High Temperature Signals for Thermal-Stimulated Polarization and Depolarization Experiments in Poly(DTH succinate)

M. PUMA, N. SUÁREZ

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

ABSTRACT: Thermal-stimulated polarization and depolarization experiments with and without blocking electrodes are performed on a particular tyrosine-derived polyarylate: poly(DTH succinate). The high temperature region comprising the combined effects of the glass transition relaxation peak and the conduction through the sample is modeled. Conduction through the sample is described by a simple temperature relaxation model that, in the presence of blocking electrodes, gives rise to a charge redistribution peak. The analytical expression for this peak is found and, together with a convenient description for the glass transition relaxation peak the experimental data, is closely reproduced. An estimate of the dielectric constant can be obtained with the model proposed. For the sample used, the value is equal to 2.4. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 283–291, 1998

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

INTRODUCTION

Thermal-stimulated polarization (TSP) and thermal-stimulated depolarization (TSD) experiments were conducted to characterize the high temperature region of a particular tyrosine-derived polyarylate. Tyrosine-derived polyarylates are systems where either the pendent chains or the backbone length can be independently altered. 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 work was prepared by copolymerizing of the desaminotyrosyl-tyrosine hexyl (DTH) ester with the succinic natural diacid. The resulting polymer, referred to as poly(DTH succinate),[1]

has six carbons in the pendent chain and two methylene groups between the carboxylic acid end groups into the polymer backbone as shown in Figure 1. The high temperature currents induced by the depolarization and polarization experiments under different experimental conditions are not well described by existing theories or are usually ignored. To be able to study aging effects on these samples using stimulated thermal current experiments, it is first necessary to have a reliable model that can be used to describe the high temperature current region. To find such a model, TSP and TSD experiments were performed with and without blocking electrodes. The scope of this article is limited to the description of the high temperature signals above the glass transition relaxation peak. Despite the complicated kinetic effects exhibited by polymeric materials, the current rise observed after the glass transition temperature by TSP and TSD experiments without blocking electrodes is described by a simple temperature exponential rise. The observed peak
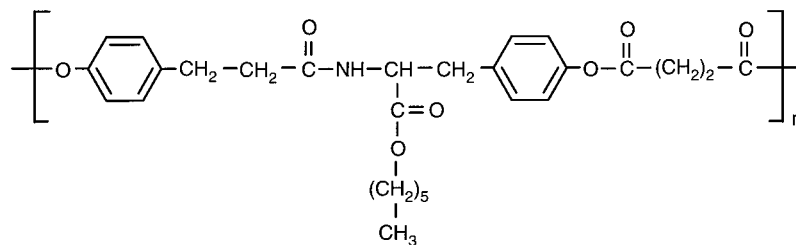

Correspondence to: M. Puma.

Figure 1 Chemical structure of poly(DTH succinate). The backbone includes the diacid component, succinate, whereas the pendent chain has the DTH ester.

for TSP experiments in the presence of blocking electrodes is explained using the same current dependence and the redistribution of the charges among the sample capacitor plates and the blocking electrode capacitors. This charge redistribution of the system takes place as the temperature increases or the polarizing field changes, and it continues until a stationary state with zero current flow is reached. Knowing the values of the blocking capacitor, the relative dielectric constant of the sample can be estimated. To describe the high temperature region, we use a convenient phenomenological model for the characterization of the glass transition relaxation peak. This model allows the description of this peak using a minimum number of parameters whose values depend on the thermal and electrical history of the sample. A thorough review of the effects taking place in the glass transition region of polymeric substances was written by McKenna.[2]

TSD AND TSP EXPERIMENTS WITHOUT BLOCKING ELECTRODES

These experiments were performed with a thin film sample of poly(DTH succinate), 0.488 mm thick, which is placed inside a parallel plate capacitor whose electrodes are disks of 18 mm in diameter. The surfaces of the poly(DTH succinate) sample were aluminized to ensure a constant potential on its surfaces. For the first TSD experiment, a polarizing voltage of 5 V was applied to the capacitor plates, while the sample was at a temperature of about 325 K. With this voltage applied, the sample was cooled to low temperature with a constant rate of approximately 1 Ks^{-1}, where the relaxation time is very high. The potential difference was then removed, and the sample included into the electrometer loop. At this point, the current through the electrometer was monitored, and when the background current was close

to 0 (typically $\leq 10^{-14}$ A), the sample was heated with a constant temperature rate b, of approximately 0.07 Ks^{-1}, whereas the current is detected by a Cary Vibrating Reed Electrometer model 401M across a measuring resistor of 10^{11} Ohm. When the temperature reached approximately 345 K above the glass transition relaxation peak and into the rise of the conduction current, the first cycle of the experiment was concluded. At this temperature, the poly(DTH succinate) sample was cooled down well below the glass transition relaxation peak where the second cycle of the experiment was conducted. For the second cycle of the experiment, the sample is heated again and the current rise recorded a second time up to the previous temperature without having applied any additional polarization voltage to the sample.

