Aging Effects in Poly(DTH succinate) Observed with Thermal-Stimulated Polarization and Depolarization Experiments

N. SUÁREZ, M. PUMA

Instituto de Ingenieria, POBA International #438, P.O. Box 02-5255, Miami, Florida 33102-5255

ABSTRACT: Thermal-stimulated polarization and depolarization experiments with blocking electrodes are performed on a particular tyrosine-derived polyarylate: poly(DTH succinate). Aging effects on this sample are observed for the glass transition relaxation peak and the charge redistribution peak originated by the conduction though the sample when blocking electrodes are present. The high temperature region where these peaks are present is modeled, and results are presented as a function of aging time. The model describes the experimental data to better than 1% for all the aging times. Contributions between the two peaks modeled are found to be constant and independent of aging. The glass transition temperature is constant within a fraction of a degree, and the shift of the maximum temperature of the spectrum is due to the charge redistribution peak. The results obtained suggest that the variation in shape of these peaks is originated by the change in the mobility of the polymeric chains, affecting in different manners the dipole orientation mechanism, as well as conduction through the sample. A simple logarithmic aging time dependence is found for most of the parameters used in the model. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 293–301, 1998

Key words: stimulated thermal currents; aging effects; glass transition; polarization and depolarization experiments; relaxation in polymers

INTRODUCTION

The properties of polymeric materials studied near the glass transition temperature are complicated by the thermal and mechanical history of the sample under study. Such complicated effects are originated by heating the samples above the glass transition temperature, T_g, and the value of the different relaxation times necessary to reestablish the original set of electrical, thermal, and mechanical properties. This phenomena makes it very difficult to perform repetitive experiments, as well as the comparison with results from other authors without the detailed knowledge of the complete history of the sample. The presence of these nonequilibrium states complicates the theoretical understanding and description of the properties of polymeric materials in the temperature range where these phenomena are prevalent. The effects associated with the lack of equilibrium occurring around and above the glass transition temperature are very important from a technical point of view in electrical applications,[1] as well as in biomedical applications[2] and also constitute a field of active research geared to the understanding, modeling, and description of the underlying phenomena involved.[3] As the temperature of a polymer increases above T_g, the electrical properties of the polymer change. As the temperature of the sample is again stabilized, usually at an

annealing temperature below T_g that depends on the material studied, these properties slowly recover their original values. The time involved in this reversible process depends on the annealing temperature and the sample studied. These time-temperature-dependent phenomena are usually referred to as aging effects. If the recovery time is much longer than the experimental time, such states can be probed and characterized. In this article, we will study the aging effect of a tyrosine-derived polyarylate. Tyrosine-derived polyarylates are new degradable polymers that had been identified as promising materials for the design of degradable medical implants.[4] The synthesis of tyrosine-derived polyarylates was recently reported using desaminotyrosyl-tyrosine alkyl esters and aliphatic diacids as monomers. The tyrosine-derived polyarylate studied in this study was prepared by the copolymerization of the desaminotyrosyl-tyrosine hexyl (DTH) ester with the succinic diacid. The resulting polymer, referred to as poly(DTH succinate), has six carbons in the pendent chain and two methylene groups between the carboxylic acid end groups into the polymer backbone. A series of stimulated current experiments in the high temperature range that involve the combined effect of the glass transition relaxation peak and the conduction present in these samples will be described as a function of the time elapsed from the moment the sample is quenched from a particular temperature above T_g and then kept for a certain length of time at an annealing temperature of about 300 K.

