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Antiplasticization Effects on a Secondary Relaxation in Plasticized Glassy Polycarbonates

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ABSTRACT: Recent deuteron NMR measurements of secondary relaxations in polycarbonates of Bisphenol A plasticized by addition of small-molecule liquids are analyzed and interpreted. In contrast to the primary relaxation, the effect of plasticizer on the secondary relaxation is observed to increase the mean value and spread of the activation energy and average relaxation time as well as dramatically increase the width of the distribution of correlation frequencies, i.e., antiplasticization. The coupling model of relaxation is applied to this data, taking into consideration the presence of an inhomogeneous distribution of relaxation times as suggested by NMR line-shape data. Essentially the same distribution of primitive relaxation times of the model occurs for both the unplasticized and plasticized samples. Most of the effects from an increased concentration of the plasticizers result from an increase in the coupling parameter *n*. This results simultaneously in a shift of the mean relaxation time to longer times, an increase in the mean activation energy, and broadening of the loss function. The mean of the primitive distribution can be related to dilute-solution measurements and calculations of the phenyl ring motion of a single chain. These experimental facts are given a consistent explanation by the model leading to a more precise characterization of antiplasticization.

I. Introduction

There is continued interest in the understanding of the nature of secondary relaxations in polycarbonates of Bisphenol A (BPA).[1-22] Particularly, one would like to find out why one of the secondary relaxations that arises from phenylene ring motions seems to play a role in determining the bulk mechanical properties of the BPA polycarbonate family of polymers.[1,6,9,22-24] These interesting problems related to the secondary relaxations have attracted many investigations using a variety of experimental techniques to elucidate the molecular basis of phenylene ring motions. Much valuable information has been gathered, and a picture of the motions of the phenylene rings has emerged. However, there are still issues to be resolved. In fact, proposed models of phenylene ring motions differ in detail, but all have in common that the motions are considered very local.[2-12] It is difficult to see how this local molecular motion in a chain can contribute to mechanical properties, such as ductility, impact strength, etc., unless it is coupled intermolecularly. The conclusion that the β relaxation is not a pure internal motion but is coupled to the neighboring molecules has not only been reached in the polycarbonates (PC)[1,6,10,21] but also in poly(methyl methacrylate) (PMMA)[25] by simultaneous measurements of the dynamic Young's modulus and the dynamic Poisson's ratio. Techniques based on nuclear magnetic resonance[2-18] can monitor the rotational motions of certain molecular groups, identify the local molecular motion of the phenylene rings, and measure the time scale of the internal molecular motion. The time scale measured is that of the local motion coupled to the bulk.

To model correctly the effect that this coupling to neighboring molecules has on the secondary relaxation is not an easy task because the coupling between molecules is in general dynamic and not static in nature. Local free volume together with its fluctuation in size has been used to model secondary relaxations.[9,22] The concept of free volume for a molecular relaxation process is derived from molecular crowding, which reduces the mobility of the relaxing species. Molecular crowding originates from interchain interactions or couplings. In other words, if interchain interactions were not present, there would be no crowding between molecules to be considered. Thus, local free volume is consistent with coupling between molecules, but it is a consideration that is limited to the static aspects of the latter. The dynamical aspects of molecular coupling are usually left out in the local free-volume model. Nevertheless, density fluctuations[5] do exist in glassy polymers, and if the experimental data is interpreted as local free-volume fluctuations, it would be valuable to know the size of the local free volume and its spread. Data from small-angle X-ray scattering[26] and fluorescence techniques,[27] in PMMA and unannealed polystyrene, have led to an estimate of about $(0.47\ \mathrm{nm})^3$ and $(0.65\ \mathrm{nm})^3$, respectively, for the average volume of the local free volume (hole). Ultrasonic velocity positronium annihilation data[28] have deduced that the average hole has radius of 0.17 nm in polycarbonate. The fluorescence data of PS have indicated the spread of the local free-volume fluctuations:[27] over 90% of the distribution is larger than about $(0.48\ \mathrm{nm})^3$ and practically none larger than $(0.74\ \mathrm{nm})^3$. The sizes of the free-volume fluctuations seem to be much smaller than the volume of molecular units in a chain involved in the segmental or α-relaxation, which is responsible for the glass transition. Hence, for α-relaxations, only the average free volume but not the free-volume fluctuations need to be considered. This has been pointed out repeatedly in the literature.[9,29]