Figure 2 shows the currents detected by TSD experiments in the high temperature region. The solid triangles show the first cycle of the experiment evidencing the presence of the glass relaxation peak and the conduction part of the current. The open triangles show the second cycle of the experiment, where only the conduction rise of the current is present as the signal from the glass relaxation peak was fully discharged during the first cycle. The conduction current rise for the second cycle of the experiment follows very closely the behavior of the current recorded for the first cycle. This behavior is due to the very low current intensities of the glass relaxation peak for the stated polarization conditions, in comparison with the greater current involved for the conduction part of the signal and the polarization temperature used that was equal to 325 K.

To characterize the high temperature current attributed to the conduction of the sample, it is assumed that this current can be described as

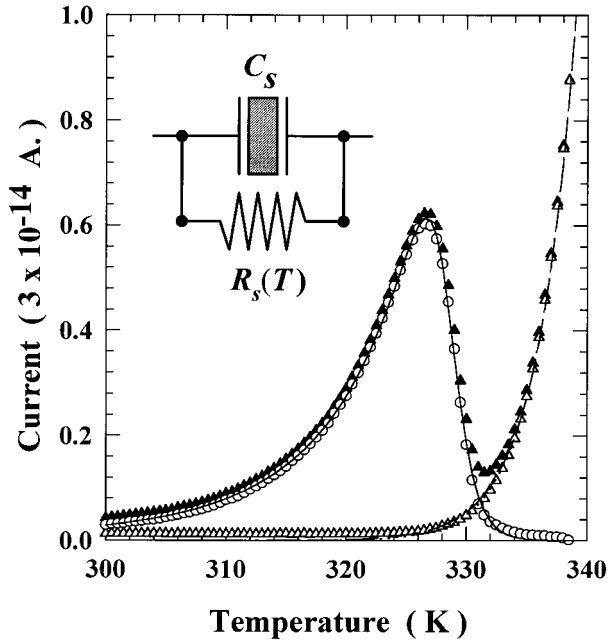$$I(T) = -\frac{dQ}{dt} = \frac{Q_0}{\tau(T)}, \qquad (1)$$

Figure 2 The first cycle of a TSD current experiment without blocking electrodes using a polarization voltage of 5 V and a polarization temperature of 325 K is shown as solid triangles. The second cycle of the experiment, after the sample was cooled again from 340 K, is shown with open triangles. The open circles represent the signal obtained from the difference of the two previous current contributions. The solid line through the open triangles is calculated with eq. (3), and the parameters used are reported in Table I. The solid line through the open circles, representing the glass transition peak, is calculated by means of eq. (4) and with the parameters given in Table II. The inset shows the $R_s - C_s$ equivalent circuit for the sample where $R_s(T)$ represents the temperature-dependent resistor responsible for the conduction. The heating rate for the TSD experiments were 0.07 Ks^{-1}.

where $Q_0 \approx V_p/C_s$, with V_p being the polarization voltage used in the TSD experiment and C_s the value of the capacitance of the sample that is assumed approximately constant in the range of interest and above the glass transition relaxation peak. The value Q_0 also depends on the effective polarization temperature, as well as the rate at which the sample is cooled through the transition. In eq. (1), the relaxation time can be thought of as the one assigned to a $R_s - C_s$ equivalent circuit similar to the one shown in the inset of Figure 2. For the relaxation time of the system, we will use an approximation around $T \approx T_g$ of the well-established WLF[3] expression. This approximation has been previously used in the KAHR model,[4] even

if the meaning of the parameters involved is not the same as the one used by the WLF expression

$$\tau(T) = \tau_0 \exp\{-\alpha(T - T_g)[1 + \lambda(T - T_g)]\}, \quad (2)$$

where α represents the zero-order and λ the first-order term, respectively. With these assumptions, the current can be written as

$$I(T) = \kappa \exp\{\alpha(T - T_g)[1 + \lambda(T - T_g)]\}. \quad (3)$$

The solid line in Figure 2 through the open triangles of the second cycle of the experiment has been calculated with eq. (3). In Table I are reported the values of the parameters obtained for the zero and first order approximation for the expression (2) of the relaxation time.

