Physical aging effects on high temperature relaxations of poly(DTH carbonate) and poly(DTO carbonate) monitored by TSPC and TSDC

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Abstract

Thermal stimulated polarization and depolarization experiments with blocking electrodes are performed on two tyrosine-derived polycarbonates: poly(DTH carbonate) and poly(DTO carbonate). Aging effects are studied in a high temperature range that involved the contribution of the glass transition relaxation peak and the charge redistribution peak originated by the conduction through the sample and the presence of blocking electrodes. A reliable new models are used to described these high temperature relaxations and the results are presented as a function of aging times, polarization conditions and changing structure. For each sample the glass transition temperature, the parameter related with the shape of the glass transition peak and the contribution between the two modeled peaks, are found to be constant and independent of aging time. The variations in shape and temperature position of the maximum of the charge redistribution peak show logarithmic time dependence with aging time. These results are compared to the ones previously reported on a particular tyrosine-derived polyarylate, and the analysis suggests that structural differences in mobility and flexibility of the polymeric chains originate the observed variations. The examination of the experimental data indicates that charge redistribution and glass transition peaks share the same origin, and that the conduction aging effects are triggered by the onset of the glass transition.
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1. Introduction

Amorphous polymers, due to their glassy nature below their glass transition temperature T_g, are not in thermodynamical equilibrium. The approach of those materials to thermodynamic equilibrium, at constant environmental conditions and temperatures below T_g, is named structural relaxation and it is also referred as physical aging [1–3]. This process can be detected through the time evolution of a variety of physical properties of thermodynamic, dielectric and mechanical nature. The physical aging is determined by slow relaxation changes that take place in time scales long when compared with typical experimental time scales. These kinetic phenomena make it very difficult to perform repetitive experiments, as well as the comparison with the

results from other authors since it is required a detailed knowledge of the complete thermal history of the sample and the temperature rate of cycling. In addition, during structural relaxation the presence of nonequilibrium states complicates the theoretical understanding and description of polymeric materials. The effects associated with the lack of equilibrium occurring around and above T_g constitute a field of active research geared to the understanding, modeling and description of the underlying phenomena involved.

Structural relaxation processes are generally believed to have a nonlinear and nonexponential behavior [4]. One of the more widely used expressions to describe nonlinearity is the Tool–Narayanaswamy–Moynihan [5–7] equation that introduces the dependence of the relaxation time, on both, the temperature and the structure of the glass. In modeling the nonexponentiality of the relaxation process, one of the most popular equations is the stretched exponential response function, referred to Kohlrausch–William–Watts (KWW) function [8,9]. The aging process observed through

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different techniques in glassy polymeric systems has been described using a variety of models [10–16], and most of the approaches share the common essential concepts already mentioned. The detailed discussion among all the existing models leads to the conclusion that no single uniform model exists that relates the molecular processes occurring to the observed physical changes, and that the observation of physical aging with different techniques leads to slightly different view of the processes that occur.

Physical aging has been widely studied experimentally by dilatometry [17] (volume relaxation) and differential scanning calorimetry DSC [18] (enthalpy relaxation). Thermally stimulated current techniques have been applied in more recent years to the study of this phenomenon [19–26]. In studying thermally stimulated depolarization currents (TSDC) a polarizing electric field is applied at a temperature high enough to activate bound and free charges in the material, then, this polarizing state is frozen in by a rapid cooling down of the sample and afterwards, the sample is heated at a constant heating rate while the depolarization current is registered as a function of temperature. In the case of thermally stimulated polarization currents (TSPC) the charges are activated by applying an electric field to the sample while heating at a constant rate, and the polarization current is recorded as a function of temperature. The depolarization and polarization currents obtained with these techniques reveal the existence of different relaxation processes such as the secondary relaxations, the space charge relaxation attributed to the activation of free charges, the dielectric manifestation of the glass transition, known as the α relaxation, etc. Among these relaxations, it is well known that at least the last one is originated by a cooperative motion of the main polymer chain segments. This is a kinetic process and therefore it must be affected by physical aging providing that the recovery time of the material is much longer than the experimental time. Previous studies by TSDC showed the progressive decrease and shift towards higher temperatures of the α relaxation in α-PET samples with physical aging [25]. TSPC measurements in the same samples reported the appearance of a dielectric relaxation attributed to the complete polarization of the polymer chain dipoles of the aged material, the evolution of this relaxation was found to change in a similar way to the structural endothermic relaxation detected by DSC. Performing TSDC and TSPC experiments on a particular tyrosine-derived polyarylate we had reported [26] aging effects in the high temperature range of the dielectric spectrum. In that work the glass transition relaxation and the space redistribution charge due to conduction through the sample were modeled and the results presented as a function of the aging time.