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However, for a secondary relaxation involving bulky molecular groups, the volume swept out by their motion is comparable in magnitude to the local density rarefractions. Both the average free volume and the fluctuations are needed for determination of the relaxation spectrum. This is likely the case for the phenylene ring motions in BPA polycarbonate as judged by the size of the units involved (see Figure 9 of ref 30). Experimentally an inhomogeneous distribution of relaxation times of the phenyl group rotation was confirmed by Schaefer and co-workers,[2-4] by Spiess,[7,10,12] and by Jones et al.[11] by using several different NMR techniques. It is interesting to point out also that an intermolecular distance of 0.55 nm has been inferred from X-ray diffraction data of BPA polycarbonate.[30] This is the same order of magnitude as the linear dimension of the local free volume. Combined consideration of the last two points leads us to conclude that the phenylene ring secondary relaxation in BPA-PC indeed couples intermolecularly to the bulk.

In this work, recent deuteron NMR measurements[9] on secondary relaxations in polycarbonates of Bisphenol A plasticized by addition of small-molecule liquids are analyzed and interpreted by using the "coupling model"[31] of relaxation. The coupling model describes the effects of intermolecular coupling on the basic relaxation rate, W_0, of an intramolecular motion. Sufficiently localized intramolecular motions of a polymer chain in a glass are expected to have an uncoupled (primitive) relaxation rate W_0, which is unaffected by intermolecular coupling. However, as discussed above, secondary relaxations of phenylene rings in BPA-PC involve sufficiently large scale motions, which are impeded by intermolecular coupling. Whereas phenyl ring motion in dilute solution involves complete anisotropic rotation, the corresponding motions in the bulk are sometimes characterized as "restricted rotations". The coupling model is consistent with such effects of intermolecular coupling, although it does not derive them from the details of the molecular motion. The coupling model, based on several different but consistent theoretical approaches, asserts that such intermolecular coupling reduces the uncoupled rate W_0 by a time-dependent factor of the form $(\omega_c t)^{-n}$. This results in a self-similar time-dependent relaxation rate of the form

$$W(t) = W_0(\omega_c t)^{-n} \qquad 0 \le n \le 1 \tag{1}$$

Here ω_c^{-1} is the time scale for the onset of rate slowing down with magnitude determined by the molecular interactions, and the fractional exponent, n, is a measure of the degree of rate slowing.

The primitive rate W_0 is determined by the local free volume and the microscopic energy barrier, E_a, that must be surmounted in executing the π flip of the phenyl rings, where a π flip consists of a jump between two potential minima separated by 180° around the C_1C_4 axis. If the local free volume defines a local friction ζ for molecular motion and a Kramers type of description[29] of the π flip is applicable, then $W_0 \propto \zeta^{-1} \exp(-E_a/RT)$. Fluctuations in local free volume give rise to an inhomogeneous distribution of W_0. Thus, we have a distribution of primitive rates W_0 or, equivalently, an inhomogeneous distribution $g(\log \tau)$ of the logarithm of primitive relaxation time τ, where $\tau = W_0^{-1}$. A version of the coupling model, which includes an inhomogeneous distribution of the primitive relaxation times τ, is appropriate for application to the phenylene ring motions. This was introduced in ref 22 and employed there to deduce the coupling parameter n and the quantity ω_c from NMR spin-lattice relaxation data and carbon-13 chemical shift anisotropy line-shape analysis of bulk BPA-PC from the laboratory of Jones and Inglefield.[11] NMR spin-lattice relaxation data of the same phenylene ring motions of BPA polycarbonate dissolved in dilute solution[14-18] as well as theoretical calculations of energy barriers[19,20] were used to provide the value for the primitive attempt frequency τ_∞, and activation energy, E_a. The results obtained through NMR data were then used to calculate the mechanical shear loss modulus from the phenylene ring motions in bulk BPA-PC. It was found that indeed there is an inhomogeneous distribution of primitive relaxation times, and only when this is incorporated into the coupling model will the prediction fit the loss modulus data.[1] We refer the reader to ref 22 for a detailed discussion of the coupling model with inclusion of an inhomogeneous distribution of primitive relaxation times $\tau = \tau_\infty \exp(E_a/KT)$ and its application to explain and correlate the NMR data and dynamical mechanical data.