It is to be pointed out that the value of κ and T_g are not independent from each other. If we change T_g into $T_g + \Delta T_g$, then the same result will be obtained if we replace κ with $\kappa \exp(\alpha \Delta T_g)$ for the zero-order approximation. Therefore, the value of T_g used is the one obtained from the analysis of the glass transition temperature, and it is assumed as the pertinent temperature that must be used to describe the thermal changes that the sample is undergoing in this temperature region. For the first approximation, a similar relation can be found among κ and T_g; but, in this last case, the values of α and λ also are slightly affected. The difference between both approximations is mainly responsible for how well the low temperature tail of the signal and the elbow of the current rise can be described.

Also, it should be pointed out that the experi-

Table I Parameters for Eq. (3) for the TSD Data Without Blocking Electrodes

	0th Order	1st Order
κ (A)	0.118	0.114
α (K^{-1})	0.323	0.346
λ (K^{-1})	0.0	−0.008
T_g (K)	332.4	332.4

The line through the open triangles of Figure 2 was obtained from eq. (3) using a standard nonlinear-fitting algorithm for a value of T_g equal to 332.4 K. The value used for the glass transition temperature is the one obtained from the independent analysis of the glass transition relaxation peak for the experiments using blocking electrodes. The parameters corresponding to the zero- and first-order approximation are shown. Despite a better quality factor, when the first-order approximation is used, the precision of the data is compatible with both approaches.

Table II Parameter of Eq. (4) for the Glass Transition Relaxation Peak Data of Figure 2

	0th Order	1st Order
I_0 (A)	0.876×10^{-11}	0.932×10^{-11}
β (K^{-1})	0.131	0.155
η	359.1	328.4
λ (K^{-1})	0.0	0.0073
T_g (K)	328.6	328.4

This data, shown as open triangles in Figure 2, was obtained by subtracting the currents from the first and second cycles of the TSD experiment. Also, the parameters from the zero- and first-order approximation are shown. The line shown through the open circles is the one corresponding to the zero-order approximation. The agreement between data and the model more than justifies its use as a way to characterize the glass relaxation peak.

mental current signals are dependent on the thermal and electrical history of the sample. Therefore, the values of the parameters will depend on the same history and can be used to characterize the state of the sample. The open circles in Figure 2 are obtained by subtracting the signal from the first cycle of the experiment with the one from the second cycle of the experiment. The signal obtained represents the glass relaxation peak for the poly(DTH succinate) sample for the given experimental history and conditions stated previously.

To characterize the glass transition relaxation peak, a convenient phenomenological model[5] that simplifies the description of such relaxation peak is used. Equation (4) constitutes the model representing the glass relaxation peaks, and the solid line through the open circles in Figure 2 is the first-order approximation obtained with the set of parameters specified in Table II. The parameters were found using a standard nonlinear fitting algorithm. The glass transition temperature measured by our experiments and described by means of eq. (4) is found to be 328.5 K for the TSD experiments without blocking electrodes.

$$I(T) = I_0 \frac{e^{\beta(T-T_g)[1+\lambda(T-T_g)]}}{e^{\eta(T-T_g)/T} + 1}, \qquad (4)$$

Also, a set of TSP experiments is performed on the same samples without blocking electrodes. The experimental procedure is almost the same, except that the polarizing field is applied when the sample is at very low temperature and the relaxation time of the system is very long. The current obtained for the second cycle of the TSP experi-