EXPERIMENTAL

To evidence aging effects on poly(DTH succinate), a combined set of temperature-stimulated polarization (TSP) and temperature-stimulated depolarization (TSD) experiments using blocking electrodes were conducted. The measurements were performed on a thin paper-like sample of poly(DTH succinate) of 0.488 mm thick whose faces were evaporated with aluminum to maintain a constant potential surface. On each side of this sample are placed two thin flat circular sapphire disks of 19 mm in diameter and 0.216 mm thick. This sandwich is then placed inside a parallel plate capacitor whose electrodes are disks of 18 mm in diameter. Once prepared, the sample is maintained at 300 K for a long time so that its electrical properties are not changing with time in any appreciable way. The sample can be described

with an equivalent circuit model consisting of a capacitor with a parallel resistor possessing a temperature-dependent relaxation time. In series with the sample, there is an ideal capacitor with a capacitance equal to the parallel capacitance of the two sapphire disks. The sequence of experiments performed on the sample consists of two consecutive experimental cycles. The first cycle consists of a TSP experiment where the sample temperature is lowered from 300 K to liquid nitrogen temperatures at a rate of approximately 1 Ks^{-1}. At this point, a polarization field of 100 V is applied to the sample and simultaneously the current is detected with a Cary Vibrating Reed Electrometer model 401M across a measuring resistor of 10^{11} Ohm. When the transient currents are below the background current of the electrometer, the temperature of the sample is increased linearly with time at a rate of about 0.07 Ks^{-1}, and the current *versus* temperature is digitally recorded simultaneously. After the recorded polarization current that is present at high temperature, in the form of a composite relaxation current peak, is close to 0, approximately, at a temperature of 340 K, the first cycle of the experiment is concluded. Henceforth, without removing the external field, the temperature of the sample is lowered back again to liquid nitrogen temperatures at a rate of approximately 1 Ks^{-1}, where the second cycle or a TSD experiment begins. When the sample again has reached liquid nitrogen temperatures, the polarization field is removed, and the sample is short-circuited through a temporary short and the electrometer. Once again, after all transient currents are down below background values, the temperature is raised at the same constant rate, while the depolarization current is detected up to the same temperature as the one reached for the previous TSP run. After the end of the second cycle, the sample is stored in the sample cell at the annealing temperature of 300 K until a new experiment is performed. This experimental sequence, in exactly the same order, is conducted as a function of the time-elapsed counting from the end of the second cycle of each experiment.

The results obtained by the TSP cycles of the experiments as a function of the time elapsed between experiments or aging time are shown in Figure 1, whereas the TSD cycle of the experiments is shown in Figure 2. From the preliminary results of Figure 1 and Figure 2, it is evident that every time a TSD experimental cycle is concluded, the aging time is reset to some initial value be-
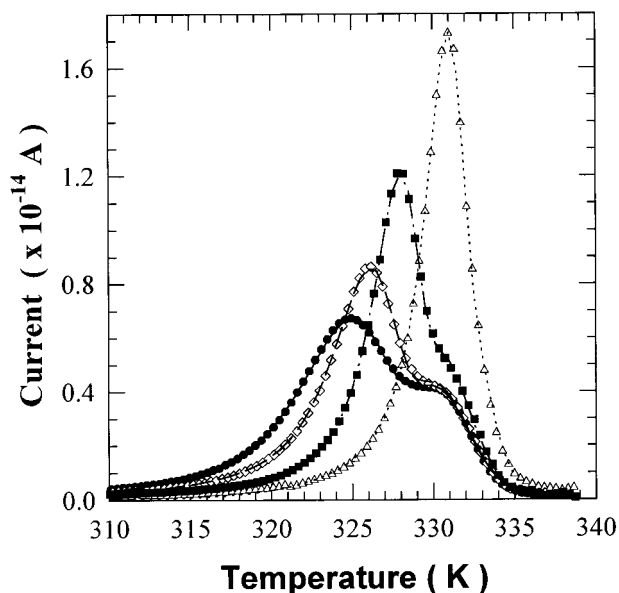
Figure 1 TSP currents *versus* temperature for the different aging experiments are shown with different symbols. TSP signals from the aging experiments performed after 22, 46, and 166 h, and on the as-given sample are represented by ●, ◇, ■, and △, respectively. Experimental points corresponding to these symbols are a subset of all of the points digitally recorded. Different lines through these points represent the fitting obtained with the model used to describe the high temperature region of the experimental spectra.

cause all of the subsequent TSD experimental traces that follow are equal within experimental uncertainties. Their shapes do not depend on the time elapsed between the TSP cycle of the experiments that clearly show a time dependence. The symbols shown in Figure 2 are time-related to the ones in Figure 1; the corresponding sequences of TSP and TSD experiments share the same symbols. Among the TSD curves, only the result corresponding to the aging time of 46 h shows a small departure from the others. The times shown in Figure 1 are measured from the end of the second cycle (i.e., the end of the prior TSD experiment).

