Positronium Annihilation Lifetime and Dynamic Mechanical Studies of γ-Relaxation in BPA-PC and TMBPA-PC Plasticized by TOP

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ABSTRACT: Positronium annihilation lifetime spectroscopy (PALS) was employed to study the structure and dynamic properties of glassy BPA-PC and TMBPA-PC containing tris(2-ethylhexyl) phosphate (TOP) as diluent molecules. For BPA-PC/TOP blends, the results showed that the total hole volume fraction is insensitive to the addition of TOP up to 10 wt % but increases at higher TOP concentration. However, in the case of TMBPA-PC/TOP blends, a different trend was observed. The total hole volume fraction decreases monotonically with TOP concentration up to 15% and thereafter increases slightly from 15 to 20%. Dynamic mechanical relaxation was also used to monitor the dynamics of the blends. This part of the work was motivated by a prediction of the coupling model (made before the experimental measurement was carried out) that addition of TOP should have opposite effects on the γ-relaxation times of BPA-PC and TMBPA-PC. Indeed, it was found by dynamic mechanical measurement at constant frequency that, while the γ-relaxation peak temperature of BPA-PC was shifted to *higher* temperature with addition of TOP, the opposite effect was found in TMBPA-PC. The γ-relaxation peak temperature of TMBPA-PC was shifted to *lower* temperatures upon addition of TOP with little change in the width of the peak as predicted by the coupling model. The predictions of the coupling model and the dynamic mechanical results are supported by (1) dielectric relaxation measurements of the γ-relaxation performed on the same TMBPA-PC/TOP blends by Rizos and co-workers [accompanying paper] and also (2) the phosphorus-31 nuclear magnetic resonance data on diluent dynamics in the same BPA-PC/TOP and the TMBPA-PC/TOP blends obtained by Bergquist et al. [accompanying paper], which is shown by them to be also consistent with the lattice model for diluent dynamics.

Introduction

The antiplasticization effect in bisphenol A polycarbonate (BPA-PC) has been extensively studied using dynamic mechanical relaxation, dielectric relaxation, and NMR techniques.[1−4] Both dielectric relaxation and dynamic mechanical relaxation spectra showed that the low-temperature γ-relaxation peak of BPA-PC/diluent systems is suppressed, broadened, and shifted to higher temperatures (at a constant frequency).[1,2] Similar conclusions have been reached by NMR studies.[3,4] We reserve β-relaxation to designate the structural relaxation always found on the low-temperature side of the α-relaxation. Some authors designate our γ-relaxation as β-relaxation and ignore the existence of the structural relaxation. These experimental works have laid the foundation of the antiplasticization effect in BPA-PC. A free volume fluctuation model[1] and a lattice model[3] have been developed to explain the experimental observations. The coupling model has also been used to explain this phenomenon.[5] There are differences among the models as to the physical origin of antiplasticization. In the free volume fluctuation model, it is proposed that the γ-relaxation is intermolecularly uncooperative, and the strength of the relaxation is proportional to the local free volume fluctuation. The addition of diluent molecules leads to a decrease in the local free volume fluctuation, thus suppressing the γ-relaxation peak. This is a pioneering work, which has stimulated many experimental investigations to follow. The lattice model[3] uses both free volume and dynamic arguments. The number of nearest-neighbor contacts assumed to influence local dynamics is counted. When applied to the polymer chain, the presence of one diluent−polymer repeat unit contact is considered to suppress sub-glass transition motion through improved packing. By contrast, polymer repeat units on the lattice in contact with more than one diluent molecule are presumed to have enhanced mobility. On the basis of this model, the free volume of the polymer/diluent system should suffer a slight decrease initially with increasing diluent concentration. The lattice model has been used successfully to describe the diluent dynamics in BPA-PC glasses.[3] The coupling model, on the other hand, interprets the relaxation behavior from the standpoint of dynamic interactions and constraints between the polymer and diluent molecules.

In applying the coupling model to the problem of antiplasticization in BPA-PC,[5] an inhomogeneous dis-

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tribution of primitive γ-relaxation times due to density fluctuations has been taken into account, consistent with NMR line-shape data.[6-11] The primitive relaxation time of a molecular moiety in the coupling model[12-21] is defined as the reciprocal of the relaxation rate before intermolecular interaction starts to slow it down. Actually, even in the absence of an inhomogeneous distribution of primitive relaxation times, the relaxation is already dynamically heterogeneous in the coupling model.[22] Most of the effects on the γ relaxation from the increased concentration of the plasticizers result from an increase in the coupling parameter n_γ of the γ relaxation. This increase in n_γ produces, through a result of the coupling model, simultaneously a shift of the mean γ relaxation time to longer times, an increase in its mean activation energy, and a broadening of the mechanical loss peak,[5] in agreement with experimental data. At the same temperature, the γ-relaxation time of glassy BPA-PC is short relative to the structural relaxation (α) time of many platicizers such as Aroclor.[1-5] Thus, the condition that the relaxation times of diluent molecules in glassy BPA-PC are longer than the γ relaxation times generally holds. This proviso is met in BPA-PC plasticized by Aroclor because the γ-relaxation peak of pure BPA-PC at 1 Hz occurs at -100 °C and the glass transition temperature, T_g, of neat Aroclor is approximately -44 °C. With the addition of Aroclor, the phenylene rings of BPA-PC executing the γ relaxation now see an environment of increasing number of immobile replacement Aroclor molecules. The dynamic constraint imposed on the γ relaxation is therefore enhanced. In the context of the coupling model, the coupling parameter n_γ is proportional to the dynamic contraints, and hence n_γ increases. Indeed, this effect of a diluent on the mechanical response of the γ relaxation had been observed in BPA-PC plasticized by Aroclor[1,4,5] and other small molecule liquids.[2,3]