ments is similar to the one found for TSD experiments, with the difference that the glass transition relaxation is not as evident because the conduction current component now overwhelms the contribution of the glass temperature signal as can be seen in Figure 3. For these experiments, a polarization field of 5 V is applied from low temperature, and the sample is then heated to about 335 K with a constant temperature rate of about 0.07 Ks^{-1}. To limit the value of the current at the end of the TSP experiment, it was terminated at a slightly lower temperature than the one used for the TSD runs. In Figure 3, the solid triangles describe the signal observed as we heat the sample through the first cycle of the experiment with the field applied. After we reach a temperature of
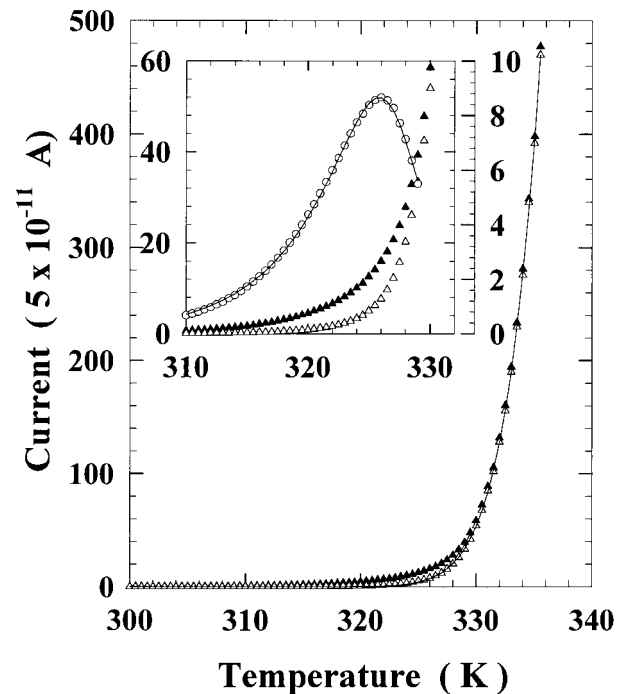

Figure 3 The first cycle of a TSP current experiment without blocking electrodes is shown with solid triangles. The second cycle of the same experiment is shown with open triangles. In this experiment, a polarization voltage of 5 V was established at low temperature and kept constant across the sample through both cycles. The heating rate for both experiments was 0.07 Ks^{-1}. The line through the open triangles is calculated with eq. (3), with the parameters reported in Table III. The inset shows the extra current contribution present during the first cycle of the experiment. The open circles are obtained subtracting both current signals. The intensity of this resulting signal can be read in the scale to the right of the inset and using the same current unit shown.

Table III Parameters of Eq. (3) for the TSP Data Without Blocking Electrodes

	1st Order
κ (A)	150.3×10^{-11}
α (K^{-1})	0.40
λ (K^{-1})	-0.027
T_g (K^{-1})	332.4

The line through the open triangles of Figure 3 was obtained using a standard nonlinear-fitting algorithm for a value of T_g equal to 332.4 K. The value used for the glass transition temperature is the one obtained from the independent analysis of the glass transition relaxation peak for the experiments using blocking electrodes. Only the parameters corresponding to the zero-order approximation are shown.

about 330 K, the sample is cooled again below the relaxation peaks without removing the applied field, and then is heated a second time with the same heating rate. The open triangles represent the signal as observed in the second cycle of the experiment. The glass relaxation peak just appears as some extra current contribution during the first heating cycle. The inset in Figure 3 shows in more detail the region where the extra current exists, and the open circles represent the signal obtained by subtracting these two signals. The current rise for the second cycle of the experiment again can be described with the first-order approximation of the WLF relaxation time for eq. (3). The parameters obtained for the TSP current rise are consistent with the one reported in Table I for the TSD experiments. The differences are the intensity, that grew by a factor of almost 10^3, and the fact that the thermal history of the sample has been changed by the previous cycle of the experiment. Also, the same parameters of Table II used to describe the glass transition relaxation peak in the TSD experiment very closely reproduce the curve representing the same peak in the TSP experiments, considering the difference already stated plus the fact that the signal has more intrinsic noise due to the extraction process of the data. In Table III, the parameters obtained for the description of the TSP current rise are reported.

These results can be modeled with a simple equivalent circuit for the sample that is shown in the inset of Figure 2. The variation of the relaxation time with temperature in this temperature region can mainly be assigned to the variation of the sample resistance to the conduction current. Such assumption is justified with the identification $\tau(T) = R_s(T)C_s$ and assuming that the capacitance C_s is almost constant in the tempera-

ture range of interest above T_g. Even if C_s is slowly varying with temperature, it does not vary as strongly as would R_s.

TSD AND TSP EXPERIMENTS WITH BLOCKING ELECTRODES

The same experiments were performed adding to both sides of the sample a pair of blocking electrodes. They were formed with a pair of sapphire disks of 19 mm in diameter and 0.216 mm thick. To model our sample, we used the equivalent circuit shown in the inset of Figure 4, where the two extra blocking electrodes are added as two ideal capacitors.

