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On the Molecular Motions Originating from the Dielectric γ-Relaxation of Bisphenol-A Polycarbonate

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ABSTRACT: We have investigated the molecular motions responsible for the dielectric γ-relaxation of bisphenol A polycarbonate (BPA−PC) by taking advantage of the unbalanced influence of cold-drawing in the dielectric losses. The direct comparison of the dielectric relaxation curves measured on the BPA−PC samples uniaxially stretched below the glass transition temperature with those corresponding to the nonstretched samples allowed us to resolved two main components of the dielectric γ-relaxation. The characteristic times of each of these components nearly coincide with those derived by neutron scattering and deuterium nuclear magnetic resonance for two well-defined jumps of the phenylene rings, evidencing the cooperativity among the motions of the different molecular groups forming the polycarbonate repeating unit. A more detailed analysis of the orientation effects on the dielectric γ-relaxation reveals a weaker third component with characteristic time scales close to those reported in the literature for the fast phenylene ring oscillations. On the basis of these three components we have been able to accurately describe the relaxation behavior of both oriented and nonoriented samples over an extremely wide temperature interval (50−350 K). From these results, we conclude that the low temperature dielectric behavior is mainly driven by the phenylene π-flips, but at temperatures above 200 K, the dielectric relaxation becomes increasingly governed by the concurrent rotation of the carbonate/phenylene units, being these motions those more strongly hindered by chain orientation. Some implications of these finding on the mechanical properties of polycarbonate are discussed.

Introduction

The secondary relaxation of polycarbonate and other related engineering thermoplastics have been extensively investigated over the past decades because this relaxation process is believed to be directly related with the excellent mechanical properties of bisphenol A polycarbonate (BPA−PC) (see for example references[1−8] and the references therein). A broad variety of experimental techniques and computational methods have been used in these investigations, being one of the most fruitful approaches the combination of dynamic mechanical analysis (DMA) and nuclear magnetic resonance (NMR). Despite of the huge effort, the microscopic origin of the secondary relaxation process of BPA−PC has not been completely elucidated. Nevertheless, there is a rather general consensus about the utmost relevance of phenylene ring π-flips for both, the secondary relaxation and the mechanical properties of BPA−PC. Moreover, it has been evidenced that these local molecular motions are coupled to other motions of the groups forming the BPA−PC repeating unit and also that there is a in-chain correlation among the motions in different repeating units.[5−7]

Most of these results have been derived by investigating polymers with modified chemical groups and by following the resulting effects on the secondary relaxation processes of the corresponding family of polymers. More recently, a similar approach has been used by investigating the secondary relaxation of block copolymers with varying size of the block containing the unit of interest. In such a way, it has been evidenced that the strength of the mechanical loss peak decreases significantly as the size of the BPA−PC block is reduced below 7−9 monomers. This latter finding has been often interpreted as a clear evidence that the molecular motions responsible for the γ-relaxation involve in-chain cooperation along such a large number of consecutive repeating units.[9,10] Further investigations have also suggested that this large scale character of the molecular cooperativity is closely related with the mechanical properties of the polymer.[11]

Despite the ability of the dielectric relaxation (DS) techniques to cover an extremely broad frequency range with high sensitivity, DS has been much less used than DMA to this kind of studies. Among others, a main reason for this would be the rather weak dielectric dispersion associated with the secondary relaxation of BPA−PC and the high sensitivity of the resulting relaxation spectra to very small traces of moisture. Nevertheless, early dielectric relaxation investigations on the γ-relaxation of BPA−PC already evidenced that it can be hardly associated with a single molecular motion.[12,13] Indeed, in a recent work where DS technique has been used to investigate a series of poly(ester carbonates)[14] it was concluded that there are two main contributions to the dielectric γ-relaxation of BPA−PC, one assigned to the libration of the carbonyl group alone (as it was previously suggested[13]) and the other to the combined motion of the carbonyl and phenylene groups. On the other hand, some other dielectric investigations have shown a significant effect of small molecule plasticizers[15] and the molecular orientation[12,16−18] on the secondary γ-relaxation of BPA−PC.

Very recently, quasielastic neutron scattering (QENS) techniques have been used to investigate the phenylene ring dynamics in a series of phenylene containing engineering thermoplastics, namely BPA−polysulfone,[19] poly(ether sulfone),[20] BPA−PC,[21] and BPA−poly(hydroxyether).[22] As was

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anticipated from previous ^{2}H NMR studies on this kind of polymers,[23−26] the QENS experiments confirmed the presence of phenylene π-flip motions with characteristics that change only slightly from polymer to polymer. Moreover, these measurements also indicated the presence of fast phenylene ring oscillations of increasing amplitude, being the dynamic characteristics of this motion essentially the same for the four polymers investigated, although the observed increasing amplitude of the oscillation with temperature was found to be less pronounced in the case of BPA−poly(hydroxyether). Interestingly, regardless of these similarities, an additional motion was found for BPA−PC only. Furthermore, it has been shown that the corresponding QENS signal can be well accounted for by assuming the presence of ∼90° phenylene rotations,[21] the existence of which was previously envisaged from computational studies.[27,28] Besides, the time scale of such additional phenylene motion was found to agree well with that measured by DS at high temperatures/frequencies. In this temperature range, the contribution of the relaxation component previously associated with the librations of the isolated carbonyl group is found to be dominant.[16] Therefore, the QENS results put into question the independence of the carbonyl group motions and instead, they again point to the cooperative character among the motions of the different molecular groups forming the BPA−PC unit.

In this work, we have performed broadband DS experiments over a very wide temperature range on BPA−PC in order to gain new insight on the molecular origin of the γ-relaxation. Our approach has been to compare the dielectric γ-relaxation measured on both oriented and nonoriented BPA−PC samples. The dielectric γ-relaxation loss intensity of the uniaxially stretched BPA−PC is known to be significantly lower than that of the nonoriented samples.[12,16−18] However, it has been recently found that the loss reduction is not uniform over the whole frequency range,[16] which reflects the different influence of molecular orientation on the γ-relaxation components. Taking advantage of this feature, it has been possible to obtain the characteristics of the BPA−PC dielectric relaxation components. This procedure has the advantage that, opposite to using chemical modifications, the overall polymer structure is not changed much by cold-drawing, being the main effect an increasing of the local packing and the molecular orientation.[17] Furthermore, it has been suggested that cold-drawing of BPA−PC will affect mainly those regions that are loosely packed, which would be those having a higher molecular mobility, without changing much the overall polymer structure.[29]

The paper is organized as follows. In the next section, the details of the experimental methods used are summarized. In the Results, the dielectric γ-relaxation data of both nonoriented and oriented BPA−PC are presented and the characteristic times of the two main relaxation components are extracted by the direct comparison between the loss curves collected on both samples. Next, the comparison of these relaxation times with those derived previously by means of different techniques for the phenylene dynamics is used to obtain a molecular assignment of the motions originating the two resolved components. Finally, at the end of the Discussion, we present a detailed quantitative analysis of the loss curves measured on BPA−PC, providing a complete description of the experimental data and a simple explanation of the observed effects of orientation on the dielectric relaxation. The conclusions are summarized in the last section.

