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Citation: *Journal of Applied Physics* **99**, 113524 (2006); doi: 10.1063/1.2205354

View online: <http://dx.doi.org/10.1063/1.2205354>

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## High-temperature polarization and depolarization experiments on poly( $\epsilon$ -caprolactone)

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(Received 3 August 2005; accepted 17 April 2006; published online 13 June 2006)

Thermally stimulated depolarization current (TSDC) and thermally stimulated polarization current (TSPC) techniques are compared, and the results obtained for semicrystalline poly( $\epsilon$ -caprolactone) (PCL) are reported in this work. It is shown that concerning the glass transition relaxation, both techniques give the same information, provided that for the TSDC case the polarization temperature is above the temperature range where the labeled  $\rho$  peak occurs. The current reversal observed in TSPC spectrum of this polymer is originally reported here, and its presence predicted by a simple phenomenological model taking into account the  $T^{-1}$  dependence of the equilibrium polarization. The current reversal observed in the TSDC experiments when the sample is polarized at high temperatures is an evidence of the existence of an internal field applied during the heating cycle. Performing two consecutive TSPC experiments (TSPC2) two current reversal temperature zones were observed. The comparison of the dielectric spectra obtained in the same temperature zones by the different techniques envisages the possible presence of a dipolar mechanism contributing to the  $\rho$  peak. Further modeling and data treatment need to be done in order to corroborate this hypothesis. © 2006 American Institute of Physics. [DOI: [10.1063/1.2205354](https://doi.org/10.1063/1.2205354)]

### I. INTRODUCTION

The method of field-induced thermally stimulated currents<sup>1-5</sup> consists of measuring, with a defined heating scheme, the currents generated by the buildup and /or the release of a polarized state in a solid dielectric located between two electrodes. In order to observe current peaks due to the thermally activated transition from neutrality to a polarized state, the sample temperature must be increased at a constant rate, while applying the dc field. This technique is generally named thermally stimulated polarization currents (TSPC). Current peaks are also obtained due to the thermally activated transition from the initial polarized state to the equilibrium state. To detect these depolarization currents the field is applied at a starting temperature above the relaxation processes to be observed, then the sample is cooled under the applied field to some lower temperature, and afterwards, with the field switched off the sample is heated at a constant rate. This is the well-known thermally stimulated depolarization current (TSDC) technique. Both techniques, TSPC and TSDC, are very sensitive, since electrometers that can detect currents down to  $10^{-17}$  A are available. For the study of dipolar relaxations, the theoretical formulations of TSPC and TSDC are usually restricted to the case that the equilibrium polarization depends on the temperature according to the Langevin function.<sup>1,2,6,7</sup> With this assumption TSPC and TSDC classical theories provide similar current peaks, the main differences being that (1) the polarization current is of opposite sign, (2) the appearance of a current reversal on the

high-temperature side of the dipolar TSPC peak due to the decrease in the equilibrium polarization which varies as  $T^{-1}$ , and (3) TSPC dipolar peaks are superimposed onto the normal dc conduction current.

Poly( $\epsilon$ -caprolactone) (PCL) is a typical polyester with repeating units arranged head-to-tail and ester dipoles that exhibit a dipolar electric moment with perpendicular and parallel components to the chain contour. The perpendicular component produces the dielectric response of local and segmental relaxations while the parallel component contributes to the dielectric relaxation associated with the so-called normal modes. These modes, related with the longest relaxation times, have been reported in dilute and semidilute solutions of PCL studied by dielectric spectroscopy<sup>8-10</sup> However, no evidence has been found about the existence of these normal modes in field-induced thermally stimulated currents experiments in this polymer. The relaxation process located in a high-temperature zone, where the normal modes are supposed to be active, has been explained in terms of space-charge accumulation at the phase crystalline boundaries<sup>11</sup> or ions migrations at the sample surfaces.<sup>12</sup>

It is the purpose of this paper to make a direct comparison of TSDC and TSPC experiments performed on poly( $\epsilon$ -caprolactone) in order to obtain information regarding the origin of the high-temperature dielectric relaxations. To check the effect of the conduction current and carrier injection the experiments are performed with and without blocking electrodes. A simple phenomenological model is presented to characterize the observed dielectric manifestation of the glass transition in polarization experiments.

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## II. EXPERIMENTS

The PCL studied is an aliphatic semicrystalline polyester supplied by Sigma Aldrich. Its weight-average molecular mass is  $M_w=130\,000$  g/mol and the sample is a compressed molded film from pellets. Its crystallinity is 61%, calculated from the heat of fusion values obtained from PCL fraction  $T_m$  endotherms.

