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Study of poly(methyl methacrylate) space charge relaxation by TSDC

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A windowing polarization technique has been applied to form PMMA thermoelectrets. The stimulated depolarization currents of these electrets in the range of polarization temperatures between 380 and 405 K show only a ρ peak which is attributed to space charge relaxation. The area of this peak exhibits a maximum at a certain polarization temperature (the optimal polarization temperature). The results obtained by fitting the depolarization currents to the general kinetic order model are consistent with the existence of a space charge polarization mechanism with a distribution of trapping depths, which can be qualitatively described. Moreover, the Arrhenius-like kinetic parameters deduced from the relaxation times can be interpreted in terms of a compensation law. Finally, the optimal polarization in PMMA can be described by means of a distribution of trapping levels. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The technique of thermally stimulated depolarization currents (TSDC) has proved to be most useful in studying the electrical properties of polymers, and their variations when the material is subjected to treatments which lead to configurational changes[1–3]. A generic TSDC experiment can be described as follows. The sample, furnished with suitable electrodes (usually in a sandwich configuration), is heated up to a temperature T_p (polarization temperature) above the room temperature. Then, an electric field E_p (polarizing field) is applied to the sample for a time t_p (isothermal polarization time). After this, the sample is cooled and subjected to the polarizing field, as can be seen in *Figure 1a*. In the conventional formation process of an electret (described above) we may distinguish two steps. The first, isothermal, along which the polarizing field is applied to the sample, and a second step along which the sample is cooled at a controlled rate while the field remains applied to it. During both steps the field activates the conduction mechanisms and dipole orientation mechanisms which are temperature dependent, and during the second step those mechanisms are frozen. Because of this treatment, the sample becomes an electret, that is, dielectric material which exhibits a quasi-permanent charge. Afterwards, the sample is heated at a constant rate while it is short-circuited through an ammeter and the intensity is recorded as a function of temperature. The plot of the intensity as a temperature function shows several peaks which correspond to the relaxation of dipole orientation and trapped charges activated during the polarization. The electret formation and depolarization processes have been widely described in the literature[1–3].

The possibility of removing the polarizing field before the end of the non-isothermal step has given rise to a technique called windowing polarization (WP)[4–10]. The polarizing field may be removed just at the beginning of the cooling step or a few degrees below, so that the range of temperatures over which the field is applied determines the window width. In our study we have used null width windows. The differences between conventional and windowing polarization (null width window) processes can be seen in *Figure 1*. This polarization technique has been used in previous work[10–12], and has resulted in a useful way to avoid the overlapping of conduction mechanisms that are activated during the isothermal step with the mechanisms which may become activated during the cooling step.

In contrast to the experimental simplicity of the TSDC technique, the analysis of the resulting experimental data to evaluate parameters is not easy, as the polarization may be due to several different microscopic processes (associated with dipolar or free charge mechanisms), whose relaxation will contribute to the depolarization current[2]. In the case of free charge relaxation, one of the most used approximate expressions is the Randall and Wilkins equation[13], valid in the slow retrapping case. They assumed that the thermally stimulated current is proportional to the rate at which trapped charge carriers are thermally released, and that this rate is proportional at any moment to the trapped carrier population