Let us now focus our attention on the TSP experiment, where a voltage of 100 V is established while the sample is at low temperature. At these low temperatures, all capacitors can be considered as ideal capacitors without losses. With the presence of the polarizing field, they will acquire a charge Q_0 across their plates. As the temperature increases with a constant rate b, the temperature-dependent resistor of the sample starts diminish-
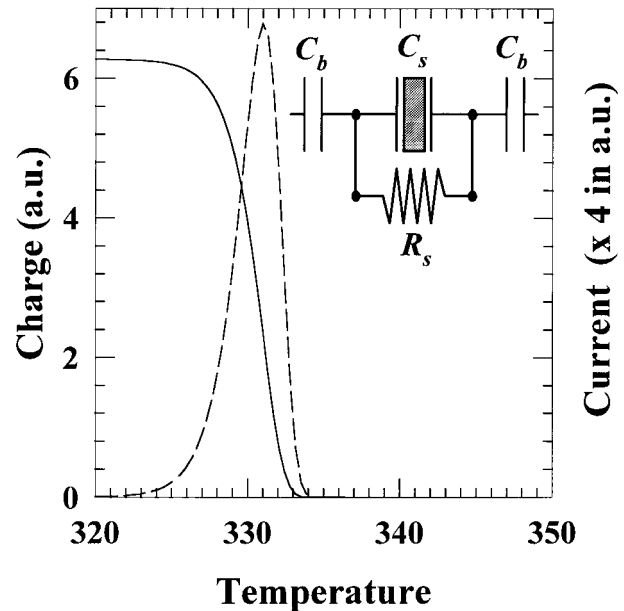

Figure 4 The charge $Q(T)$ as a function of the temperature is shown with a continuos line. The relaxation time used for the calculations is the zero-order approximation of eq. (1). The current $I(T)$ calculated with eq. (6) is shown with a dashed line. The inset represents the sample equivalent circuit, where two additional ideal capacitors, C_p, are added to describe the blocking electrodes.

ing. As the value of the relaxation time becomes smaller, the charge on the sample capacitor starts to diminish according to

$$Q(T) = Q_0 e^{-T/b\tau(T)}, \qquad (5)$$

where we have used the fact that time t is related linearly to the temperature through $T = bt$ and $\tau(T) = (C + C_s)R_s(T)$, with C being the equivalent capacitance of the blocking electrodes. Equation (5) is a well-known expression that shows how, at high enough temperature, the charge originally accumulated in the sample capacitor is short-circuited. In this process a redistribution of charges on the blocking electrodes takes place in order to keep the voltage constant and equal to the one applied externally. The current due to this charge redistribution is obtained by taking the derivative of eq. (5) with time or temperature. To calculate such derivative, the zero-order approximation for the relaxation time of eq. (1) is used. The current can then be expressed as

$$I(T) = Q_0 f(T)\left(\alpha + \frac{1}{T}\right)e^{-f(T)}, \qquad (6)$$

with

$$f(T) = \frac{T}{b\tau_0} e^{\alpha(T-T_g)}.$$

Figure 4 shows the variation of the charge on the capacitor plates representing the sample and the current obtained with eq. (6) for a set of testing parameters. The current just obtained contributes to the relaxation spectrum as an extra peak whose presence is due to the existence of blocking electrodes. The observed peak in Figure 4 is due to the dissipation of the charge across the capacitor plates of the sample that induces the charge on the blocking electrodes, because the current is not allowed to flow into the external circuit. This charge redistribution on the blocking electrodes takes well in account the main features of the experimental data for the poly(DTH succinate) samples studied. For TSD and TSP experiments using blocking electrodes and a fixed polarization voltage, the total charge on the system is known if enough time is allowed to elapse for the current transients to vanish.
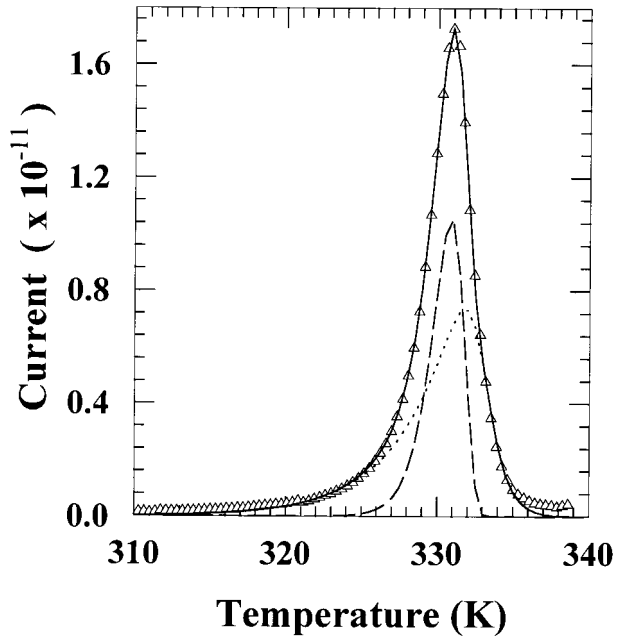

