Macromolecules **1993,** *26,* 3075–3080

Broadband Dielectric Study on Binary Blends of Bisphenol-A and Tetramethylbisphenol-A Polycarbonate

G. Katana,* F. Kremer, and E. W. Fischer

Max-Planck-Institut für Polymerforschung, Postfach 3148, W-6500 Mainz, FRG

R. Plaetschke

Zentrale Forschung/Polymerphysik, Bayer AG, W-5090 Leverkusen, FRG

Received November 30, 1992; Revised Manuscript Received March 11, 1993

ABSTRACT: Broadband dielectric spectroscopy (10^{-1} to 10^7 Hz) and differential scanning calorimetry (DSC) have been used to study the α- and β-relaxations in blends of bisphenol-A polycarbonate (BPA-PC) and tetramethylbisphenol-A polycarbonate (TMBPA-PC) in the temperature range from 93 to 553 K. All blends show one broadened α-relaxation as compared with the homopolymers. At temperatures below T_g the β-relaxations corresponding to both homopolymers are observed in the blends. The β-relaxation strength obeys dilution laws with no indication of a critical TMBPA-PC concentration above which the β-relaxation in BPA-PC is totally suppressed.

Introduction

Several studies have been carried out on the secondary relaxation behavior of bisphenol-A polycarbonate (BPA-PC) and its plasticized form.[1–7,35] The motivation in these studies lies on the fact that the secondary relaxation process is related to the mechanical properties of the polymer and on the industrial importance of the effect of plasticizers on polymer properties. Blending of polycarbonate-based polymers has been widely used to modify their properties. Thus, studies looking into the effect of blending BPA-PC with other solid polymers on its local molecular motions[8–10] have become of increasing interest for both basic and applied research.

Suppression of the β-relaxation has been observed in BPA-PC in cases of both plasticizer–polymer[1] and polymer–polymer[9,12] combinations. The suppression of the β-relaxation is generally thought to be related to the antiplasticization effect which can have a strong influence on the mechanical properties of the polymer.[10,11] Blending homopolymers changes their molecular environment. This may lead to new backbone or side-chain conformational states with a wide distribution of orientational energy barriers. The motion of individual molecules will therefore be determined by both inter- and intramolecular interactions within their immediate surrounding. The size of the region in which the molecule is influenced by its neighbors is dependent on the specific interactions between the blend components.

Relaxation processes offer a direct way of studying molecular dynamics in polymers. Information about the transitions between equilibrium states and the kinetics involved can be obtained from these processes characterized by a relaxation strength and a relaxation time distribution. The relaxation strength measures the long time limit of the change of any linear susceptibility, such as the dielectric permittivity, as the system relaxes, and therefore it can be treated as a quasiequilibrium property of the system. The dynamics of the relaxation processes is described by a distribution of relaxation times with a characteristic width and mean relaxation time. The temperature dependence of the relaxation time shows the type of activation processes present in the system. Typically, relaxation processes below T_g exhibit an Arrhenius behavior while the dynamic glass transition (α-relaxation) has a William–Landel–Ferry (WLF)[32] or a Vogel–Fulcher–Tammann temperature dependence.

New orientational energy barriers are expected in blends, and these determine not only the length of the relaxation time but also the width of the relaxation time distribution. The nature of the intermolecular interactions between the blend components can be determined by obtaining the scaling behavior of the relaxation strength as a function of blend composition. Despite the fact that various methods have been applied to the investigation of the molecular motions in the blends of bisphenol-A polycarbonate (BPA-PC) and tetramethylbisphenol-A polycarbonate (TMBPA-PC), some questions are still controversial. Different explanations of the origin of the secondary molecular motions in the pure polymers have been proposed,[6,9,10,27] and in the blends it is not clear whether these motions of the components are cooperative or totally independent. These discrepancies might be caused by the difference in the sensitivity of the methods used (i.e., to what concentration level can the molecular motion of the minor component in the blend be detected).

In this paper, we present broadband dielectric spectroscopy measurements on the homopolymers BPA-PC and TMBPA-PC and blends of these two polymers. With a broad frequency (10^{-1}–10^7 Hz) and temperature range (93–553 K), we were able to examine both the α- and the β-relaxation processes. The frequency-dependent loss curves of both the α- and the β-relaxation were quantitatively analyzed, and the temperature dependence of the relaxation times in various blends was obtained. The composition dependence of the relaxation strength was examined at temperatures corresponding to the β-relaxations of BPA-PC and TMBPA-PC in the blends. This analysis was also carried out for the α-relaxation at the same intervals from the glass transition temperature of the blend. It will be shown that the temperature range over which the β-relaxations occur for the two components are not influenced by blending and that their relaxation strengths vary according to dilution laws. Contrary to recent dynamic mechanical measurements,[29] our results show no evidence of a critical TMBPA-PC concentration of 75% above which the β process peak in BPA-PC is totally suppressed.