Recently a comprehensive study of secondary relaxations in BPA-PC plasticized by addition of small-molecule liquids was published.[9,10] The effect the plasticizer has on the α relaxation is well-known.[9,29,35] Addition of a plasticizer shifts its relaxation time to shorter times. As a result the glass temperature, T_g, of the polymer is reduced. In the framework of conventional free-volume theory, this effect has been rationalized as due to an increase in free volume with addition of the plasticizer.[28,35] The effect of some plasticizer on the secondary relaxation in some amorphous polymers, including BPA-PC, is very different. Deuteron NMR[9,10,12] measurements of phenyl motion in PC were analyzed, assuming distributions of activation energies and correlation frequencies for the phenyl π flips. It was found that the plasticizers used not only increase the mean value and spread of the activation energy, and the average relaxation time, but also lead to a dramatic increase of the width of the distribution of correlation frequencies. Thus, plasticizers hinder the phenylene ring mobility, while on the other hand they facilitate the segmental mobility. They broaden drastically the relaxation spectrum of the phenylene ring motion but leave that of the segmental motion unchanged or possibly even narrow it. These opposite effects that the plasticizers have on the primary (segmental) and the secondary relaxations justify the use of the term "antiplasticization" to describe the effects they have on the secondary relaxation. Originally the term was used to describe the property of a plasticized polymer in the glassy state at temperatures well below T_g as being harder and more brittle than the neat polymer.[36,37]

More recently Wehrle, Hellmann, and Spiess (WHS)[38] have successfully fit deuteron NMR line shapes using distributions (both symmetric and asymmetric) of correlation rates, $P(\Omega)$, for the phenylene ring motions in glassy Bisphenol A polycarbonate. The parameters of the distribution required to fit line shapes for samples both with and without plasticizers were found. For instance, for the log Gaussian distribution

$$P(\Omega) = \frac{1}{\sigma(2\pi)^{1/2}} \exp[-[\ln (\Omega/\Omega_0)]^2/2\sigma^2] \tag{2}$$

the parameters are the variance, σ^2, and the mean jump rate, Ω_0, which is taken to follow an Arrhenius law:

$$\Omega_0 = \tau_\infty^{-1} \exp(-E_A{}^0/RT) \tag{3}$$

They found that addition of plasticizer causes the average ring-flip rate to decrease and its distribution to broaden. Thus addition of plasticizer required a new set of parameters for the distribution. They interpreted this as being due to both a shift and broadening of a corresponding distribution of activation energies. Although the deuteron NMR line shapes can be reproduced rather well by this approach, it is important to point out that this does not rule out other interpretations. It is possible that the deuteron NMR line shapes could be explained by another approach different from that offered by WHS. It has not been determined whether the distributions of activation energies obtained by WHS for different plasticizer concentrations actually represent the physics of these systems or they are merely representations of the experimental data. In this work we offer an alternative interpretation, which can reproduce essentially the same relaxation spectrum of WHS and hence the deuteron NMR line shape at each plasticizer concentration. As in the WHS approach, we also use a distribution of activation energies to address the deuteron NMR data. However, the distribution in our treatment is for the primitive relaxation times $\tau = W_0{}^{-1}$ of the coupling model. This means that, in addition to this distribution, we require the coupling model parameters n and ω_c. However, we use essentially the *same* distribution for both the unplasticized and plasticized samples. Most of the effects from *an increased concentration of the plasticizers result from* an increase in the coupling parameter n. From this, we obtain simultaneously (1) a shift of the mean relaxation time to longer times, (2) an increase in the mean activation energy, and (3) broadening of the loss function. The mean of our primitive distribution can also be related to dilute solution measurements and calculations of the phenyl ring motion of a single chain.[22] The coupling model is able to address not only the NMR line shapes but additional phenomena that are beyond the scope of the WHS method. Our previous paper[22] on unplasticized polycarbonates was able to use the coupling model, including the parameters n and ω_c, to explain (1) the large difference in activation energies of the phenylene ring motion in bulk and in dilute solution, (2) the fact that the activation energy of the phenylene ring motion is smaller than that of the methyl group motion in dilute solution but that the situation is reversed in the bulk, (3) the discrepancy between the measured activation energy and MNDO and ab initio calculations of the activation energy, and (4) the magnitude of the attempt frequency. In the case of plasticized polycarbonate, we retain the parameters n and ω_c along with their physical interpretation, in addition to the distribution of activation energies. A system as complicated as plasticized polycarbonate cannot presently be modeled with no adjustable parameters. However, the additional parameters n and ω_c within the coupling model significantly broadens the scope of this approach.