In this article we will study the aging effects of two tyrosine-derived polycarbonates which differ in the length of the alkyl ester pendent chain. The pendent chain length of these polycarbonates increases from six to eight carbons by the use of hexyl and octyl esters as C terminus protecting

groups (Fig. 1). The resulting monomers are desamonityr-osyl-tyrosine alkyl esters (DTH, DTO) which can be readily polymerized to polymers of high molecular weight by conventional techniques of polycarbonate synthesis [27,28]. Poly(DTH carbonate) and poly(DTO carbonate) are being investigated for medical applications such as drug delivery and bone fixation. Previous studies have confirmed that these amorphous materials are generally biocompatible, possesses favorable physicomechanical properties, and can be fabricated readily into devices useful for medical applications [27,29]. A model TSDC study in these controlled structures [30] has shown a correlation between secondary relaxation processes and the increasing number of methylene groups in the pendent chain, and a correspon-dence of the temperature position of the α relaxation process with the associated glass transition temperature measured by differential scanning calorimetry (DSC). In the present study a series of carefully designed TSDC and TSPC experiments were performed in a temperature range that involved the combined effect of the glass transition relaxation and the conduction of the samples. The changes observed in both contributions were described as a function of the time elapsed from the quenching of the sample at a particular temperature above T_g and then kept for different aging times at an annealing temperature of about 300 K. A single phenomenological pseudo-equilibrium dipolar model was used to characterize the relaxation associated to the glass transition, while the charge redistribution relaxation originated by the conduction of the sample was described by a simple temperature relaxation model. The effect of aging in the evolution of these high temperature currents was analyzed for the first time in these materials as a function of different aging times, polarization conditions and changing structure. The obtained results were compare to the ones previously reported in a particular tyrosine-derived poly-arylate referred to as poly(DTH succinate) [26].

2. Experimental

2.1. Polymer characterization and film preparation

The chemical structure of the polymers was confirmed by infrared and nuclear magnetic resonance spectroscopy [27, 28]. Polymeric films were cast on glass plates from a filtered
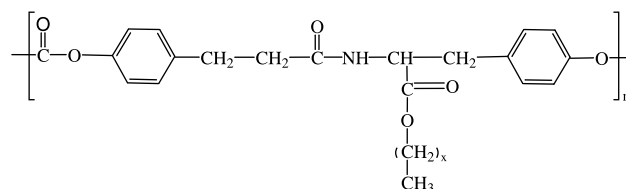

Fig. 1. Chemical structure of polycarbonates used in this study. The length of the pendent chain was varied from six, poly(DTH carbonate), to eight carbons, poly(DTO carbonate), by choosing the number of methylene groups, $x=5$ and 7.

glass wool 10% w/v solution in methylene chloride. The solvent was evaporated at room temperature under nitrogen. Molecular weights were determined by gel permeation chromatography (GPC) [27]. The films were pressed for 10 min at 14,000 lb at a temperature of $T_g + 40$ K between two heated, polished steel plates using a Carver Laboratory Press Model 2625. Before releasing the pressure, the plates were water-cooled to room temperature. The faces of the polymeric films, about 200 mm thickness, were evaporated with aluminum to maintain a constant potential surface. The samples were prepared and maintained at 300 K for a long time enough for its electrical properties do not change with time in an appreciable way.

2.2. TSPC and TSDC experiments

To perform the dielectric measurements two thin flat circular sapphire disks were placed on each side of the sample. The diameter and the thickness of the sapphire disks are 19 and 0.216 mm respectively. Then, this sandwich is placed between two spring-loaded metallic electrodes in contact with the sapphire disks. The sequence of experiments performed on the samples consists of two consecutive cycles. The first cycle is a TSPC experiment where the sample temperature is lowered from 300 K to liquid nitrogen temperatures at a rate of about 1 K s^{-1}. Then an electric polarization field, typically of 2×10^6 V/m, is applied to the sample and simultaneously the current is detected with a Cary Vibrating Reed Electrometer model 401 M across a measuring resistor of 10^{11} Ω. Once the transient currents are below the background current of the electrometer, the sample temperature is increased at a constant rate of 0.099 K s^{-1}, and the current versus temperature is digitally recorded. The first experimental cycle is concluded at a temperature of about 350 K, when the recorded polarization current is close to zero. Then, without removing the external electric field, the sample temperature is lowered back again to liquid nitrogen temperature, at a rate of approximately 1 K s^{-1}. At this temperature the field is switched off, and the sample is short-circuited through the temporary short and the electrometer. After all transient currents are well below background currents, the second cycle or a TSDC experiments begins. In this second cycle the sample temperature is raised at a constant rate of 0.099 K s^{-1} while the depolarization current is registered up to the temperature of about 350 K. After the end of the second cycle, the sample is stored in the system cell at the annealing temperature of 300 K, during a controlling time period, until a new sequence of identical experiments is started.

2.3. Analysis of TSPC and TSDC spectra

The high temperature currents induced by the polarization and depolarization experiments under different experimental conditions are usually not well described by existing theories or are most times ignored. To be able to study aging effects in polymers using stimulated thermal current experiments we have modeled the high temperature region comprising the combined effects of the glass transition relaxation peak and the charge redistribution peak, originated by the conduction through the sample when blocking electrodes are present [26]. The relaxations peaks were described by a model in which the sample is thought as a capacitor with a parallel temperature dependent relaxation time resistor in series with an ideal capacitor that represents the blocking electrodes. Under these conditions it was shown that, in the presence of blocking electrodes, the conduction part of the current originates a charge redistribution peak that can be described as [31]:

$$J_Q(T) = Q_0 f(T)\left(\alpha + \frac{1}{T}\right)\exp(f(T)) \qquad (1)$$

Where $f(T) = (T/b\tau_0)\exp(\alpha(T - T_g))$, b is the heating rate, α and τ_0 are constants related to the approximation of the WLF [31] relaxation time, and Q_0 is a constant proportional to the intensity of the charge redistribution peak. In TSPC experiments with blocking electrodes, the charge redistribution peak is observed when the relaxation time of the sample decreases and the conduction charges accumulated at low temperature on its plates are shorted out due to the diminishing value of the sample parallel resistance. In TSDC experiments, during the polarization step, the time spent above T_g is usually much longer than the relaxation time of the sample. Therefore, under these conditions the sample acquires zero voltage across its plates. Once low temperature is reached, the field switched off and the sample shorted out through the measuring electrode, the very long sample relaxation time allows the sample to acquire a charge on its plates. This is possible due to the redistribution of the initial charges present in the blocking electrodes among all the capacitors. As well as it occurs in TSPC experiments, in TSDC experiments as the temperature is raised, a diminishing of the sample relaxation time at high temperatures will originate again the redistribution of charges.