Experimental Section

Sample Preparation and Characterization. The polymers used were poly(bisphenol-A) carbonate (Makrolon 2808) and poly(tetramethylbisphenol-A) carbonate provided by Bayer, Le-

0024-9297/93/2226-3075$04.00/0

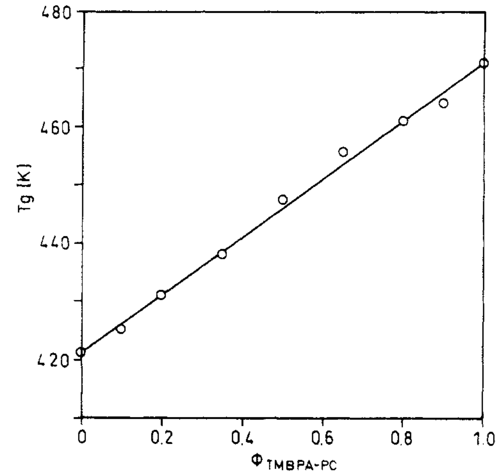

Figure 1. Glass transition temperature (T_g) as a function of composition.

Table I. Properties of the Pure Polymers

polymer	M_w	$T_g \pm 1$ K	density (at 296 K) (g/cm^3)	thermal expansivity (cm^3/K/10^{-4})
BPA-PC	28 000	421	1.208	1.20
TMBPA-PC	30 000	471	1.083	1.28

verkusen. These polymers have no side chains and therefore have β-relaxation maxima which are suppressible according to the Heijboer classification.[16] Films of the pure polymers and their mixtures were prepared by dissolving the individual polymers in dichloromethane (CH_2Cl_2) at a 10% level (g/mL). The films were air dried for 2 days at 296 K and then for a further 5 days under vacuum at 353 K. Before measurements, the films were annealed for 24 h at 20 K above T_g. The resultant films were 0.2 ± 0.01-mm thick. The glass transition temperatures (T_g) were determined using a Mettler DSC 30 at a heating rate of 10 K/min. Each blend showed a single T_g which is equal to the volume fraction average of the glass transition temperatures of the component polymers (Figure 1). The densities of the homopolymers and their blends were determined by using a gradient column composed of 2-propanol, distilled water, and calcium nitrate. All density values were measured at 296 K. The specific volumes of the pure polymers were measured in a GNOMIX PVT machine by heating the samples to temperatures between 473 and 503 K and cooling at 1 K/min. Table I shows a summary of the polymer properties.

Dielectric Measurements. Dielectric measurements were performed on the polymers and their blends with a TMBPA-PC composition by weight varying from 10% to 90%. Self-supporting gold-plated films were placed between two gold-plated stainless steel electrodes that were pressed together by a micrometer screw. The effective diameter of the samples was 20 mm, and their thickness was 0.2 ± 0.01 mm. Measurements of the complex dielectric function were made in the frequency range 10^{-1}–10^6 Hz using a frequency response analyzer (Solartron-Schlumberger FRA 1260 with a high impedance preamplifier of variable gain) and a Hewlett-Packard impedance analyzer (HP4192A, frequency range from 10 to 10^7 Hz)[17]. The frequency response analyzer has a resolution of 5×10^{-5} in the loss tangent, tan δ, and is therefore specially suitable for studying the weak β-relaxations. In contrast, the impedance analyzer has only a resolution of 10^{-3} and was therefore used to measure the much stronger α-relaxations. The measurements covered a temperature range from 93 to 553 K. Below 450 K the temperature was controlled by a nitrogen gas heating system which covers a range from 90 to 450 K with a temperature stability within ±0.2 K.

The data were quantitatively analyzed by fitting the experimental relaxation curves using the Havriliak-Negami function.[18] This function can be viewed as a superposition of individual Debye-like processes. It accounts for the unsymmetrical frequency distribution with respect to the logarithm of frequency log ω and within the experimental error describes our data well (Figure 2). The function can be written in the form