Figure 5 The result of a TSP current experiment using blocking electrodes is shown. A polarization voltage of 100 V, established at low temperature, is used. The experimental points are presented as open triangles. The solid line through those points is the result of the overlapping signals from the glass relaxation peak and the signal originated by the presence of the blocking electrodes. The heating rate for this experiment is 0.07 Ks^{-1}. Table IV reports the values found for eq. (4) that describe the glass relaxation peak and the charge redistribution peak of eq. (6). The dotted line represents the glass transition peak component and the dashed line the contribution of the charge redistribution peak. The parameters were found by a nonlinear-fitting algorithm exploring the neighborhood of the possible values to find the true minimum.

Figure 5 shows with open triangles the actual peak obtained by the TSP experiment described on an "as given" sample (i.e., one without any previous thermal or electrical history). The region where the experimental signal appears contains the contributions from the glass relaxation peak and the conduction current peak just described, because both relaxations span the same temperature range for the particular thermal history of this sample. Therefore, to describe such peak, we use a superposition of the glass relaxation peak, as expressed through the model of eq. (4), plus the conduction peak, described by eq. (6) just obtained. Figure 5 shows with open triangles the experimental data and with a solid line the overall behavior obtained by a standard nonlinear fitting algorithm with the above expressions. The decom-

Table IV Parameters Obtained from the Combination of Eq. (4) and Eq. (6) Describing the Glass Relaxation Peak and the Charge Redistribution Peak of Figure 5

Glass Transition		Charge Redistribution	
I_0 (a.u.)	1.191	Q_0 (a.u.)	2.951
β (K^{-1})	0.275	α (K^{-1})	0.974
η	489	τ_0 (s)	701
λ (K^{-1})	0	T_g (K)	332.8
T_g (K)	332.8	b (Ks^{-1})	0.0727
Q_g (C)	6.32×10^{-10}		
Q_c (C)	4.06×10^{-10}		
Q_T (C)	10.38×10^{-10}		

The glass transition temperature T_g is considered a unique parameter. Furthermore, the values of the heating rate b and the total charge under each of the relaxation peaks are reported together with the parameters. Data described correspond to the TSP experiment of Figure 5 shown as open triangles. To obtain a convergence, a standard nonlinear-fitting algorithm was used.

position of the experimental peak among these two relaxations is represented with a dotted line for the glass transition relaxation peak and with a dashed line for the charge redistribution peak caused by the conduction current and the presence of blocking electrodes. Table IV shows the parameter used for the two components of the observed relaxation, as well as the charge that each peak contributes to the total signal. The glass transition temperature is the same for both contributions as it is constrained to be equal.

For a TSD experiment, the same eq. (6) describes the general behavior for the current. From the experimental point of view, there are important differences. Usually, when a normal TSD experiment is performed, the sample is polarized at high temperature. At these temperatures, only the blocking electrodes are charged, because the sample capacitance is usually short-circuited by the low value of its parallel resistor. Subsequently, the temperature of the sample is lowered and the polarizing field is removed. Then, the sample is short-circuited for some time by an actual short or through the measuring electrometer. At this low temperature and after the sample is short-circuited, there is a charge redistribution among the capacitors, because now the sample can be considered as an ideal capacitor with zero loss. Once this redistribution of charges has taken place, the temperature of the sample is increased at a constant rate. In this process, the thermal

and electrical history of the sample has been modified in comparison to the previous experiment that was performed on an annealed system at about 300 K for about 3 months. To perform a TSD experiment, the sample must be heated up to the polarization temperature used, that in this case is above the annealing temperature reported previously. Therefore, it is not expected that the signal be the same as the corresponding TSP signal recorded from a sample that was not previously cycled above the annealing temperature and kept at this temperature for the length of time specified. A study of these signals as a function of the sample thermal history showing the aging effect exhibited by poly(DTH succinate) in this temperature region is out of the scope of this article and will be presented separately.

