Comparative Broad-Band Dielectric Study on Poly(ester carbonate)s with 1,4-Cyclohexylene Linkages

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ABSTRACT: Broad-band dielectric spectroscopy (10^{-1}−10^{7} Hz) has been used to study the molecular dynamics in a set of bisphenol A poly(ester carbonate)s (BPA-PECs) and tetramethylbisphenol A poly(ester carbonate)s (TMBPA-PECs) containing 1,4-cyclohexylene dicarboxylate (CHDC) linkages. Four dielectric relaxation processes are observed: The dynamic glass transition (α-relaxation) being characterized by a Williams−Landel−Ferry (WLF-behavior) temperature dependence. Additionally three secondary relaxations (β-, γ'-, and γ*-relaxation) exist. The β-relaxation is related to the flip-flop motion of the cyclohexylene rings and becomes dielectrically active because of a coupling to the neighboring carbonyl units. The γ'- and γ*-relaxations originate from fluctuations of the carbonyl groups as well, either by their own librational motions or by a coupling to the flips of the adjacent phenylene groups. Replacing the hydrogen atoms in the phenylene rings ortho to the carbonate units (BPA-PEC) by methyl groups (TMBPA-PEC) alters drastically the molecular dynamics below and above the calorimetric glass transition.

1. Introduction

The secondary relaxations of bisphenol A polycarbonate (BPA-PC) have been extensively studied since they are believed to be closely related to their mechanical properties.[1−6] As part of an ongoing investigation on the relationship between polymer structure and dynamics, we have in this study analyzed the dielectric behavior of a series of systematically modified poly(ester carbonate)s. Apart from the dynamic glass transition, we have observed three well-separated secondary relaxations showing Arrhenius behavior. As there is only one dielectrically active group present in the polymer—the carbonyl group—the secondary relaxations reflect the coupling of the different neighboring group onto its dynamics.

On the basis of mechanical investigations on a series of alternating multiblock copolymers of BPA-PC and tetramethylbisphenol A polycarbonate (TMBPA-PC, for the structural formula see Table 1), Jho and Yee[7] have suggested that the γ-relaxation, which usually is a local process, is to some extent cooperative, involving several repeat units. This was concluded from the observation that the relaxation appears as a broad composite peak arising from the contributions from the BPA-PC and TMBPA-PC blocks, but on increasing the block lengths of BPA-PC and TMBPA-PC units beyond six, two separate peaks are observed corresponding to each block. This means that the intrachain correlation distance of the mechanical secondary relaxational motion extends to several repeat units.

To investigate how a local molecular motion—the conformational transition of a cyclohexylene ring—interacts with neighboring segments, Liu and Yee[8] recently performed dynamic mechanical measurements on two series of poly(ester carbonate)s (PECs) containing 1,4-cyclohexylene dicarboxylate linkages (CHDC). They concluded that incorporating CHDC units in the main chain enhances the mobility in the secondary relaxation of BPA-PC and TMBPA-PC. This observation was assigned to cooperative conformational fluctuations of neighboring cyclohexylene units which, in turn, activate motions of the linked carbonate segments. A similar conclusion had previously been made in the work of Chen et al.[9] on copolymers based on poly(ethylene terephthalate) and poly(cyclohexylene dimethylene terephthalate).

Earlier dielectric investigations on BPA-PC have been able to split up the γ-relaxation into a lower- and higher-temperature component which were assigned to carbonyl and carbonyl−phenyl motions, respectively.[10−12] Whereas the latter relaxation is much stronger in TMBPA-PC, the former relaxation is weaker because of interactions between the methyl and the carbonyl groups. Using molecular orbital calculations, Sung et al.[13,14] have shown that the motion of the carbonyl group in BPA-PC is only weakly hindered by the phenylene rings whereas it is strongly hindered in TMBPA-PC. Therefore, it is of interest to analyze the effect of these components on the γ-relaxation in a homologous series of copolymers.

In this paper, we present broad-band dielectric measurements on two series of PECs containing CHDC linkages. Specifically, we varied the length of the BPA-PC chain between the cyclohexylene units and studied how this variation affects the relaxation processes observed. The effect of substituting the hydrogen atoms ortho to the carbonate unit by methylene groups (in TMBPA-PC) was investigated as well.