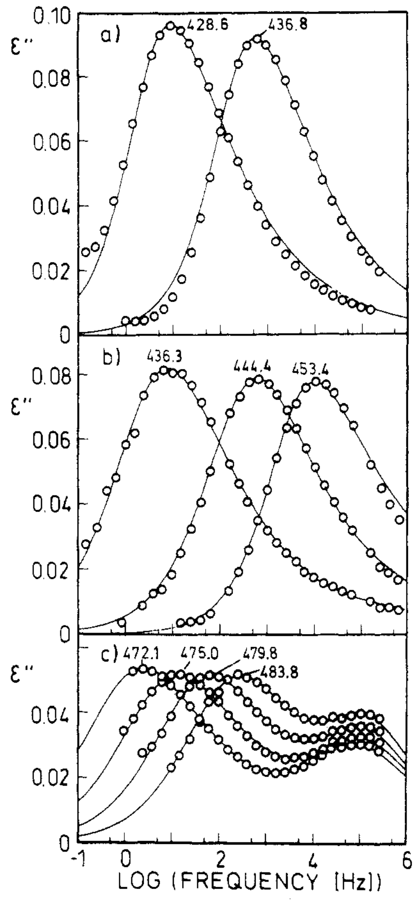

Figure 2. Dielectric loss $\epsilon''(\omega)$ as a function of frequency for (a) BPA-PC, (b) blend with $\Phi_{TMBPA\text{-}PC} = 0.1$, and (c) TMBPA-PC at various temperatures. The symbols denote the experimental data, and the solid lines are fits according to the Havriliak–Negami function (eq 1). In a and b only the α-relaxation is observable within the experimental frequency and temperature window, while in c and β-relaxation occurs on the high frequency side.

$$\epsilon^* = \epsilon_\infty + \frac{(\epsilon_S - \epsilon_\infty)}{((1 + i\omega\tau)^\alpha)^\gamma} \tag{1}$$

with $0 < (\alpha, \gamma) \leq 1$. α and γ are dimensionless parameters describing the symmetric and asymmetric broadening of the loss function respectively, τ is the relaxation time scale for this function, ϵ_S and ϵ_∞ are the values of the real part of the complex dielectric function with $\omega\tau \ll 1$ and $\omega\tau \gg 1$. The dielectric relaxation strength, $\Delta\epsilon$, is then given by $\epsilon_S - \epsilon_\infty$. At frequencies below 10^3 Hz a conductivity contribution adds up to the measured dielectric loss. It obeys the power law

$$\epsilon'' \propto \omega^{s-1} \tag{2}$$

with $0.5 \leq s \leq 1$. Due to the strongly differing functional form of the relaxation process and the conductivity contribution, the two can easily be separated. The following analysis was carried out after the conductivity contribution was subtracted from the relaxation process. In the case where both the α- and the β-relaxation processes occurred, a twofold Havriliak–Negami function was fitted (Figure 2c), and the parameters α, γ, τ, and $\Delta\epsilon$ for the relaxation peak were obtained.

Results and Discussion

α-Relaxation. Figure 2 shows the plot of the dielectric loss ϵ'' against the logarithm of frequency for the α-process in the homopolymers and the blend with $\Phi_{TMBPA\text{-}PC} = 0.1$. By comparison of the dielectric absorption in the homopolymers (Figure 2a,c) with that of the blend two features are evident. Firstly, the blend exhibits a single

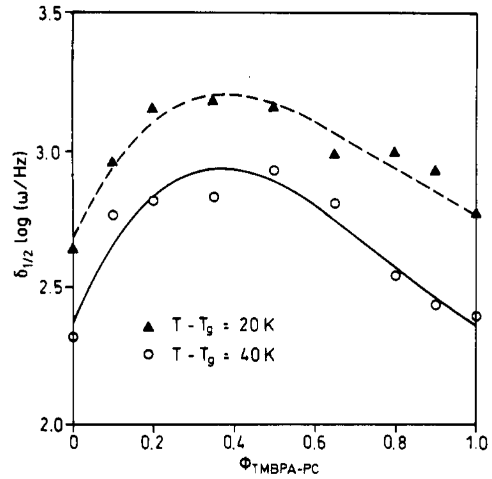

Figure 3. Halfwidth $\delta_{1/2}$ log ω as a function of $\Phi_{TMBA\text{-}PC}$ for the α-peak plotted at $T - T_g$ = 20 and 40 K.

but broadened α-peak, and secondly, the peak is shifted in the frequency position as compared to the pure components (Figure 2a,b). For TMBPA-PC both the α- and the β-relaxations appear in the frequency window (Figure 2c) between 10^{-1} and 10^6 Hz.

The broadening of the α-relaxation in compatible polymer blends is a well-known effect.[20,21] However, it is notable that in many systems this broadening is directly linked with the broadening of the glass transition as observed by calorimetry.[22-27]

In contrast, the width of the glass transition for the blends of BPA-PC and TMBPA-PC at a scanning rate of 10 K/min showed no systematic variation with composition. All blends had an average glass transition width of 8.9 ± 0.5 K whereas the homopolymers BPA-PC had a width of 8.8 ± 0.1 K and TMBPA-PC a width of 9.7 ± 0.1 K, respectively. The same is true for the heat capacity change occurring through the glass transition. The blends showed an average heat capacity change of 0.27 ± 0.02 as compared to the heat capacity change of 0.25 ± 0.01 in BPA-PC and of 0.27 ± 0.01 in TMBPA-PC. This strongly indicates the collective participation of the components in the transition particularly taking into account that the samples used had almost equal molecular weights. The question is, however, what the broadening observed in the dielectric relaxation curves signifies.