$$I = -\frac{dn}{dt} = s_0 n \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where I is the current intensity, n the trapped charge, T the absolute temperature, k the Boltzmann constant, E_a the activation energy (or trap depth) and s_0 the pre-exponential frequency factor. The solution of this
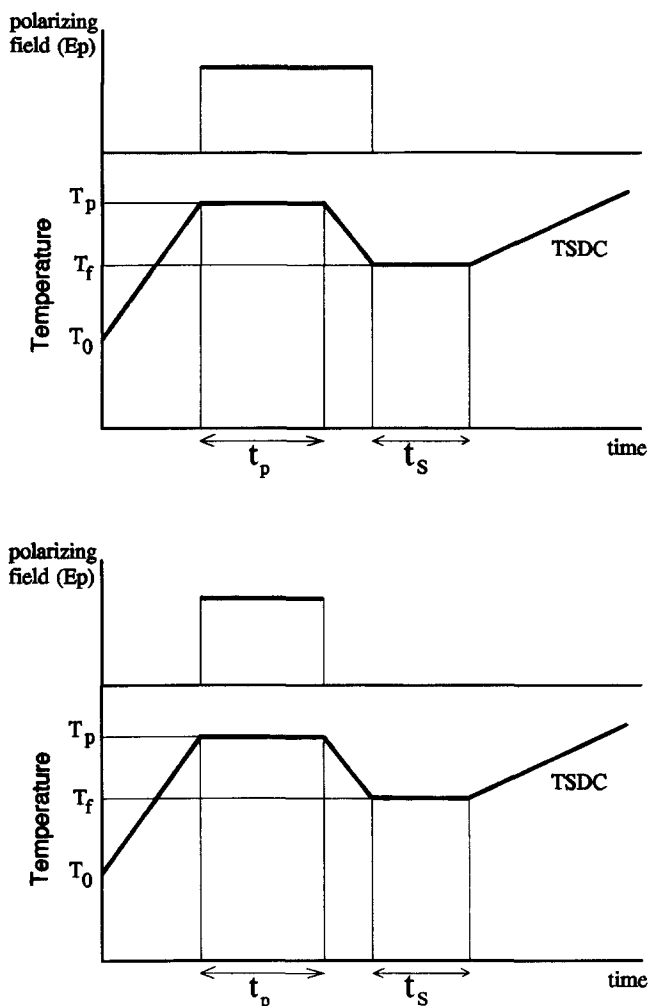
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Figure 1 Differences between conventional polarization (a) and WP (b) processes

equation in the case of a constant heating rate β is

$$I(T) = n_0 s_0 \exp\left(-\frac{E_a}{kT} - \frac{s}{\beta}\int_{T_0}^{T}\exp\left(\frac{E_a}{k\theta}\right)d\theta\right) \quad (2)$$

which is the well known 'first order kinetics' equation. In this equation n_0 and T_0 are the initial trapped charge and temperature respectively. Garlick and Gibson[14] suggested a 'second order kinetics' equation, on the basis of a strong retrapping probability

$$I = -\frac{dn}{dt} = s_0' n^2 \exp\left(-\frac{E_a}{kT}\right) \quad (3)$$

Many researchers[15-17] have found that these models do not describe properly the whole variety of all possible kinetic phenomena. For this purpose, an empirical equation was proposed

$$I = -\frac{dn}{dt} = s_0' n^b \exp\left(-\frac{E_a}{kT}\right) \quad (4)$$

where b (the 'kinetic order') is an empirically determined parameter which can have values other than 1 or 2. Although the cases of b different from 1 or 2 do not have correspondence to physical reality, the activation energy calculated using this model is very close to its true value[18].

The temperature variation of the relaxation times

(the frequency factor inverse) has been assumed to follow the Arrhenius equation

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{kT}\right) \quad (5)$$

If the logarithm of the pre-exponential factor τ_0 varies linearly with the activation energy, as has been often found experimentally in polymers, one observes a compensation law

$$\tau_0 = \tau_c \exp\left(-\frac{E_a}{kT_c}\right) \quad (6)$$

where τ_c and T_c, respectively known as the compensation time and the compensation temperature, are phenomenological introduced parameters. The expression for the relaxation time then becomes[19]

$$\tau = \tau_c \exp\left[\frac{E}{k}\left(\frac{1}{T} - \frac{1}{T_c}\right)\right] \quad (7)$$

The compensation rule has been studied in polymers in both dielectric and mechanical relaxation[20-22]. The physical meaning of the parameters involved is not clear yet, but the compensation law has been used for comparing the molecular mechanisms that initiate a relaxation by different thermally stimulated techniques[22].

Vanderschueren[23] made a study of the TSDC spectrum (for temperatures above room temperature) of conventionally poled PMMA electrets and concluded that his results were consistent with the existence of three distinct polarization mechanisms with activation energies of 0.8, 2.1 and 2.4 eV respectively. The first two mechanisms could be related to uniform polarization or, more probably, to local displacements of ions which are subsequently trapped. The third mechanism was probably related to space charge polarization. Solunov and Vassilev[24] proposed the same origin for this third mechanism. In this paper, we have fitted experimental TSDC data to the general kinetic order model to explain the space charge polarization in PMMA.