2. Experimental Section

2.1. Sample Preparation. The chemical structures of the homopolymers and block copolymers used in this investigation and their thermal properties are given in Table 1. Details concerning the synthesis are given elsewhere.[8] In the B_mC and T_mC copolymer series, *m* stands for the average number of BPA-PC or TMBPA-PC units in the chain and C is the cyclohexylene linkage. The polymers were obtained in powdered form. Films of the polymers were prepared by dissolving

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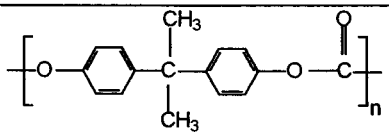
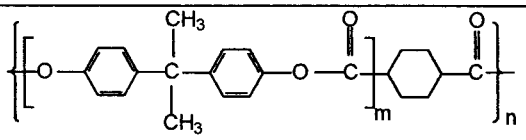
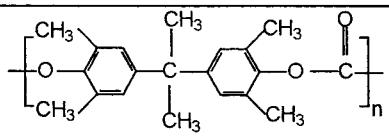
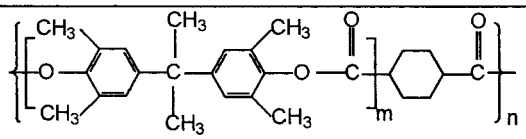
Table 1. Structures, Number of BPA-PC or TMBPA-PC Units in PECs (m), Number-Average Molar Masses ($\bar{M}_n$), Polydispersity Index PDI = $\bar{M}_w/\bar{M}_n$, Glass Transition Temperatures (T_g), and Densities (ρ) of the Poly(ester carbonate)s under Study[a]

Polymer	Repeat Unit	m	$\bar{M}_n$ (g/mol)	PDI	T_g (K)	ρ (g/cm^3)
BPA-PC		-	36,000	2.5	423	1.195
(BPA-PECs)						
B_9C		9	36,000	2.3	431	–
B_7C	"	7	36,000	2.3	432	1.187
B_5C	"	5	28,000	2.3	434	1.185
TMBPA-PC		-	31,000	2.6	473	1.085
(TMBPA-PECs)						
T_9C		9	30,000	1.6	471	–
T_5C	"	5	33,000	1.7	475	1.083
T_3C	"	3	32,000	1.8	479	1.080

[a] PDI was determined by GPC in tetrahydrofuran. The T_g's were measured at a heating rate of 10 K/min.[9] The densities were determined using the immersion method based on the Archimedes principle and have uncertainties below 0.001.

them in dichloromethane at a mass ratio polymer:solvent = 0.1:1. To remove water and solvent, the films were air-dried for 2 days at room temperature and for further 5 days under vacuum at 353 K. Before the measurements, the samples were annealed for 24 h at 20 K above T_g. The resulting films were about 0.15 mm thick.

2.2. Dielectric Measurements. Self-supporting films with evaporated gold electrodes were placed between two gold-plated brass plates that were pressed together by a micrometer screw. The measurements of the complex dielectric function were made in the frequency range between 10^{-1} and 10^7 Hz using a Solartron-Schlumberger frequency response analyzer together with a Novocontrol interface (broad-band dielectric converter). The measurements covered a temperature range from 123 to 523 K using a nitrogen gas-controlled heating system (Quatro Novocontrol). The frequency sweeps were carried out when the sample temperature was stable within ±0.2 K.

To describe the dielectric spectra quantitatively, a superposition of model functions according to Havriliak and Negami[15] and a conductivity contribution have been fitted (Winfit Novocontrol) to the isothermal dielectric loss data ϵ'':

$$\epsilon'' = \frac{\sigma_0}{\epsilon_0}\frac{a}{\omega^s} - \sum_{k=1}^{3}\mathrm{Im}\left[\frac{\Delta\epsilon_k}{[1+(i\omega\tau_k)^{\alpha_k}]^{\beta_k}}\right] \qquad (1)$$

In this notation, ϵ_0 is the vacuum permittivity, σ_0 the dc conductivity, $\Delta\epsilon$ the dielectric strength, and τ the mean relaxation time. The index k refers to the different processes that contribute to the dielectric response. α_k and β_k describe the symmetric and asymmetric broadening of the relaxation time distribution. The first term on the right-hand side of eq 1 is caused by translational diffusion of mobile charge carriers. For Ohmic behavior, s equals 1; deviations ($s < 1$) are caused by electrode polarization; and a is a factor having the dimensionality $[a] = (\mathrm{Hz})^{s-1}$.