If, on the other hand, that the α-relaxation time of a diluent used to plasticize a polymer is shorter than that of the γ-relaxation of the neat polymer, the effect of the diluent molecule on the γ relaxation may shift it to *shorter* times when a certain condition is met. Although this expectation by the coupling model is by no means a rigorous prediction and other factors have not been considered, this opposite effect on the γ-relaxation could possibly be found in plasticized tetramethylbisphenol A polycarbonate (TMPC). TMPC is a good candidate because its γ-relaxation at 1 Hz peaks at a much higher temperature of about 41 °C, and the condition for the occurrence of the opposite effect of diluent on the γ-relaxation of TMPC could be met for some suitable choice of diluent such as TOP. A typical antiplasticization effect was observed experimentally already in BPA-PC/tris(2-ethylhexyl) phosphate (TOP) blends.[2] In the present study, the γ-relaxation behavior of BPA-PC/TOP blends and TMBPA-PC/TOP blends was investigated by mechanical spectroscopy and compared in order to test the above-mentioned prediction provided by the coupling model on the possible occurrence of a reversal of the antiplasticization phenomenon in TMBPA-PC/TOP. The choice of TMBPA-PC/TOP is made because pure TMBPA-PC has a much longer γ-relaxation time than the structural relaxation time of neat TOP ($T_g = -130$ °C) at the same temperature. An NMR study had concluded that the phenylene ring flips such as in the case of BPA-PC is correlated with the γ-relaxation of TMBPA-PC.[23] Therefore, a comparative study of the γ-relaxations in BPA-PC/TOP and TMBPA-PC/TOP is meaningful. The possible observations of a spectacular reversal of the effect TOP has on the γ-relaxation time when going from BPA-PC to TMPC motivate us to carry out the experimental work to be reported in this paper and the accompanying papers.

In this work, positronium annihilation lifetime spectroscopy (PALS) was employed to monitor the change in total hole volume fraction of the blends as a function of diluent concentration. It is a tool uniquely suited for probing the size and density of nanometer-sized holes in polymers. Dynamic mechanical relaxation spectroscopy (DMS) was used to characterize the shift of the γ-relaxation. The results of the two sets of experimental data are compared with the predictions of the models on the γ-relaxation. Diluent (TOP) motion has been measured on the same samples by Bergqvist et al.[24] using a phosphorus-31 NMR experimental technique. Also, γ-relaxation in the TMBPA-PC/TOP blends has been measured by Rizos et al. by dielectric relaxation spectroscopy.[25] Results of these two complementary investigations are reported in two accompanying papers[24,25] that follow. The information on the γ-relaxation dynamics and the TOP dynamics obtained by them, in conjunction with our dynamic mechanical data of the γ-relaxation, is used to support the claim that TOP addition has opposite effects on the γ-relaxations in BPA-PC/TOP and TMBPA-PC/TOP.

Experimental Section

Materials. BPA-PC/TOP blends with various concentrations of the diluent were kindly supplied by Dr. Roger Kambour of the General Electric Co. TMBPA-PC was synthesized by solution condensation polymerization at the University of Michigan. It was purified twice by dissolving in CH_2Cl_2 and reprecipitating from isopropyl alcohol and dried at 110 °C under vacuum. TOP was purchased from Aldrich and was used without further purification. TMBPA-PC/TOP blends were prepared by codissolving TMBPA-PC and TOP in CH_2Cl_2 and casting onto glass slides. The films were removed from the glass slides and dried under vacuum and heated at 10 °C above their respective T_g's for 15 min before making the dynamic mechanical measurements. Five blends with different TOP concentration were prepared. TOP concentrations are 0, 5, 10, 15, and 20 wt %. All blends are transparent with no sign of phase separation. This is to be contrasted with the 20% sample studied previously by Kambour et al., which showed evidence of phase separation.[2]

PALS. A 30 μCi ^{22}Na positron source was deposited on the surface of a copper disk and covered with a 3 μm nickel foil. This source assembly was then placed on the surface of the polymer sample. The PALS measurements were performed with a conventional fast-timing coincidence method. About 1.8×10^7 counts were collected for each lifetime spectrum in approximately 3 h. All the measurements were conducted at 23 °C. All samples were heated above their melting temperatures and quenched to room temperature right before the measurements. The lifetime spectra were resolved into three components using the program PFPOSFIT.

A count rate of 1700 counts/s is not excessive. The electronics used are capable of handling such rates. For example, the TAC, an Ortec 566, has a 50 ns full scale setting, which we typically use to collect the polymer data. For a full scale of 50 ns this allows 200 000 counts/s. This is roughly an order of magnitude larger than the typical START and STOP rates we get using the bulk PALS systems with a 30 μCi source. The MCA used to digitize the TAC pulses is a model 8715 Canberra ultrafast ADC for high count rate γ-ray spectroscopy. Its conversion time is fixed at 800 ns, which is almost 3 orders of magnitude smaller than the inverse coincidence rate of 1700 counts/s. Thus, the MCA is more than fast enough to handle the coincidence rate.

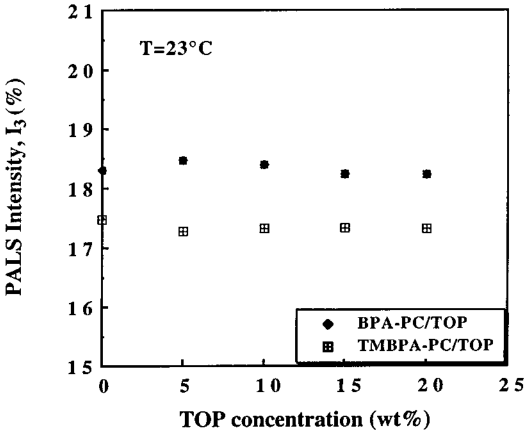

Figure 1. o-Ps intensity, I_3, versus TOP concentration at room temperature.