EXPERIMENTAL

PMMA samples were cut from commercial sheets of 1 mm thickness. Circular aluminium electrodes of 2 cm diameter were vaporized in vacuum on both sides of all samples. In order to form conventionally polarized electrets, an electric field E_p was applied to the sample at a temperature T_p for a time t_p and then the sample was cooled to a temperature T_f at the rate of 2.5°C min^{-1}. The electric field was removed at this temperature. For electrets formed by WP, the polarizing field was removed at the beginning of the cooling step. Once the electrets had been formed, they were depolarized by TSDC at a rate of 2.5°C min^{-1} in all cases.

The experimental set up consisted of a measuring cell placed in an air-forced Selecta oven, modified to be controlled by an Eurotherm model 818 temperature programmer. Current was measured by a Keithley 610C electrometer. Data of temperature and current were collected by a PCLAB 814B A/D converter card in a computer. Collected data (current vs. temperature) were

fitted to the general kinetic order equation

$$I = s_0 n_0 \exp\left(\frac{E_a}{kT}\right)$$

$$\times \left[\frac{(b-1)s}{\beta} \int_{T_0}^{T} \exp\left(\frac{E_a}{KT'}\right) dT' + 1\right]^{-b/(b-1)} \quad (8)$$

which results from integration of equation (4) in the case of a constant heating rate β. The fitting processes were performed by multidimensional χ^2 function minimization, with n_0, s_0, E_a and b as variable parameters, using software developed in our laboratory, which is based on routines described by other authors[25]. As the formal covariance matrix that comes out of a χ^2 minimization has meaning only if the measurement errors are actually normally distributed[25], in our case no meaningful confidence limits on the estimated model parameters can be given. Because of this reason, some comparison examples between calculated and experimental data will be given as examples of the fitting accuracy.

RESULTS AND DISCUSSION

The thermally stimulated current spectrum of conventionally polarized PMMA electrets (dotted line in *Figure 2*) is composed of three overlapping peaks in the range of temperatures above room temperature. The temperatures of their maxima are only well defined in the case of the two peaks that appear at higher temperatures. In the case of the two more evident peaks, the one whose maximum appears at lower temperature (α, at approximately 378 K) is associated with an uniform mechanism, whereas the one whose maximum occurs at higher temperatures (ρ, at approximately 403 K) is attributed to space charge polarization[11,23,24]. The interpretation of the experimental data in order to study the mechanisms that initiate these relaxations is difficult due to the peak overlapping. In order to study both relaxations separately, the peak cleaning technique[26] can be applied. In *Figure 2* (continuous line), it can also be seen as these two relaxations are separated by the peak cleaning technique.

On the other hand, TSDC discharge of PMMA electrets formed by WP show only ρ relaxation for the polarization temperature range between 380 K and 405 K (*Figure 3*). The differences between the ρ peak isolated by peak cleaning and the one obtained by windowing polarization lies in the fact that the former is related to charge trapped over a wide temperature range and the latter is associated with a narrow temperature range which is determined by the polarization window width. For this reason, it can be expected that in the case of windowing polarized electrets the activated charge is associated with a definite energy level and it may be considered an elementary relaxation[22] (or at least approximately non-distributed), so that TSDC discharges of PMMA electrets formed by WP in the aforementioned temperature range results in a very convenient way to study the space charge relaxation in this polymer.

In *Figure 3* the shift in the ρ peak with T_p, the poling temperature, for PMMA electrets formed by WP can be observed. The area increases with T_p, exhibits a maximum at a temperature that we call the optimal
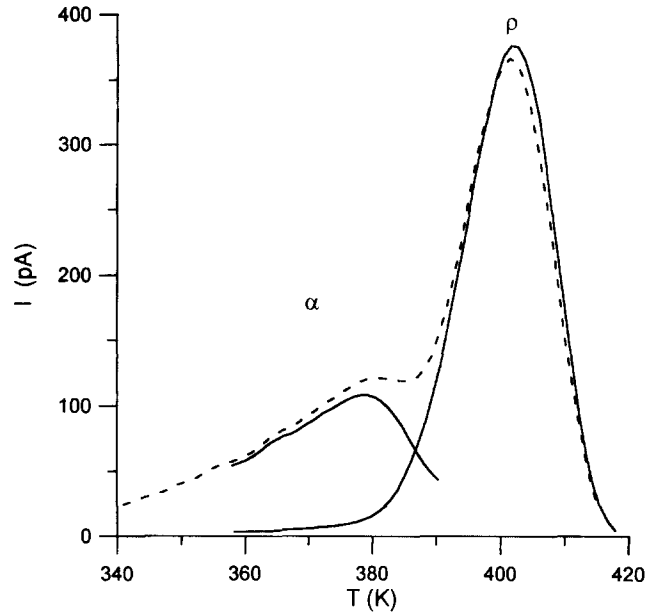