Besides the charge redistribution peak, the glass transition relaxation peak is also observed in the high temperature region. This peak will be described by the phenomenological expression [32]:

$$J_g(T) = J_0 \frac{\exp(\beta(T - T_g))}{1 + \exp(\eta(T - T_g)/T)} \qquad (2)$$

Where β, η, J_0 and T_g are constants that characterize the shape and position of the glass transition relaxation peak. The above equation was written using the zero order approximation of the WLF expression of the temperature dependence of the relaxation time.

2.4. TSPC and TSDC results

Figs. 2 and 3 show, in the cases of poly(DTH carbonate) and poly(DTO carbonate) respectively, the results obtained by the TSPC cycles of the experiments for different times elapsed between experiments or aging times. The times shown in the inserts are measured from the end of the second cycle, i.e., the end of the prior TSDC experiment. These figures clearly show the dependence of the spectra with the annealing times, generally it can be stated that the width and height of the spectra vary with the annealing time. Figs. 4 and 5 show the corresponding results of the TSDC cycles of the experiments, each one performed immediately after the previous TSPC presented in Figs. 2 and 3. The corresponding sequences of TSPC and TSDC experiments share the same symbols. Among the TSDC curves, only the result corresponding to the aging time of 22 h for the poly(DTH carbonate) sample shows some dispersion from the others. From the results presented in Figs. 4 and 5 it is clear that the shapes of the subsequent TSDC spectra do not depend on the time elapsed between the TSPC cycle of the experiments. From this observation it can be concluded that each time a TSDC experimental cycle is finished the aging time is reset to some initial value.

To analyze the TSPC and TSDC relaxation peaks obtained in both samples, we use a combination of Eqs. (1) and (2) and a standard nonlinear algorithm plus a search region for some of the parameters to make sure than an absolute minimums obtained for the least mean square deviations between the combined expression and the data analyzed. None of the parameters were fixed a priori, and
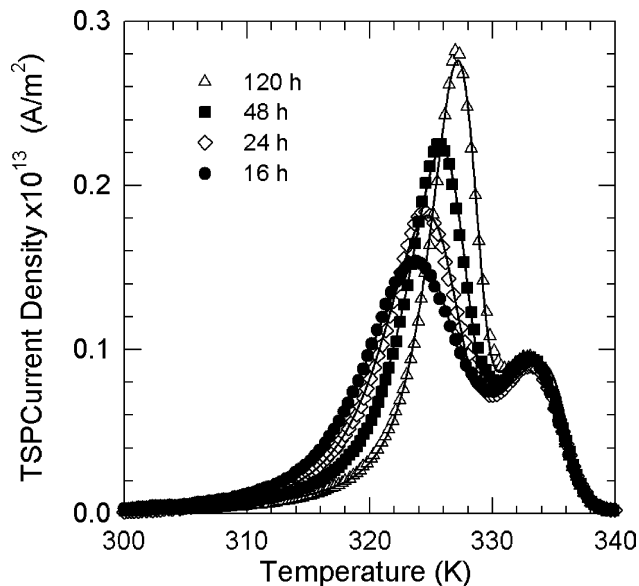
Fig. 3. TSPC spectra of poly(DTO carbonate) for the aging experiments performed after 16, 24, 48 and 120 h. Experimental points represented with different symbols are a subset of all the points digitally recorded. The continuous lines through these points represent the fitting obtained with the model used to describe the high temperature region of the experimental spectra.