A significant charging effect, i.e., changes in the o-PS intensity, is observed only if the experiment lasts for days. Our data were collected in a matter of a couple of hours. Thus, the charging effect was minimal. Besides, all the specimens were subjected to the same procedure and thus the same amount of irradiation. The trend we observe should therefore be independent of the charging effect, if any.

DMS. All the dynamic mechanical relaxation spectra of the blends were obtained from a spectrometer built in our laboratory, which is based on a linear motor driver unit and a Hewlett-Packard data acquisition unit controlled by a HP computer. The measurements of the complex Young's modulus $E^* = E' + iE''$ in tension were performed at a constant frequency of 1.0 Hz in a temperature range from −150 °C to the T_g of the blends with a scan rate of 1.5 °C/min.

Results and Discussions

PALS. The PALS data due to o-Ps pick-off annihilation provide information that can be translated into hole size and number density of holes from the τ_3 and I_3 results, respectively.[26] The product of the hole size and the density then gives a value proportionate to the hole volume fraction, i.e., $f_h = cI_3\tau_3$. c is dependent on the polymer and can be evaluated from volume expansivity measurement. However, we have found c to fall in a narrow range of values. Therefore, for the present series we shall assume c to be constant. Figure 1 is a plot of o-Ps annihilation intensity, I_3, versus TOP concentration in the two types of blends. It shows that there is little change in I_3 with diluent concentration in both systems, which means that the total number of nanometer-sized holes sampled by o-Ps remains virtually constant with the addition of TOP. The size of the holes in the blends, however, does change as a function of TOP concentration. Figure 2 is a plot of o-Ps annihilation lifetime, τ_3, versus TOP concentration. The size of the error bar is approximately equal to the size of the symbols. In the TMBPA-PC/TOP system, the τ_3 value decreases rather rapidly initially with increasing TOP concentration and then levels off. Thus, the average size of the holes decreases with increasing TOP concentration. These observations agree quite well with the lattice model, which proposes that the small molecules occupy the free volume and consequently cause improved packing.

However, the same arguments cannot be applied to the BPA-PC/TOP system since an opposite trend of τ_3 is observed (see Figure 2). The τ_3 of the BPA-PC/TOP blends does not change much at low TOP concentrations, but beyond 10% it increases with increasing TOP concentration. This dependence on addition of TOP means that initially the average hole size does not change, but then it increases at the higher concentrations. This observed behavior in BPA-PC/TOP is at variance with the lattice model, indicating that the lattice model, although successful in many respects,[3] has limitations in predicting the packing and free volume of plasticized polymer systems in a totally consistent manner. The opposite trends displayed by the two polymer/plasticizer systems are maintained when the relative hole fractions are plotted against TOP content. In general, the different trends of τ_3 in BPA-PC/TOP and in TMBPA-PC/TOP indicate that volume or packing may not be the ultimate determining factor in the consideration of the γ-relaxation in these systems.

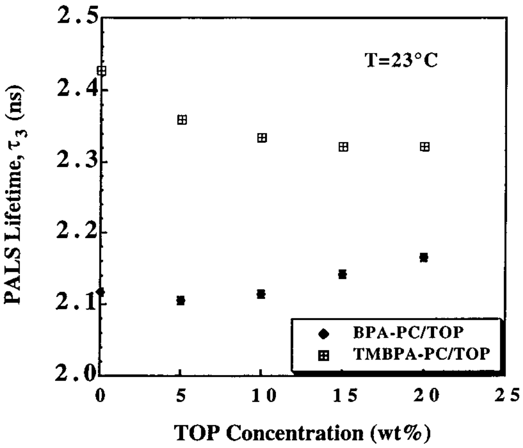

Figure 2. o-Ps lifetime, τ_3, versus TOP concentration at room temperature.

Nevertheless, in the case of diluent dynamics, the lattice model does adequately account for the bimodal population of the diluents found by a phosphorus-31 NMR measurement on the same samples by Bergqvist et al.[24] The NMR data indicate that the dynamics of TOP are bimodal with diluent molecules in contact with other diluent molecules (as microclusters) displaying much greater mobility than diluent molecules surrounded by polymer.[24]