The experiments without blocking electrodes were performed with a thin-film sample of 1.04 mm thickness, placed inside a parallel-plate capacitor whose electrodes are disks of 19 mm in diameter. For TSDC experiments a polarizing field of  $5 \times 10^5$  V/m was applied to the capacitor plates. In order to obtain the whole high-temperature dielectric spectrum the sample was polarized at a temperature of about 300 K. A polarization temperature of 220 K was chosen to isolate the dielectric manifestation of the glass transition from the high-temperature dielectric spectrum. After polarizing the sample for a time  $t_p=3$  min, holding the field on, it was cooled, at a rate of approximately  $1\text{ K s}^{-1}$ , to a temperature where the relaxation time is very high. The applied field 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 closed to zero, the sample was heated with a constant temperature rate  $b$  of  $0.1\text{ K s}^{-1}$ , while the current is detected across a measuring resistor of  $10^{11}\ \Omega$ . Also TSPC experiments were performed on the sample 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. Simultaneously with the switching on of the field the current is detected with the electrometer. When the transient currents are below the background currents, the temperature of the sample is increased at a constant rate of  $0.1\text{ K s}^{-1}$  and the current recorded. At a temperature of about 300 K, the actual TSPC experiment is concluded. Henceforth, without removing the external field, the sample temperature is lowered back to liquid nitrogen at a rate of approximately  $1\text{ K s}^{-1}$ , where the second TSPC experiment begins (TSPC2). In TSPC2 experiments and, without changing the polarizing field, the sample is heated again at a constant rate of  $0.1\text{ K s}^{-1}$  while the current is recorded.

The same TSDC, TSPC, and TSPC2 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.

## III. TSPC MODEL CALCULATIONS

According to previous work,<sup>13</sup> assuming a dipolar system formed by a number of permanent dipole moments fixed to some mobile polymer chains, the polarization of the TSDC  $\alpha$  peak is given by

$$P_{\text{TSDC}}(T) = P_o \frac{1}{\exp\left[\frac{2p_o E(\alpha(T - T_g) - 1)}{kT}\right] + 1}. \quad (1)$$

In expression (1)  $p_o$  is the average dipole moment,  $E$  is the applied electric field, and  $T_g$  and  $\alpha$  depend on the thermal history of the sample.<sup>13</sup>

To obtain the polarization for the TSPC we need to revert the initial and final states of the polarization. This is easily done by subtracting the equilibrium polarization  $P_o$  from Eq. (1) to obtain

$$P_{\text{TSPC}}(T) = P_o(T) \frac{f(T)}{f(T) + 1}, \quad (2)$$

where

$$f(T) = \exp\left[\frac{2p_o E(\alpha(T - T_g) - 1)}{kT}\right]. \quad (3)$$

In expression (2) we explicitly wrote the equilibrium polarization,  $P_o(T)$ , as a function of the temperature  $T$  and whose dependence is known to behave as  $1/T$ . Now we know that for  $T \sim T_g$  the behavior is not the one in equilibrium and for  $T < T_g$  there is no temperature dependence and for  $T \gg T_g$  the dependence is  $1/T$ . We should switch the dependence with temperature on, according to the value of the relaxation time. Once the relaxation time is greater than the typical time of data acquisition, irrespectively of its value, the dependence of  $P_o$  with temperature remains  $1/T$ . Therefore we will switch on the dependence with a continuous function that changes its value from 0 to 1 in the neighborhood of  $T_g$ . This function can be readily written as

$$w(T) = 0.5 \left[ \tanh\left(K \frac{T - T_g}{T}\right) + 1 \right], \quad (4)$$

where the constant  $K$  has the function of varying the range where the function changes from zero to one. Its value is chosen in order to make sure that the transition from zero to one is smooth and around the relaxation maximum; that is, it will go from zero to one in an interval  $\Delta T$  around  $T_g$ . With this definition now we can turn on the dependence with  $T$  of the polarization in such a way that at low temperatures its value is one (no temperature dependence) and at high temperature will show a  $1/T$  dependence. For this purpose we define the additional function that will be one at low temperature and at high temperature it will approach  $1/T$  as

$$w'(T) = 1 - w(T) \tanh\left(\frac{T - T_g}{T}\right). \quad (5)$$

The function  $w'(T)$  modulates the value of the equilibrium polarization and at high temperatures it will show a  $1/T$  dependence. To obtain the polarization for the TSPC case we can rewrite Eq. (2) as

$$P_{\text{TSPC}}(T) = P_o w'(T) \frac{f(T)}{f(T) + 1}. \quad (6)$$

To calculate the current for the TSPC we generally need to take the derivative with time of the polarization. However, as we are not in equilibrium this operation cannot be performed and is customary to write

$$\frac{dP_{\text{TSPC}}}{dt} = \frac{P(T) - P_o(T)}{\tau(T)} + \frac{dP_o(T)}{dt}. \quad (7)$$