3. Results and Discussion

3.1. The α-Relaxation. Figure 1 shows a plot of the dielectric loss ϵ'' versus the logarithm of the frequency for the α-process in BPA-PC and the BPA-PEC samples at different temperatures. One broadened relaxation process is observed in all samples. It is shifted to lower frequencies with decreasing length of the BPA segment. It should be noted that in going from BPA-PC to BPA-PEC the mole fraction of the carbonate moieties decreases by a factor of 2; i.e., the mole fraction of the carbonyl moieties increases by a factor of 2 (Table 1). Also, due to the partial double-bond character of the C(carbonyl)−O(ether) bonds in BPA-PC,[16,17] the carbonate linkage has a lower rotational/torsional freedom than the carbonyl group in the CHDC unit.

The temperature dependence of the mean relaxation times (Figure 2) for the α-process for all samples investigated follows the WLF law[18]

$$\log\left(\frac{\tau(T)}{\tau(T_g)}\right) = \frac{C_1(T-T_g)}{C_2+T-T_g} \qquad (2)$$

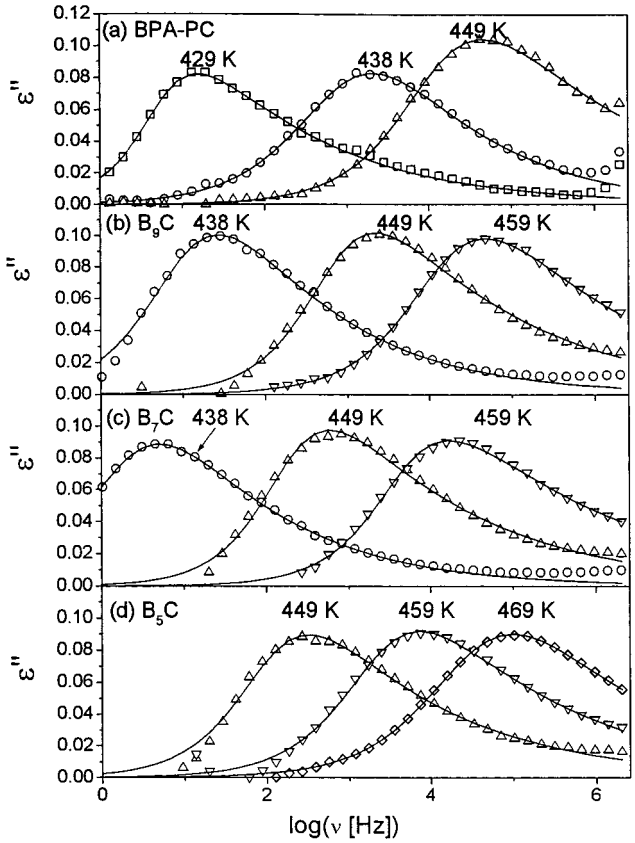


Figure 1. Dielectric loss $\epsilon''(\nu)$ as a function of the logarithm of frequency for (a) BPA-PC, (b) B_9C, (c) B_7C, and (d) B_5C at various temperatures. The symbols denote the experimental data, and the solid and dashed lines are fits according to the Havriliak−Negami function. The conductivity contribution has been subtracted from the experimental data. The increase in ϵ'' at high frequency arises from lower-frequency tails of the β- and γ*-processes. The limit of experimental uncertainty is smaller than the size of the symbols.