The bimodal population consisting of isolated diluent molecules and microclusters is a special way to describe concentration fluctuation. Concentration fluctuation is more general and known to be present in miscible blends.[27,28] It is possible to discuss the TOP rotational dynamics in the blends according to the conceptual basis of the coupling model for mixtures that incorporate concentration fluctuations.[29−31] Above the glass transition temperature of the mixture, the dynamics of the diluent as well as that of the polymer are determined by at least two factors: concentration fluctuation and the interactions between molecular units of the same as well as different components of the blend.[29−31] The local segmental motion of the polymer usually occurs at a much longer time scale than the time scale of diluent rotation and is principally responsible for the slowing down of diluent rotation in the mixture. The dynamics, including the most probable relaxation times of the relaxation spectra of the two components of the mixture, can be described via theoretical models of blends.[29−32] When the mixture initially in thermodynamic equilibrium is cooled to temperatures significantly below T_g, where physical aging is negligible, local segmental relaxation is arrested, and the structure is frozen essentially in the equilibrium liquid state before it falls out of equilibrium. The large disparity in the time scales of TOP rotation and local segmental motion of either BPA-PC and TMBPA-PC makes their difference in T_g immaterial in determining the most probable relaxation time, τ^*_{TOP}, of the distributed TOP components in the blends. Instead, the determining factors are the interactions among the TOP molecules and between the TOP molecules and the repeat units of the polymer. The two polymers BPA-PC and TMBPA-PC are miscible with a very small heat of mixing.[1] Thus, as far as the TOP molecule is concerned, the monomers of BPA-PC and TMBPA-PC are chemically very similar, and we may expect that τ^*_{TOP} is to a first approximation the same in both blends. This behavior of τ^*_{TOP} is in fact verified by Bergquist et al.[24] with their NMR data which show that at an experimental frequency of 1 Hz the relaxation spectrum of the fast component has a maximum at −56 °C for the two blends. This is to be compared with −130 °C, the glass transition temperature of pure TOP. Also, τ^*_{TOP} has the same activation enthalpy of 56 kJ/mol in both blends. The lattice model can also explain these same facts by identifying τ^*_{TOP} with that of the microclusters, which by definition is the same in both blends. In the context of the coupling model,[5,7,29−31] the same activation enthalpy of τ^*_{TOP} is equivalent to the TOP having the same most probable coupling parameter n_{TOP} and coupling parameter distribution, $\{n_{TOP}\}$, in the two blends. Let us compare the coupling model with the lattice model. The isolated diluent molecules of the bimodal distribution in the lattice model correspond to one extreme in the concentration fluctuation of the coupling model.[29−31] This extreme, envisaged in the lattice model, consists of isolated diluent molecules completely surrounded by polymer. In the coupling model, the dynamics of these isolated diluent molecules will be determined by the local segmental motion of the surrounding polymer molecules. The latter impose more constriant on the motion of the isolated TOP molecule and bequeath to it a larger coupling parameter n_{TOP} than in neat TOP. It follows along the same way as in previous applications of the coupling model to blends[29−31] that rotational motion of these isolated TOP molecules is slowed down and tends to be suppressed in the glassy state of the plasticized polymer. On the other hand, a microcluster of TOP molecules is another extreme in the concentration fluctuations that have minimal contacts with polymer molecules. TOP molecules with environments richer in TOP molecules have a smaller coupling parameter than the isolated TOP molecules and relax as a fast component in the glass. Although, the inevitable presence of polymer molecules in the blend means that even the relaxation spectrum of this fast component is shifted to longer times than pure TOP at the same temperature. Thus, as far as diluent dynamics is concerned, the lattice model and the coupling model[29−31] lead to similar conclusions.

Figure 3 is a plot of the total calculated hole volume fraction determined by PALS versus TOP concentration. In the case of BPA-PC/TOP, the total hole volume fraction is insensitive to the addition of TOP up to 10% in concentration. As the TOP content is increased further, the hole volume fraction increases. In the case of TMBPA-PC/TOP, a reversal of this trend is observed. Instead, the total hole volume fraction decreases rapidly with addition of TOP up to 15%, levels off, and then increases slightly in going from 15% to 20%. Orthopositronium sees both static (unoccupied) volume and free volume fluctuation as static holes due to its short lifetime (∼2 ns). Therefore, the amount of free volume fluctuation cannot be resolved from PALS data taken at a single temperature. The separation of static volume and free volume fluctuation could be accomplished if we perform the measurements at very low temperatures at which all the motions of the molecules that have contribution to the free volume fluctuation are frozen. Nevertheless, the PALS results of distinctly different dependences of the hole volume fraction on TOP concentration in BPA-PC/TOP and in TMBPA-PC are noteworthy when considering free volume as the determining factor of the γ-relaxation. We discuss this point in the following section on DMS results.

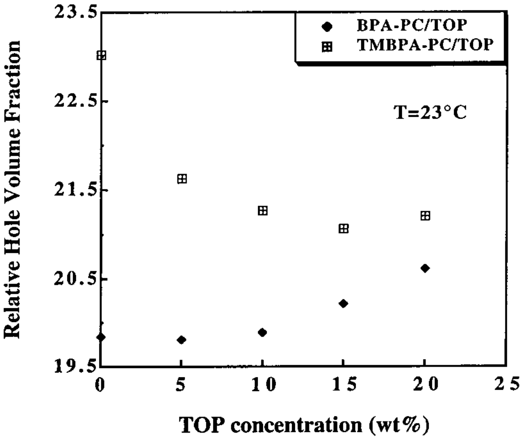

Figure 3. Hole volume fraction detected by PALS versus TOP concentration at room temperature.

DMS. The dynamic mechanical relaxation of neat TMBPA-PC and TMBPA-PC/TOP blends with 5, 10, 15, and 20% TOP are shown all together in Figure 4a−c. There, the storage Young's modulus E' and the loss tangent, $\tan \delta = E''/E'$, at a constant frequency of 1.0 Hz are plotted against temperature T in the γ-relaxation temperature range. The rapid decrease of E' and the concomitant increase of $\tan \delta$ with T at higher temperatures is due to the onset of the α-relaxation of the polymer blend as the glass transition temperature T_g is approached. For both neat TMBPA-PC and TMBPA-PC/TOP with 5% TOP, T_g is sufficiently high (203 and 168 °C, respectively) that the tail of the $\tan \delta$ coming from the α-relaxation has negligible effect at least on the position of the maximum of the γ-relaxation peak. By inspection of Figure 4b, it is clear that the γ-relaxation peak has been shifted to *lower* temperatures with the addition of 5% TOP. The γ-relaxation peak of neat TMBPA-PC located at 41 °C is shifted down to 29 °C when diluted 5% by TOP. Furthermore, there is no broadening of the relaxation peak. The experimental γ-relaxation peak temperature at 1 Hz of neat TMBPA-PC and of TMBPA-PC/5%TOP blend is shown in Figure 5 (open triangles). On further increase of the weight percentage of TOP to 10% or higher, there is a rapid reduction of T_g (142, 115, and 98 °C for 10, 15, and 20% TOP, respectively), and the tail of the $\tan \delta$ from the α-relaxation increasingly distorts the γ-relaxation peak to the extent that at 20% TOP the peak is totally obscured, leaving behind only a shoulder. At intermediate TOP concentrations it is necessary to somehow subtract the low-temperature tail of the α-relaxation to reveal the γ-peak. By any reasonable extrapolation of the data in Figure 4c, the difference exhibits a peakthat is identified with the γ-relaxation. However at concen-