There are two terms that we will discuss separately. The initial term shows that the polarization at temperature  $T$  is not in equilibrium with the expected equilibrium polarization. Therefore, it predicts the presence of a current flow that is proportional to the departure from the equilibrium state and is inversely proportional to the relaxation time at that temperature. The temperature dependence of the relaxation time follows the William-Landell-Ferry (WLF) approximation.<sup>13</sup> If  $P_o$  were independent of  $T$ , then the expression for the current would be exactly the same as the one for the TSDC case, except that would flow in the opposite direction. Now we know that for  $T < T_g$  the polarization  $P_o$  does not vary with  $T$  for all practical purposes. Therefore at the offset of the TSPC current we expect exactly the same behavior found for a TSDC experiment. For  $T$  greater than  $T_g$ , where the relaxation time is shorter than the typical experimental data acquisition time, then the variation of the current is just  $b dP_o(T)/dT$  as we are heating the sample at a constant rate  $b$ . The second term of Eq. (7) will give rise to a negative contribution of the current due to the equilibrium depolarization of the dipolar chains. Now that we know the limiting cases it is easy to find the expression of the current in the following way:

$$I_{\text{TSPC}}(T) = w'(T)I_{\text{TSDC}}(T) + b \frac{P_o(T)}{dT}. \quad (8)$$

The above expression is not surprising since the initial term is the contribution of the departure from equilibrium of the polarization value, which is given in the same way as for the regular TSDC experiments. The only fact to notice is that now this value is modulated by the function  $w'(T)$ . The second term shows the typical derivative with respect to time or temperature through the factor  $b$  that exists because of the linear heating rate.

When we perform the derivative of  $w(T)$  it is always zero but in a small region around  $T_g$  that we neglected without any quantitative consequence. Also, the only term that switches on the equilibrium temperature dependence of the polarization is the  $w'(T)$  function and is the only term that changes with time. The rest of the time dependence of the polarization is only due to the change in the relaxation time and therefore should not be taken into consideration here as it was already derived in the initial term of Eq. (7).

So the general expression for the current can be written as

$$I_{\text{TSPC}}(T) = I_0 w'(T) \frac{e^{\beta(T-T_g)}}{e^{\eta(T-T_g)/T} + 1} + \gamma \frac{f(T)}{f(T) + 1} w(T) \frac{1}{T^2}. \quad (9)$$

Equation (9) will be used for describing the current in a TSPC experiment and will show the negative part of the curve due to the behavior of the equilibrium polarization. In this expression  $\eta = 2\rho_o E a / k$ , and  $\beta$  is the preexponential factor of the relaxation time. There is only one more parameter in relation of the TSDC current,<sup>13</sup>  $\gamma$ , that is proportional to the depolarization current. The extra parameter in the function  $w$  is never changed but just chosen with the criteria already described. To fit the experimental data to Eq. (9) we performed a standard nonlinear fitting procedure.

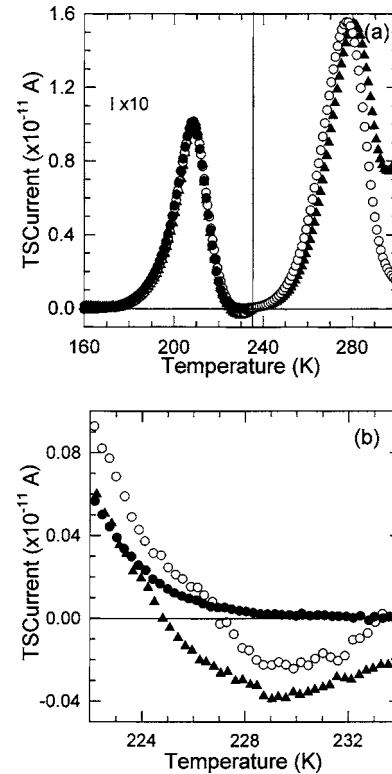


FIG. 1. a) High temperature TSDC and TSPC spectra of PCL without blocking electrodes: (●) TSDC  $T_p=220$  K; (○) TSDC  $T_p=296$  K; (▲) TSPC. (b) Shows the detail of the small region where the current reversal is present. The density current was normalized to an electric field of 1 MV/m.