Experimental Section

Samples. The BPA−PC samples used in this work were supplied by Goodfellow (CT301310) (sheets 0.175 mm thick). The characteristics of this polymer, and in particular the molecular weight distribution ($\bar{M}_n$=20.7 kg mol^{-1} with polydispersity index = 2.66 as determined by means of gel permeation chromatography (GPC) using polystyrene as standard), are similar to those of a more standard BPA−PC as that produced by Bayer AG ($\bar{M}_n$=19.1 kg mol^{-1} with polydispersity index = 2.56), which has been extensively investigated in the literature. Furthermore, both polymers have the same glass transition temperature, T_g = 150 K (as determined by means of standard differential scanning calorimetry), and more interestingly, they depicted indistinguishable dielectric losses in the γ-relaxation range. The reason for using the BPA−PC sheets was related with the fact that using specimens of well-defined thickness provides a much better control of the degree of orientation obtained after cold-drawing.

Before any measurement or mechanical treatment, the sheets were maintained under vacuum (about 0.1 Torr) at about 380 K for several hours to remove any trace of moisture. This care is of great importance because water molecule dipoles, even in amounts undetectable by using standard methods, will contribute significantly to the dielectric losses in the BPA−PC secondary relaxation range.

To obtain uniaxially oriented samples, the specimens were placed in a circulating nitrogen atmosphere inside the heating chamber of the miniature material tester MINIMAT 2000 (Rehometrics Scientific). When the sample temperature was stabilized at 340 K, the sample (of ribbon shape, typically 8 × 30 mm^2) was stretched at a rate of 1.7 mm/s to achieve draw ratios in the range 1.5−4.0. Once the desired draw ratio was obtained, the specimen was rapidly cooled to room temperature. Only at the end of the cooling process the mechanical stress maintaining the desired draw ratio was removed. The sample orientation achieved was characterized by means of birefringence measurements performed by using a prism coupler refractometer (Metricon 2010). The corresponding values of the birefringence index Δn ($\Delta n = n_{\|} - n_{\perp}$) were in the range 0.03−0.05.[16] To avoid any moisture absorption, all the samples were stored under a dry nitrogen atmosphere before the subsequent dielectric experiments.

Dielectric Relaxation Experiments. Broadband dielectric spectroscopy (BBDS) experiments over a wide frequency range, 10^{-2}−10^7 Hz, were performed by using an ALPHA-S impedance analyzer (Novocontrol) in combination with a Quattro temperature control system. Both oriented and nonoriented BPA−PC samples were measured isothermally in the temperature range from 120 to 420 K with stability better than 0.05 K. The sample capacitor was formed with gold plated electrodes. For nonoriented BPA−PC samples, a single piece of sheet was placed between two electrodes of 30 mm diameter. For the measurements on oriented samples, 20 mm diameter gold-plated electrodes were used. Four pieces of stretched specimen having the same birefringence were necessary to fill the electrode surface. It is noteworthy that in the experiments on oriented samples the electric field was always perpendicular to the stretching direction and all the results below correspond to such geometry. To confirm that the detected effects on the dielectric relaxation were only related to the molecular orientation, after the measurements the sample capacitor containing the stretched specimens was annealed slightly above T_g. In this way, the molecular orientation was lost and the measurement over the whole temperature range was repeated without removing the sample from spectrometer. The dielectric relaxation behavior resulting from the latter run was that corresponding to a nonoriented BPA−PC sample.

Two additional equipments have been used in order to extend the investigated frequencies and temperatures. On one hand, a Hewlett-Packard impedance analyzer HP4291B was used to cover the high-frequency range 10^6−10^9 Hz at temperatures above 150 K. In this setup, a sheet piece was placed between two gold-plated electrodes 10 mm diameter. Isothermal frequency sweep measurements were carried out with temperature stability better than 0.05 K. The combination of the data collected in this high-frequency

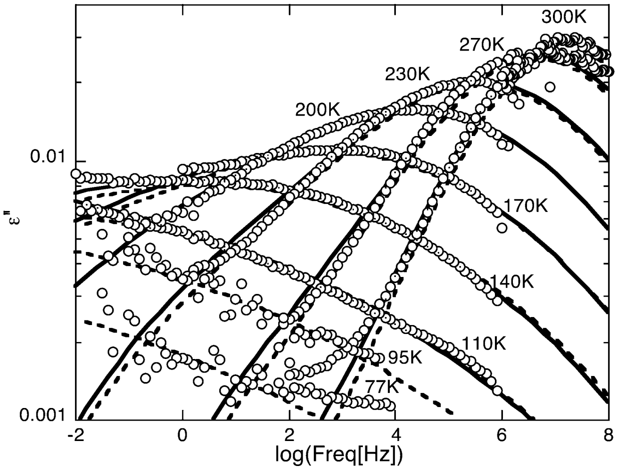

Figure 1. Dielectric relaxation losses of nonoriented BPA−PC on the whole temperature range investigated. The solid lines correspond to the fitting of the data as originated for three distinct components (see the text for details). The dashed lines correspond to the final description in terms of this model.

range with those measured at the same temperature at lower frequencies was performed using a minor correction, accounting for the uncertainties in the determination of the capacitor geometry. The value of the correction factor was chosen to allow a good matching of the permittivity values determined by means of both setups in the common decade ($10^6 < f(\mathrm{Hz}) < 10^7$). On the other hand, isothermal low-temperature measurements, below 110K, were performed using a SI1260 Impedance/gain-phase analyzer complemented with a MESTEC interface covering a frequency range 10^{-2}−10^4 Hz. The sample capacitor, formed with gold plated electrodes of 20 mm diameter, was mounted on the cold head of a close-cycle helium refrigerator system CTI−Cryogenics 8200 connected to a Lake Shore temperature controller.

The more limited accuracy in the determination of the dielectric losses in these two additional equipments (uncertainty in tan $\delta > 10^{-4}$) precluded a proper characterization of the effects of sample orientation on the dielectric response and therefore the results presented below in these extended ranges correspond only to nonoriented BPA−PC.