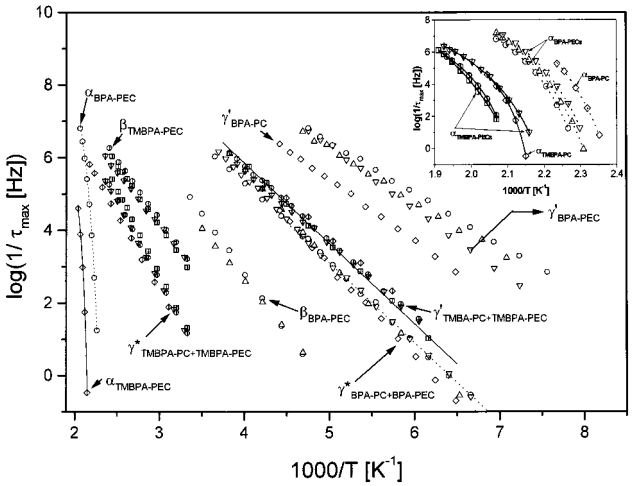


Figure 2. Temperature dependence of the relaxation rate for the α-, β-, γ*-, and γ'-processes for various poly(ester carbonate)s (PECs). The symbols correspond to BPA-PC (◊), B_9C (▽), B_7C (△), B_5C (○),TMBPA-PC (stroked ◊), T_9C (stroked ▽), T_5C (stroked ○), and T_3C (stroked □). The limit of experimental uncertainty is smaller than the size of the symbols.

Table 2 gives a summary of WLF parameters obtained for the samples investigated. The calorimetrically and dielectrically measured T_g values show the same trend. However, they do not coincide within the limits of experimental accuracy which is caused by the fact that

Table 2. WLF Parameters of the α-Relaxation of the Poly(ester carbonate)s under Study[a]

polymer	C_1	C_2	T_g^{BDS}	T_g^{DSC}
BPA-PC/-PEC	± 2	± 3 [K]	± 2 [K]	± 2 [K]
BPA-PC	25	40	429	423
B_9C	20	32	438	431
B_7C	20	33	443	432
B_5C	18	25	445	434
TMBPA-PC/-PEC	± 3	± 3 [K]	± 2 [K]	± 2 [K]
TMBPA-PC (TMBPA-PECs)	26	39	474	473
T_9C	20	48	468	471
T_5C	25	54	484	475
T_3C	26	60	487	479

[a] T_g^{BDS} corresponds to the temperature at which the dielectrically determined mean relaxation rate has a value of 0.01 Hz. T_g^{DSC} is the glass transition temperature determined by differential scanning calorimetry (DSC) at a heating rate of 10 K/min.

the dielectric method senses the fluctuations of the dipolar units only in contrast to calorimetry. The changes observed with both methods reflect the change of chain flexibility and of segment packing. The density decreases with increasing content of CHDC linkages (Table 1).

Changing the phenyl structure in going from BPA-PC to TMBPA-PC shifts the α-peak to much higher temperature (Figure 2) which we attribute to the increased energy barrier to phenyl rotation arising from steric hindrance:[19] The TMBPA chain is stiffer than BPA as the phenyle flip is not as easily possible because of the sterical hindrance of the methylene groups. In addition, a high-frequency process (γ*) appears which will be discussed later (Figure 3). Unlike in the BPA-PECs, the frequency position of the α-process shows only a weak dependence on the length of the TMBPA-PC chain which we ascribe to the weakened polar interactions resulting from the higher specific volume of TMBPA-PC compared with BPA-PC.

Parts a and b of Figure 4 give a summary of the variation of the relaxation strengths and shape parameters of the α-process as a function of the mole fraction of the CHDC linkages determined at $T = T_g^{BDS} + 15$ K, respectively. It can be seen that the dielectric strength of the α-process in the B_mC copolymers increases with decreasing length of the polycarbonate chain (Figure 4a). This can be explained by the increase in the fraction of dipolar carbonyl moieties replacing the carbonate moieties. For the T_mC copolymers, no significant changes in the dielectric strength are observed with varying content of CHDC linkages. We attribute this fact to the increasing distance between the carbonyl groups which render the dipole−dipole interactions ineffective. In addition, because of imperfect sequence homogeneity in these systems, concentration fluctuations of the regions exhibiting the polar interactions are expected. This effect is expected to become more important with the amount of polar carbonyl groups. In other words, the distribution of relaxation times is expected to become broader (decrease in α) with increasing molar fraction of CHDC linkages, which indeed is observed in the B_mC copolymers. On the other hand, due to the increased distance between the CHDC linkages in the T_mC copolymers, the secondary bonds are weak and do not play a significant role as seen by the weak dependence of the shape parameter on the length of the TMBPA-PC chain.