At the glass transition, the discontinuity of the heat capacity implies a gain in the configurational entropy. At the onset of the glass transition, a discontuity in the thermal expansivity also sets in due to the sudden increase in the free volume leading to a configurational freedom. The α-relaxation is then only evident when a critical free volume is acquired which allows for cooperative motion. Since the two polymers have almost the same thermal expansivity in the glassy state (Table I) and they have equal temperature ranges of their glass transition, it can be inferred that in the vicinity of the glass temperature these polymers experience equal changes in their configurational entropy and free volume. The observed broadening of the α-relaxation in the blends can therefore be attributed to local concentration fluctuations which may not be detectable using DSC measurements since the two polymers are structurally similar and their glass transition temperatures vary only by 50 K.

Figure 3 shows the composition dependence of the halfwidth of the relaxation frequency distribution. The halfwidths of relaxation curves were evaluated at the same distances, from T_g. This ensures that in all compositions the widths of loss curves in the same frequency window are compared.

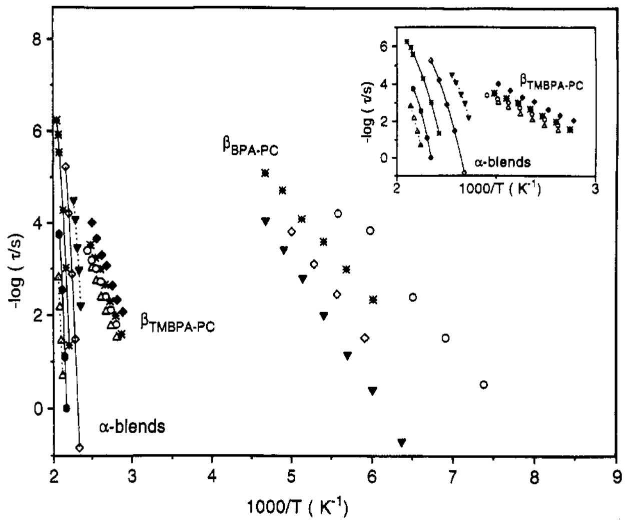

Figure 4. Activation plot for various BPA-PC/TMBPA-PC blends showing the temperature dependence of the relaxation time for both α- and β-processes. The symbols correspond to blends with TMBPA-PC volume fraction: ▼ = 0, ◇ = 0.11, ◆ = 0.22, * = 0.38, ● = 0.68, ○ = 0.82, △ = 1.

Table II. WLF Fit Parameters Obtained for the α-Relaxation in the Blends

vol fraction ($\Phi_{TMBPA\text{-}PC}$)	$C_1 \pm 3$	$C_2 \pm 3$ K	$T_0 = T_g - C_2$ (K)
0.11	15	43	382
0.22	17	59	373
0.38	20	76	363
0.53	22	90	357
0.68	25	101	355

The maximum shown by the halfwidth of the relaxation frequency distribution when plotted against blend composition (Figure 3) is not a feature unique to this system. A similar behavior has been observed in the binary blends of polystyrene and poly(2-chlorostyrene) (PoClS/PS),[20] polystyrene and poly(vinyl methyl ether) (PS/PVME),[24] and in supercooled binary liquid mixtures.[28] The position of the maximum relative to the pure components is surprising. Whereas in the binary liquid mixtures where the maximum favored the component with a higher T_g, in PoClS/PS blends the maximum was observed toward PS which has a lower T_g than PoClS and the lowest relaxation strength. As can be seen in Figure 3, the BPA-PC/TMBP-PC system shows a maximum that lies more toward BPA-PC which has the lowest T_g and the highest relaxation strength. This shows that the position of the maximum is not determined only by T_g or the relaxation strengths of the blend components.

An activation plot summarizing the dynamics of the α- and β-processes in the blends is shown in Figure 4. Due to the concentration dependence of T_g the blends exhibit a WLF temperature dependence with the WLF curves shifted from each other. The α-relaxation data was fitted using the WLF equation

$$\log a_T = \frac{C_1(T - T_g)}{C_2 + T - T_g} \qquad (3)$$

Table II gives a summary of WLF parameters obtained for some blends with the corresponding Vogel temperatures evaluated using the relation $T_0 = T_g - C_2$. Fitting the 90/10 blend with the Vogel–Fulcher–Tammann equation gave T_0 = 381.8 ± 11.6 K and log τ_0 = 13.3 where τ_0 is the relaxation time at the Vogel temperature.