Results

Figure 1 shows a series of dielectric loss curves corresponding to a nonoriented BPA−PC sample, covering the whole temperature and frequency ranges investigated. From simple inspection of the figure, a marked asymmetry of the loss peak is apparent in the intermediate temperature range. A rapid narrowing of the loss peak on increasing temperature is also noteworthy. Figure 2 depicts the temperature dependence of the characteristic time determined from these data sets as the reciprocal of the angular frequency at the maximum of the loss peak. It is observed that, when the whole experimental frequency range—covering nearly 9 decades—is considered, the resulting temperature variation deviates clearly from the linear behavior expected on such a representation from an Arrhenius-like behavior.

Figure 3 shows a set of dielectric loss curves measured on an oriented BPA−PC sample ($\Delta n = 0.043$). To highlight the effect of orientation on the dielectric losses, some curves corresponding to the nonoriented BPA−PC have also been included in the same frame. The overall appearance of the loss curves measured on the oriented sample is not very different from that measured on nonoriented BPA−PC. However, the comparison of the loss curves recorded at the same temperature evidences a significant reduction of the dielectric loss peak intensity, in agreement with literature results.[12,16−18] Nevertheless, this is an unbalanced effect since, for instance, the reduction of the dielectric losses at 200 K is significantly less pronounced in the low frequency flank of the loss peak (see Figure 4). Moreover, when the same kind of comparison is performed for samples with different level of orientation, it is found that the loss reduction depends almost linearly on the molecular orientation as determined by birefringence measurements, irrespective of the frequency range considered (see inset of Figure 4). The fact that changing the molecular orientation level yields no significant displacement of the peak frequency suggests that the sample orientation achieved by cold drawing does not affect noticeably the characteristics of the γ-relaxation components, but mainly modifies their contribution to the whole relaxation process. Furthermore, what is of utmost relevance for our further analysis is the unbalanced reduction of the dielectric losses, which in a two-component view of the γ-relaxation would indicate that the contribution of the slowest component is less reduced by sample orientation, at least at 200 K. This quite surprising finding has been unambiguously established and will be rationalized below.

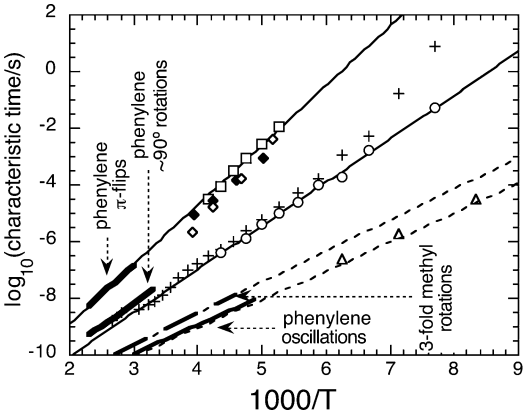

Figure 2. Temperature dependence of the characteristic relaxation times determined from dielectric experiments as the reciprocal of the angular frequency at the peak maxima: (+) whole γ-relaxation of nonoriented BPA−PC, (□) component **I**, (○) component **II**, and (△) component **III**. Thick lines are the time scales derived from QENS ref 21 for the indicated motions and the diamonds correspond to ^{2}H NMR data taken from ref 23 (filled) and from ref 24 (empty). The solid lines represent the fitting of the dielectric data and the dashed lines correspond to the extrapolation to the low-temperature side of the time scales obtained from QENS.

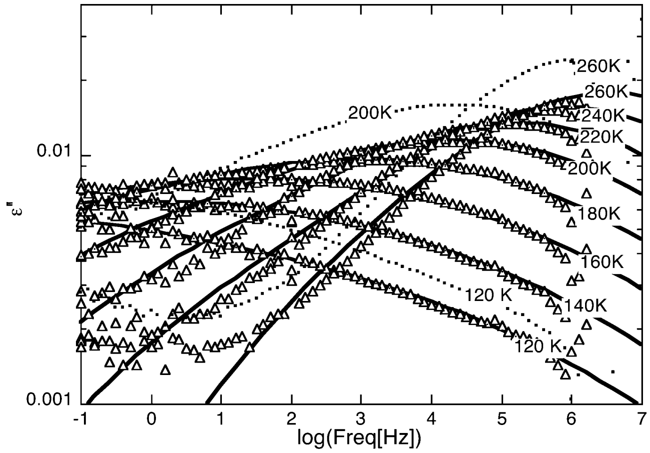

Figure 3. Dielectric relaxation losses of cold-drawn BPA−PC ($\Delta n = 0.043$) in the temperature range from 120 to 260 K measured in steps of 20 K. Data measured on the nonoriented sample at 120, 200, and 260 K are also included as dotted lines for comparison.

The simplest way to account for the dielectric γ-relaxation of BPA−PC as originated from two distinct components is to

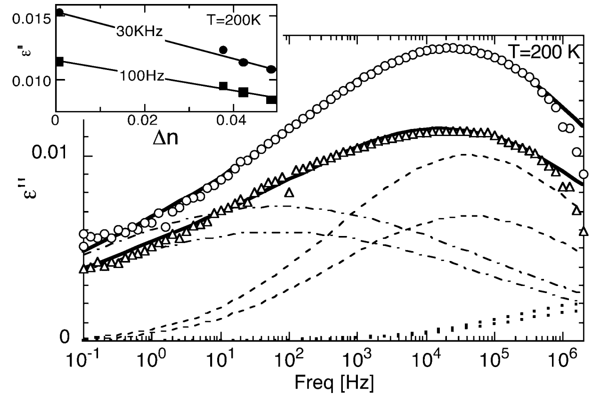

Figure 4. Detailed comparison between the dielectric relaxation losses at 200 K of nonoriented (○) and cold-drawn (△) BPA−PC. The inset shows the linear dependence of the dielectric losses on Δn, determined at 200 K for two different frequencies. The solid lines in the mainframe show the final description of the data: component **I** (dotted-dashed lines), component **II** (dashed lines), and component **III** (dotted line).