Figure 2 TSDC curve resulting from a conventionally polarized PMMA electret. Polarization conditions: $T_p = 398$ K; $t_p = 1200$ s; $T_f = 333$ K; $t_s = 300$ s; $E_p = 1250$ kV m^{-1} (dotted line). Isolation of α and ρ relaxations by thermal cleaning (continuous line)
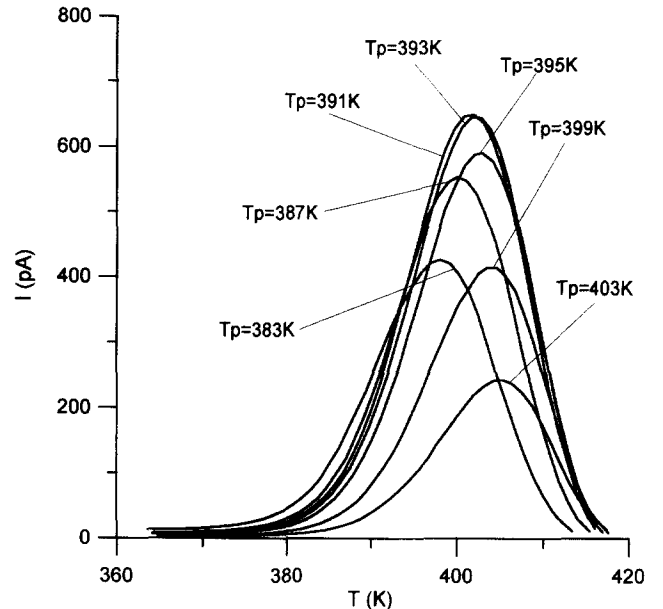

Figure 3 TSDC discharges of windowing polarized PMMA electrets ($E_p = 3750$ kV m^{-1}; $t_p = 600$ s; $T_f = 363$ K; $t_s = 180$ s; T_p as indicated in the figure)

polarization temperature[10,11] (T_{po}), which is approximately 391 K in this case and gives a TSDC maximum at about 402 K, and finally tends to vanish for higher polarization temperatures. The parameters that characterize the TSDC curves, the intensity of the maxima (I_m), the temperature at which they appear (T_m) and the peak areas were determined for these discharges. The areas result from the evaluation of

$$\int I(T) dT \quad (9)$$

over the whole discharge, so they are proportional to the

Table 1 Parameters that characterize the TSDC curves in the case of PMMA WP electrets ρ relaxation as a function of polarization temperature

T_p (K)	I_m (pA)	T_m (K)	Area (μC)
383.0	426	398.0	0.187
387.0	553	400.0	0.233
391.0	649	401.9	0.271
393.0	645	401.7	0.268
395.0	590	402.9	0.244
399.0	414	403.5	0.167
403.0	243	405.3	0.097

Table 2 General kinetic order trapping parameters in the case of ρ relaxation for PMMA WP electrets

T_p (K)	n_0 (μC)	s_0 (10^{26} s^{-1})	E_a (eV)	b
383.0	0.200	0.014	2.07	1.20
387.0	0.247	4.132	2.29	1.27
391.0	0.288	7.991	2.32	1.25
393.0	0.285	13.76	2.34	1.26
395.0	0.257	259.3	2.44	1.31
399.0	0.175	414.4	2.46	1.24
403.0	0.100	613.4	2.48	1.21