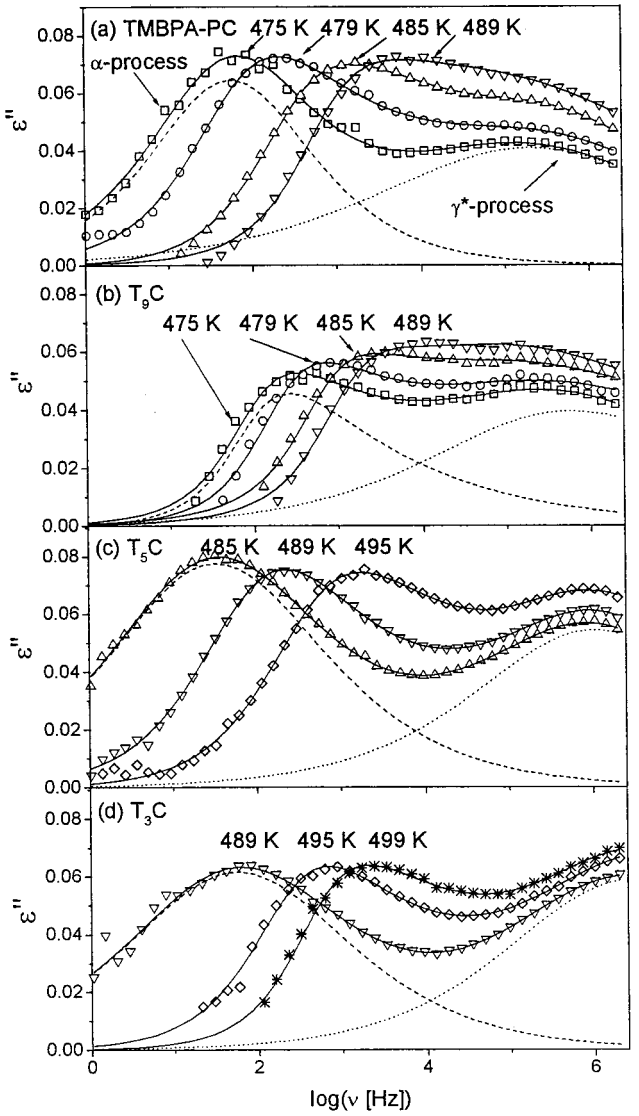


Figure 3. Dielectric loss $\epsilon''(\nu)$ versus logarithm of frequency for (a) TMBPA-PC, (b) T_9C, (c) T_5C, and (d) T_3C at various temperatures. The symbols denote the experimental data, and the solid and dashed lines are fits according to the Havriliak–Negami function. The conductivity contribution was subtracted. The limit of experimental uncertainty is smaller than the size of the symbols.

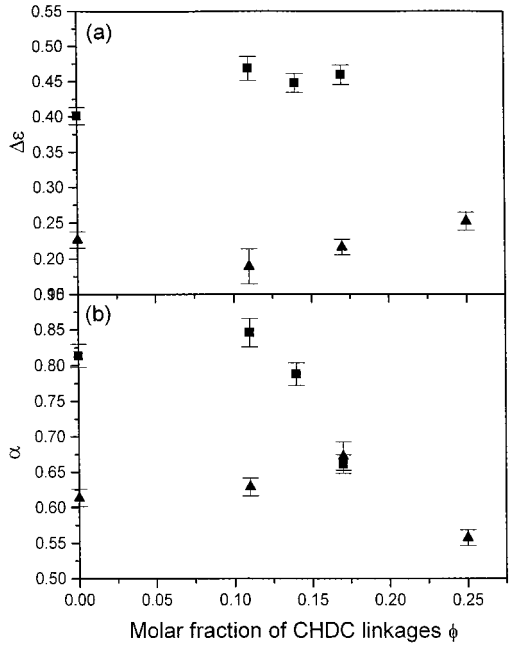


Figure 4. (a) Relaxation strength $\Delta\epsilon$ and (b) shape parameter α of the α-process of the poly(ester carbonate)s at $T - T_g = 15$ K as a function of the molar fraction of the CHDC linkages. The symbols correspond to B_mC (■) and T_mC (▲). $\phi = [1/(m + 1)]$.