DESCRIPTION OF THE RELAXATION

To describe the relaxation peaks, we use a model in which the sample is described by a capacitor with a parallel resistor possessing a temperature-dependent relaxation time in series with an ideal capacitor that represents the blocking electrodes. Under these conditions, we have already shown that the conduction part of the current existing

for these kind of substances and in the presence of blocking electrodes originates a charge redistribution peak that can be described with the expression[5]

$$I(T) = Q_0 f(T)\left(\alpha + \frac{1}{T}\right)e^{-f(T)}, \qquad (1)$$

with $f(T) = (T/b\tau_0)e^{\alpha(T-T_g)}$, b the constant heating rate, α and τ_0 are two constants related to the approximation of the WLF[6] relaxation time, and Q_0 is a constant proportional to the intensity of the charge redistribution peak. The charge redistribution peak for a TSP experiment with blocking electrodes is observed when the relaxation time of the sample decreases and the charges responsible for the conduction that were accumulated on its plates at low temperature are shorted out by the diminishing value of the sample parallel resistance. In the case of a TSD experiment, the only charges existing at low temperature while the polarizing field is present are located on the blocking
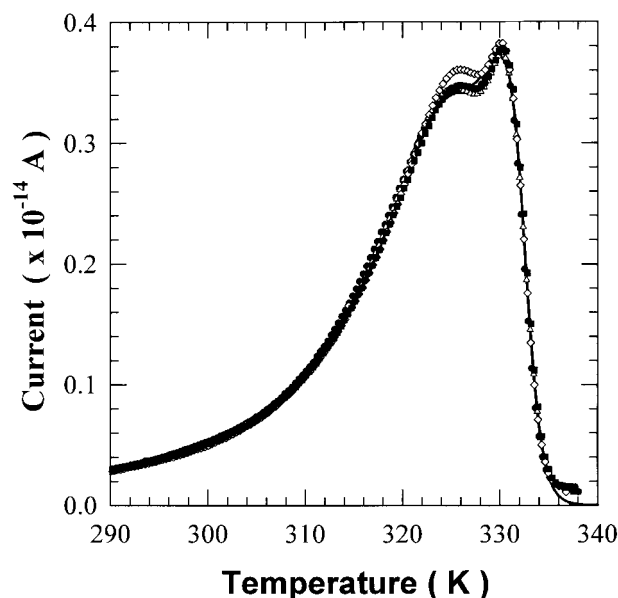
Figure 2 TSD currents *versus* temperature for the different aging runs are shown with different symbols. TSD signals from the aging experiments performed after 22, 46, and 166 h, and on the as-given sample are represented by ●, ◇, ■, and △, respectively. Solid line through these points does not represent any of the individual experimental sets of data, but is the one calculated with the average of all of the parameters obtained with the model used. We assume that all of the different experiments are best described by the average curve obtained.

capacitors. This fact is strictly related to the amount of time spent above T_g during the polarization stage, which is usually long enough for the sample to acquire zero voltage across its plates. The time spent around T_g is usually much longer than the relaxation time of the sample at that same temperature; therefore, the charge on the sample capacitor is completely shorted out. Once low temperature is reached, where the relaxation time of the sample is very long, the polarizing field is removed and the sample is shorted out through the measuring electrometer. At this point, the initial charges present on the blocking electrodes are redistributed among all the capacitors and the sample acquires a charge on its plates. For the same reason stated in the case of the TSP experiments, as the temperature is raised, the charges again are redistributed due to the diminishing relaxation time of the sample at high temperature.