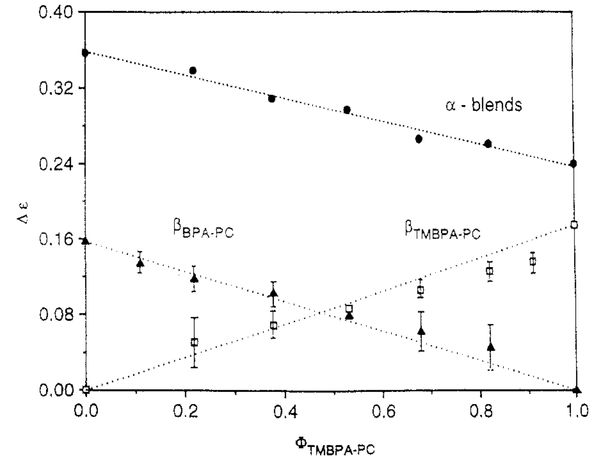

Figure 5. Relaxation strength $\Delta\epsilon$ of α- and β-relaxation processes as a function of TMBPA-PC volume fraction ($\Phi_{\text{TMBPA-PC}}$). The relaxation strength of the α-relaxation (•) was measured for all blends at $T - T_g = 15$ K and for the β-relaxation in BPA-PC (▲) at 194 K and at 380 K for the β-peak in TMBPA-PC (□).

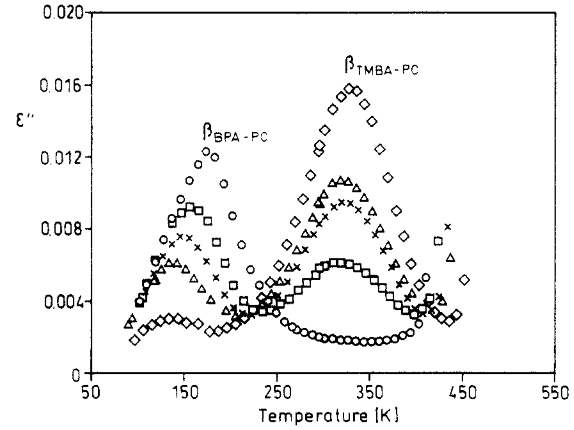

Figure 6. Isochronal plot of the dielectric loss (ϵ'') obtained at 10 Hz for various blends. The blends contain TMBPA-PC volume fraction $\Phi_{\text{TMBPA-PC}}$: ○ = 0, □ = 0.22, × = 0.38 △ = 0.53, ◇ = 0.82.

Figure 5 gives a summary of the variation of the relaxation strengths of both the α- and β-relaxations as a function of blend composition. The strengths of the α-relaxation were determined at a temperature interval $T - T_g = 15$ K for all the blends while the β-relaxation strengths were determined at 194 K for BPA-PC and at 380 K for TMBPA-PC. The relaxation strengths were corrected for density effects. It is shown that the α-relaxation strength decreases with an increase of $\Phi_{\text{TMBPA-PC}}$. Using a model based on concentration fluctuations in binary polymer blends, Fischer et al.[26] have recently shown that, within the glass transition, the α-relaxation is strongly governed by the volume of cooperatively relaxing domains. In view of this model, the decrease of the α-relaxation strength seems to suggest an increase of the volume of cooperativity as the volume fraction of TMBA-PC is increased. A quantitative analysis to obtain the size of this volume will be reported later.

β-Relaxation. Figure 6 shows an isochronal plot (10 Hz) for the loss factor ϵ'' of the β-relaxation in the blends. The β-relaxation of both homopolymers could be detected down to concentration levels of 10%. Contrary to the dynamic mechanical results reported by Jho et al.,[29] a critical TMBPA-PC concentration of 75% above which the BPA-PC β-peak is completely suppressed was not observed in our measurements.

It can be seen in Figure 6 that the TMBPA-PC β-peaks in the blends have curve forms similar to that of the homopolymer. The temperatures of the maxima for the blend β-peaks are close to that of the homopolymer and shift very slightly to lower temperatures with increasing BPA-PC concentration. The peak shifts by 17 ± 2 K at a BPA-PC concentration of 80%. This is in agreement with observations from DMS measurements carried out by Hörth[14] and those reported recently by other workers.[29] On the other hand, at a TMBPA-PC composition of 90% the BPA-PC β-relaxation peak temperature is shifted by almost 40 K.

Various explanations for this observed shift have been proposed. Hörth[14] has attributed the shift of the BPA-PC in BPA-PC/TMBPA-PC blends to the strong suppression of the high temperature tail of the β-process. In this case it was postulated that the BPA-PC β-relaxation could consist of two parts with different relaxation time distributions with the higher temperature part being easier to suppress. A similar argument has been given by Landry and Heinrich[9] for the BPA-PC β-peak suppression in BPA-PC/PMMA binary blends. They attributed the peak shift to selective inhibition of the local motion in BPA-PC.