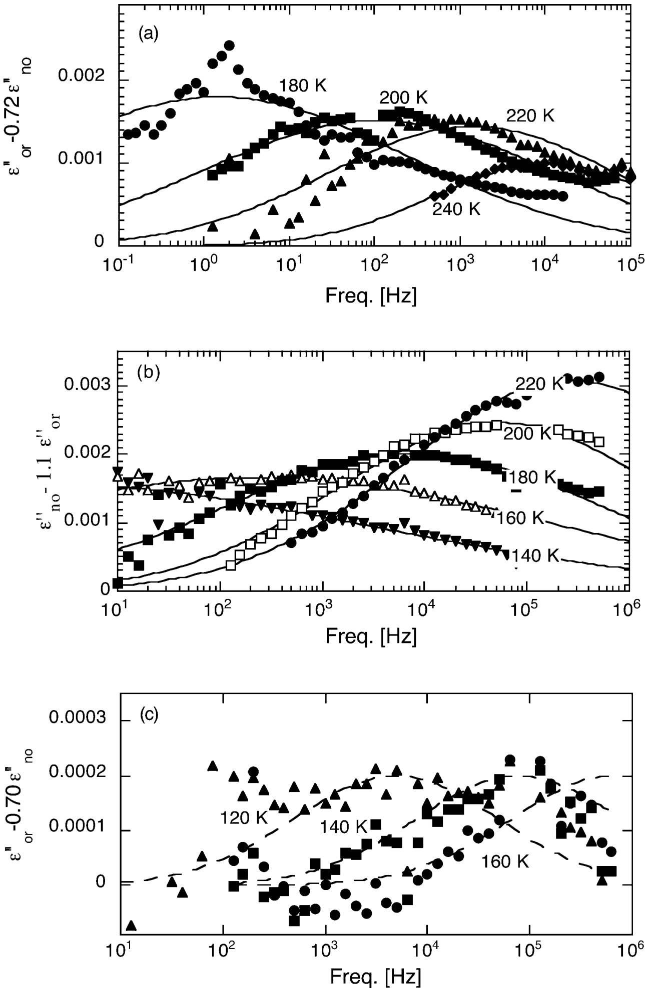

Figure 5. Dielectric loss differences obtained by using the signal measured both, on the nonoriented samples and on that with a birefringence index $\Delta n = 0.043$: (a) losses reflecting the dynamics of the slowest component **I**, (b) losses reflecting the dynamics of the best resolved component **II**, and (c) losses reflecting the dynamics of the hardly resolved fastest component **III**. The solid lines correspond to the fitting of the data according to Gaussian functions. The dashed lines are only guides to the eye.

consider that the measured losses are the result of the simple addition of the corresponding dielectric losses, which will be referred to as ϵ''_{I} and ϵ''_{II} in the following. In this simple approach one can write:

$$\epsilon''_{no} = \epsilon''_{I} + \epsilon''_{II} \quad \epsilon''_{or} = w_{I}\epsilon''_{I} + w_{II}\epsilon''_{II} \tag{1}$$

where ϵ''_{no} and ϵ''_{or} are the experimental losses corresponding to the nonoriented and to the oriented samples, respectively, and w_I and w_{II} would account for the loss reduction produced by molecular orientation on each of the relaxation components. Note that, as commented on above, it is assumed that the sample orientation does not modify the dynamic characteristics of the components. From the two-equation system (eq 1) it follows that

$$\epsilon''_{I} \propto \epsilon''_{or} - w_{II}\epsilon''_{no}\epsilon''_{II} \quad \propto \epsilon''_{no} - w_{I}^{-1}\epsilon''_{or} \tag{2}$$

According to this new set of two equations, in principle, the dynamic characteristics of ϵ''_{I} and ϵ''_{II} can be determined from the above presented experimental results. However, the temperature range where eq 2 can be applied using experimental data is limited because of both the intrinsic experimental uncertainties and the accuracy in the evaluation of w_I and w_{II}. To determine these values, it is necessary to access experimentally the dielectric losses in the very high or in the very low-frequency side of the whole relaxation process. Actually, w_I and w_{II} can be properly determined only at high and low temperatures, respectively. Nevertheless, when analyzing the data shown in Figures 1 and 3 we have found that the values of w_I and w_{II} are essentially temperature independent, in the accessible range: $w_I = 0.91 \pm 0.02$ and $w_{II} = 0.72 \pm 0.02$. Therefore, by means of eq 2, we determined the characteristics of both ϵ''_{I} and ϵ''_{II}, over the whole temperature range where measurements on the effect of orientation on the dielectric γ-relaxation are reliable. The so obtained results are shown in Figure 5, parts a and b (for the sake of clarity, data for some intermediate temperatures have been omitted). The smaller effect of orientation on component **I** causes the corresponding data to be more scattered. Despite that, from the results depicted in Figure 5, parts a and b, the dynamic characteristics of the two components can be accessed, mainly the corresponding characteristic times. The values resulting from a Gaussian description of the data points around each loss peak are included in Figure 2. Note that no curve fitting procedure is involved in the deconvolution method followed above, opposite to previously published works on the dielectric γ-relaxation of BPA−PC,[8,14] The characteristics of the components we obtained result from the direct comparison between the dielectric response measured on the nonoriented and oriented samples, respectively. On the other hand, the results shown in Figure 5, parts a and b, indicate that component **II** is better resolved at high temperatures, whereas the signatures of component **I** are significantly reduced at the highest temperatures investigated. This anticipates the increasing relevance of component **II** in determining the characteristics of the whole dielectric γ-relaxation of BPA−PC at high temperatures.

Discussion

Molecular Motions Responsible for the Two Resolved γ-Relaxation Components. The comparison of the temperature dependence of the main relaxation times of the two resolved components with that determined directly from the maximum of the whole loss peak evidences that the characteristic time of the whole γ-relaxation is intermediate to that of the two components at the lowest temperatures and, on the contrary, much closer to component **II** at higher temperatures. This behavior suggests that the molecular mechanisms provoking the dipole fluctuations responsible of the fast component have to be less efficient at low temperatures. This result provides a simple explanation of the unconventional temperature dependence of the dynamic characteristics of the whole dielectric γ-relaxation process. On one hand, the curvature (and also the high value of the apparent activation energy) observed in the Arrhenius representation would just be a consequence of the increasing relevance of component **II** at higher temperatures. On the other hand, the increasing contribution of this faster component also would explain the rapid narrowing of the loss peaks with temperature as depicted in Figure 1.