they were allowed to vary within certain limits. There was only one constrain on the analysis, the parameter T_g was taken to be the same for both relaxations, i.e., the space charge relaxation and the glass transition peaks. In Figs. 2 and 3 the lines represented the calculated peaks while the
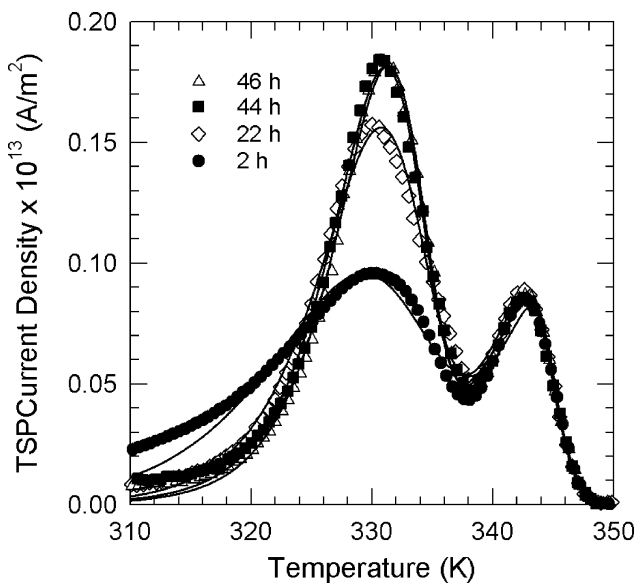
Fig. 2. TSPC spectra of poly(DTH carbonate) for the aging experiments performed after 2, 22, 44 and 46 h. Experimental points represented with different symbols are a subset of all the points digitally recorded. The continuous lines through these points represent the fitting obtained with the model used to describe the high temperature region of the experimental spectra.
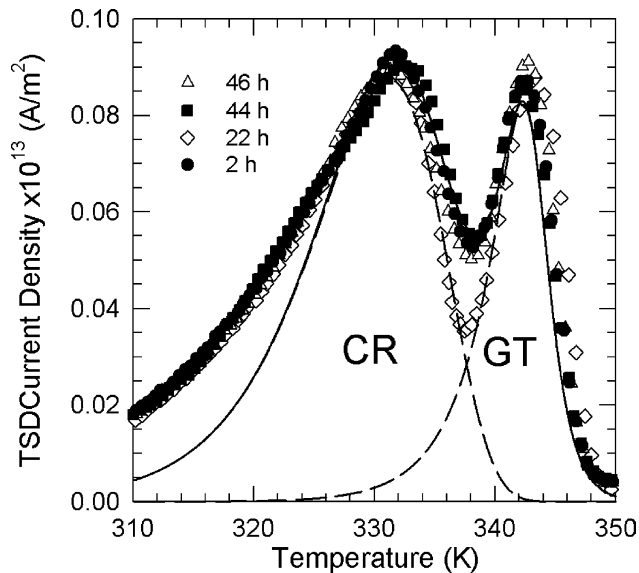
Fig. 4. TSDC spectra of poly(DTH carbonate) for the aging experiments performed after 2, 22, 44 and 46 h. Experimental points represented with different symbols are a subset of all the points digitally recorded. The continuous line through these points is calculated with the average of all of the parameters obtained with the model used. The partial contribution to the spectra from the charge redistribution peak (CR) and the glass transition relaxation peak (GT) are represented with broken lines.
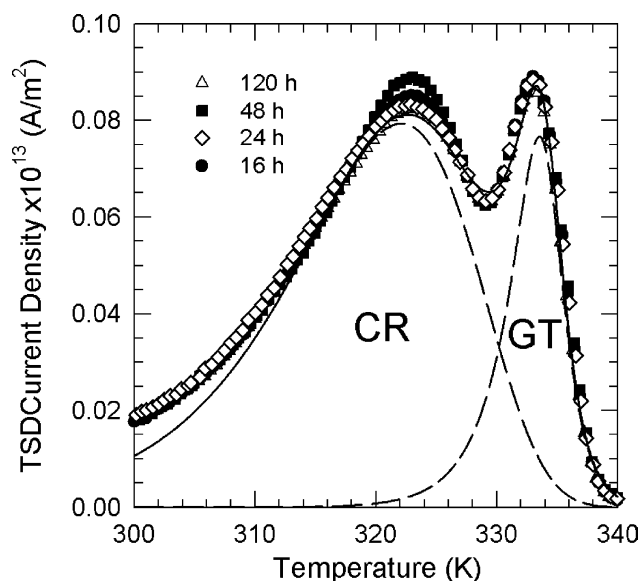
Fig. 5. TSDC spectra of poly(DTO carbonate) for the aging experiments performed after 16, 24, 48 and 120 h. Experimental points represented with different symbols are a subset of all the points digitally recorded. The continuous line through these points is calculated with the average of all of the parameters obtained with the model used. The partial contribution to the spectra from the charge redistribution peak (CR) and the glass transition relaxation peak (GT) are represented with broken lines.

symbols represent the experimental points. The agreement between experimental points and calculated data is quite good, especially for the case of poly(DTO carbonate) (Fig. 3), where the coincidence is remarkably close. In previous TSDC studies performed in a series of tyrosine-derived polycarbonates with different lengths [30], it was reported that in increasing the length of the pendent chain from 6 to 8 carbons, the contribution of secondary relaxations to the dielectric spectrum decreases by a factor of 1/2. In consequence the low temperature tail of the high temperature spectrum was found to be less affected by the presence of these secondary relaxations in the case of poly(DTO carbonate) that in the case of poly(DTH carbonate). As we do not perform any kind of cleaning technique, this observation can be account by explaining the differences in the quality of the fitting presented in Figs. 2 and 3. In fact, the coincidence between experimental points and calculated data is greater in the case of poly(DTO carbonate) sample, which is also the one whose high temperature dielectric spectrum is less affected by the presence of the low temperature relaxations.

In TSDC results presented in Figs. 4 and 5, the lines represented the calculated peaks while the symbols represent the experimental points. In these figures, the calculated peaks labeled CR (charge redistribution peak) and GT (glass transition peak) and shown with a short broken line are the ones corresponding to the average calculated curves obtained by the TSDC experiments. For these peaks the samples are cycled from 300 to 340 K and back to 300 K in about 20 min. No extra time is allowed at

300 K before cooling the samples down for the TSDC cycle of the aging experiments. In both figures the combination of these two peaks is represented by a continuous line. As well as in the case of TSPC results, the coincidence between experimental points and calculated data is greater in the case of poly(DTO carbonate) sample. The average T_g parameter found is approximately the same for all the relaxations of the same sample, regardless of their aging time and equal to 344.6 ± 0.3 K and 335.1 ± 0.6 K for poly(DTH polycarbonate) and poly(DTO carbonate) respectively. The errors involved are the mean standard deviations. All of the aging experiments performed in each sample were conducted with the same thermal history therefore, it is consistent that the glass transition temperature should not change in the same material as the kinetic effects related with this parameter depends on the thermal history and the temperature rate of cycling [33], and both of them were kept constant during the TSDC experiments.