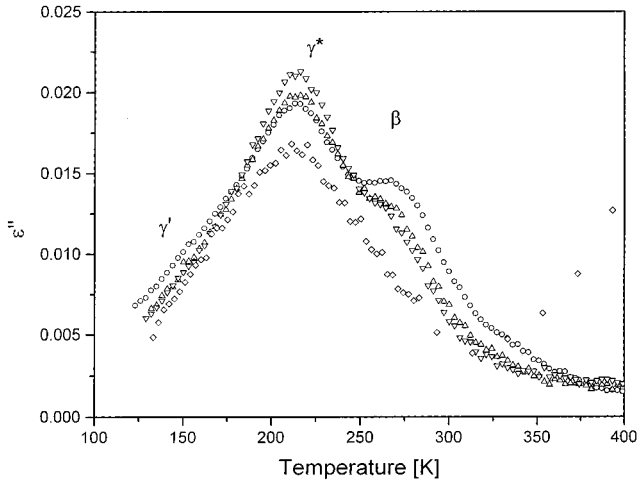


Figure 5. Isochronal plot for the β-, γ*-, and γ'-processes of the dielectric loss (ϵ'') obtained at 1.9 kHz for BPA-PC (◊) and BPA-PECs: B_9C (▽), B_7C (△), and B_5C (○). The limit of experimental uncertainty is smaller than the size of the symbols. The increase in ϵ'' in BPA-PC at high temperature is due to the low-frequency tail of the α-process.

3.2. The β-Relaxation. Figure 5 shows isochronal plots of the loss factor ϵ'' of the secondary relaxations in BPA-PC and the BPA-PECs at 1.9 kHz. Three relaxation regions (around 170, 210, and 270 K) can be distinguished. The high-temperature peak around 270 K is the β-relaxation which is assigned to motion induced by the "chair–chair" conformational transition of cyclohexylene rings on the adjacent carbonyl group through C(cyclohexyl)–C(carbonyl) bond as shown schematically in Figure 6b. The temperature position is unaffected by the length of the BPA-PC chain segment. However, the peak strength (Table 3) increases monotonically with decreasing length of the BPA-PC chain due to increasing mole fraction of the cyclohexylene rings. The temperature dependence of the mean relaxation time follows an Arrhenius law (Figure 2). Also, in previous mechanical measurements performed on acrylic polymers containing cyclohexylene rings pendant to the polymer backbone, a loss peak was observed near 193 K at 1 Hz.[20] This process was attributed to the chair–chair conformational exchange motion of the cyclohexylene ring, and its activation energy was calculated as 48.1 kJ/mol. The activation energies we have determined from our experimental data fall in the range between 54 and 66 kJ/mol (Table 3) and do not show any systematic dependence on the separation between the CHDC linkages. It can be concluded that, by tethering the cyclohexylene units at both ends to the main chain, the activation energy of the chair–chair motion is larger than when they are pendant to the polymer backbone.[20]

Changing the phenyl structure in going from BPA-PC to TMBPA-PC shifts the β-peak to higher temperatures (Figure 2). Figure 7 shows an isochronal plot for the loss factor ϵ'' for TMBPA-PC and TMBPA-PECs at

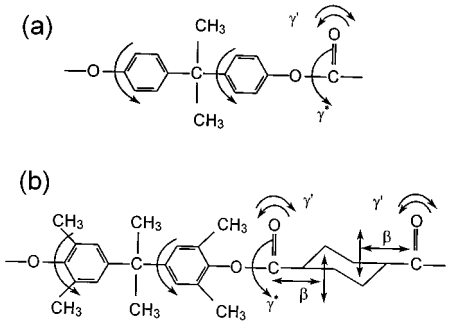


Figure 6. Schematic illustration of the β-, γ*-, and γ'-processes in (a) the polycarbonates and (b) the poly(ester carbonate)s under study.