Together with the charge redistribution peak just described, there exists the glass transition relaxation peak. This peak will be described by the following phenomenological expression[7]

$$I(T) = I_0 \frac{e^{\beta(T-T_g)[1+\lambda(T-T_g)]}}{e^{\eta(T-T_g)/T} + 1} , \qquad (2)$$

where β, λ, η, and I_0 are constants that characterize the shape of the peak together with the common T_g. Even if both expressions use an equivalent approximation of the WLF relaxation time, the conduction phenomena and the glass relaxation peak are due to different physical properties and therefore the constants involved do not necessarily have similar values and temperature dependence under thermal treatment. Conduction energies and reorientation energies are generally different functions of temperature and therefore such differences are to be expected. For both phenomena, a common T_g is assumed because we deem that these share the same origin and both are triggered by the onset of the glass transition. To find the temperature T_m, at which the maximum of the current described by eq. (1) occurs, it is necessary to solve the following transcendental equation

$$e^{\alpha T_m} = b\alpha\tau_0 e^{\alpha T_g} \frac{2 + \alpha T_m}{(1 + \alpha T_m)^2} , \qquad (3)$$

where T_m can be computed once the parameters

defining the charge redistribution peak are known.

DESCRIPTION OF THE EXPERIMENTAL RESULTS

To analyze the relaxation peaks obtained from the TSP and TSD experiments, we combine eqs. (1) and (2) and use a standard nonlinear algorithm plus a search region for some of the parameters to make sure than an absolute minimum is obtained for the least mean square deviation between the combined expression and the data analyzed. None of the parameters included in the previously described expressions were fixed *a priori,* and they were allowed to vary within certain limits. The only constraint on the analysis was on the temperature T_g that was taken to be the same parameter for both relaxation peaks. This limitation is of little practical consequence because the parameters T_g and α in eq. (1) do not uniquely define the value of $f(T)$ as explained in ref. 5.

In Figure 1, the different line types represent the calculated peaks while the symbols represent the obtained experimental points. The agreement between experimental data and combined eqs. (1) and (2) is remarkably close. In Table I, all of the parameters obtained by the minimization procedure are reported for the different experimental aging times. Also, additional information pertaining to the charge under the glass transition relaxation peak Q_g, as well as the one under the charge redistribution peak Q_c, is reported. These partial charges are calculated from the knowledge of the parameters describing each relaxation and the actual heating rate measured from the data of temperature *versus* time. The total charge Q_T shown in Table I is the addition of $Q_c + Q_g$ that agrees with the total charge calculated from the experimental curve to better than 1%. Therefore, we are only reporting the values obtained from the model presented.

From the previously described data, some immediate results can be deduced. The average glass transition temperature found is approximately the same for all of the relaxation peaks, regardless of their aging time and equal to 331.9 ± 0.5 K, wherein the error is the mean standard deviation. The glass transition temperature is known to show kinetic effects that depend on the thermal history of the sample, as well as the temperature rates of cycling.[8] All of the aging experiments were conducted with the same thermal history

Table I   Parameters for Eq. (1) (Describing the Charge Redistribution Peak) and for Eq. (2) (Describing the Glass Transition Relaxation Peak) Are Obtained from the TSP Experiments as a Function of Aging Time

| Δt 22 H | | | | Δt 166 H | | | |
Glass Transition		Charge Redistribution		Glass Transition		Charge Redistribution	
k (a.u.)	0.629	Q_0 (a.u.)	2.664	k (a.u.)	0.894	Q_0 (a.u.)	2.627
β (K^{-1})	0.136	α (K^{-1})	0.430	β (K^{-1})	0.208	α (K^{-1})	0.817
η	331.00	τ_0 (s)	214.3	η	359.25	τ_0 (s)	230.9
λ (K^{-1})	0	T_g (K)	331.65	λ (K^{-1})	0	T_g (K)	331.54
T_g (K)	331.65	b (Ks^{-1})	0.0742	T_g (K)	331.54	b (Ks^{-1})	0.0726
Q_g (C)	6.12×10^{-10}	63.07%		Q_g (C)	6.26×10^{-10}	63.35%	
Q_c (C)	3.58×10^{-10}	36.93%		Q_c (C)	3.62×10^{-10}	36.65%	
Q_T (C)	9.71×10^{-10}			Q_T (C)	9.88×10^{-10}		