The dielectric relaxation of BPA−PC mainly reflects the molecular motions involving the carbonate (or carboxyl) group since the rest of the molecular groups forming the repeating unit, namely two phenylene rings and two methyl groups, do not present significant dipole moment. However, as already commented in the Introduction, there is a rather general consensus on the idea that the motions of the different groups of the BPA−PC unit are somehow correlated. With this idea in mind, literature values of the characteristic time scales for the motions of both the phenylene rings and methyl groups of the BPA−PC unit, as determined from quasi-elastic neutron scattering QENS[21,30] and ^{2}H NMR[23,24] measurements, have also been included in Figure 2. It is clear from this comparison that the molecular motions responsible of components **I** and **II** would be strongly related to the phenylene π-flips and to the phenylene ~90° rotation, respectively. A reasonable extrapolation of the dielectric relaxation values to higher temperatures, where the QENS values were derived, make the corresponding times to nearly coincide. Furthermore, the characteristic times for pheneylene π-flips derived from ^{2}H NMR line shape analysis[23,24] compares very well with that obtained dielectrically for component **I**. Thus, the two components resolved in the dielectric γ-relaxation of BPA−PC result to be directly connected with two well-defined jump motions of the phenylene rings. Consequently, our findings would confirm the cooperative interaction or coordination between the carbonate and phenylene groups. From the published molecular dynamics simulations and quantum mechanics calculations,[31,32] it could be inferred that this coordination would be originated by the intramolecular conformational energy map of the isolated diphenyl carbonate molecule. In these molecules, the orientation between the planes of the phenylene ring and the carbonate group is about 45° as a result of the competition between the two effects: the steric hindrance, which tries to separate as much as possible the orthohydrogen from the double bonded oxygen; and the electronic delocalization, which tries to get them as close as possible. As a consequence, the conformational map for the torsional angle between the two groups shows, in addition to two main maxima in the coplanar configuration (0 and 180°), two smaller relative maxima in the perpendicular configuration (90 and 270°).[27] Thus, a phenylene ring would be able to undergo ~90° rotation over these relative maxima, which would imply a concomitant jump of the adjacent carbonate group, therefore, contributing particularly to the dielectric relaxation. On the other hand, the phenylene ring would also undergo π-flips over the main potential barrier, which according to the dielectric results would also involve some dipole fluctuations. However, since after phenylene π-flip the ring orientation remains the same, the observed dielectric relaxation component should be originated by dipole moment fluctuations due to carbonate motions taking place during the rearrangement of the surrounding units,[7] likely including those belonging to other nearby repeating units of the same chain (as suggested by literature results[33,34]). Although the dipole moment fluctuations would also be related to the carbonate group motions, it is evident from the above comparison that the characteristic time of the resulting dipole moment fluctuation is indeed determined by the phenylene π-flip probability.

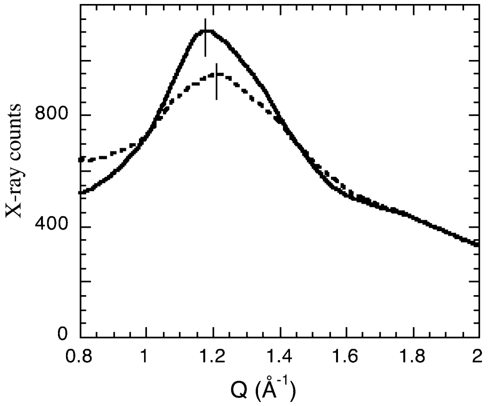

Figure 6. Comparison between the X-ray diffraction intensity recorded on nonoriented (solid line) and oriented (dashed line) BPA−PC samples. In the experiments the samples were rotated around the axis defined by the incident beam to average the influence of sample orientation in the scattering geometry. The vertical lines mark the corresponding peak positions.

On the other hand, the assignment of component **II** to the rotation of the carbonate groups in conjunction with the ~90° rotation of the adjacent phenylene rings provides a quite simple explanation for the stronger reduction of component **II** observed for the orientated samples. In the stretched sample, there would be a preferential local orientation of the chain such that the phenylene rings would become more closely packed.[17,35] This is in fact supported by the significant effect of sample orientation on the position of the main peak of the X-ray diffraction intensity (see Figure 6). It is rather apparent that for the oriented sample the maximum intensity is found to be located at higher angles. Moreover, the measured X-ray diffraction pattern of the nonoriented sample compares well, as should be expected, with the coherent intensity determined by neutron scattering on a fully protonated BPA−PC.[36] In particular, the maximum intensity occurs in both cases in the same range. Moreover, by comparing the coherent scattering from several BPA−PC samples with selective deuteration, the neutron scattering investigations also showed that the interchain carbon−carbon correlations contributes as a peak around 1.3 Å^{-1}, i.e., in the same range where the maximum X-ray intensity is observed. Therefore, the shift of the peak position to higher Q values in the oriented samples provides a direct evidence of the increasing packing density. The better packing of the polymer chains would produce an increase of the steric hindrance for the 90° rotations since it would be difficult for a ring to find an environment with enough room to be well accommodated after a 90° jump. Furthermore, the effect of chain orientation would be weaker on the phenylene π-flip jumps since in this case the initial and final states of the molecular groups of the corresponding monomer are indistinguishable and likely the position of the surrounding units would become only slightly disturbed. Nevertheless, it would be expected that chain orientation would also affect the in-chain cooperativity between the phenylene π-flips and the carbonate motions. Regarding this, it is also worth mentioning that there are some evidences in the literature pointing out to the kind of picture discussed above.[35] Particularly, phenylene rings are found to preferentially orient parallel to each other in the oriented samples, however, being the dihedral angles between the carbonate and the phenylene groups in BPA−PC unaffected, to within experimental precision. Also, experiments on cold-rolled BPA−PC showed a decreasing concentration of free volume holes[2], where the phenylene ∼90°-rotations are expected to be less hindered.

With the arguments discussed above, one should also expect the probability of phenylene ∼90°-rotations to increase with temperature due to the effect of thermal expansion on the available space around a phenylene ring. This would yield and increasing contribution of such molecular motions to the whole dielectric γ-relaxation, as it has been evidenced experimentally above (see peak intensities in Figure 5b), and will be further apparent in the detailed quantitative analysis that will be presented below. Summarizing, the stronger effect of chain orientation on the fastest of the two relaxation components can be rationalized by the fact that although the thermal energy necessary for this jump is smaller than that for a phenylene π-flip, the number of units participating in these events is limited by packing.

Finally, it has to be pointed out that the molecular assignment presented above is different from that proposed recently by Merenga et al.[14] In that work, the characteristics of the two components on the γ-relaxation of BPA−PC were inferred from the comparison among the dielectric relaxation of a series of poly(ester carbonate)s. On this basis, these authors attributed the faster component to the librational motions of the carbonyl group alone and the slower one to the motions carbonyl group coupled with the phenylene motions. Although the latter assignment is compatible with our results, the former is not because of the clear correlation we obtain between the dielectric component **II** and the phenylene ∼90° rotations detected by QENS.