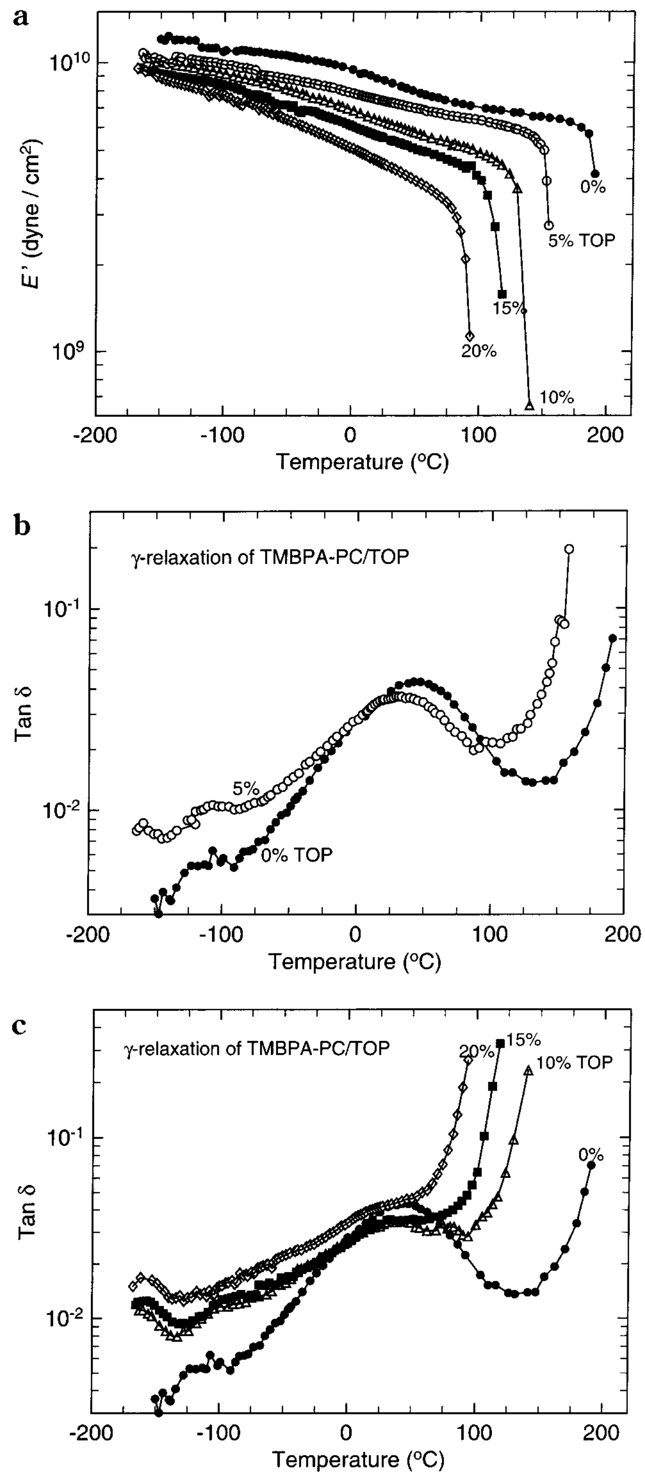

Figure 4. (a) The storage Young's modulus, E', of TMBPA-PC/TOP blends measured at 1 Hz. The number in the figure represents the weight percent of TOP in the blend. (b) The loss tangent, tan δ, of TMBPA-PC/TOP blends measured at 1 Hz. Only data for 0 and 5 wt % of TOP are shown in this figure to demonstrate clearly that the γ-relaxation peak is shifted to lower temperature with addition of 5% TOP to TMBPA-PC. (c) The loss tangent, tan δ, of TMBPA-PC/TOP blends measured at 1 Hz. Only data for 0, 10, 15, and 20 wt % of TOP are shown in this figure. The overlapping contributions from the γ-relaxation and the α-relaxation in blends containing 10% or more TOP makes it difficult to isolate the γ-relaxation peaks in them.

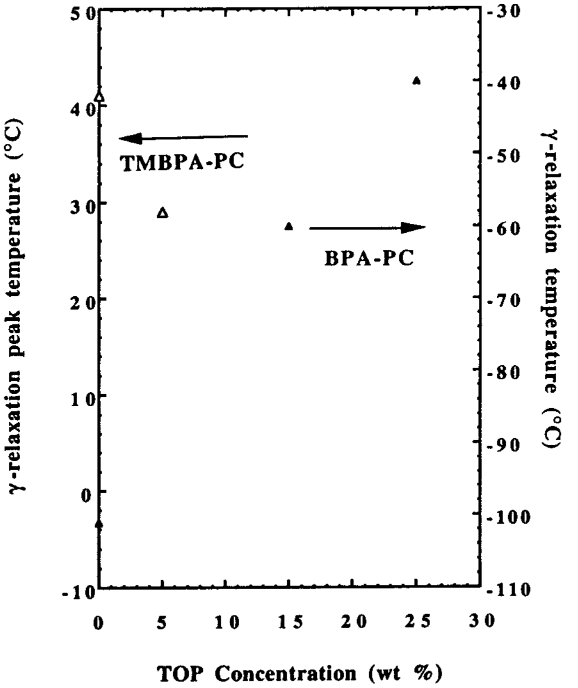

Figure 5. γ-relaxation peak maximum temperatures versus TOP concentration of BPA-PC/TOP and TMBPA/TOP blends. For TMBPA/TOP blends only the data of the 0 and 5% TOP samples in which the positon of the γ-relaxation peak maximum can be clearly identified are shown.

