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A Dielectric Relaxation Study of the γ-Relaxation in Tetramethylbisphenol A Polycarbonate Plasticized by Tris(2-ethylhexyl) Phosphate

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ABSTRACT: Dielectric relaxation spectroscopy (DR) was employed to study the dynamics of glassy tetramethylbisphenol A polycarbonate (TMBPA-PC) containing various amounts of tris(2-ethylhexyl) phosphate (TOP) added as diluent molecules. The present data confirm that the γ-relaxation dynamics, at constant frequency, shift to lower temperatures with increasing TOP content, an effect observed for the first time by dynamic mechanical measurements. This behavior of the γ-relaxation in TMBPA-PC plasticized by TOP is to be contrasted with that in bisphenol A polycarbonate (BPA-PC) plasticized by TOP. In the latter case, the γ-relaxation dynamics, at constant frequency, shift to higher temperatures with addition of TOP. These opposite trends of the γ-relaxation dynamics in two similar polycarbonates are surprising. However, the results can be rationalized by the coupling model.

Introduction

In recent years there has been continued interest in the understanding of the nature of secondary relaxations in bisphenol A polycarbonate (BPA-PC)—in particular the γ-relaxation that relates to phenylene rings motion, since it seems to play a significant role in determining the desirable mechanical properties of the polymer.[1−15] The effect on the γ-relaxation caused by plasticization of BPA-PC by the addition of a diluent has been studied repeatedly by many workers.[2−4,8] The γ-relaxation peak of BPA-PC at a constant frequency is suppressed, broadened, and shifted to higher temperatures with the addition of a smaller molecular diluent. Thus, even though the α-relaxation in BPA-PC is sped up to indicate the effect of lowering the glass transition temperature by plasticization, the γ-relaxation exhibits the opposite behavior of being slowed down. This is well-known as the effect of antiplasticization. The antiplasticization of the γ-relaxation in BPA-PC is a challenging problem that has attracted much attention and has been the subject of many investigations using different techniques including dynamic mechanical[1,2,4−6] relaxation, NMR,[2,7−15] and dielectric relaxation.[16−18] Some theoretical considerations[2,6,7] have been given to explain the antiplasticization of the γ-relaxation in BPA-PC/diluent systems.

Recently, a similar study of the effect of diluent on the γ-relaxation in tetramethylbisphenol A polycarbonate (TMBPA-PC) has been carried out.[3] TMBPA-PC, having four additional methyl groups present on the two phenyl rings, is very similar in structure to BPA-PC. The diluent is tris(2-ethylhexyl) phosphate (TOP) which, when added to BPA-PC, antiplasticizes its γ-relaxation[3,4] like other diluents such as Aroclor studied previously.[2] Oddly enough, on blending TMBPA-PC with TOP the dynamic mechanical measurement at constant frequency shows that the γ-peak temperature of the blends decreases with increasing TOP concentration,[3] at least at low concentrations. This is a surprising result because this observed behavior of γ-relaxation in TMBPA-PC/TOP is contrary to that in BPA-PC plasticized by TOP.[3,4]

In the present study, dielectric relaxation spectroscopy was employed to monitor the dynamics of the γ-relaxation in TMBPA-PC/TOP blends. The objective of this work is to use another technique to check the unusual properties of the γ-relaxation found in the dynamic mechanical study of TMBPA-PC/TOP blends.[3]

Experimental Section

Samples. TMBPA-PC/TOP blends were prepared by codissolving TMBPA-PC and TOP in dichloromethane at room temperature and casting onto glass slides. The films were dried under vacuum at 45−50 °C for about 48 h to remove any residual solvent. All blends with the diluent TOP concentration of 5, 10, 15, and 20 wt % were transparent with no sign of phase separation as evidenced by wide-angle X-ray scattering (WAXS).

Dielectric Relaxation Spectroscopy (DR). The real and imaginary parts of the complex dielectric permittivity ϵ^* were measured with a Novocontrol BDC-S system composed of a frequency response analyzer (Solartron Schlumberger FRA 1260) and a broad dielectric converter with an active sample cell in the frequency range 10^{-2}−10^{6} Hz. The samples were kept between two gold-plated stainless steel plates, with the sample temperature controlled ($\pm$0.1 °C) by a Novocontrol Quatro system between 290 and 380 K.