| Δt 46 H | | | | As-Given Sample | | | |
Glass Transition		Charge Redistribution		Glass Transition		Charge Redistribution	
k (a.u.)	0.670	Q_0 (a.u.)	2.655	k (a.u.)	1.191	Q_0 (a.u.)	2.951
β (K^{-1})	0.152	α (K^{-1})	0.581	β (K^{-1})	0.275	α (K^{-1})	0.974
η	324.73	τ_0 (s)	180.3	η	488.55	τ_0 (s)	700.95
λ (K^{-1})	0	T_g (K)	331.54	λ (K^{-1})	0	T_g (K)	332.81
T_g (K)	331.54	b (Ks^{-1})	0.0711	T_g (K)	332.81	b (Ks^{-1})	0.727
Q_g (C)	6.21×10^{-10}	62.47%		Q_g (C)	6.32×10^{-10}	60.88%	
Q_c (C)	3.73×10^{-10}	37.53%		Q_c (C)	4.06×10^{-10}	39.12%	
Q_T (C)	9.95×10^{-10}			Q_T (C)	1.04×10^{-09}		

These parameters are obtained with a standard nonlinear fit, where the total experimental signal is described by the superposition of the two peaks mentioned previously. Also, the values of the partial charges under the charge redistribution peak Q_c, the glass relaxation peak Q_g, and the total charge Q_T are given.

(e.g., the maximum temperature reached, as well as the same cooling and heating rate used to cycle the sample, were kept the same); therefore, it is consistent that the glass transition temperature should not show any significant kinematic departure among the aging experiments. Furthermore, it is observed that the partial contributions to the total charge from the charge redistribution peak and the glass transition relaxation peak are practically constant and independent of aging time for all of the TSP experiments. Naturally, the total charge under the composite peak must be constant, because the polarization voltage was always kept equal to 100 V. Table II shows the average values of the charge $\langle Q_g \rangle$ under the glass transition relaxation peak, the charge $\langle Q_c \rangle$ under the charge redistribution peak, and the total charge $\langle Q_T \rangle$, together with their standard mean deviation ΔQ calculated from the four different TSP runs.

Because part of the relaxation related to the glass transition relaxation peaks is originated by the viscous movements of the dipolar side chains units present in the sample, partial contribution from this relaxation to the whole relaxation peak should remain constant if the polarization conditions are fixed. Therefore, it is not surprising that the charge under the glass relaxation peak is con-

Table II   Average Values of the Partial Charge Under the Glass Relaxation Peaks Q_g, the Charge Redistribution Peaks Q_c, and the Total Charge Q_T Under the TSP Experimental Runs

	Q (C)	ΔQ (C)	Distribution (%)
$\langle Q_g \rangle$	6.23×10^{-10}	7×10^{-12}	62.42
$\langle Q_c \rangle$	$3.7 \ \times 10^{-10}$	2×10^{-11}	37.58
$\langle Q_T \rangle$	$10.0 \ \times 10^{-10}$	2×10^{-11}	

The mean standard deviation and the percentage obtained for each partial relaxation are also reported.

Table III Average Parameters for Eq. (1) (Describing the Charge Redistribution Peak) and for Eq. (2) (Describing the Glass Transition Relaxation Peak) Are Obtained from the Different TSD Experiments

Glass Transition		SD	Charge Redistribution		SD
k (a.u.)	0.460	2×10^{-3}	Q_0 (a.u.)	0.836	7×10^{-3}
β (K^{-1})	0.0676	3×10^{-4}	α (K^{-1})	0.265	4×10^{-3}
η	399	1	τ_0 (s)	336	10
λ (K^{-1})	0	—	T_g (K)	332.40	5×10^{-2}
T_g (K)	332.40	5×10^{-2}	b (Ks^{-1})	0.0725	3×10^{-4}