In all the TSPC experiments performed in the same sample the fitted partial contribution to the total polarization from the charge redistribution peak, P_{0Q}, and the glass transition relaxation peak, P_{0g}, are practically constant and independent of aging time. The average values originated by these two high temperature relaxations are $\langle P_{0g} \rangle = (0.86 \pm 0.04)10^{-12}$ C/m^2, $\langle P_{0Q} \rangle = (1.5 \pm 0.1)10^{-12}$ C/m^2 and $\langle P_{0g} \rangle = (1.16 \pm 0.03)\ 10^{-12}$ C/m^2, $\langle P_{0Q} \rangle = (1.04 \pm 0.01)10^{-12}$ C/m^2 for poly(DTH carbonate) and poly(DTO carbonate) respectively. The errors involved are the mean standard deviations. The total polarization, P_{0T} is the addition of $P_{0g} + P_{0Q}$ that agrees with the total polarization calculated from the experimental curves to better than 1% for poly(DTO carbonate) and 5% for poly(DTH carbonate). Obviously, as the polarization electric field was kept constant in all the experiments, it should be expected that for the same sample the polarization originated by the composite relaxation peak must be the same. As total and partial polarizations due to the high temperature relaxations peaks are constant in each sample, we can conclude that the aging conditions do not change the concentration of the available dipoles contributing to the glass relaxations, but only the shape of the charge redistribution peak. This property is in agreement with the model used to describe them.

In the analysis of the TSDC experiments we found for the same sample very little variation among all the fitting parameters. The average total polarization originated by the charge redistribution peak and the glass transition peak, calculated from the experimental spectra were $\langle P_{0T} \rangle = (2.2 \pm 0.1)10^{-12}$ C/m^2 for poly(DTH carbonate) and $\langle P_{0T} \rangle = (2.13 \pm 0.05)10^{-12}$ C/m^2 for poly(DTO carbonate). On each sample this total polarization coincides, within the mean standard deviations, with the one obtained in TSPC experiments. Of course, the total polarization of the composite peak should be the same because in each sample the polarization field used in both experiments was the same. The average β parameter obtained in the analysis of

the TSDC experiments increases from 0.12 K^{-1} to 0.15 K^{-1} as the pendent chain decreases, in fact, the diminishing of 25% in the number of methylene groups in poly(DTH carbonate) with respect to poly(DTO carbonate) coincides with 25% of increment of the β parameter in the former sample. In modeling the endothermic C peak of aged amorphous linear polyesters, Cortés et al. [34] had found that the nonexponentiality parameter of the KWW function, β_{KWW}, decreases with the length of the polymer chain. Gómez et al. [35] had also reported the same effect in studying structural relaxations in polymethacrylates. This effect has been interpreted by Hodge [14] as a measure of the degree of cooperativity of the relaxation process, or the number of chain segments involved in a particular relaxation event. Low values of β_{KWW} correspond to a high degree of cooperativity and a large number of chain segments. Our results seem to confirm this last statement, although the meaning of the β parameter is not the same in both models. The β parameter of Eq. (2) is inversely related with the broadening of the glass transition peak while β_{KWW}, is inversely related to the width of the distribution of relaxation times.

Figs. 6 and 7 show the partial contribution to the dielectric signal of the glass transition and the charge redistribution peaks for the different aging experiments for the poly(DTH carbonate) and poly(DTO carbonate) samples respectively. Both contributions were plotted using the parameters obtained with Eqs. (1) and (2) for all the different aging experiments. The model used to describe the high temperature relaxation peaks represents quite well the experimental data. This result together with the fact that the partial charges under the corresponding relaxations are constant, is evidence that the model describes the system
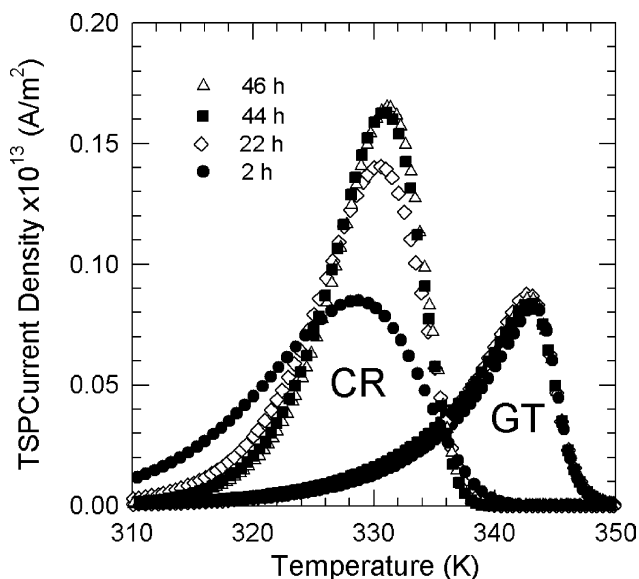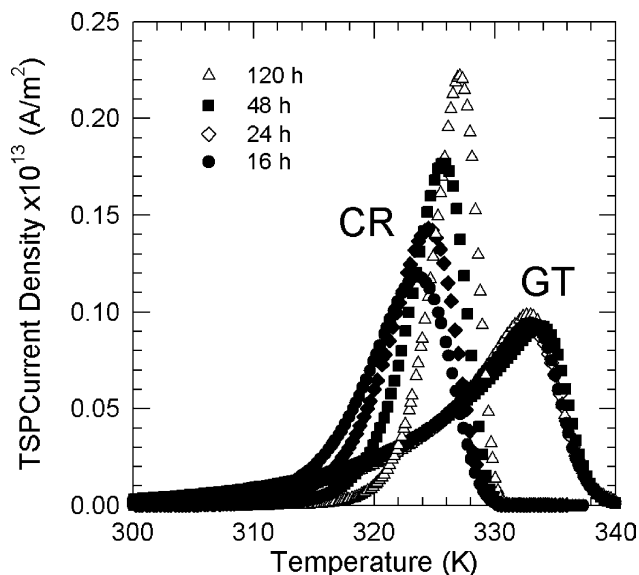