Figure 5 Intensity of the maxima I_m ($\triangle$), peak areas ($\square$) and initial trapped charge n_0 (O) as a function of the polarization temperature
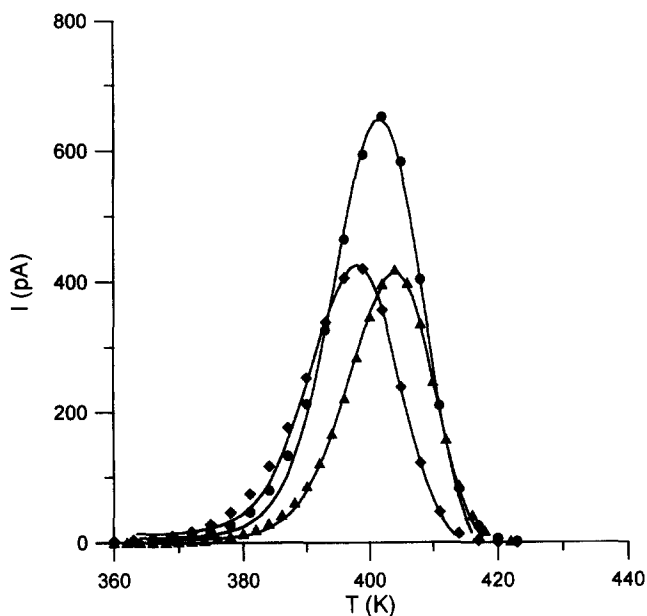

Figure 4 Examples of experimental data fitting to general order kinetics model (——, experimental data; $\blacklozenge$, $\bullet$ and $\blacktriangle$, calculated data). The polarization parameters were $E_p = 3750 \text{kV m}^{-1}$; $t_p = 600 \text{s}$; $T_f = 363 \text{K}$; $t_s = 180 \text{s}$; T_p: ($\blacklozenge$) 383 K; ($\bullet$) 393 K; ($\blacktriangle$) 399 K

Figure 6 Temperature of the maxima T_m ($\blacksquare$) and calculated activation energy E_a ($\blacktriangle$) vs. the polarization temperature T_p

released charge.

$$Q = \int I \, \mathrm{d}t = \frac{1}{\beta} \int I \, \mathrm{d}T$$

and will be calculated in charge units. These results are shown in *Table 1*.

These curves were fitted to the general kinetic order model to study the change in the relaxation parameters with the poling temperature. These parameters are n_0 (the initial trapped charge), s_0 (a frequency factor), E_a, the trapping depth and b the kinetic order. The obtained results can be seen in *Table 2*. Some examples of the curve fitting procedures are plotted in *Figure 4*. They show a good agreement between the experimental and calculated data.
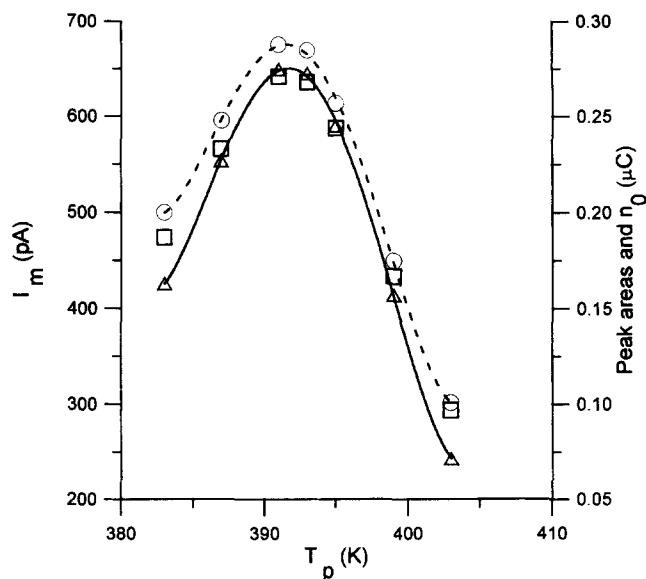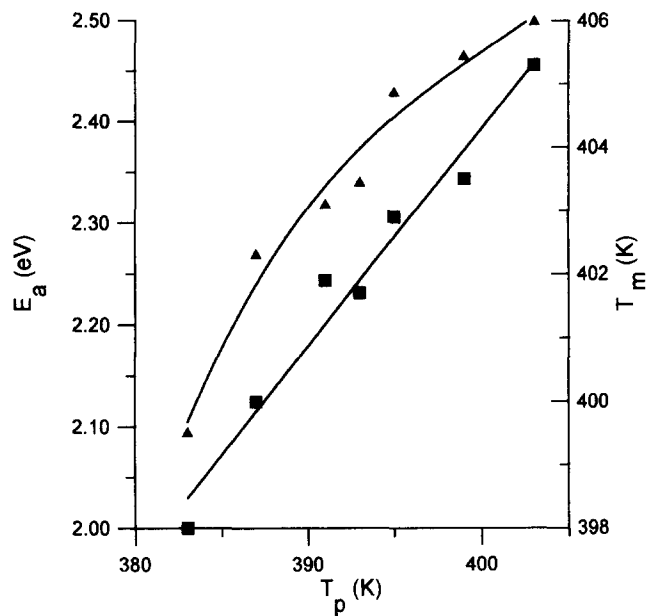
For windowing poled PMMA electrets, the effect of polarization temperature on the discharge parameters can be seen in *Figures 5* and *6*. In *Figure 5* it can be noted that the current at the peak maxima (I_m) and the released charge (peak area) reach a maximum value at the optimal polarization temperature ($T_{po} \approx 391 \text{K}$). This effect is also evidenced for the initial trapped charge, n_0 (*Figure 5*), which also goes through a maximum at the same polarization temperature. In *Figure 6* it can be seen that the temperatures at which the maxima appear (T_m) are approximately linear with the polarization temperature.