In addition to the deuteron NMR experiments, dynamic mechanical measurements and local density fluctuation measurements by small-angle X-ray (SAXS) scattering were made by Fischer et al.[9] in a thorough study of antiplasticization of secondary relaxations of PC. These studies (except deuteron NMR) were carried over to orthotetramethyl Bisphenol A polycarbonate (TMPC), poly(methyl methacrylate) (PMMA), and poly(cyclohexyl methacrylate) (PCHMA). The rich information provided by these investigations has enhanced the potential for an improved understanding of antiplasticization of secondary relaxations. In fact, based on the free-volume fluctuation model for the secondary relaxation, Fischer et al.[9] suggested that the distribution function, $P(\delta f)$, of the relative free-volume fluctuations $\delta f = \delta V/\langle V\rangle$ narrows with increasing plasticizer content. Then, assuming there is a critical value δf^* such that only secondary motion units with $\delta f > \delta f^*$ can contribute to the secondary relaxation and δf^* lies in the tail of the distribution so that $P(\delta f)$ is small for $\delta f > \delta f^*$, Fischer et al. have shown that the number of motion units contributing to secondary relaxation decreases with increasing plasticizer content. As a consequence, the strength of the secondary relaxation is expected to decrease, a behavior that was observed by dynamic mechanical measurements in BPA–PC and referred to as the β-suppression effect.[9] Although the concept of free-volume fluctuations is useful for secondary relaxation, nevertheless, considerations based on molecular interaction potentials are more fundamental. The static or "mean-field" approximation to the interactions may indeed be adequately described as free-volume distributions. Our previous work[22] on unplasticized BPA–PC is consistent with the concept of free-volume fluctuations. We also agree with Fischer et al.[9] that free-volume fluctuations are not important for the more spatially extensive and cooperative α relaxation. The α relaxation responsible for T_g is controlled, as far as the free volume is concerned, by the average free volume.[29] The coupling model introduces additional physics associated with the dynamical aspects of the molecular interactions. However, neither our treatment of the NMR data in this paper nor that of WHS[38] address the problem of the β-suppression effect.

II. Coupling Model Explanation of Antiplasticization

We limit our consideration mostly to the data obtained by the deuteron NMR[9,10,12] in the study of antiplasticization of the phenylene secondary relaxation in BPA–PC. In this experimental investigation, the experimental data of the line shapes were analyzed to yield a distribution of correlation times at each temperature and plasticizer content. The distribution of correlation times was proven to be heterogeneous in nature, consistent with the picture of free-volume fluctuations. It was argued that structural heterogeneity in the amorphous glassy state will lead to a distribution of activation energies, E_a, which results in a distribution of correlation frequencies. From the log Gaussian distributions of correlation frequencies, the distributions of activation energies were deduced.

In unplasticized BPA–PC, the mean activation energy, $\bar{E}_a{}^*$, for the phenyl flip was given to be 38 kJ/mol and a distribution of $\bar{E}_a{}^*$ values with a width between 32 and 44 kJ/mol. In a mixture of BPA–PC with 25% polychlorinated biphenyls, the values become considerably larger, $\bar{E}_a{}^* = 50$ kJ/mol and a width of 35–64 kJ/mol.

Recently, we have applied the coupling model[22] to understand the local molecular motions in unplasticized bulk BPA–PC and its dilute solutions by an analysis of NMR spin–lattice and carbon-13 chemical shift anisotropy (CSA) line-shape data of Jones, Inglefield, and coworkers. The coupling model approach and the method of inclusion of an inhomogeneous distribution of primitive relaxation times τ were detailed in ref 22, which henceforth will be referred to as I. The present work is a sequel to I and applies the model now to explain the antiplasticization of the phenylene secondary barrier relaxation. For this reason and for economy of space, the reader is asked to consult ref 22 in reading the rest of this paper. The only slightly deviation from the previous approach is the representation of the inhomogeneous distribution of primitive τ's (i.e., the log Gaussian distribution $g(\log \tau)$ in I) by a log Gaussian distribution

$$h(E_a) = (1/\Delta E_a\sqrt{\pi}) \exp[-(E_a - \Delta E_a)^2/\Delta E_a{}^2] \qquad (4)$$

of primitive activation energy barriers. In doing so, we

Table I
Parameters Characterizing the Distribution of Correlation Frequencies of the Phenyl Ring Motion in BPA-PC Deduced from the Published Data of Spiess and Co-workers and Obtained from a Coupling Model Analysis of the Same Data at a Temperature of 250 K

polychlorinated biphenyls, wt %	τ^*, s	E_a^*, kJ/mol	ΔE_a^*, kJ/mol	τ_∞^*, s	E_a, kJ/mol	ΔE_a, kJ/mol	τ_∞, s	ω_c, s^{-1}	n
0	7.2×10^{-7}	38	6	8.3×10^{-15}	13	2.04	6.2×10^{-13}	8.4×10^{11}	0.66
25	1.77×10^{-4}	50	14	6.38×10^{-15}	13	3.64	6.2×10^{-13}	2×10^{12}	0.74