We extend this argument to explain the BPA-PC β-peak shift. Wehrle et al.[15] using pulsed ^{2}H NMR and Phillips et al. using ultrasonic measurements[33] have shown, particularly for the case of BPA-PC, that the β-relaxation is due to cooperative motion of the phenylcarbonyl groups. It is also known that the carbonyl group motion occurs at lower temperatures than the ring motion.[4] The dipole moments that form the dielectric probe are found in the polar carbonate group of the polycarbonates and not in their phenylene rings. It would be expected that if the β-relaxation was due only to the low-temperature carbonyl group motion the peak should be observed at the same temperature in both TMBPA-PC and BPA-PC. However, changing the phenyl ring structure (by attaching methyl groups) in going from bisphenol-A to tetramethylbisphenol-A polycarbonate shifts the β-peak by 150 K higher and the peak height increases. This is an indication of how strongly the carbonyl group motion is coupled to the motion of the phenylene rings. From DMS measurements it has been shown that the β-relaxation is to some extent cooperative.[29]

As shown in Table I, the specific volume of bisphenol A is less than that of TMBPA-PC. It would be reasonable to consider that the free volume of the polymer is increased with the introduction of the methyl groups in the phenylene rings. This has been shown to be the case by Kim et al.[30] who used the Bondi's group contribution method to estimate the specific free volume in blends of BPA-PC and TMBPA-PC. Increasing the free volume usually lowers the peak temperature as suggested by free volume theories.[39–41] The shift to higher temperatures of the β-peak in TMBPA-PC implies that the mobility in the tetramethylbisphenol-A segment is lower than that of the bisphenol-A segment. This is supported by the observation that the radius of gyration of the TMBPA-PC molecules is larger than that of the BPA-PC.[19]

The presence of specific interactions between the blend components may lead to negative volume of mixing resulting in denser blends than the pure components. This has been shown to be case in the blends of poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) and polystyrene.[31,36,37] At low temperatures the directional character of the specific interactions led to the total elimination of the β-relaxation process in PPO at a PS concentration level of 15%. Specific volumes for PPO/PS blends at room temperature were shown to be smaller than the values predicted by simple addition laws. The BPA-PC/TMB-

Table III. Activation Energies (E_a) and Relaxation Time ($-\log \tau_0$) for BPA-PC and TMBPA-PC β-Relaxations at Various Blend Compositions

vol fraction ($\Phi_{\mathrm{TMBPA\text{-}PC}}$)	E_a ($\beta_{\mathrm{BPA\text{-}PC}}$) ± 2 (kJ/mol)	E_a ($\beta_{\mathrm{TMBPA\text{-}PC}}$) ± 2 (kJ/mol)	$-\log \tau_0$ ($\beta_{\mathrm{BPA\text{-}PC}}$)	$-\log \tau_0$ ($\beta_{\mathrm{TMBPA\text{-}PC}}$)
0.00	53.8		17.2	
0.11	48.0		17.0	
0.22	47.2	99.5	16.4	16.9
0.38	40.5	98.1	14.8	16.3
0.53	39.3	98.8	14.6	16.2
0.68	36.3	92.4	14.5	15.6
0.82	37.8	98.3	14.7	15.5
0.91		95.1		15.7
1.00		95.0		15.5

PA-PC blends show a T_g variation which is proportional to the blend composition, and the measured density at room temperature decreased monotonically with increasing TMBPA-PC concentration.

In the absence of specific interactions, the blend components will exhibit their characteristic local motions governed by the flexibility and degrees of freedom of the molecular segments.[38] The existence of specific interaction between BPA-PC and TMBPA-PC has been demonstrated by the pronounced suppression of the higher temperature tail of the BPA-PC β-relaxation peak as compared with its lower temperature counterpart.[9,29] This effect is also evident in our results (Figure 6). To our knowledge there are no sufficient explanations to describe suppression of the higher temperature tail, the shift of the peak temperature, and the composition insensitivity of the lower temperature tail of the BPA-PC β-peak. It seems conceivable that the suppression and the shift of the peak temperature is a consequence of the coupling of the ring motion in BPA-PC with the limited ring motion in TMBPA-PC. This results in a decoupling of the ring motion from the carbonyl group, an effect which is felt more by the flexible BPA-PC molecules. Pochan et al.[8] have reported similar peak shifts in the sub-T_g relaxations of Lexan^{R} polycarbonate when blended with *n*-butyl 4,5,7-trinitrofluorenone-2-carboxylate (BuTNF). They observed that the major relaxation of the lower temperature region associated with the carbonyl motion was plasticized with an increase of BuTNF and exhibited a plasticization similar to the α-relaxation.