Fig. 7. Partial contribution to the TSPC spectra of poly(DTO carbonate) from the charge redistribution peak (CR) and the glass transition relaxation peak (GT). The different symbols represent the fittings obtained with the models for the aging experiments performed after 16, 24, 48 and 120 h.

under study accurately. Due to the slightly small changes of the glass transition temperature and the variations of the shape and maximum of the charge redistribution peaks in the aging experiments, the assumption that the main electrical property mostly affected by the aging process is the conductivity of the sample can be sustained. These results are in complete agreement with the ones reported in a previous study of a particular tyrosine-derived polyarylate: poly(DTH succinate) [26]. In that study the chosen polymer had six carbons in the pendent chain and two methylene groups between the carboxylic acid end groups.

To quantify the effect of the aging processes in the high temperature dielectric spectrum of the samples, we try to establish how the maximum of the charge redistribution and the glass transition peaks behaves with aging time. In Fig. 8(a) the open and solid circles represent the temperature of the current maximum of the glass transition peak as a function of aging time for the poly(DTH carbonate) and poly(DTO carbonate) samples respectively. We also include in this figure the corresponding points previously reported for poly(DTH succinate) [26], represented by solid triangles. From this figure we can conclude that within the standard deviation of the generated points, the glass transition maximum remains constant with aging time for the three samples. These glass transition maximum values are comparable to the ones reported in previous works [30, 36], the differences can be account by variations in the experimental conditions and thermal histories of the samples. Fig. 8(b) shows the temperature of the current maximum of the charge redistribution peak as a function of aging time for the poly(DTH carbonate) (open circles) and poly(DTO carbonate) (solid circles) samples. The corresponding points for the case of poly(DTH succinate) are also

Fig. 6. Partial contribution to the TSPC spectra of poly(DTH carbonate) from the charge redistribution peak (CR) and the glass transition relaxation peak (GT). The different symbols represent the fittings obtained with the models for the aging experiments performed after 2, 22, 44 and 46 h.
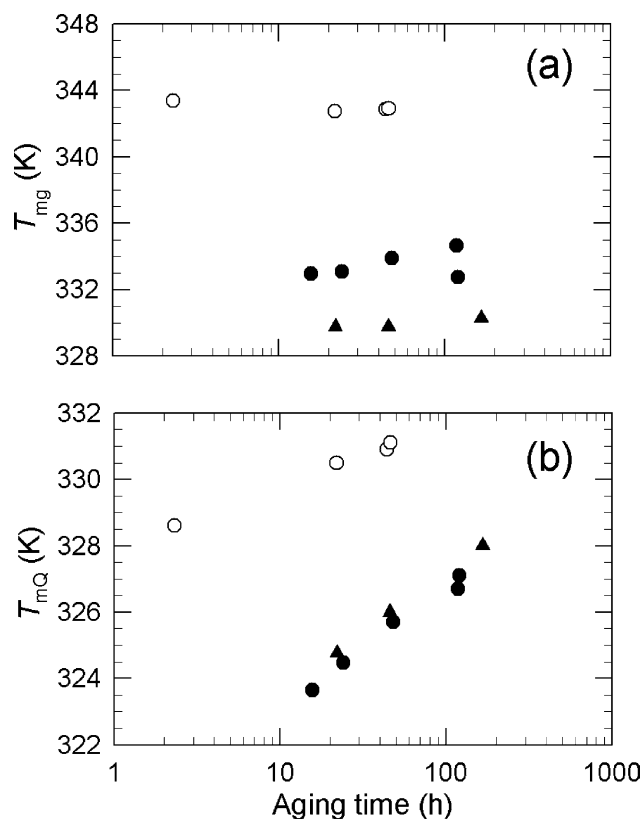
Fig. 8. Aging time dependence of different parameters. (a) Temperature of the current maximum of the glass transition peak as a function of aging for poly(DTH carbonate) (open circles), poly(DTO carbonate) (solid circles), and poly(DTH succinate) (solid triangles). (b) Temperature of the current maximum of the charge redistribution peak as a function of ageing time for poly(DTH carbonate) (open circles), and poly(DTO carbonate) (solid circles), and poly(DTH succinate) (solid triangles).