Table 3. Relaxational Strengths ($\Delta\epsilon$) for the β-, γ*-, and γ'-Relaxations of the Poly(ester carbonate)s under Study

polymer	β-relaxation	γ*-relaxation	γ'-relaxation
BPA-PC/-PEC	$\Delta\epsilon$ at 230 K	$\Delta\epsilon$ at 194 K	$\Delta\epsilon$ at 194 K
BPA-PC		0.038	0.10
B_9C	0.035	0.075	0.11
B_7C	0.039	0.067	0.12
B_5C	0.051	0.061	0.15
TMBPA-PC/-PEC	$\Delta\epsilon$ at 303 K	$\Delta\epsilon$ at 303 K	$\Delta\epsilon$ at 191 K
TMBPA-PC		0.25	0.056
T_9C	0.010	0.25	0.056
T_5C	0.042	0.24	0.062
T_3C	0.090	0.23	0.067

1.5 Hz where three relaxation regions (around 160, 265, and 300 K) can be distinguished. It can be conjectured that the coupling between the cyclohexylene rings and the adjacent polar groups is strong because of the stiff TMBPA-PC segments.

3.3. The γ'-Relaxation. In Figure 5, the peaks at 170 K (γ') and 210 K (γ*) are the lower- and higher-temperature components of the γ-relaxation in BPA-PC, respectively.[21,22] The broad γ'-peak is assigned to librational motion of the carbonyl group alone[21,22] as illustrated schematically in Figure 6a,b. The repulsion between the carbonate carbonyl group and the hydrogen ortho to the carbonate group is weak.[14] The temperature dependence of the mean relaxation time follows an Arrhenius law (Figure 2). The activation energy of the γ'-peak of BPA-PC determined in this study (Table 4) is 32 ± 2 kJ/mol, showing close agreement with reported values (~30 kJ/mol).[10−12]

In the B_mC copolymers, the γ'-peak frequency (Figure 2) and strength (Table 3) increase with decreasing length of the BPA-PC segments. The former observation can be attributed to the increase in degree of freedom of the carbonyl groups whereas the latter can be explained by the increased number of highly mobile carbonyl units.

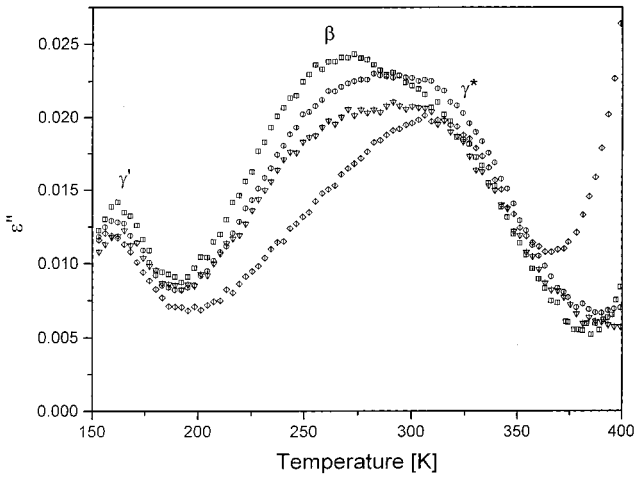


Figure 7. Isochronal plot for the β-, γ*-, and γ'-processes of the dielectric loss (ϵ'') obtained at 1.5 Hz for TMBPA-PECs. The symbols correspond to TMBPA-PC (stroked ◇), T_9C (stroked ▽), T_5C (stroked ○), and T_3C (stroked □).

In going from BPA-PC to TMBPA-PC the γ'-peak frequency decreases (Figure 2), suggesting inhibition of the local motion of the carbonyl group by the pendant methyl groups. Using molecular orbital calculations, Sung et al.[14] have shown that the presence of methyl substituents in TMBPA-PC significantly decreases the rotational/torsional freedom around the carbonate linkage due to strong repulsion between the ortho methyl and the carbonate carbonyl groups, leading to an increase in activation energy, which is consistent with our results. In addition, the hindrance of carbonyl motion would decrease the size of the molecular environment as revealed by decrease in dielectric strength (Table 3).