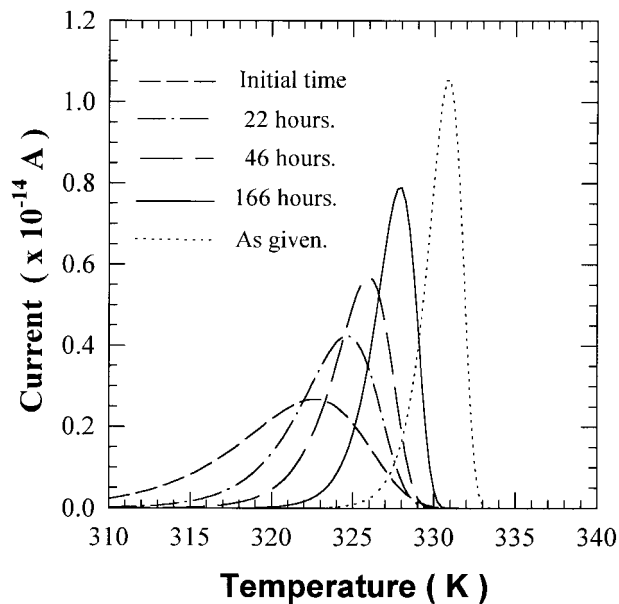|	Q (C)	ΔQ (C)	Distribution (%)
Q_G	8.92×10^{-10}	7×10^{-12}	88.56
Q_c	1.15×10^{-10}	2×10^{-12}	11.44
Q_T	10.07×10^{-10}	8×10^{-12}	—

Average values are obtained from all of the TSD runs. Average values of partial charges under the charge redistribution peak Q_c, the glass relaxation peak Q_g, and the total charge Q_T are also given, together with their mean standard deviation (SD).

stant for all of the equivalent TSP aging experiments. The charge redistribution peak must be responsible for the additional polarization necessary to complete the total polarization charge present on the plates of the capacitors. Because total and partial charges under the different high temperature relaxation peaks are constant, these results indicate that the aging conditions do not change the concentration of available dipoles contributing to the glass relaxation peak, but only the shape of it. This last remark is linked to the model used to describe the relaxation. It is remarkable that the minimization process produces such results without using any constraints.

For the TSD experiments, similar results as the one reported in Table I would show very little variation among the parameters. Therefore, for the TSD experiments, we are reporting in Table III the average values obtained for the parameters. These parameters are the average from the different values obtained from all the TSD aging experiments. Also, the standard mean deviation that resulted from their different values is given. In Figure 2, the solid line represents the average curve produced by the use of these averaged parameters, and it is assumed to be the best approximation for all the TSD aging experiments performed. The proportion of the charge accumulated under the charge redistribution peak and the glass transition peak is different from the one obtained for the TSP experiments (see ref. 5), even if the total charge under the composite peak is the same. The difference in the distribution of the

charges among the two relaxation peaks reflects the different polarization conditions existing for the TSD experiments even if the polarization voltage is the same. Despite the fact that distribution of the partial charges among the different contributions to the high temperature peak is different from the one found for the TSP experiments, the total charge under the combined peak is the same because the same polarization voltage was used.