trations higher than 5%, the location of the peak maximum depends on the procedure used to subtract the α-relaxation from the γ-relaxation. At these higher concentrations of diluent, other experimental probes may be better suited than dynamic mechanical measurement to isolate the γ-relaxation peak. The fact that the effect is certainly real, as evidenced by the comparison between the 0% and the 5% TOP dynamic mechanical data (Figures 4b and 5), has helped to promote the undertaking of additional experimental investigations that employ dielectric relaxation spectroscopy[25] and the nuclear magnetic resonance technique.[26] These works confirm that there is a trend beyond 5% TOP. In particular, the dielectric relaxation data obtained by Rizos and co-workers in the same samples (see figures in ref 25) show that the γ-relaxation peak temperature of the TMBPA-PC/TOP blends decreases with increasing TOP concentration. Dynamic mechanical measurements of the γ-relaxation peak in BPA-PC/TOP blends do not encounter the problem of overlap of the α- and γ-relaxations contributions. This favorable situation for BPA-PC/TOP blends occurs because the γ-relaxation peak temperature is far below the T_g of the blends up to 20% TOP. The experimental γ-relaxation peak temperature at 1 Hz of neat BPA-PC and BPA-PC/TOP blends is shown also in Figure 5 as a function of TOP concentration (filled triangles). Our data are in good agreement with the previous work on BPA-PC/TOP blends by Kambour et al.[2] Figure 5 shows that the γ-relaxation peak shifts to higher temperatures with addition of TOP in the BPA-PC/TOP blends. This behavior is to be contrasted with the γ-relaxation temperature of the TMBPA-PC/TOP blends (open triangles in Figure 5), which instead shifts to lower temperatures with increasing TOP concentration.

The PALS results have already indicated that TOP molecules reduce the amount of fluctuation in the TMBPA-PC/TOP blends. Thus, free volume fluctuation arguments would predict that the γ-relaxation peak should be broadened, suppressed, and shifted to higher temperatures. The lattice model has similar predictions although a slightly different argument is used. According to this model, the mobility of TMBPA-PC should decrease at low TOP concentration since most TOP molecules are dispersed in the form of single molecule, filling in the free volume and causing improved packing. Consequently, the γ-relaxation peak should shift to higher temperatures and become broadened at the same time.

Let us recall the PALS data of BPA-PC which indicate that (1) the average hole size does not change initially and then increases at higher concentrations and (2) the total hole volume fraction is insensitive of TOP up to 10% in concentration and increases with TOP content from there on. Using these volume information from PALS as inputs to the lattice model or free volume fluctuation arguments, we are led to conclude that they predict that the γ-relaxation peak temperature of BPA-PC/TOP blends should shift to lower temperatures with addition of TOP. From the above discussion, it is clear that neither the free volume fluctuation argument nor the lattice model in its present form can give an explanation to the dynamic mechanical and dielectric[25] γ-relaxation results of the TMBPA-PC/TOP and BPA-PC/TOP blends and at the same time be consistent with the PALS data. Modifications of these approaches possibly may bring them back to consistency. We mention also the interpretation by Bergquist et al.[24] which follows from previous NMR studies of the polymer motion in BPA-PC/dibutyl phthalate of ref 3. They interpret the shift to higher temperatures of the γ-mechanical loss of BPA-PC/TOP as caused by the presence of diluent rotation on the high-temperature side of the original loss peak and not to a shift of the γ-relaxation of the polymer. This interpretation differs from others[1,4,5] and is a possibility that should be considered further. We note, however, that this interpretation is inappropriate for the TMBPA-PC/TOP system.

As we have already mentioned in the Introduction, this “anomalous” behavior of the TMBPA/TOP blends which is opposite to that found in closely related BPA-PC/TOP blends was expected conceptually from the coupling model. In the coupling model, for any relaxation process including the γ-relaxation, the observed relaxation time τ^* and the primitive relaxation time τ_0 (i.e., the relaxation time before intermolecular interaction has an effect) are related by

$$\tau^* = [t_c^{\ -n}\tau_0]^{1/1-n} \tag{1}$$

where n is the coupling parameter of the relaxation process and t_c is the temperature-independent crossover time from independent dynamics ($t < t_c$) to coupled dynamics ($t > t_c$).[12,14,15] Recent quasielastic neutron scattering experiments in several homopolymers[20,21] and analysis of molecular dynamics simulation data of a small molecule liquid, *o*-terphenyl,[18] have found the crossover from $\exp(-t/\tau_0)$ relaxation to $\exp[-(t/\tau^*)^{1-n}]$ as predicted by the coupling model at $t_c \approx 2 \times 10^{-12}$ s. The results of these experiments confirm the existence of the primitive relaxation time, τ_0. Earlier in this paper, we have discussed how the interplay of concentration fluctuation and interactions between the molecular species (polymer−polymer, polymer−diluent, and diluent−diluent) determines the relaxation spectra of both the polymer segmental motion and of the diluent rotational motion above T_g and in the glassy state. We have further argued that, at the same concentration, the relaxation spectrum of the diluent is nearly the same in either BPA-PC/TOP or TMBPA-PC/TOP. Phosphorus-31 NMR data[24] of the TOP motion have confirmed this expected result. The most probable relaxation times, $\tau^*_{\mathrm{TOP,blend}}$, of the fast TOP component found by NMR in the blends to be the same in TMBPA-PC/TOP[24] and in BPA-PC/TOP[3] are shown as points represented by the filled circles (15% TOP) and open diamonds (20% TOP) in a plot of relaxation time versus reciprocal temperature in Figure 6. Shown also are the most probable γ-relaxation time, τ^*_γ, of neat BPA-PC (dashed line in Figure 6) and neat TMBPA-PC (solid line in Figure 7) from dynamic mechanical measurements, and each has been extrapolated by its Arrhenius temperature dependence to wider ranges of temperature. These relaxation times satisfy the relation