have brought the analysis to be considered here in line with the presentation of deuteron NMR data in terms of a distribution of effective activation energies, E_a^*, by Fischer et al. Effects of the distribution of free volume and possible fluctuations in the coupling parameter are incorporated into the distribution of E_a^*. For unplasticized bulk BPA-PC, the results of the deuteron NMR data[9,10] are not in complete agreement with those of the other NMR data[11] analyzed in I. Notably, the average activation energy $\bar{E}_a^*$ is 38 kJ/mol for the former and the somewhat larger $E_a^* = 50 \pm 8$ kJ/mol for the latter. This discrepancy could be the result of different methods of data treatment by the two experimental groups. This cannot be resolved at this time. The only sensible thing we can do is to take each set of data seriously but separately in the coupling model analysis. The essentials of the conclusions reached in I and in the present work remain unchanged even in the event that the values E_a^* and/or $\bar{E}_a^*$ have to be adjusted.

We start from the activation barrier energy, E_a, of the primitive relaxation time

$$\tau = \tau_\infty \exp(E_a/RT) \qquad (5)$$

of phenyl group rotations of an isolated polymer chain obtained experimentally from NMR measurements in dilute solution of BPA-PC and from theoretical calculations.[22] The experimental and theoretical values are, respectively, 13 ± 5 and 13.8 kJ/mol, in good agreement with each other. We continue to take the primitive τ to be characterized by $E_a = 13$ kcal/mol and $\tau_\infty = 6.2 \times 10^{-13}$ s (Table I of I). From the relation between E_a^* and E_a (similar to eq 8, of I)

$$\bar{E}_a^* = E_a/(1-n) \qquad (6)$$

we deduce

$$n = 0.66, \quad \text{unplasticized} \qquad (7)$$

and

$$n_p = 0.74, \text{ plasticized, } c = 0.25 \qquad (8)$$

for phenylene ring motions in unplasticized and plasticized BPA-PC, respectively. The difference between the present value of 0.66 and the values 0.70 obtained in I for unplasticized BPA polycarbonates is the immediate consequence of discrepancy between $E_a^* = 38$ kJ/mol of refs 9 and 10 and $E_a^* = 50 \pm 8$/kJ/mol of ref 11. It should not be considered as an inconsistency inherent of the coupling model. Continuing the analysis, the frequency $\bar{\Omega}$ at which the log Gaussian distribution of correlation frequencies at $T = 250$ K is maximum[9] is equated to $1/2\pi\tau^*$, where $\tau^* = [[(1-n)\omega_c{}^n\tau]^{1(1-n)}$ and τ is given in eq 5. Then, from the second relation of the coupling model (eq 7 in I)

$$(2\pi\bar{\Omega})^{-1} = [(1-n)\omega_c{}^n\tau]^{1/(1-n)} \qquad (9)$$

The values 8×10^{11} and 2×10^{12} s^{-1} are deduced for ω_c of unplasticized and plasticized BPA-PC, respectively. The ω_c value for unplasticized BPA-PC is about a factor of 2 longer than those determined in I, and again the discrepancy is merely a reflection of the difference in the activation energy between the two sets of experimental data.[9,11]

Our main intent here is to demonstrate how the antiplasticization of secondary relaxation can be explained by the coupling model. Thus there is no need to give a quantitative fit of the deuteron NMR data. An approximate account is already sufficient for our purpose. In fact, it is more convenient for us to calculate a loss function, $R(\Omega)$, instead of the distribution function of correlation frequencies, $P(\Omega)$. This loss function, to be defined below, is closely related to $P(\Omega)$. The NMR data were interpreted[9] as a distribution of activation energies, E_a^*, about the mean value, $\bar{E}_a^*$. The half-widths ΔE_a^* are 6 and 14 kJ/mol for unplasticized PC and PC plasticized with 25 wt % of pentachlorophenyl, respectively. From a collorary of the second relation (eq 8 of I), we deduce the corresponding half-widths ΔE_a of the primitive activation energies, E_a, to be

$$\Delta E_a = (1-n)\Delta E_a^* \qquad (10)$$

In this equation, possible fluctuations of the coupling parameter, which may be concomitant with local free-volume fluctuations, are not considered. We find, using eqs 7 and 8 for the coupling parameters, the values of $\Delta E_a = 2.04$ and 3.64 kJ/mol for unplasticized and plasticized BPA-PC, respectively. All parameters essential to the coupling model have now been determined, and their values for $T = 250$ K are listed in Table I. The next step is the computation of the relaxation spectrum or alternatively the loss function, $R(\Omega)$, as follows. Each primitive process governed by activation energy E_a has a corresponding rate $W_0 \equiv (1/\tau_\infty)\exp(-E_a/RT)$. This rate becomes slowed down by coupling in the manner of eq 1 (eq 3 of I). The relaxation function, $\phi(t)$, has the form of eqs 6 and 7 of I. Written out explicitly