3.4. The γ*-Relaxation. The γ*-relaxation is assigned to fluctuations of the carbonyl group being coupled to phenylene motions (Figure 6). Using molecular orbital calculations, Sung et al. have shown that the motion of the carbonate linkage in BPA-PC is weakly coupled to rotation of phenylene rings since the repulsion between the carbonate carbonyl and the hydrogen ortho to the carbonate group is low.[14] This is expected to weaken the dielectric strength. The activation energy of the γ*-relaxation determined in BPA-PC in this study (Table 4) is 49 ± 2 kJ/mol, which is in the range of the reported values for the same system (~45 kJ/mol).[10−12]

In the B_mC copolymers, the γ*-peak frequency is nearly unaffected by the length of the BPA-PC chains,

Table 4. Activation Energies (E_a) and Characteristic Frequencies (log f_0) for the β-, γ*-, and γ'-Relaxations of the Poly(ester carbonate)s under Study

polymer	β-relaxation		γ*-relaxation		γ'-relaxation	
BPA-PC/-PEC	$E_a \pm 0.9$ [kJ/mol]	log(f_0[Hz]) ± 0.6	$E_a \pm 0.8$ [kJ/mol]	log(f_0[Hz]) ± 0.6	$E_a \pm 0.5$ [kJ/mol]	log(f_0 [Hz]) ± 0.7
BPA-PC			48.5	15.0	32.3	13.1
B_9C	66.3	15.9	42.2	13.4	33.2	14.2
B_7C	54.1	13.2	46.6	14.6	27.6	12.7
B_5C	62.8	15.2	43.2	13.7	27.0	12.2
TMBPA-PC/-PEC	$E_a \pm 1.2$ [kJ/mol]	log(f_0[Hz]) ± 0.6	$E_a \pm 0.4$ [kJ/mol]	log(f_0[Hz]) ± 0.7	$E_a \pm 0.5$ [kJ/mol]	log(f_0[Hz]) ± 0.7
TMBPA-PC			80.0	14.1	39.3	13.3
T_9C	56.2	12.2	84.0	15.0	38.6	12.9
T_5C	62.8	13.4	85.8	15.3	39.7	13.3
T_3C	64.7	13.5	88.7	16.0	42.4	13.9

indicating that the relaxation takes place only locally, i.e., via specific interactions of the carbonyl groups with the phenylene rings (Figure 2). However, the γ*-peak strength abruptly increases on going from BPA-PC to B_9C and then decreases with decreasing length of the BPA-PC chain. The abrupt increase of the γ*-peak strength (Table 3) can be attributed to an increased number of carbonyl moieties as well as an increased motional freedom of the carbonyl groups compared to the restricted one in the carbonate moieties.

In going from BPA-PC to TMBPA-PC, the γ*-peak frequency decreases significantly (Figure 2) because of greater steric hindrance imposed by the methyl-substituted phenylene rings. However, the dielectric strength of the γ*-process is larger than in BPA-PC, suggesting that in order for internal motion of the carbonyl group to take place, a larger region of intra- and intermolecularly correlated methyl-substituted phenylene rotations must take place, relieving steric hindrance. The activation energy of the γ*-relaxation determined in this study (Table 4) is 80 ± 2 kJ/mol, showing close agreement with values reported from dynamic mechanical spectroscopy ($\sim$80 kJ/mol) on the same system.[1]

Like in the B_mC copolymers, the length of the TMBPA-PC chain segment has no effect on the γ*-peak frequency, at least at low temperatures. However, at higher temperatures (Figure 3), the process becomes faster with decreasing TMBPA-PC chain length. By contrast, in TMBPA-PEC the cyclohexylene rings, being comparatively more mobile due to higher specific volume of TMBPA-PC, mitigate the dynamic contraints acting on this process. Thus, one observes a reversed trend in the secondary relaxations: in B_mC the γ'-peak shifts to lower temperatures with decreasing BPA-PC chain length with the γ*-peak being unaffected whereas in T_mC it is the γ*-peak which is shifted to lower temperatures with decreasing TMBPA-PC chain length with the γ'-peak remaining unaffected.

4. Conclusion

Broad-band dielectric spectroscopy has enabled to elucidate the molecular dynamics in two sets of polycarbonates with 1,4-cyclohexylene linkages. The extraordinary sensitivity of this method allows to analyze the dynamic glass transition (α-relaxation) as well as the secondary relaxations in detail. The latter are characterized by the coupling of the dielectrically active carbonyl groups to the flip-flop motions of the adjacent phenylene rings and the chair-to-chair conformational transitions of the cyclohexylene moieties. Our analysis is in close agreement with previous dynamic mechanical measurements in identical polymeric systems.

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