Results and Discussion

Isothermal dielectric loss, ϵ'', data in the γ-relaxation region of TMBPA-PC/TOP blends with 5, 10, 15, and

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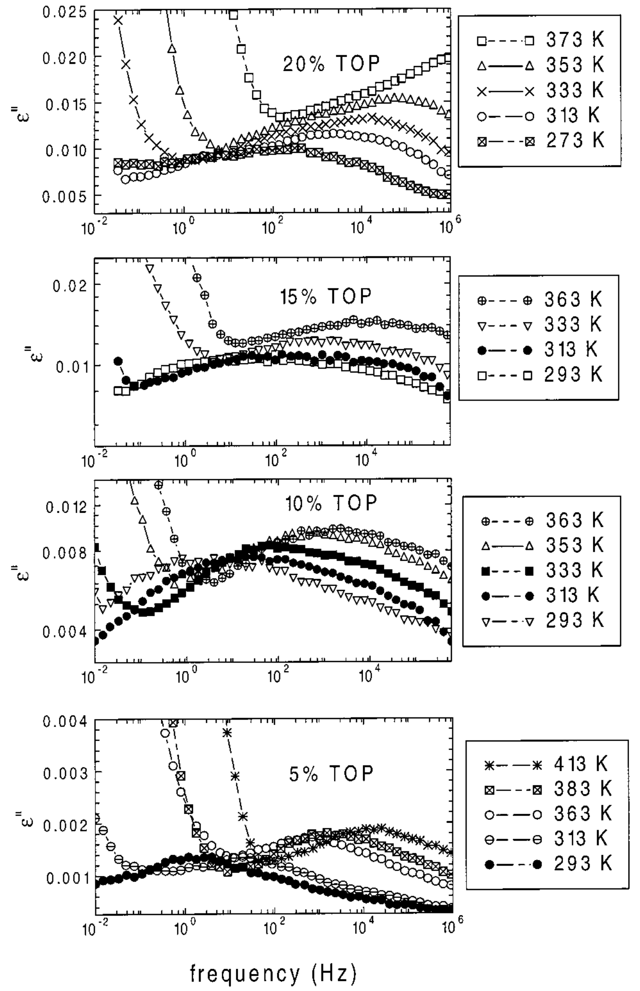

Figure 1. Dielectric loss data in the γ-relaxation region of TMBPA-PC/TOP blends. From bottom to top: blend containing 5% TOP at 293, 313, 363, 383, and 413 K; blend containing 10% TOP at 293, 313, 333, 353, and 363 K; blend containing 15% TOP at 293, 313, 333, and 363 K; and blend containing 20% TOP at 293, 313, 333, 353, and 373 K. The rise of ϵ'' toward low frequencies is the conductivity contribution as indicated by the dashed line through the data points.

20% TOP at a number of temperatures are shown in Figure 1. The γ-relaxations in the blends are very broad, similar to the γ-relaxation in BPA-PC/diluent systems observed by others.[4,8,18,19] The steep rise of ϵ'' at low frequencies is caused by electrical conductivity within the sample which is assumed to fall as f^{-1} with frequency f. The empirical Havriliak–Negami[20] (HN) equation

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau_\gamma)^\alpha]^\beta} \qquad (1)$$

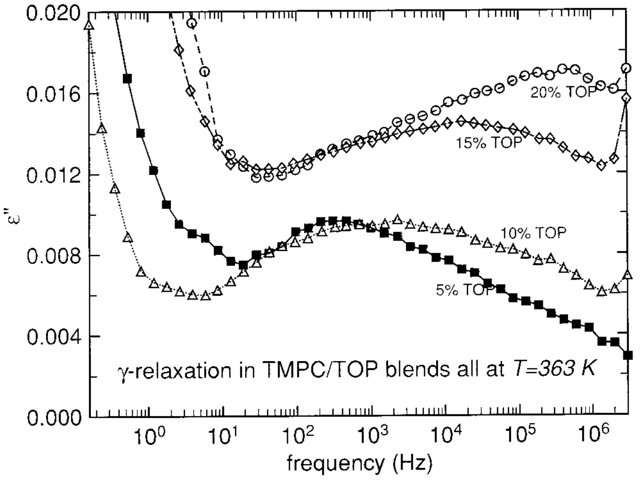

Figure 2. Dielectric loss data in the γ-relaxation region of four blends containing 5, 10, 15, and 20% TOP at a common temperature of 363 K showing the shift of the γ-relaxation to higher frequencies with increasing TOP content.