$$\phi(t) = \exp[-(t/\tau^*)^{1-n}] \qquad (11)$$

where a second relation relates τ^* to the primitive relaxation time

$$\tau^* = [(1-n)\omega_c{}^n\tau_\infty \exp(E_a/RT)]^{1/(1-n)} \qquad (12)$$

From $\phi(t)$ we calculate the loss function $r(\omega)$ from the formula

$$r(\omega;E_a) = \mathrm{Im}(\mathrm{FT}\ (-\mathrm{d}\phi/\mathrm{d}t)) \qquad (13)$$

where FT denotes the operation of taking the Fourier transforms in angular frequency space ω and Im is the operation of taking the imaginary part of a complex number. The loss function $R(\omega)$ is the sum of all these contributions $r(\omega;E_a)$

$$R(\omega) = \int P(E_a)\, r(\omega;E_a)\, \mathrm{d}E_a \qquad (14)$$

weighted by the Guassian distribution

$$P(E_a) = (1/\pi\Delta E_a)\exp[-(E_a - \bar{E}_a)^2/(\Delta E_a)^2] \qquad (15)$$

Identifying $\omega = 2\pi\Omega$, we obtain the loss functions $R(\Omega)$ as

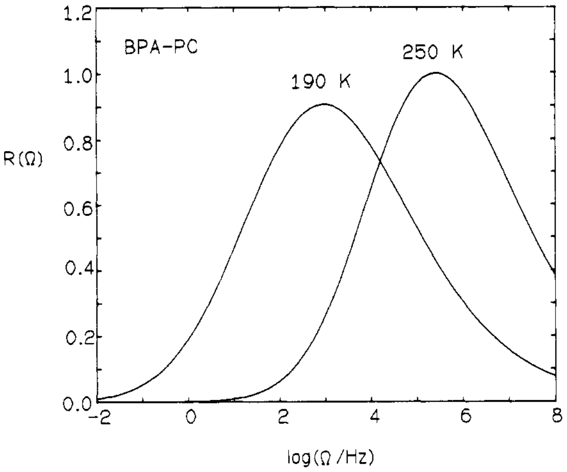

Figure 1. Loss function $R(\Omega)$ of phenyl secondary relaxation calculated as a function of frequency, Ω, in hertz for unplasticized BPA-PC at 250 and 190 K according to the coupling model by eqs 9–13 with parameters given in Table I.

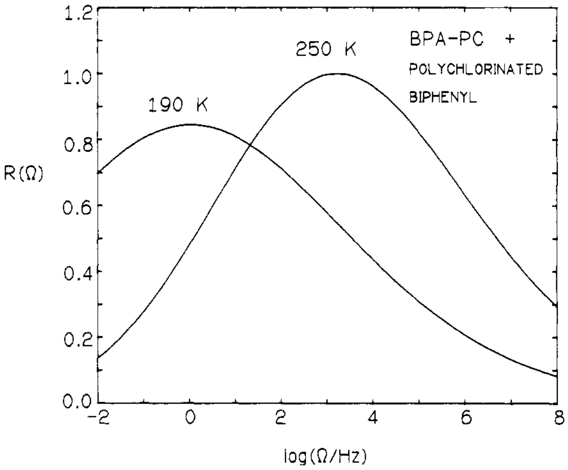

Figure 2. Loss function $R(\Omega)$ of phenyl secondary relaxation calculated as a function of frequency, Ω, in hertz for plasticized BPA-PC with 25 wt % polychlorinated biphenyls at 250 and 190 K according to the coupling model by eqs 9–13 with parameters given in Table I.