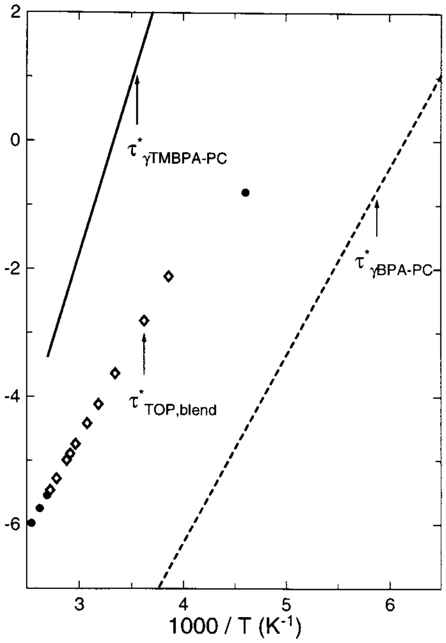

Figure 6. Effective relaxation time, $\tau^*_{\gamma\mathrm{BPA\text{-}PC}}$, of neat BPA-PC γ-relaxation (dashed line). Effective relaxation time, $\tau^*_{\mathrm{TMBPA\text{-}PC}}$, of neat TMBPA-PC γ-relaxation (solid line). The lines are extrapolations of the Arrhenius temperature dependences of the mechanical γ-relaxation times to wider temperature ranges. The effective α-relaxation times, $\tau^*_{\mathrm{TOP,blend}}$, of TOP in the blend deduced from phosphorus-31 NMR data of Berquist et al.[24] are points represented by the symbols (circles for 15% TOP, diamonds for 20% TOP).

$$\tau^*_{\gamma\mathrm{BPA\text{-}PC}} \ll \tau^*_{\mathrm{TOP,blend}} \ll \tau^*_{\gamma\mathrm{TMBPA\text{-}PC}} \tag{2}$$

With the diluent relaxation spectrum in the glassy blends determined, the effect of the presence of the diluent on the γ-relaxation of the polymer can be considered in the framework of the coupling model. We shall take into account the experimental facts as stated by inequality (2) that in the blends the TOP motion occurs at a *higher* temperature than the γ-relaxation of neat BPA-PC but at a *lower* temperature than the γ-relaxation of neat TMBPA-PC (see Figure 6). This relation between the times scales of TOP rotation and the γ-relaxation of BPA-PC means that, as far as the γ-relaxation of BPA-PC is concerned, the added TOP molecules in its neighborhood, being relatively immobile, impose increased dynamic constraints to the γ-relaxation process. Consequently, the coupling parameter n_γ of the γ-relaxation of BPA-PC/TOP will

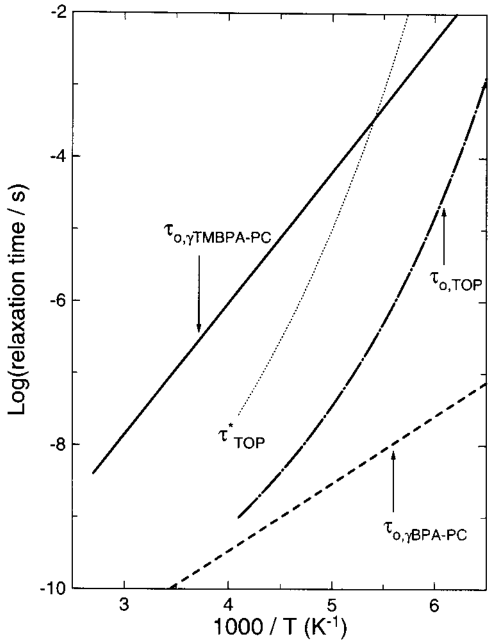

Figure 7. Dotted curve represents the Vogel−Fulcher fit to the effective relaxation time, τ^*_{TOP}, of pure TOP obtained from dielectric measurement by Rizos et al.[25] The corresponding primitive relaxation time of TOP, $\tau_{0,TOP,}$ is shown as a dashed−dotted curve. Shown also are the primitve relaxation times $\tau^*_{0,\gamma BPA\text{-}PC}$ (solid line) and $\tau^*_{0,\gamma TMBPA\text{-}PC}$ (dashed line) calculated from the mechanical γ-relaxation times given in Figure 6.

increase with increasing TOP concentration. By contrast, in TMBPA-PC/TOP the added TOP molecules, being comparatively more mobile, mitigate the dynamic constraints acting on the γ-relaxation process and decrease its coupling parameter n_γ. From the coupling model, an increase (a decrease) in n_γ leads to an increase (a decrease) in τ^*_γ. This result follows in a straightforward manner as a consequence of eq 1 if the primitive relaxation time $\tau_{0\gamma}$ is unchanged with the addition of TOP, because

$$\tau^*_\gamma = \tau_{0\gamma}(\tau_{0\gamma}/t_c)^{n_\gamma/(1-n_\gamma)} \tag{3}$$

$\tau_{0\gamma}/t_c \gg 1$, and $n_\gamma/(1 - n_\gamma)$ is a monotonically increasing function. Hence, the coupling model expects a shift of the γ-relaxation spectrum of BPA-PC to longer times with the addition of TOP, but the opposite effect when the polymer is TMBPA-PC.