In Figure 3, contribution of the charge redistribution peaks for the different aging experiments is presented. These peaks were plotted using the parameters obtained for eq. (1) for all the different aging experiments. The peak labeled initial time and shown with a short dashed line is the one corresponding to the average curve obtained by the TSD experiments. To compare it with the TSP runs, the charge under its curve was normalized to the average charge obtained by this peak in the TSP runs. For this peak, the sample is cycled from 300 K to 340 K and back to 300 K in about 20 min. No extra time is allowed at 300 K before cooling the sample down for the TSD cycle of the aging experiments. Therefore, it is very difficult to guess an effective aging time, because there are many factors that are impossible to quantify properly. The three intermediate peaks in Figure 3 correspond to well known aging times. The as-given sample has been at 300 K temperature for over 1 month after its surfaces were aluminized. In Figure 4, the different peaks shown represent the partial contribution to the signal of the glass transition relaxation peak. These peaks
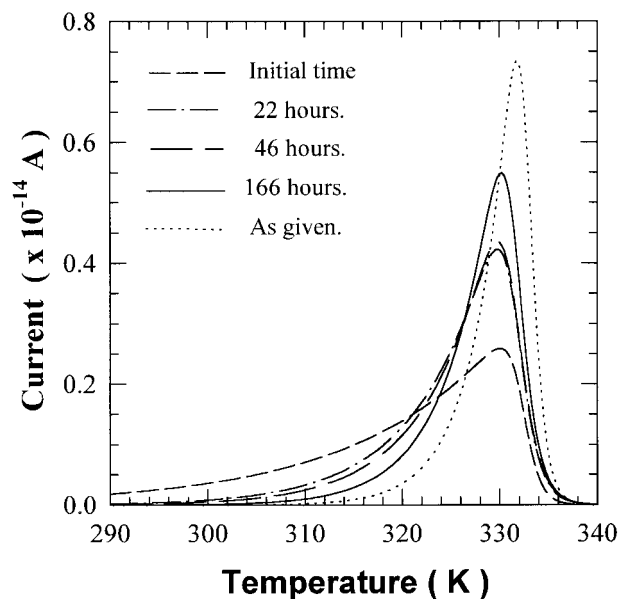
Figure 3 Partial contribution to the high temperature signal from the charge redistribution peak is shown. (− − −) Contribution from the TSD experiment and corresponds to an initial time. (− · −) Aging time of 22 h; (—) aging time of 46 h; and (——) aging time of 166 h. (· · · ·) As-given sample.

were plotted using the parameters obtained for eq. (2) for all of the different aging experiments. The peak labeled initial time and shown with a short dashed line is the one corresponding to the average curve obtained by the TSD experiments. To compare it with the TSP runs, the charge under its curve was normalized to the average charge obtained by this peak in the TSP runs in a similar fashion as for the previous peak.

The fact that the model used to describe the high temperature relaxation peaks agrees well with the data, together with the fact that the partial charges under the corresponding relaxation are constant, indicates that the model describes the system under study accurately. Because the glass transition temperature does not vary appreciably in the aging experiments—but the shapes of the curves and maximum of the charge redistribution peaks are affected—we assume that the main electrical property that is mostly affected by the aging process is the conductivity of the sample. To try to quantify such an observation, we try to establish how the temperature of the maximum of the charge redistribution peak behaves with aging time. Once this time scale is established, the parameters responsible for the current rise on the low temperature side of the relaxation

peaks—together with the shift of the maximum temperature of the charge redistribution peak—are plotted on the same time scale. In Figure 5, the open and solid circles represent variation of the maximum of the current *versus* temperature of the different contributions of the charge redistribution peak as a function of aging time. The three empty circular points correspond to the maximum of the charge relaxation peak for the well-known aging times. With these three points and a logarithmic regression, we determined the effective aging times of the as-given sample and the one labeled initial time on the supposition that the same dependence is valid and therefore their aging times are found. The solid circles show the times found by this procedure. Using the aging times just determined, the parameter α of eq. (1) represented by open squares and β of eq. (2) represented by solid triangles, is plotted. These last two parameters show a similar logarithmic time dependence with aging time as the one established for the temperature of the maximum of the charge redistribution peak. The similar aging time dependence between α and β seems to imply a common phenomenological origin between the conduction current through the sample and the

Figure 4 Partial contribution to the high temperature signal from the glass transition relaxation peak is shown. (− − −) Contribution from the TSD experiment and corresponds to an initial time. (− · −) Aging time of 22 h; (—) Aging time of 46 h; (——) aging time of 166 h. (· · · ·) Charge redistribution peak for the as-given sample.
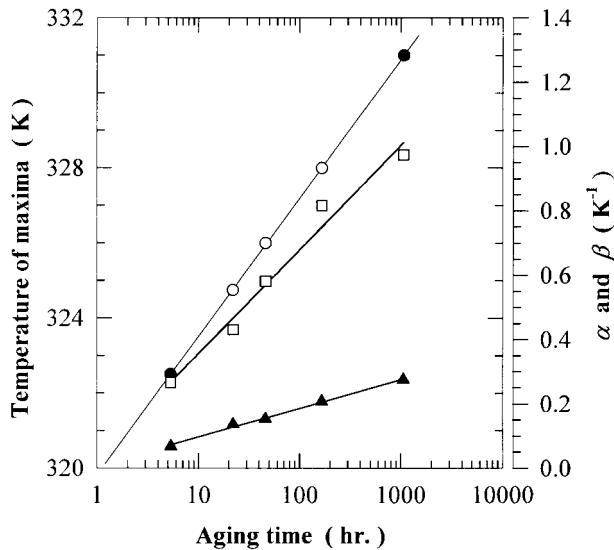
Figure 5 Aging time dependence of different parameters is shown. (○) Temperatures of the maximum of the charge redistribution peaks for the well-known aging times. (●) Same information for the initial time and the as-given sample. (□) Variation with aging time of the parameter α, whereas (▲) is the same information for β.