represented as solid triangles. A simple logarithmic time dependence was founded for the temperature of the maximum of the charge relaxation peak in the three samples. The similarity between the slopes obtained for the fitted straight lines for the poly(DTO carbonate) and poly(DTH succinate), together with the comparatively smaller slope founded for the poly(DTH carbonate), allows to correlate these slopes with the 'flexibility index' (FI), defined as the number of the carbon atoms present in the alkyl pendent chain and the number of methylene groups contained within the variable portion of the polymer backbone. In fact, the two polymers with similar slopes have also the same FI equal to 8, while for the poly(DTH carbonate) this value is 6. These results can be related with the ones founded by Tangpasuthadol et al. [37,38], in studying thermal properties and physical aging behavior of tyrosine-derived polycarbonates and tyrosine-derived polyarylates. The conclusion of these authors was that these polymers become more flexible with an increasing on methylene groups in either the pendent chain or polymer backbone. Therefore, from the results presented in Fig. 8(b) we can conclude that, as the polymer becomes more flexible, the rate of displacement of the maximum of the

space charge relaxation peak with aging time increases. A logarithmic time dependence had been also reported [25] for the temperature of the maximum of the TSDC glass transition peak of aged α-PET samples. This observation was explained by the decreased in the mobility of the molecular chains, which was related to the reduction of the free volume in the sample. However, due to the experimental conditions used in that work, together with the existence of additional relaxations in the high temperature side of the spectrum, it is not clear that they were looking at an isolated peak. Probably the superposition of at least part of a reported higher temperature relaxation is affecting the temperature displacement with aging time. In that work TSPC experiments in aged sample were also reported. In these experiments a dipolar peak cleaning technique was performed, trying to erase from the spectrum the contribution of the glass transition relaxation. The results show a complex broad relaxation (labeled α_a), that was identified as a polarization process associated to the recovery of the mobility in the amorphous region above the glass transition, whose evolution shows a shift towards higher temperatures and an increase in area as the annealing time increases. This behavior was related with that of the endothermic peak associated with the enthalpy recovery process at T_g. The annealing process affecting the whole high temperature spectrum, including the free charge polarization, together with the cleaning technique used in that work do not allow the clear identification of an isolated relaxation, therefore the temperature displacement of the complex spectrum with aging time cannot be identified with a single process. Performing DSC experiments in α-form PVDF samples, Neidhofer et al. [39] had reported a similar logarithmic time dependence of the annealing peak temperature. In that work the authors could fit satisfactorily the linear dependence with the equation proposed by Marand et al. [40]. The conclusion was that the PVDF structural evolution during annealing was assigned to secondary crystallization accompanied by increasing conformational constrains in the residual amorphous material. However, as our samples are amorphous materials, the annealing effects observed mainly in the charge redistribution peak can be attributed to the change in the mobility and flexibility of the polymeric chains, affecting the conduction through the sample while the material properties slowly recover their equilibrium values.

The parameters α of Eq. (1), represented by circles and β of Eq. (2), represented by squares are plotted in Fig. 9 as a function of aging time for the two samples studied. We also include in this figure the corresponding points previously reported for poly(DTH succinate). The α parameter of the three samples shows a similar logarithmic time dependence with aging time as the one established for the temperature of the maximum of the charge redistribution peak. For poly(DTH carbonate) and poly(DTO carbonate) the β parameter does not appreciable change (within the mean standard deviations) during the aging process, contrary to
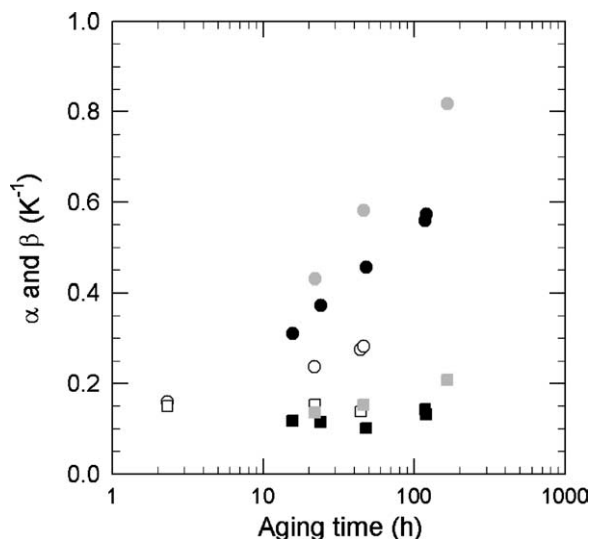
Fig. 9. Aging time dependence of α (circles) and β (squares) parameters for poly(DTH carbonate) (open symbols), poly(DTO carbonate) (black symbols), and poly(DTH succinate) (grey symbols).