Detailed Analysis of the Dielectric γ-Relaxation. The relaxation components depicted in Figure 5, parts a and b, can be further analyzed by in an attempt to describe in detail the whole γ-relaxation process of BPA−PC. In the procedure followed below, we have assumed that the two dielectric loss contributions resolved in Figure 5, parts a and b, are the results of simple molecular motions involving jumps between two equivalent energy minima separated by an energy barrier. For component **II**, this energy barrier would be that separating two equilibrium positions of the carbonate unit, which would also correspond to that of a ∼90° phenylene rotation. The energy barrier for component **I** would rather correspond to that of a phenylene π-flip. Because of the intrinsic structural disorder of an amorphous polymer, the barrier height for each process will be distributed. In this simple picture, the dielectric losses associated with each relaxation component would be just a consequence of the superposition of single Debye processes given by

$$\epsilon''(f) = \Delta\epsilon \int_0^\infty \frac{2\pi f \tau(E)}{1 + [2\pi f \tau(E)]^2} G(E)\, \mathrm{d}E \tag{3a}$$

with

$$\tau(E) = \tau_\infty \exp\left(\frac{E}{RT}\right) \quad G(E) = \frac{1}{\sqrt{2\pi}\sigma_E}\left(\frac{(E - \langle E\rangle)^2}{2{\sigma_E}^2}\right) \tag{3b}$$

R being the gas constant, E the activation energy, $\langle E\rangle$ the average value, σ_E the standard deviation of the distribution, and $\Delta\epsilon$ the measurement of the dielectric strength associated with this component. Note that we have also made the assumption that the energy barrier distribution is of Gaussian shape.

Table 1. Characteristics of the Three Components of the Dielectric γ-Relaxation of BPA−PC[a]

component	τ_∞ (s)	$\langle E\rangle$ (kJ mol^{-1})	σ_E (kJ mol^{-1})	$\Delta\epsilon_{\mathrm{or}}/\Delta\epsilon_{\mathrm{no}}$
I	7.8×10^{-14} [b]	40 ± 1	11.4 ± 1.7	0.86
II	7.8×10^{-14}	29.4 ± 0.5	7.1 ± 0.3	0.65
III	1×10^{-13} [c]	19[c]	6.5 ± 0.5	∼0.80

[a] The last column gives the estimates of the effect of orientation on the dielectric strength of each component. [b] Fixed in the fitting procedure. [c] Data from ref 21.

As a first step in this approach, we have fitted the temperature dependence of the relaxation times of components **I** and **II** (see Figure 2) by an Arrhenius equation to get the corresponding values of the average activation energies and the preexponential factors τ_∞. The values of the resulting fitting parameters are included in Table 1. Because of the higher uncertainty in the relaxation time values corresponding to component **I**, for those data, τ_∞ has been assumed to take the same value than that corresponding to component **II**. As can be seen in Figure 2, this assumption allows a good description of the observed temperature dependence. Furthermore, the value for τ_∞ is on the order of the reciprocal of a typical vibrational frequency as should be required for any simple molecular jump. Note that this is not the case of the parameters obtained when fitting the time characterizing the maximum of the whole dielectric γ-relaxation losses (neither for the mechanical relaxation[5,37,38]). To fit the loss curves corresponding to component **II**, the values of $\langle E\rangle$ and τ_∞ appearing in Table 1 have been fixed in eq 3. In this step, the fitting was limited to those few temperatures where the shape of the dielectric peak is sufficiently well-defined by the experimental data. The average value of σ_e for component **II** resulting from that fitting is shown in Table 1, where the uncertainties have been estimated to account for the values derived at different temperatures. When the same procedure was applied to the data of component **I** (Figure 5a) the values of σ_e resulted to be very much scattered, with values in the range 7−13 kJ/mol.

In the following, we will focus on the determination of the contribution of each of the two isolated components to the whole dielectric γ-relaxation of BPA−PC. To obtain this information, in the next step of the fitting procedure, the dielectric loss data of nonoriented BPA−PC were fitted as a superposition of the two components (each contributing as indicated in eq 3a and with the above derived parameters) allowing the corresponding dielectric strengths as fitting values. However, this procedure does not allow a good fitting of the data at temperatures below 220 K, the experimental data showing significantly more losses in the high-frequency side of the measured window. Although one could consider this discrepancy to be due to the high uncertainties of the values of σ_e for component **I**, if this parameters is let free in the fitting procedure the resulting values are, not only incompatible with the results shown in Figure 5a, but also unphysically large (the slower process would contribute more at high frequencies than the faster one). A possibility to explain all these features is that there is some other weak and faster contribution to the dielectric γ-relaxation of BPA−PC. Such a possibility is strongly supported by the measurable dielectric losses observed at temperatures as low as 77 K (see Figure 1) where taking into account that the time scales corresponding to components **I** and **II** are both larger than 10^6 s, any significant contribution from these components is expected in the experimental frequency window. If this additional contribution is either, relatively weak or hardly sensitive to sample orientation (or both), it would not be easily detectable by the procedure followed above. Since this extra contribution would be faster than those previously resolved, it should be more relevant at low temperatures. Looking for any signature of such an third component, we have made a direct comparison between the measured losses on the oriented and nonoriented samples at low temperatures (namely 120−160 K). The orientation effect on the dielectric relaxation at these low temperatures also results in an unbalanced loss decreasing, being slightly more pronounced in the low-frequency side of the measured window (see curves at 120 K in Figure 3), where component **II** would be the main contribution. Thus, by applying eq 2 at these low temperatures we have tried to obtain some information on this third component (Figure 5c). Despite the large uncertainties resulting from that procedure, when the resulting characteristic times are included in Figure 2, it seems that the additional component of the dielectric γ-relaxation could again be directly connected with some phenylene motion, namely with the fast angular oscillations around the C4 axis detected by QENS not only in BPA−PC but also in other polymers containing phenylene rings.

By assuming the presence of a third faster contribution to the dielectric γ-relaxation of BPA−PC, the fitting procedure was repeated by assuming that this faster component is also described by the set of eq 3 with the same Arrhenius dependence of the time scale than that obtained in ref 21 for the fast phenylene angular oscillations ($\tau_\infty = 10^{-13}$ s, $\langle E \rangle = 19$ kJ/mol). Since the large uncertainties of the data depicted in Figure 5c do not allow one to obtain a meaningful estimate of σ_E for this component, we have allowed this parameter to be free in the fitting of the low-temperature data of BPA−PC ($T < 170$ K). The average of the resulting values is $\sigma_E = 6.7 \pm 0.8$ kJ/mol. It is noteworthy that the so derived energy barrier distribution is not easily connected with a particular molecular jump, but it should be considered as a measure of the time scales of a variety of ill-defined fast molecular motions, likely those including the methyl group 3-fold rotation, that makes the local environment of both the phenylene rings and the carbonate groups to fluctuate. This could explain why the dielectric relaxation times of this fast component agree well with those accounting for the phenylene ring oscillations as observed by QENS.