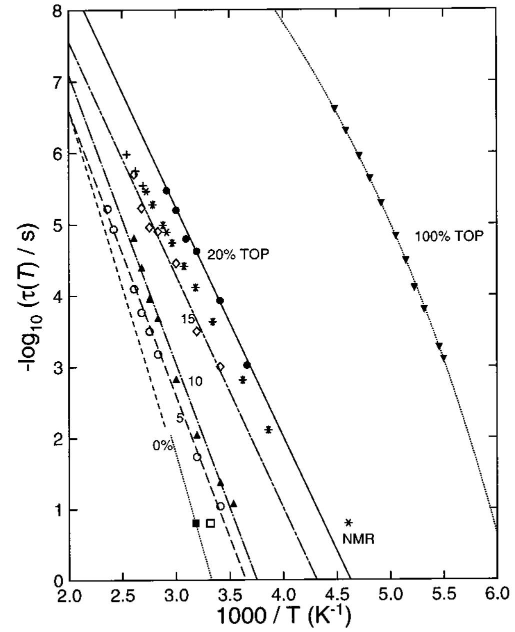

Figure 3. Relaxation map, [−log(relaxation time)] versus 1000/T, for the γ-relaxation process of the TMBPA-PC/TOP solutions (5, 10, 15, and 20% TOP) obtained from dielectric relaxation measurements. Shown also are the α-relaxation times of pure TOP, the γ-relaxation times of pure TMBPA-PC obtained by dielectric measurement (dashed line)[21] and by mechanical measurement (thicker dashed line and the lone filled square),[3] and the rotational relaxation time of TOP in microclusters obtained by ^{31}P NMR (+) for 20% and (*) for 5% TOP) [ref 22].

was used to fit and characterize the observed γ-relaxation process. In the above equation ϵ_0 and ϵ_∞ are respectively the low- and high-frequency values of the real part of the dielectric permittivity, and τ_γ is the characteristic relaxation time. The two parameters α and β ($0 < \alpha, \beta$ and $\alpha\beta \leq 1$) are used to characterize the symmetric and asymmetric broadening of the distribution of relaxation times, respectively. Fits to the experimental ϵ'' data by the sum of the conductivity contribution (shown as examples by dashed lines in Figure 1) and the γ-relaxation according to eq 1 have enabled the parameters of the γ-relaxation including the relaxation time τ_γ to be determined. An interesting feature of this relaxation is the very broad distribution of relaxation times with very small HN parameters. The shape parameters α and β (0.38, 0.48) at 370 K were found for the 10% TOP blend, which are approximately the same as found in earlier DS studies[16−18] of the γ-relaxation of polycarbonates.

The dielectric data of four blends all taken at the same temperature of 363 K (Figure 2) show that there is a shift of the γ-relaxation peak monotonically to higher frequencies as the TOP content is increased from 5 to 20%. In Figure 3 the dependencies of the γ-relaxation time τ_γ on temperature in the blends are shown in an Arrhenius plot. Open circles, filled triangles, open

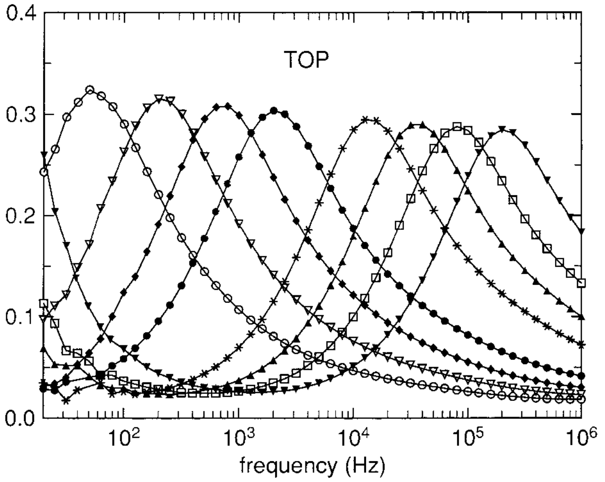

Figure 4. Dielectric loss data of pure TOP at eight different temperatures. From left to right, loss curves are for $T = 179$, 183, 188, 192, 201, 206, 210, and 216 K.

diamonds, and filled circles represent the data points for samples containing 5, 10, 15, and 20% TOP, respectively. The solid straight lines are fits to these data points by the Arrhenius temperature dependencies. We have included in Figure 3 also the dielectric γ-relaxation time, τ_γ, of undiluted TMBPA-PC[21] (dashed line labeled 0%) and the α-relaxation time, τ_{TOP}, of pure TOP (filled inverted triangles) together with a fit to the latter by the Vogel−Fulcher equation, $\log(\tau_{\mathrm{TOP}}) = -13.2 + 784.8/(T - 104.3)$. The dielectric loss data of pure TOP are shown in Figure 4 for eight temperatures.