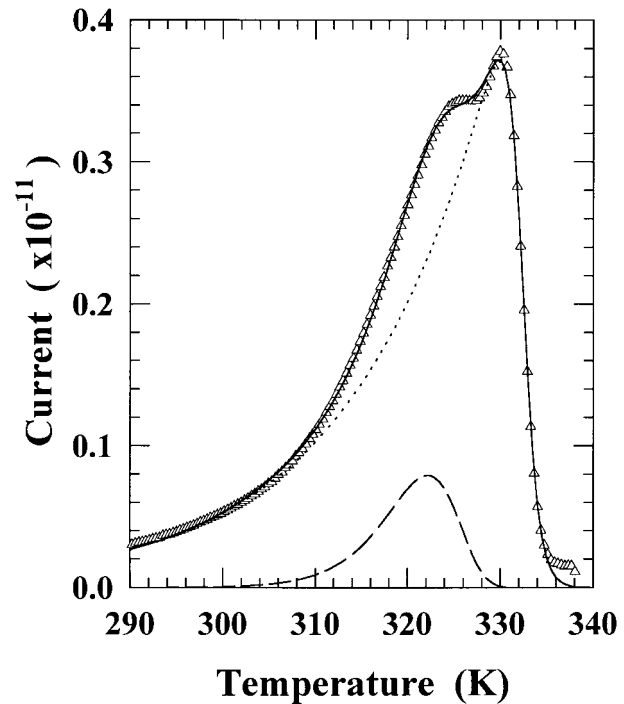Figure 6 shows with open triangles the TSD signal observed. The contribution of the glass

Figure 6 The result of a TSD experiment using blocking electrodes is shown as open triangles. The polarization voltage used is 100 V and the polarization temperature was 340 K. The heating rate while recording the current is 0.07 Ks^{-1}. The solid line through the triangles is obtained with the contribution of the glass relaxation peak and the charge redistribution peak. The dotted line represents the glass transition peak component and the dashed line the contribution of the charge redistribution peak. The parameters used for eqs. (4) and (6) are reported in Table V.

Table V   Parameters Obtained from the Combination of Eq. (4) and Eq. (6) Describing the Glass Relaxation Peak and the Charge Redistribution Peak of Figure 6

	Glass Transition		Charge Redistribution
I_0 (a.u.)	0.461	Q_0 (a.u.)	0.838
β (K^{-1})	0.0674	α (K^{-1})	0.254
η	397	τ_0 (s)	337
λ (K^{-1})	0	T_g (K)	332.3
T_g (K)	332.3	b (Ks^{-1})	0.0736
Q_g (C)	8.82×10^{-10}		
Q_c (C)	1.14×10^{-10}		
Q_T (C)	9.96×10^{-10}		

The glass transition temperature T_g is considered a unique parameter. Furthermore, the values of the heating rate b and the total charge under each of the relaxation peaks are reported together with the parameters. To obtain a convergence, a standard nonlinear-fitting algorithm was used.

transition relaxation peak and the conduction current redistribution peak is now evident from the observation of the current signal. As already pointed out, the sample cannot be considered without previous thermal history and also, as the internal field is produced on the sample by the redistribution of charges at low temperature, the relative intensities of the signal are different from the TSP experiments; however, the total charge under the composite signal must be conserved if the same polarizing voltage is used for the TSD and TSP experiments. In Figure 6, the open triangles represent the experimental data, with a solid line the description of the data obtained by the combination of the two relaxations described, with dotted lines as the component of the glass transition relaxation peak and with a dashed line as the contribution of the charge redistribution peak caused by the conduction current and the presence of blocking electrodes. Table V reports the values of the parameters found that describe both relaxations obtained in the same manner as previously described. We would like to point out that the temperatures obtained for the glass transition temperature in the experiments using blocking electrodes are consistently about 2 degrees above the ones obtained without blocking electrodes.

ESTIMATE OF THE DIELECTRIC CONSTANT

For the TSD experiments with blocking electrodes, the electric polarization field is applied at high enough temperature and for a sufficient length of time that the charge across the sample capacitor is discharged completely through its temperature-dependent resistor. At these temperatures, the value of this resistance is low and the associated relaxation time short, compared with the polarization time and other characteristic times involved in the experiment. Therefore, if we assume C as the equivalent capacitance of the blocking electrodes, the charge on this capacitor is equal to $Q_0 = CV_p$, where V_p is the polarization voltage used in the TSD experiment. After the temperature is lowered, the polarizing field is removed, and the sample is short-circuited through an external resistance or the measuring instrument. At this point, the original charge present on the blocking electrodes is redistributed among the blocking electrodes and the sample capacitor, because now the resistance has a very high value and the capacitor can be considered an ideal one. When the equilibrium configuration is reached at this low temperature, the charges are redistributed according to

$$\frac{Q'}{C} = -\frac{Q_s}{C_s} \quad \text{with} \quad Q' + Q_s = Q_0, \qquad (7)$$