The values of I_m have been plotted vs. the peak areas (*Figure 7*). The correlation between these magnitudes suggests that the changes in I_m are a reliable indicator of the trapped charge progression in the polarization process. The peak areas vs. the initial trapped charge,
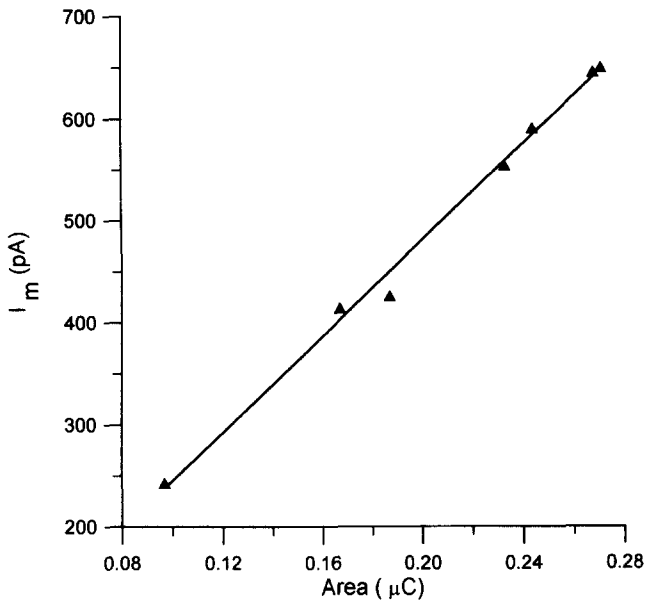
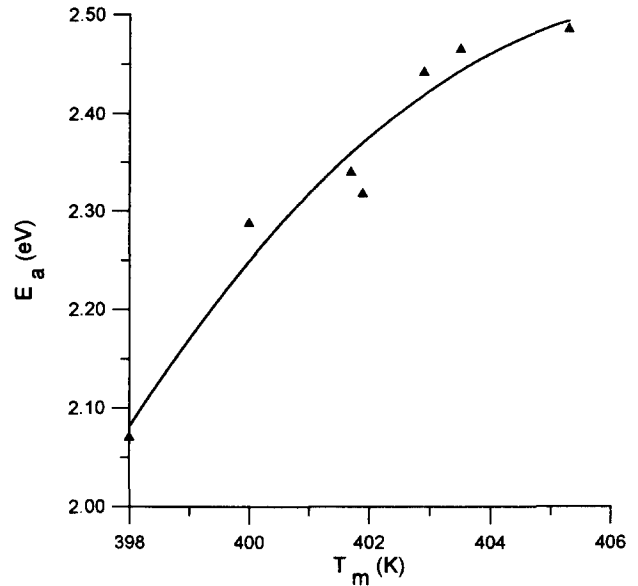**Figure 7** Intensity of the maxima I_m vs. the peak areas