By inspection of Figure 3 it is clear that at any temperature τ_γ becomes *shorter* with the addition of TOP up to 20%. Equivalently, at constant frequency (or at constant $\log(\tau_\gamma)$) the γ-relaxation dielectric loss peak is shifted toward lower temperatures by the addition of TOP. In the same figure we have plotted τ_γ obtained from dynamic mechanical measurement at 1 Hz on neat TMBPA-PC (filled square) and at other frequencies (thicker dashed line) and at 1 Hz on TMBPA-PC with 5% TOP (open square).[3] From the experimental data of these two samples for which the γ-relaxation have been unambiguously extracted from mechanical and dielectric data, there is reasonably good agreement in the values of τ_γ obtained from the two techniques. Therefore, our dielectric data confirm the observation by dynamic mechanical relaxation data of the same blends[3] that addition of TOP speeds up (i.e., plasticizes) the γ-relaxation in TMBPA-PC, opposite to what was found in BPA-PC/TOP.[3,4]

Phosphorus-31 NMR measurement made on the same TMBPA-PC/TOP blends has led Bergquist et al. to the same conclusion.[22] The phosphorus-31 NMR probed the motion of the TOP molecules in the blends and detected two populations. One population was interpreted to consist of isolated TOP molecules completely surrounded by polymer. The rotational motion of the isolated TOP molecules is confined to a cone, and the rate and amplitude of this motion increase slowly with temperature. The other population consists of TOP molecules in contact with other TOP molecules (microclusters) which undergoes isotropic Brownian rotational diffusion with an apparent activation energy of 56 kJ/mol. Fitting the ^{31}P NMR spectra, Bergquist et al. found that the relaxation of TOP molecules in the microclusters was characterized by a stretched exponential correlation function, $\exp(-(t/\tau_p)^{\beta'})$, where $\beta' = 0.7$ and is the same for 5, 10, 15, and 20% TOP. The large stretch exponent, i.e., $\beta' = 0.7$, indicates that the relaxation spectrum of TOP molecules in the microclusters is quite narrow, with full width at half-height (fwhh) equal to about 1.57 decades. The correlation times τ_{NMR} were determined as a function of temperature, and they are plotted as a function of temperature for 15% (*) and 20% (+) TOP in Figure 3. As can be seen, τ_{NMR} is rather insensitive to diluent concentration and falls between the dielectric γ-relaxation times of TMBPA-PC containing 15 and 20% TOP. Therefore, we could expect some contribution to the broad dielectric loss peak of the 15 and 20% blends in Figure 1 from motions of TOP molecules in the microclusters. However, the dielectric relaxation spectrum of the TOP being narrow (fwhh = 1.57 decades according to NMR) indicates that the principal contribution to the broadened dielectric loss peaks (fwhh > 4 decades) in Figure 1 has to come from the γ-relaxation of TMBPA-PC in the blends. This conclusion holds even better for the 5 and 10% TOP blends because there the observed τ_γ is much longer than τ_{NMR} (see Figure 3), and the dielectric loss peaks should have negligible contribution from the TOP in microclusters. Thus, after taking into consideration the NMR data of TOP molecular motions in the blends, we are still led to the result that TOP plasticizes the γ-relaxation of TMBPA-PC, contrary to the effect of antiplasticization it has on BPA-PC.

As discussed in ref 3, the coupling model is able to explain consistently the experimental observations of the opposite changes of the dynamics of the γ-relaxation in BPA-PC and TMBPA-PC when blended with TOP. The coupling model[23,24] when applied to the γ-relaxation can rationalize both the “antiplasticization” of the γ-relaxation of BPA-PC by TOP, as discussed in previous works,[3,6,9,19] and the reversal of the effect on the γ-relaxation in the TMBPA-PC/TOP blends. The surprising reversal of the effect in TMBPA-PC was first found by dynamic mechanical spectroscopy,[3] and we now have confirmed it by dielectric spectroscopy here and also by Bergquist et al. by phosphorus-31 NMR measurement.[22]

Conclusions

Dielectric relaxation data of TMBPA-PC/TOP blends show that the γ-relaxation peak, at constant frequency, shifts to *lower* temperatures with increasing diluent (TOP) content. The present experimental results support the finding by a recent dynamic mechanical study of the same blends. This behavior of the γ-relaxation in TMBPA/TOP is to be contrasted with the shift of the γ-relaxation peak to *higher* temperatures with increasing TOP in BPA-PC/TOP blends. As discussed before in the preceding paper (ref 3), the coupling model provides consistent descriptions of the opposite trends of the γ-relaxation dynamics in these two similar polycarbonate/diluent blends.

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