where Q' is the charge on the blocking electrodes and Q_s the charge on the sample capacitor. It is straightforward to write the value of the sample capacitance in terms of the charge present on it as

$$C_s = C \frac{|Q_s|}{Q_0 - Q_s}. \qquad (8)$$

It is necessary to calculate the equivalent capacitance of the blocking electrodes that in our case is 54.3 pF, and the initial charge Q_0 that for a polarization voltage of 100 V is equal to 5.43×10^{-9}C. As the measured total charge under the TSD composite relaxation curve is equal to 9.96×10^{-10}C, a value of approximately 12.2 pF is obtained for the capacitance of the sample. From the geometry of the sample, the same capacitance can be calculated to be equal to $C_s = 5.14\varepsilon_r$ pF, giving an approximate value of 2.37 for the relative dielectric constant. A similar argument can be made for the TSP experiment. The polarization field is now applied at low temperature, and the charged Q' is now distributed on the sample and blocking capacitors according to

$$V_p = Q'\left(\frac{1}{C} + \frac{1}{C_s}\right), \qquad (9)$$

where again C is the equivalent capacitance of the blocking electrodes. As the temperature increases at constant rate b, the charge on the sample capacitance is discharged due to the smaller value of the relaxation time of the $R_s - C_s$ system, whereas the voltage difference must be compensated by an extra charge on the capacitance of the blocking electrodes. When the discharged process of the sample capacitor is completed at high temperature and, consequently, the recorded current is 0, the charge on the blocking electrodes is again equal to the value Q_0 previously calculated. Equation (8) also applies for this situation, and the value for C_s can again be calculated using the total charge measured under the high temperature relaxation peaks. The value obtained for Q_s is, for the TSP experiment, equal to 1.04×10^{-9}C, which gives the value for C_s of 12.9 pF and 2.50 for the relative dielectric constant of the sample. Both values obtained for the relative dielectric constant of poly(DTH succinate) are within 5% of each other and can be considered to be the same within our experimental errors. The value of ε_r of about 2.44 corresponds to a temperature just below the glass transition temperature, where the charge configuration obtained starts diminishing as the effective relaxation time of the system becomes comparable with the characteristic experimental times. Also, when blocking electrodes are present, the current detected is the one flowing through the external circuit and not directly dQ_s/dt. For both TSD and TSP experiments, there is an attenuation factor that is equal for both configurations as long the same blocking electrodes are used.

CONCLUSIONS

The glass relaxation peak plus the conduction current present in the same temperature range for TSD and TSP experiments with and without blocking electrodes is described and modeled for poly(DTH succinate). The part of the signal attributed to the conduction is described by a simple relaxation model. The model uses a simple approximation of the WLF relaxation time for temperatures in the vicinity of the glass transition. The presence of blocking electrodes modifies the shape of the conduction current and is responsible for the extra relaxation peak. This peak is produced by the redistribution of the charges among the sample capacitance and the blocking electrodes capacitance. The shape of this peak is calculated and, together with a model that easily describes the glass relaxation peak, experimental data are reproduced with high accuracy. For the description of the glass relaxation peak, a useful phenomenological model is used. Furthermore, using the redistribution of charges on the capacitance present in the system, the relative dielectric constant for the poly(DTH succinate) sample is estimated and found to be of the order of 2.4 for an estimated temperature of about 310 K.

REFERENCES

1. J. Kohn, 20th Annual Meeting of Science for Biomaterials, Boston, MA, Society for Biomaterials, Minneapolis, MN, 1994, p. 67; J. Kohn and J. J. Fiordeliso, U.S. Pat. 5,216,115 (1993); J. Fiordeliso, M.Sc. Thesis, Rutgers University, 1993; J. Kohn, *Trends Polym. Sci.,* **1,** 206 (1993); J. Fiordeliso, S. Bron, and J. Kohn, *J. Biomater. Sci. (Polym. Ed.),* **5,** 497 (1994).
2. G. B. McKenna, *Comprehensive Polymer Science,* Vol. 2. *Polymer Properties,* C. Buoth and C. Price, Eds., Pergamon Press, Oxford, 1989.
3. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.,* **77,** 3701 (1955).
4. A. J. Kovac, J. J. Aklonis, J. M. Hutchinson, and A. R. Ramos, *J. Polym. Sci., Polym. Phys.* **17,** 1979 (1979).
5. M. Puma, *Polym. Adv. Technol.,* **8,** 39 (1997).