When blending two components together, it is nontrivial to predict how the relaxation of one component will be affected by the other component in general. Only in the extreme limit of dilute concentration of one component in the other can the prediction be easily made. As previously demonstrated in considering the component dynamics in several blends in the context of the coupling model, it is also useful to compare the primitive γ-relaxation time of the polymer molecule, $\tau_{0,\gamma}$, with the primitive relaxation time of the diluent molecule in the pure form, $\tau_{0,TOP}$, in the consideration of the component dynamics in the blend.[29−31,33,34] If $\tau_{0,\gamma}$ is shorter (or longer) than $\tau_{0,TOP}$, then τ^*_γ of the polymer in the blend is likely to be increased (or decreased) relative to the pure state due to enhanced (or reduced) coupling of the molecular moieties in the polymer undergoing the γ-relaxation by the presence of TOP molecules with longer primitive relaxation time. Although this criterion is by no means rigorous, it is worthwhile to compare these primitive relaxation times. From eq 1, one can calculate $\tau_{0,\gamma P}$ from $\tau^*_{\gamma P}$ and $n_{\gamma P}$, the coupling parameter of the γ-relaxation of polymer P, according to

$$\tau_{0,\gamma P} = (t_c)^{n_{\gamma P}}(\tau^*{}_{\gamma P})^{1-n_{\gamma P}} \tag{4}$$

Both $\tau^*_{\gamma P}$ and $n_{\gamma P}$ can be experimentally determined as demonstrated in refs 5 and 17. A similar expression,

$$\tau_{TOP} = (t_c)^{n_{TOP}}(\tau^*{}_{TOP})^{1-n_{TOP}} \tag{5}$$

is used to calculate $\tau_{0,TOP.}$

The coupled relaxation dynamics of the γ-relaxation in the polymers and the rotation of TOP are different. The γ-relaxation in pure BPA-PC and TMBPA-PC involve stronger coupling than the rotational relaxation of TOP. The difference in coupling strength is manifested in terms of a difference in the values of their coupling constants, $n_{\gamma P}$ and n_{TOP}. For the γ-relaxation in BPA-PC, $n_{\gamma P}$ is around 0.68.[5,17] The γ-relaxation in TMBPA-PC is similar in nature to that of BPA-PC except that it occurs at a much higher temperature (50 °C at 1 Hz). We assume that its $n_{\gamma TMBPA-PC}$ is also 0.68. The value of n_{TOP}(neat) for neat TOP is about 0.40 as estimated from a fit to the frequency dependence of dielectric relaxation measurement under isothermal conditions[25] by the stretched exponential relaxation function. We calculate $\tau_{o,\gamma P}$ and $\tau_{o,TOP}$ according to eqs 4 and 5, respectively. The τ^*_{TOP} in eq 5 obtained from a Vogel−Fulcher fit, $\log(\tau^*_{TOP}) = -13.2 + 784.8/(T - 104.3)$ to dielectric relaxation measurement of τ^*_{TOP} of neat TOP[25] is plotted as the dotted curve and $\tau_{0,TOP}$ as the dashed−dotted curve in Figure 7. $\tau_{0,\gamma BPA-PC}$ and $\tau_{0,\gamma TMBPA-PC}$ are represented by the solid and dashed lines in Figure 7, respectively. The results in the figure indicate that

$$\tau_{0,\gamma BPA-PC} \ll \tau_{0,TOP} \ll \tau_{0,\gamma TMBPA-PC} \tag{6}$$

These relationships between $\tau_{0,\gamma BPA-PC}$, $\tau_{0,\gamma TMBPA-PC}$, and $\tau_{0,TOP}$ are similar to those between $\tau^*_{\gamma BPA\text{-}PC}$, $\tau^*_{\gamma TMBPA\text{-}PC}$, and $\tau^*_{TOP,blend}$ given before by eq 2. Consequently, from either points of view based on the effective relaxation times (eq 2) or the primitive times (eq 6), γ-relaxation times of BPA-PC and TMBPA-PC are related in opposite ways to the rotational relaxation time of TOP molecules in the blends. Naturally, opposite effects of the diluent on the γ-relaxation, i.e., antiplasticization but plasticization of the γ-relaxation respectively in BPA-PC and TMBPA-PC are predicted. These effects are consistent with the dynamic mechanical experimental data shown in Figures 4b and 5. A similar conclusion has been reached by Berquist et al. from NMR data[24] and by Rizos et al. from dielectric relaxation data.[25]

Conclusions

PALS data show that the total number of nanosized holes remains constant in both BPA-PC and TMBPA-PC when TOP was used as a plasticizer. The average hole size decreases in the TMBPA-PC/TOP blends with increasing TOP concentration but increases in the BPA-PC/TOP blends. Thus, the total hole volume fraction of TMBPA-PC decreases with addition of TOP whereas in the case of BPA-PC, the total hole volume fraction increases. Dynamic mechanical relaxation spectra of TMBPA-PC/TOP blends show that the γ-relaxation peak shifts to lower temperatures, at least at low concentrations of TOP, opposite to the trend found in BPAPC/TOP blends. This plasticization of the γ-relaxation in TMBPA-PC by the addition of a typical diluent TOP is dramatically different from the commonly known effect of antiplasticization of the γ-relaxation in BPA-PC by the same diluent. The effect observed by dynamic mechanical measurement is corroborated directly by dielectric relaxation measurement by Rizos and coworkers[25] and indirectly by Bergquist et al. by NMR measurements.[24] Theoretically, the coupling model provides a consistent rationalization of the opposite behaviors of the γ-relaxation dynamics observed in BPA-PC/TOP and TMBPA-PC/TOP blends.

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