm)^3 and practically none larger than (0.74 nm)^3. The volume swept out by the motion of the phenylene rings in polycarbonate is comparable with the average size of the density fluctuation. Hence, we expect an inhomogeneous distribution of primitive relaxation times τ. This however is not true for the primary α-relaxation responsible for the glass temperature. The α-relaxation involves segmental motions in which many monomers participate. The volume of the molecular units involved in α-relaxation is much larger than the average hole size. In one theoretical model,[32] the rearranging segment volume of 4.3–6.5 (nm)^3 is proposed for polystyrene which is more than 1 order of magnitude larger than the maximum cutoff size[31] of 0.4 (nm)^3. Effects of density fluctuations on the α-relaxation are averaged out; consequently an inhomogeneous distribution of primitive relaxation times does not arise and only an average free volume leading to an average friction needs to be considered for α-relaxation[9] as is also conventionally done.[33]

The coupling model is still necessary even in the presence of an inhomogeneous distribution of primitive relaxation times. The latter alone cannot explain many pieces of data: the large difference of the activation energies of the phenylene ring motion in the bulk E_a^* and in dilute solution E_a; the activation energy of the phenylene ring motion is smaller than that of the methyl group motion in dilute solution, but the situation is reversed in the bulk; the discrepancy between the measured E_a^* and MNDO and ab initio (Gaussian) calculation of the activation energy;[6] and the unphysical nature of the magnitude of the attempt frequency. Application of the inhomogeneous distribution version of the coupling model has resolved these problems.

We have considered the methyl group relaxation also in dilute solution and bulk polycarbonates. The methyl motion is found to be uncoupled, and the coupling parameter n is nearly zero. This result is consistent with the fact[1,9] that the methyl motion is not coupled to mechanical deformations and does not contribute to dynamical mechanical loss and dispersion.

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Registry No. BPA (copolymer), 25037-45-0; BPA (SRU), 24936-68-3; chloral (copolymer), 29057-43-0; chloral (SRU), 31546-39-1.

References and Notes

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