As shown in Figure 4, in both homopolymers and the blends, the β-relaxation obeyed the Arrhenius equation

$$\tau = \tau_0 \exp[E_a/RT] \tag{4}$$

The activation energies for the homopolymers BPA-PC and TMBPA-PC determined in this study are 54 ± 2 and 95 ± 2 kJ/mol, respectively, showing close agreement with reported values measured with dynamic mechanical spectroscopy[29] and by ^{13}C solid-state NMR.[13] The activation energy of TMBPA-PC is nearly constant throughout the full composition range whereas the activation energy of BPA-PC decreases with increasing TMBPA-PC concentration (Table III). It is interesting to note that the size of τ_0 for $\beta_{\mathrm{TMBPA\text{-}PC}}$ decreased from $10^{-15.5}$ s for pure TMBPA-PC to $10^{-16.9}$ s for the blend with 80% BPA-PC. In comparison, τ_0 for $\beta_{\mathrm{BPA\text{-}PC}}$ increased from 10^{-17} s for pure BPA-PC to a maximum of $10^{-14.5}$ s with increasing concentration of TMBPA-PC.

In Figure 5, the variation of the β-relaxation strength $\Delta\epsilon$ in BPA-PC and TMBPA-PC is shown as a function of blend composition. The relaxation strength can be approximated using the Onsager equation[37]

$$\Delta\epsilon = \epsilon_s - \epsilon_\infty = 4\pi n \mu^2/9kT \tag{5}$$

where n is the number density of dipole moments and μ is the diple moment. This approximation gives a relaxation strength which at a given temperature is proportional to the number of dipole moments. It is shown in Figure 5 that the relaxation strengths evaluated at 194 K for the $\beta_{\mathrm{BPA\text{-}PC}}$-relaxation process and at 380 K for β-relaxation corresponding to TMBPA-PC decrease with increase of the volume fraction of the second component. The variation of the β-relaxation strength with blend composition strongly show for both components a peak attenuation that results mainly from dilution effects (dotted line in Figure 5). In fact, for a given concentration (Table IV), the relaxation strengths of the β-processes in the blends add up to those of the pure components. Our results are in agreement with the dynamic mechanical measurements recently reported by Kim et al.[30] It is important to note that tan δ which is commonly used in the literature[8,29] as an indicator of the type of interactions present in blends may be misleading because this quantity combines both the loss and storage effects.

Table IV. Relaxation Strengths $\Delta\epsilon$ of the α- and β-Relaxations Shown in Figure 4

vol fraction ($\Phi_{\mathrm{TMBPA\text{-}PC}}$)	$\Delta\epsilon$ (α-relaxation) at $T - T_g = 15$ K	$\Delta\epsilon$ ($\beta_{\mathrm{BPA\text{-}PC}}$) at 194 K	$\Delta\epsilon$ ($\beta_{\mathrm{TMBPA\text{-}PC}}$) at 380 K
0.00	0.36	0.16	
0.11		0.13	
0.22	0.34	0.12	0.05
0.38	0.31	0.10	0.07
0.53	0.30	0.08	0.09
0.68	0.27	0.06	0.11
0.82	0.26	0.05	0.13
0.91			0.14
1.00	0.24		0.18

Conclusions

Broadband dielectric spectroscopy has enabled the investigation of the molecular dynamics in the blends of BPA-PC and TMBPA-PC both above and below their glass transition temperatures. All blends were miscible in the temperature range investigated and displayed only one α-relaxation and a single calorimetric glass transition temperature. The temperature range of the glass transition in the blends determined from DSC thermograms was constant for all compositions and equal to that of the homopolymers. The observed broadening of the α-relaxation is attributed mainly to the local composition fluctuations. At lower temperatures, two β-relaxation peaks were observed at the peak temperatures corresponding to the pure blend components. An explanation of the β-relaxation peak temperature shift in BPA-PC in view of selective decoupling of the phenylene ring motion from the carbonyl group motion due to free volume constraints has been proposed. The reduction of the β-relaxation strength in both BPA-PC and TMBPA-PC obeys mainly dilution laws. A critical TMBPA-PC concentration above which the β-relaxation in BPA-PC is totally suppressed was not observed.

Acknowledgment. The financial support for G.K. by the Germany academic exchange service (DAAD) is highly acknowledged.