the observed logarithmic time dependence of this parameter in poly(DTH succinate). The constant values of β for poly(DTH carbonate) could be explained as its glass transition temperature is more than 40 degrees above room temperature, and therefore the experimental time scale chosen for aging the sample at this temperature could be not high enough to make a proper observation of aging effects in this relaxation. However, the glass transition temperatures of poly(DTO carbonate) and poly(DTH succinate) are both located about 30° above room temperature thus, in order to explain the invariance of β with aging time in the former sample we have to consider the differences between polymer structures. Investigating by DSC the structural relaxation of amorphous polymethyl(α-n-alkyl)acrylates, Godard et al. [41] have found practically no change in the nonexponentiality parameter (inversely related to the width of a distribution of relaxation times) as the number of carbons in the side alkyl chain increases. In studying enthalpy relaxation kinetics in structurally related tyrosine-derived polyarylates and tyrosine-derived polycarbonates Tangpasuthadol et al. [37,38] reported that beyond a minimum length of four carbons the size of a pendent chain did not affect the limited segmental mobility occurring in the glassy state, thus, the rate of enthalpy relaxation was limited by the mobility of the polymer backbone. As the pendent chains of poly(DTO carbonate) and poly(DTH succinate) are beyond the minimum length (8 and 6 carbons, respectively), the aging effects in the β parameter (logarithmic time dependence with aging time) can be though as a result of a greater mobility of the poly(DTH succinate) backbone due to the increase in the number of backbone methylene groups as compared with poly(DTO carbonate). The parameters α and β are both related to the approximation used for the relaxation time whose variation is mainly attributed by the model [32] to the variation with

temperature of the sample parallel resistance. Under these assumptions the aging time dependences showed in Fig. 9 and their further correlation with polymer structure contradicts the belief that the shape of the glass transition peak is mostly due to the presence of an energy distribution for the dipolar motion. On the contrary, it seems to confirm that the onset of both, the glass transition and the charge redistribution peak, are related to the changes of viscosity that change the mobility of the polymeric chains, affecting in a different manner the reorientation of the dipoles and the conduction through the sample. It is also worth to note that the observed time dependence on the parameters presented in Figs. 8(b) and 9 agrees with the predictions of Struik [1] for his tensile compliance experiments, even if for the electric case the change appears as a change in the shape of the relaxation peak and not as a shift of the data.

Fig. 10 presents the rate of variation with aging time of the α parameter (obtained from Fig. 9) as a function of T_g, for the two tyrosine-derived policarbonates studied and the tyrosine-derived polyarylate previously reported. As a common T_g was assumed in the models describing the conduction and the glass transition phenomena a straight line dependence observed is an evidence that the conduction aging effects are triggered by the onset of the glass transition. A common origin between the space charge and the glass relaxation processes have been previously proposed by explaining the influence of physical aging processes on electret properties of amorphous poly(methyl methacrylate) [42] and polymer blends of varying composition [43]. The authors tentatively concluded that the basic molecular relaxations process was identical for the two processes and that the ion conductivity of the sample was controlled by the glass transition process. Our observations
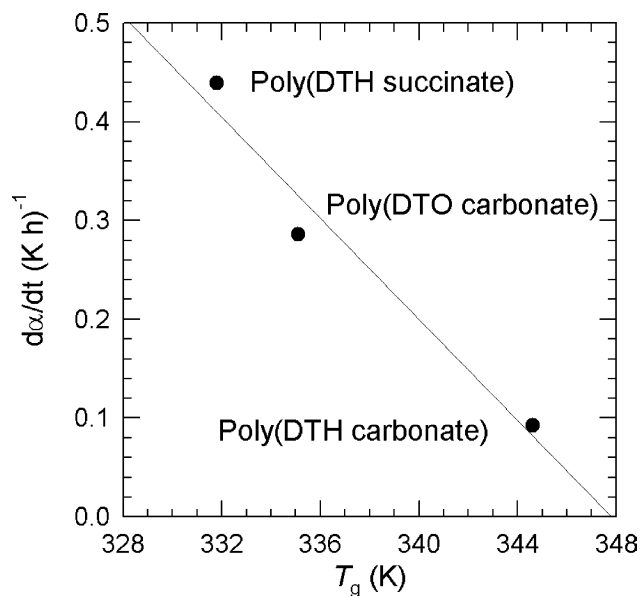

Fig. 10. Rate of variation with aging time of the α parameter as a function of T_g for poly(DTH carbonate), poly(DTO carbonate), and poly(DTH succinate).

seem also to confirm the assumption that both phenomena, charge redistribution and glass transition, share the same origin although they are due to different physical properties.

3. Conclusions

The glass transition relaxation peak plus the charge redistribution peak present in the TSDC and TSPC spectra of poly(DTH carbonate) and poly(DTO carbonate) with blocking electrodes are described and modeled as a function of aging time. The results are compared to the similar ones previously reported for poly(DTH succinate). The glass transition relaxation peak is described with a useful phenomenological model. As it was expected the glass transition temperature, T_g, is founded not to change when the samples were annealed with similar previous thermal history as well as similar heating and cooling rates. The calculated shape of this peak does not appreciable change with aging time. This result, contrary to the logarithmic time dependence founded for poly(DTH succinate) was explained in terms of differences in backbone mobility. The broadening of the glass transition peak is related to the increase in the length of the pendent chain. The charge redistribution peak that arises by the distribution of the charges among the sample capacitance and the blocking electrodes capacitance is described by a simple relaxation model. For this peak the dependence with aging time of the different parameters is founded to be logarithmic. This dependence is the same one found by Struik for the creep compliance of poly(vinyl chloride). It is observed a correlation between the rate of variation of the temperature of the maximum of the charge redistribution peak with aging time and the flexibility index. For the same polarization conditions, contributions to the total polarization from the glass transition and charge redistribution peaks remain constant for all the TSPC experiments. This implies that the aging conditions do not change the concentration of available dipoles contributing to the glass relaxation peak. All of these observations deduced using these simple models seem to indicate that charge redistribution and glass transition peaks, share the same origin and that the conduction aging effects are triggered by the onset of the glass transition.

Acknowledgements

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