Thus, in the subsequent step, the characteristic times of the three resolved components and the distribution broadening of components **II** and **III** were fixed in order to fit BPA−PC losses in the intermediate temperature range (200−240 K). In this temperature range the time scales of processes I and II are included in the measured window allowing to obtain a more confident estimate of σ_E for process I. The resulting value is shown in Table 1. Finally, in the last step of the fitting procedure, the dynamic characteristics of all the components were fixed over the whole temperature range, allowing the three corresponding dielectric strengths as the free-fitting parameters.

The temperature dependence of the so obtained $\Delta\epsilon$ values for component **III** is depicted in Figure 7. From these data, it is evident that the contribution of this component to the whole γ-dielectric relaxation process is relatively weak, but significant, and tends to decrease smoothly by reducing temperature. A linear temperature variation ($\Delta\epsilon_{\mathrm{III}} = 0.0096 + 3.1 \times 10^{-5}$ T) is able to provide a reasonable description of the dielectric strength of this fast component. This temperature dependence of $\Delta\epsilon_{\mathrm{III}}$ can be easily rationalized because the increasing amplitude of the phenylene ring oscillations detected by QENS[21] would be accompanied by an increase of the amplitude of the oscillation in the neighboring carbonate units. In fact, a power law increasing, similar to that used to account for the average angular phenylene oscillation in ref 21, is also able to describe well the experimental $\Delta\epsilon_{\mathrm{III}}(T)$ behavior.

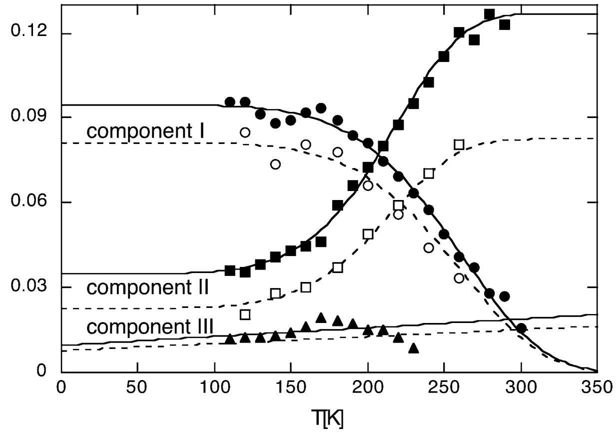

Figure 7. Dielectric strength of the three components of the BPA−PC dielectric γ-relaxation. Solid symbols correspond to the nonoriented samples and empty symbols to the oriented one. The lines correspond to a smooth description of the temperature behavior.

On the other hand, the deviations from the low temperature extrapolation observed at high temperatures are very likely related with the fact that component **III** is completely out of the experimental frequency window in this temperature range. Actually, the fitting quality is hardly affected when the values of $\Delta\epsilon_{\mathrm{III}}(T)$ are fixed in the fitting procedure to those extrapolated from low temperatures. The solid lines in Figure 1 are the results of such a fitting procedure. A remarkable good description of the experimental data is achieved using the above indicated $\Delta\epsilon_{\mathrm{III}}(T)$ and allowing now the two amplitude factors of components **I** and **II** as the only two fitting parameters. The corresponding temperature variations are depicted in Figure 7. It is found that the dielectric strength of component **I** decreases rapidly at temperatures above 200 K and eventually vanish at about 350 K. Concurrently, a fast increasing of $\Delta\epsilon_{\mathrm{II}}$ is apparent. These temperature variations quantify what was already anticipated qualitatively from the variation of the amplitudes of the loss peaks shown in Figure 5, parts a and b.

As a final test of the present approach, the solid lines in Figure 7 describing the temperature variation of the dielectric strength of the three components, has been used to calculate the dielectric losses of BPA−PC over the whole temperature range investigated (70−350 K). The comparison between these calculated curves (dashed lines in Figure 1) and the experimental data indicates that this approach is able to provide a good estimate of the experimental dielectric losses of BPA−PC over extremely large temperature and frequency ranges.

According to the above results, it seems that the whole dielectric γ-relaxation of BPA−PC at high temperatures (ca. $T > 280$ K) would be dominated by the carbonate reorientations occurring concurrently with the phenylene ~90° rotations. However, lowering the temperature, this mechanism would become hindered and below 200 K the slowest component, related with the phenylene π-flips, results the most prominent contribution to the whole dielectric losses. With respect to that, it is noteworthy that the mechanical relaxation measurements of the γ-relaxation of BPA−PC exploring this low-temperature range also yield relaxation times that match well to those derived for the phenylene π-flips as determined by QENS[21] and ^{2}H NMR.[23,24] On the other hand, the strong increment of the dielectric strength of component **II** in the range from 200 to 270 K would imply that in this temperature range the probability of a phenylene ring to perform a ~90° jump also increase strongly. This could allow rationalizing the apparent inconsistency between QENS and NMR results concerning this particular phenylene motion. According to the analysis of different NMR experiments on BPA−PC, the π-flips and fast oscillation of the pehnylene units are sufficient to account for the observed features.[23,24,39] On the contrary, coherent QENS[21] data on fully deuterated BPA−PC, where the phenylene π-flip motion do not contribute, clearly evidence a dynamic process that matches well with the characteristics of the phenylene ∼90° jumps. However, it is noteworthy that different times scales are explored by both experiments and, therefore, they present the best sensitivity at rather different temperatures. Namely, the QENS signal is well tuned at temperatures in the range 300−400 K where according to our dielectric results the carbonate/phenylene ∼90° rotations will be very significant. However, the typical frequencies of ^{2}H NMR are in the range of 10^{4} Hz and, thus, this technique would be sensitive to the carbonate/phenylene rotations only at lower temperatures where our analysis shows that the carbonate/phenylene ∼90° rotations are considerably hindered.

As a further test of the main features of the present approach, we have performed the same kind of fitting with the data corresponding to the oriented sample. Because of the weakness of component **III**, the dielectric strength of this contribution has been also fixed in the fitting procedure and taken to be the 80% of that used for the nonoriented BPA−PC, as suggested from the high frequency data at 120 K of Figure 3. The solid lines in Figure 3 correspond to the fitting so obtained and the corresponding values of the dielectric strength are included in Figure 7 (see open symbols). As it could be anticipated from the above results, orientation yields a weaker reduction of the dielectric strength for component **I** than that for component **II**. Dashed lines in Figure 4 show in detail the effect of orientation on the two components at 200 K. Furthermore, according to our results, the reduction factor hardly depends on temperature, and it is about a 14% (dashed−dotted line in Figure 7) reduction for component **I** and as high as a 35% reduction for component **II** (dashed line in Figure 7). It is also noteworthy that these estimates allow also to account for the measurable effect of chain orientation on the phenylene dynamics as determined by QENS.[40]