a function of frequency Ω in hertz. The calculations of $R(\Omega)$ have been carried out at two temperatures $T = 250$ and 190 K for the unplasticized and 25 wt % pentachlorodiphenyl-plasticized BPA-PC.[9] The results are given in Figures 1 and 2. By inspection, it is clear that at the same temperature the loss spectrum of the plasticized polymer is considerably broader than that of the unplasticized polymer. Moreover, the frequency of the loss maximum is significantly lower for the plasticized polymer than that of the unplasticized polymer. Both features observed in $P(\Omega)$ deuteron NMR experiments[9,10] are essentially reproduced by our calculations of $R(\Omega)$ using the predictions of the coupling model. They can be understood easily from the properties of the pair of eqs 11 and 12 together with the deduced fact that the coupling parameter n_p for plasticized BPA-PC is larger than n for the unplasticized BPA-PC. A larger n in eq 11 not only makes the relaxation function more dispersive, thereby broadening the relaxation spectrum, but also increases τ^* in eq 12. The latter becomes evident if eq 12 is rewritten as $\tau^* = \tau(1 - n)^{1/(1-n)}(\omega_c\tau)^{n/(1-n)}$, and observe that $\omega_c\tau \gg 1$. Thus, in the framework of the coupling model, the antiplasticization of the phenylene secondary relaxation of BPA-PC follows as a consequence of the increase in its coupling parameter n when the polymer is plasticized. The reason why n is expected to increase with addition of plasticizer to PC will be explained in the next section. Before that, we shall take on another secondary relaxation in BPA-PC and consider both experimentally and theoretically the effect of plasticizer addition on it.

The other secondary relaxation in BPA-PC is the rotation of the methyl group. In unplasticized BPA-PC the methyl group rotation has been studied in bulk by Spiess and co-workers[10] using deuteron NMR and in dilute solution by Jones and co-workers[14] using spin-lattice relaxation. These two data sets have previously been analyzed by the coupling model.[22] Within experimental errors the activation energy of methyl rotation is the same in dilute solution and in bulk. It follows from eq 6 that the coupling parameter n for methyl rotation of PC is zero or nearly zero. In the context of the coupling model, a zero value of n means the relaxation does not couple to other molecules. This deduction is consistent with the experimental observation that the methyl motions are not mechanically active. We have already mentioned that, from the deuteron NMR data of Schmidt et al.,[10] addition of 25 wt % polychlorinated biphenyls produces little change of the methyl relaxation times and its distribution. (See Figure 5 of ref 10.) The distribution of $P_m(\Omega)$ correlation frequencies Ω or relaxation times τ^* of the methyl motions deduced from NMR is considerably narrower than $P(\Omega)$ of the phenyl motions. Schmidt et al. presented this result again in terms of a distribution between 15 and 21 kJ/mol with a mean value of 18 ± 1 kJ/mol. The half-width of the distribution is 3 kJ/mol, which is remarkably close to the half-widths of 2 and 3–6 kJ/mol for the *primitive* phenyl motions in the unplasticized and plasticized BPA-PCs.

From the coupling model analysis, the observed fact that the methyl relaxation times and its mean activation energy remain essentially unchanged with addition of plasticizer implies likewise for the coupling parameter. It follows, from eqs 11–15, that the distribution of correlation frequencies is not going to be changed either, at least as far as the effect of n is concerned.

III. Interpretations

In the previous section we have seen how we use the mean activation energy data to deduce that the coupling parameter n for phenyl motions is increased when BPA-PC is plasticized. From the deduced increase in n, we are then able to calculate the change of the distribution of correlation frequencies, predicting correctly that its mean value is shifted to lower frequency and its width is significantly increased when plasticizer is added. In this section we explain, using a constraint dynamics formulation of the coupling model,[32-34] that n increases when polychlorinated biphenyls are added to BPA-PC. We shall contrast this behavior, i.e., antiplastization of a secondary relaxation in BPA-PC, with what may happen in PMMA and PCHMA. Fischer et al.[9] have shown by dynamic mechanical measurements that plasticizers suppress the β-relaxation peak of BPA-PC but not that of PMMA and PCHMA. These contrasting behaviors can also be explained by arguments based on a constraint dynamics formulation of the coupling model.