mechanism controlling the shape of the glass relaxation peak. The parameters α and β are both related to the approximation used for the relaxation time. Variation of the relaxation time described by the model (ref. 5) is mainly attributed to the variation with temperature of the sample parallel resistance. This last observation 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 glass transition and the charge redistribution peak are related to the change of viscosity of the polymeric sample that changes the mobility of the polymeric chains, thus affecting in a different manner the reorientation of the dipolar species and the conduction through the sample. As the samples were aged at 300 K, well below the glass transition temperature, it can be said that the hardening observed with aging has a logarithmic dependence with aging time. Lastly, the fact that the parameters α and β have a very good correlation factor with the determined aging time defined gives confidence in the way such time scale was found. Logarithmic aging time dependence has been seen before[1] in the time range span by our experiments. The variation of the temperature of the maximum of the charge redistribution peak

is such that $dT_{c,\max}/d \ln (t_{\mathrm{aging}}) = 1.60$ K, for the interval of aging times studied. The same slope for α and β is found to be 0.14 K^{-1} and 0.039 K^{-1}, respectively. It is interesting to note that this observed time dependence on most of the parameters agrees with the predictions of Struik for his tensile compliance experiments, even if for the electrical case the change does not appear as a shift of the data, but as a change in the shape of the relaxation peak.

With the exception of the parameter τ_0, all of the other parameters have a reasonable logarithmic dependence with aging time. To estimate the variation of the parameter τ_0 with aging time and because this parameter is not uniquely defined and has a very strong temperature dependence, we shift the similar glass transition temperatures obtained to its common average value. With these shifts ΔT_g, the new values of τ_0 are obtained applying the transformation $\tau_0 e^{\alpha \Delta T_g}$ (see ref. 5). After this operation, the resulting values of τ_0 are equal for all of the aging experiments to approximately 270 s, with an error of 12%.

CONCLUSIONS

Results of TSP and TSD aging experiments using blocking electrodes on samples of poly(DTH succinate) are reproduced with accuracy by the model used. This model describes the different relaxation contributions in the high temperature range comprising the glass transition relaxation peak and the charge redistribution peak that arises from the conduction current in the sample when blocking electrodes are present. Furthermore, because the thermal history previous to the annealing periods is similar for all of the experiments and the heating and cooling rates used are also similar, the glass transition temperature, T_g, should not change. The model presented agrees with the previously described consideration and within experimental errors shows a unique glass transition temperature. Shift of the maximum of the current observed is attributed to the charge redistribution peak that arises due to the presence of blocking electrodes. For the same polarization conditions, contribution to the total polarization from the glass transition temperature peak remains constant for all of the TSP experiments. This implies that the concentration of dipoles contributing to the glass transition relaxation peak is unchanged by the aging experiments. The de-

pendence with aging time of the different parameters is found to be logarithmic. This type of dependence is the same one found by Struik for the creep tensile compliance of poly(vinyl chloride). The only parameter that does not show such dependence is τ_0. After assuming a constant glass transition temperature, τ_0 is found to be constant within 12%, regardless of the aging time. All of these observations deduced using this simple model seem to indicate that the changes observed in the behavior of the shape of the current relaxation peak should be attributed to the change of the value of the electrical conduction in these samples. These changes seem linked to the change in the mobility of the polymeric chains, thus affecting in different manners the reorientation of the dipolar species, as well as conduction through the sample.

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