Supplementary Material Available: Tables of density and T_g values of BPA-PC/TMBPA-PC blends, of sample fits and fit parameters for the α-relaxation of BPA-PC/TMBPA-PC blends, and of Havriliak–Negami fit parameters for the β-relaxation of pure BPA-PC, pure TMBPA-PC, and blends of the two; figures of ϵ'' versus log frequency and an activation plot for various blends of BPA-PC/TMBPA-PC (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Fischer, E. W.; Hellmann, G. P.; Spiess, H. W.; Hörth, F. J.; Ecarius, U.; Wehrle, M. *Makromol. Chem. Suppl.* **1985**, *12*, 189.
(2) Bicerano, J.; Clark, H. A. *Macromolecules* **1988**, *21*, 585; *Macromolecules* **1988**, *21*, 597.
(3) Plaetschke, R.; Morbitzer, L.; Grigo, U.; Westeppe, U. 33rd IUPAC-International Symposium on Macromolecules, July 1990, Montreal, Canada.
(4) Aoki, Y.; Brittain, J. O. *J. Appl. Polymer Sci.* **1976**, *20*, 2879.
(5) Watts, D. C.; Perry, E. P. *Polymer* **1978**, *19*, 248.
(6) Henrichs, P. M.; Nicely, V. A. *Macromolecules* **1991**, *24*, 2506.
(7) O'Gara, J. F.; Jones, A. A.; Hung, C. C.; Ingelfield, P. T. *Macromolecules* **1985**, *18*, 1117.
(8) Pochan, J. M.; Gibson, H. W.; Froix, M. F.; Hinman, D. F. *Macromolecules* **1978**, *11*, 165. Pochan, J. M.; Hinman, D. F.; Turner, S. R. *J. Appl. Phys.* **1977**, *10*, 113.
(9) Landry, J. T. C.; Henrichs, P. M. *Macromolecules* **1989**, *22*, 2157.
(10) Brauwens, J. C. *J. Polym. Sci. C* **1971**, *33*, 123.
(11) Boyer, R. F. *Polym. Eng. Sci.* **1968**, *8*, 161.
(12) Butzbach, G. D.; Wendorff, J. H. *Polymer* **1991**, *32*, 1155.
(13) Roy, A. K.; Johns, A. A. *Macromolecules* **1986**, *19*, 1356.
(14) Hörth, F. J. Ph.D Dissertation, Mainz, 1986.
(15) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Colloid Polymer Sci.* **1987**, *265*, 815.
(16) Heijboer, J. *Ann. N.Y. Acad. Sci.* **1976**, *279*, 104.
(17) Kremer, F.; Boese, D.; Meier, G.; Fischer, E. W. *Prog. Colloid Polymer Sci.* **1980**, *80*, 129.
(18) Havriliak, S.; Negami, S. *J. Polym. Sci. C* **1966**, *14*, 99.
(19) Hellmann, E. H.; Hellmann, G. P.; Rennie, A. R. *Colloid Polym. Sci.* **1991**, *269*, 343.
(20) Karasz, F. E.; Macknight, W. J. In *Polymer Compatibility and Incompatibility*; Sol., K., Ed.; MMI Press Symposium Series; MMI Press: 1982; Vol. 2.
(21) Naito, K.; Johnson, G. E., Allara, D. L.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1260.
(22) Illers, K. H.; Heckmann, W.; Hambrecht, J. *Colloid Polymer Sci.* **1984**, *62*, 557.
(23) Casper, R.; Morbitzer, L. *Angew. Makromol. Chem.* **1977**, *58/59*, 1.
(24) Zetsche, A.; Kremer, F.; Jung, H.; Schultze, H. *Polymer* **1990**, *31*, 1988.
(25) Katana, G.; Zetsche, A.; Kremer, F.; Fischer, E. W. *ACS Polymer Preprints* **1992**, *33*, 122.
(26) Fischer, E. W.; Zetsche, A. *ACS Polymer Preprints* **1992**, *33*, 78. Fischer, E. W.; Donth, E.; Steffen, W. *Phys. Rev Lett.* **1992**, *68*, 2344.
(27) Zetsche, A. Ph.D Dissertation, Mainz, 1992.
(28) Shears, M. F.; Williams, G. *J. Chem. Soc., Faraday Trans.* **1973**, *211*, 69.
(29) Jho, Y. J.; Yee, A. F. *Macromolecules* **1991**, *24*, 1906.
(30) Kim, C. K.; Aguilar-Vega, M.; Paul, D. R. *J. Polymer Sci. B Physics* **1992**, *30*, 1131.
(31) Wellinghoff, S. T.; Baer, E. *Org. Coat Plast. Chem.* **1976**, *36*, 140. Wellinghoff, S. T.; Koenig, J. L.; Baer, E. *J. Polym. Sci., Polymer Phys. Ed.* **1977**, *15*, 913.
(32) Williams, L.; Landel, F. R.; Ferry, T. L. *Polymer Sci.* **1955**, *14*, 315.
(33) Phillips, D. W.; North, A. M.; Pethrick, R. A. *J. Polym. Sci.* **1977**, *21*, 1859.
(34) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
(35) Ngai, K. L.; Rendell, W. R.; Yee, A. F.; Plazek, D. J. *Macromolecules* **1991**, *24*, 61.
(36) Fried, J. R.; Karasz, F. E.; Macknight, W. J. *Macromolecules* **1978**, *11*, 150.
(37) Yee, A. F. *Polym. Eng. Sci.* **1977**, *17*, 213. Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(38) Flory, P. J. *Statistical Mechanics of chain Molecules*; Interscience: New York, 1969.
(39) Ferry, D. J. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(40) Baily, T. T.; North, A. M., Pethrick, K. A. *Molecular Motions in High Polymers*; Clarendon Press: Oxford, U.K., 1981.
(41) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Poymeric Solids*; Wiley: London, 1967; Chapter 13.