In pure BPA-PC, the phenyl secondary relaxation probed dynamic mechanically at 1 Hz has its loss maximum located at about −100 °C.[1,9] It is generally agreed that there is a relation between the phenylene motions and the mechanical properties of BPA-PC.[1,9] As has been amply discussed in the Introduction that, for this to be possible, the phenylene motions must be coupled intermolecularly. In the coupling model,[33,34] the emphasis is on the dynamical nature of the constraints leading to the self-similar slowed-down relaxation rate given by eq 1. The static component of the constraints and its fluctuations have been incorporated into W_0, the primitive rate. The constraints imposed on a phenylene group on one chain by intermolecule coupling from other chains are dynamical because of similar motions by phenylene groups on all chains. The size of the coupling parameter n is proportional to the strength of the mutual dynamical constraints. Strengthening the constraints will increase n, and mitigating them will decrease its value. Such variations in the strength of dynamic constraints were realized in two other problems of polymer physics that were addressed by the coupling model. The first is the diffusion of a sufficiently long chain tracer molecule in an entangled polymer matrix solution.[39] The dynamical constraints imposed on the tracer molecules together with the corresponding coupling parameter n_e arise from entanglement coupling between them. When the molecular weight and/or the concentration of the matrix polymer is decreased, the dynamical constraints will be mitigated. As a consequence, the entanglement coupling parameter, n_e, is expected to decrease,[40] a result consistent with the data of Lodge and co-workers[39] on PS diffusion in PVME solutions. The other example is the study of the modification of solvent relaxation by addition of polymer by Schrag and co-workers[41] and Lodge and co-workers.[42] When a polymer with T_g higher than that of the solvent is added, such as PS in aroclor (chlorinated biphenyls similar to the one studied here as plasticizer of BPA-PC), the relaxation of solvent molecules in the vicinity of the dissolved polymer experiences stronger dynamic constraints than that of the same molecules in the pure solvent at the same temperature. On the other hand, on addition of a polymer with T_g lower than that of the solvent, such as PI or PB in aroclor, the dynamic constraints are weakened. Electric birefringence data of Lodge[42] provided evidence for the increase of the coupling parameter of solvent relaxation in the former case.[43] These two examples in different areas of polymer physics should enhance the credibility of the following rather similar explanation of the increase in the coupling parameter of the phenyl secondary relaxation in BPA-PC with addition of the plasticizer, polychlorinated biphenyls.

The glass transition temperature, T_g, of polychlorinated biphenyls used in the deuteron NMR study[9,10] was not reported. From published[42] values of T_g for chlorinated biphenyls, a reasonable estimate of T_g is in the neighborhood of −50 to −30 °C. At −100 °C, the phenyl group moves with the frequency of about 1 Hz[1,9] and the motions of the polychlorinated biphenyl molecules are effectively frozen. Thus, in BPA-PC, with the addition of polychlorinated biphenyls, a phenylene group of the polymer will have on the average some of the much less mobile plasticizer molecules in its vicinity and experience enhanced dynamic constraints compared with that in the pure polymer. It follows from a result in the entropy reformulation[33,34] of the constraint dynamics version of the coupling model that the coupling parameter of the phenylene motion will increase with enhancement of dynamical constraints. This is the result that we have deduced from the experimental data in the previous section and now justified with the discussions here.

A further test of our model interpretation of the effect that a plasticizer has on the phenylene secondary relaxation in PC is afforded by the different behavior it has on the β relaxation in PMMA and PCHMA. It was observed[9] through dynamic mechanical measurements that the phenylene loss peak of PC was suppressed with additions of plasticizers but the β loss mechanisms of PMMA and PCHMA were not. These different behaviors are consistent with contrastingly different time scales of the polymer secondary relaxation with the primary relaxation of the plasticizer in these two types of polymers. Consider the example of PMMA. The secondary relaxation at 1 Hz in the dynamic mechanical loss peak[9,25] has its maximum at about 20 °C. For the plasticizers used, 20 °C is far above its glass temperature. At 20 °C relaxation of the plasticizer molecule occurs at a frequency much higher than 1 Hz. Therefore, as far as the secondary relaxation of PMMA is concerned, the plasticizer molecules are already fully relaxed. Their presence will not hinder the mobility of the secondary relaxations because dynamical constraints will not be enhanced. Consequently, the coupling parameter will not be increased by the plasticizer. Hence, eq 10, the second relation, tells us that the relaxation spectrum will not be shifted to longer times. The mechanical relaxation strength will not be reduced, in agreement with experimental data.[9]

IV. Summary

Antiplasticization of a polymer has the conventional definition that in the glassy state a polymer mixed with a low molar mass additive (plasticizers) is found to be harder and more brittle than the pure polymer. It has been suggested that this phenomenon is related to the effects that these plasticizers have on those secondary relaxations, which contribute to mechanical properties. Concise information from deuteron NMR measurements in glassy polycarbonates on the change of (1) the activation energy, (2) the mean frequency, and (3) the distribution of frequencies of the phenyl secondary relaxation in polycarbonate suggests that these properties give a more precise definition of antiplasticization.

We have used these deuteron NMR data to demonstrate that the coupling model with inclusion of fluctuations of local free volumes (or distributions of local energy barriers) gives a consistent explanation of the experimental facts on the effects of the additives on the phenyl secondary relaxations. The coupling model also provides a logical connection of secondary relaxations to bulk mechanical properties to which it contributes. The difference in the effects plasticizers have on the secondary relaxations in PC and PMMA can also be explained.

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