A noteworthy implication of the analysis above presented is that the peculiarities of the γ-relaxation process in BPA−PC arise as a consequence of the quite sharp increasing/decreasing of the dielectric relaxation strengths of the two main components. Actually, the dynamic characteristics of the three molecular motions considered are rather conventional; i.e., each depicts an average time scale following an Arrhenius-like temperature dependence, with a value of the prefactor of the order of the reciprocal of typical vibrational frequencies, and each is distributed according to a temperature independent distribution of activation energies. All these characteristics, however, when combined with rather sharp temperature variations of the relaxation strengths give rise to an apparently unconventional behavior of the whole relaxation peak, not only when characterized isothermally but also, more evidently, when characterized isochronally. This latter type of experiment is quite standard in mechanical relaxation investigations. These experiments have shown that the mechanical behavior of BPA−PC is closely connected with the phenylene π-flip motions. The direct relationship between mechanical relaxation and phenylene π-flips would have, according to the results presented above, two main reasons. On one hand, mechanical relaxation techniques involve low frequency experiments and subsequently explore the low-temperature range where phenylene π-flips also dominate the dielectric losses. Note that although a phenylene π-flip alone would not have any direct effect neither on mechanical nor on the dielectric relaxation, the subsequent rearrangement of the surrounding units would be detectable in both relaxation experiments. On the other hand, the relevance of phenylene π-flips to the mechanical relaxation would persists at higher temperatures since the increasing relevance on the dielectric relaxation is likely specifically related with the large amplitude of the carbonate motions. To illustrate this situation, we have calculated the isochronal loss curves of component **I**, that associated with the phenylene π-flips, at the low frequencies usually explored by mechanical relaxation techniques (in the range 10^{-2}−10^{2} Hz) (see Figure 8) and characterized the resulting isochronal curves by the temperature of loss maxima (as it is commonly done in experiments). The so obtained characteristic time values are compared with those obtained from mechanical experiments in the inset of Figure 8. As it can be observed we found a surprisingly good agreement between the mechanical data and the results from the calculation of the dielectric component **I**. This result supports again the close connection between the phenylene π-flip motions and the mechanical behavior, at least at low temperatures, even though a phenylene π-flip alone would neither be reflected as a mechanical relaxation process, nor as a dielectric one. On the other hand, it is noteworthy that the apparent activation energy that would result from an Arrhenius fit of this set of data is about 20% larger than the actual *40 kJ/mol* corresponding to that component. This apparent discrepancy evidence the difficulties, already pointed out in the literature,[41,42] in interpreting correctly the experimental data derived from isochronal experiments when the relaxation time is not the only single characteristic of the process that changes with temperature, but also the amplitude and the relaxation shape are temperature dependent. Finally, the good agreement found between what was derived for component **I** from dielectric experiments and the experimental mechanical relaxation data, does not exclude the possibility of a significant contribution of the carbonate/phenylene concurrent rotations to the mechanical properties of BPA−PC at higher temperatures. It is remarkable in this context that the brittle−ductile transition temperature for BPA−PC[7] is in the range where the strength of the dielectric component associated with the carbonate/phenylene rotations starts increas-

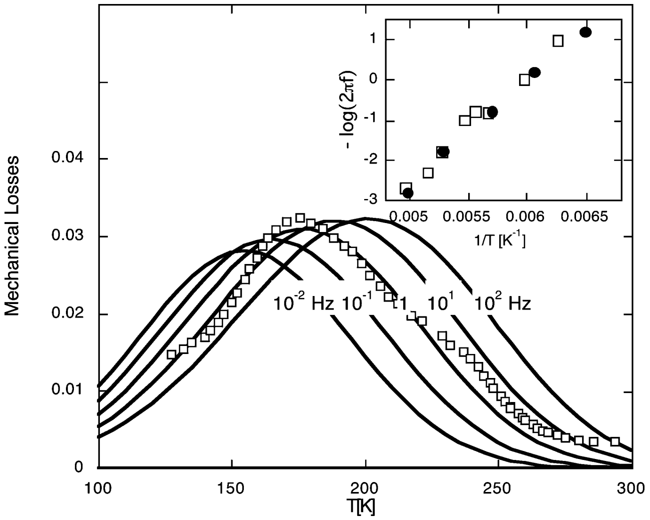

Figure 8. Comparison between the mechanical losses of BPA−PC in the γ-relaxation range,[5] (empty squares) with that calculated with component **I** modeling the dielectric γ-relaxation (solid lines). The inset shows an Arrhenius plot with the corresponding characteristic times: experimental[38] (□) and calculated (●).

ing rapidly. Furthermore, this particular component is the more strongly affected by mechanical deformation.

Conclusions

Taking advantage of the fact that the dielectric losses associated with the γ-relaxation of BPA−PC on cold drawn samples are not reduced uniformly, we have been able to investigate the molecular motions responsible for this relaxation process. The direct comparison of the dielectric relaxation curves measured on the BPA−PC sample uniaxially stretched below the glass transition temperature T_g with those corresponding to the nonstretched samples has allowed us to resolve the two main components of the dielectric secondary relaxation. The characteristic times of these components nearly coincide with those derived for two well-defined jumps of the phenylene rings, namely the phenylene π-flips correlate well with the slower component **I** and the ∼90° rotation of the phenylene rings with component **II**. This result provides additional evidence of the cooperativity among the motions of the different molecular groups forming the polycarbonate repeating unit. Furthermore, a more detailed analysis of the molecular orientation effects on the dielectric γ-relaxation suggests the existence of a weak third component that would be connected with the phenylene ring oscillations previously detected by QENS.

On the basis of this three-component picture, we have been able to accurately describe the relaxation behavior of both oriented and nonoriented samples over an extremely wide temperature interval (50−350 K). From these results, we conclude that the low temperature dielectric behavior of BPA−PC is mainly driven by the phenylene π-flips but at temperatures above 200 K the whole dielectric γ-relaxation becomes increasingly controlled by the carbonate/phenylene ∼90° rotations, being these motions those more strongly reduced by chain orientation. In addition, the presence of these three distinct molecular motions contributing to the dielectric γ-relaxation of BPA−PC provides a meaningful explanation of both the anomalous features of the whole γ-relaxation loss peaks (strong asymmetry and non-Arrhenius temperature dependence of the peak frequency) and the unbalanced effect of chain orientation on the dielectric γ-relaxation losses.

Finally, according to our results, the dielectric γ-relaxation of BPA−PC at room temperature (and above) would be entirely determined by the carbonate/phenylene simultaneous rotations, with the phenylene π-flips having a negligible effect. However, whether a similar situation would apply to the mechanical relaxation case is not obvious, since literature experimental data are well accounted for by component **I** alone.

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