#### IV. RESULTS AND DISCUSSION

Figure 1(a) shows the high-temperature thermally stimulated experiments performed on PCL without blocking electrodes, for the same polarizing voltage and heating rate. The open circles are the TSDC polarized at 296 K and the TSPC is shown as solid triangles. In these spectra two main relaxations are clearly visible, and previous studies of this polymer have associated peak  $\alpha$  with the segmental cooperative motions of important segments on the main chain,<sup>11,12</sup> while peak  $\rho$  has been attributed to free charges accumulation at crystal surfaces<sup>12</sup> or trapped charges at the crystal/amorphous interfaces in Maxwell-Wagner-Sillars (MWS) modes.<sup>11</sup> The solid circles spectrum shows the TSDC current when the sample was polarized at 220 K, and therefore it is only observed the  $\alpha$  peak. In the case of the open circles curve a current reversal appears in the high-temperature tail of the  $\alpha$  peak, which is not present in the solid circles spectrum [see Fig. 1(b)]. This is contrary to what can be expected for a TSDC curve. The results of the TSPC experiment show also the same current reversal. The current reversal in TSPC experiments had been also reported in fluorite crystals,<sup>2</sup> alkali halides,<sup>6</sup> and block copolymers;<sup>7,11</sup> its presence have been explained taking into account the temperature dependence of the equilibrium polarization. In our case the existence of a current reversal in the high-temperature tail of a TSPC dipolar peak is in complete agreement with the predicted values described by Eq. (9). These results allow us to conclude that in the TSDC experiment polarized above the peak  $\rho$ , instead of monitoring the depolarization of the sample we are mea-



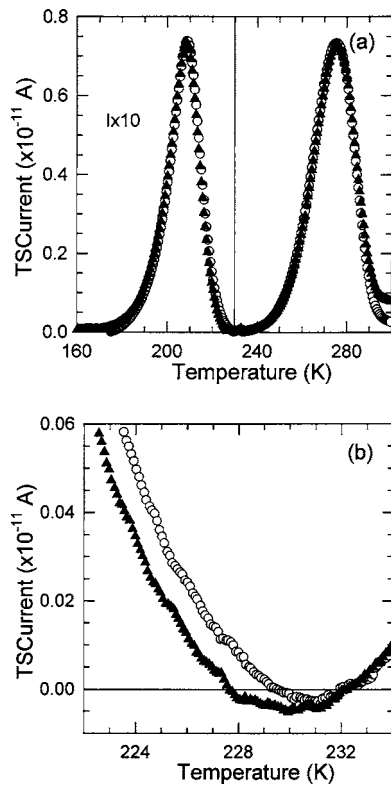


FIG. 2. (a) High-temperature TSDC and TSPC spectra of PCL with blocking electrodes: (○) TSDC  $T_p=296$  K; (▲) TSPC. (b) shows the detail of the small region where the current reversal is present. The density current was normalized to an electric field of 1 MV/m.

sureing its polarization in the presence of an internal field opposite to the initial external polarizing field. The polarization current induced by this internal field is in the same direction as the depolarization current expected in a TSDC experiment.

It is clear that the simple appearance of current reversal in the course of a real TSPC experiment cannot be considered as a definitive argument in favor of the dipolar model advocated since carrier injection, for example, could also lead to such a phenomenon. In order to check the influence of carrier injection in the reversal current detected we have performed the same TSPC and TSDC experiments (polarized at 296 K) but now with the sample sandwiched between blocking electrodes using two pairs of sapphire disks. The results are shown in Figs. 2(a) and 2(b), and they are completely in agreement with the ones presented in Figs. 1(a) and 1(b), so we can disregard any influence of carrier injection in the studied reversal current. Concerning the higher-temperature part of the TSPC spectrum, the absence of the steep increase current under blocking conditions corroborates the absence of carrier injection at sample surfaces. The presence of some background current at the highest-temperature region could be thought as due to the melting initiation of the smaller crystals present in the sample.

In Fig. 3 we present the glass transition peak of the same TSPC data shown in Fig. 2, as well as the fitting curve obtained by Eq. (9) and the polarization calculated with Eq. (6). The actual experimental data departs at high temperature due to the presence of the  $\rho$  peak. From the figure it can be seen

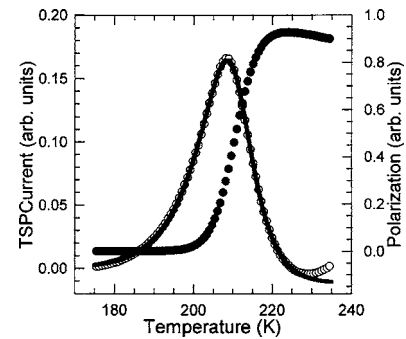


FIG. 3. Experimental and fitted TSPC  $\alpha$  relaxation together with the polarization calculated from the values obtained in fitting  $\alpha$  (Table I): (○) experimental peak; (—) fitted peak; (●) polarization. The TSPC experiment was performed with blocking electrodes. The polarization scale is the one on the right.

that the model reproduces remarkably well the experimental data. The parameters obtained in the fitting procedure are reported in Table I. The  $K$  parameter in the definition of  $w(T)$  was chosen equal to 50 in order to set the variation of the polarization in the expected temperature range. It is to be noticed that changing these parameters to higher values makes very little difference on the quality of the fit. Lowering this constant too much makes little sense as then we will observe a temperature dependence of the polarization at low temperatures where there should be none.

As the equilibrium polarization is proportional to the effective polarizing field the maximum amplitude of the current reversal must increase linearly with the applied field.<sup>2</sup> To check this dependence, and trying to isolate the current contribution due to the temperature dependence of the equilibrium polarization, TSPC2 experiments were performed varying the external applied field. It is expected that if the TSPC reversal is of dipolar origin, a current reversal must also appear during the final heating step<sup>2,6</sup> (TSPC2 experiment). The results presented in Fig. 4, besides to exhibit the predicted current-field dependence, show two current reversal zones. The primary one coincides with the location of the high-temperature side of the  $\alpha$  peak, i.e., the reverse current due to the non-negligible temperature dependence of the equilibrium polarization, and the second one is positioned in some region inside the  $\rho$  peak. This second current reversal could be interpreted as an evidence of the existence of a dipolar mechanism responsible for at least a portion of the higher-temperature relaxation mechanism ( $\rho$  peak) of PCL. With this assumption the temperature dependence of the equilibrium polarization of this dipolar mechanism could explain the observed second current reversal. Previous works have attributed the origin of the  $\rho$  peak in PCL to space-charge accumulation at the phase crystalline boundaries<sup>11</sup> or

TABLE I. Parameters of Eq. (9) obtained from the fit of the experimental TSPC  $\alpha$  relaxation peak of Fig. 3.

$I_0$ (a.u.)	0.398
$\beta(K^{-1})$	0.151
$\eta$	58.80
$T_g$ (K)	210.31

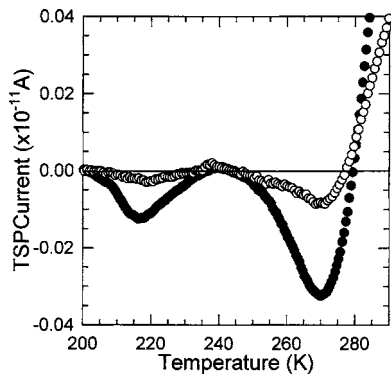


FIG. 4. TSPC2 spectra of PCL with blocking electrodes: (○)  $V_p=300$  V; (●)  $V_p=460$  V. The density current was normalized to an electric field of 1 MV/m.

ions migrations at the sample surfaces.<sup>12</sup> In this work we suggest that the above facts are consistent with the presence of a dipolar contribution to this peak. This dipolar process could be originated by the parallel dipolar moment producing the so-called normal modes observed in dilute PCL solutions by dielectric spectroscopy.<sup>8–10</sup> However, additional experiments and data processing need to be done to corroborate this hypothesis about the existence of a dipolar contribution to the  $\rho$  peak in PCL. In future work we will try to model this peak as a superposition of a dipolar and space-charges mechanisms.

## V. CONCLUSIONS

Using TSPC and TSDC methods, we have reported the original observation of a current reversal in the high-temperature tail of the glass transition relaxation peak in PCL. The presence of this current is predicted by a simple phenomenological model when the  $T^{-1}$  dependence of the equilibrium polarization is taken into account. This current reversal is also present in the TSDC spectrum when the sample is polarized at high temperatures, thus evidencing the

existence of an internal field applied during the heating cycle. This internal field irremediably transforms an intended TSDC experiment to a TSPC one when the polarization temperature is chosen above the  $\rho$  peak. In TSPC2 experiments two current reversal zones due to the temperature dependence of the equilibrium polarization were observed. The comparison of the currents obtained in the same temperature zones using the three methods envisages the possible presence of a dipolar mechanism contributing to the  $\rho$  peak. However, further work need to be done in order to elucidate the possible dipolar origin of this second current reversal zone.

## ACKNOWLEDGMENT

Financial support from FONACIT through Project No. G-2005000449 is gratefully acknowledged by two of the authors (N.S. and M.C.H.).

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