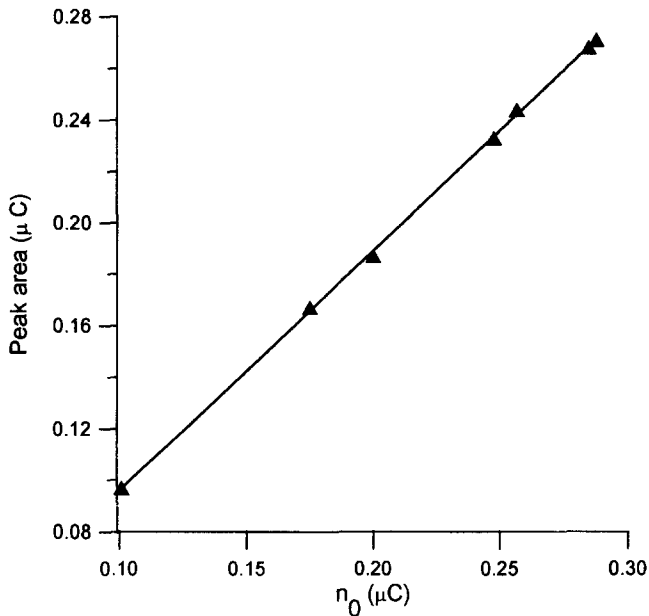**Figure 9** Calculated activation energy E_a vs. the temperature of the maxima T_m

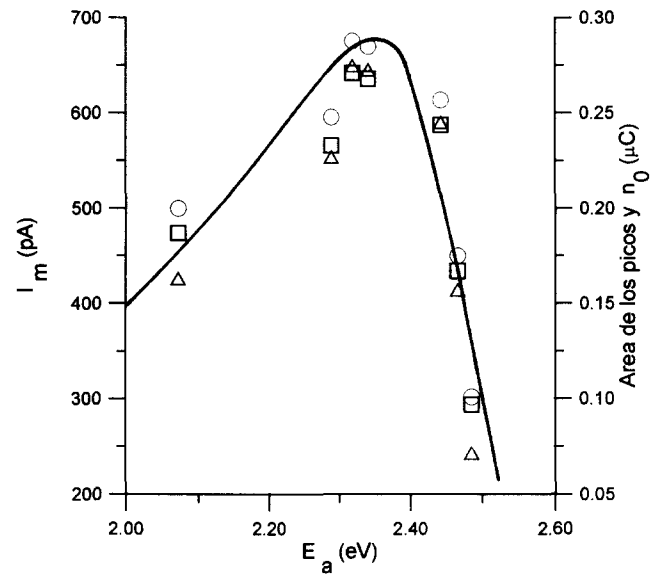**Figure 8** Peak area vs. the initial trapped charge n_0

Figure 10 Intensity of the maxima I_m ($\triangle$), peak areas ($\square$) and initial trapped charge n_0 ($\bigcirc$) as a function of the calculated activation energy E_0

n_0, plot (*Figure 8*) shows a very clear linear correlation, whose slope is very close to one. This fact can be understood as an indicator of the accuracy of the fitting process.

From a physical point of view the kinetic order, *b*, represents a balance between the first and second order kinetics, i.e. a balance between the predominance of weak or strong retrapping probability, respectively. The maximum difference between the parameters obtained is less than 9% and no correlation between the polarization temperature and the kinetic order is evident. These observations suggest that a mean value, which is close to 1.25, would be representative of the studied relaxation kinetic order.

In the case of the activation energy, which is associated with the trapping depth in the general order kinetic model, it can be noted that it is an increasing function of T_p (*Figure 6*). We have related this effect to the

windowing polarization process, because, in order to form an electret by WP, the polarizing field is switched off at the beginning of the cooling step, while there is still enough thermal energy for the carriers trapped in shallow levels to be released. As the trapping levels available for the carriers depend on the temperature, in a windowing polarization process the charges become trapped in a narrow energy level range. These reasons indicate that, applying WP technique and TSDC combined, the distribution of trapping energy levels might be determined, or at least discussed qualitatively. The fitted activation energy is an increasing function of the temperature of the maxima (*Figure 9*), so that T_m can be taken as an indicator of the changes in the trapping depth in the polarization process for windowing polarized electrets. It can be noted that in the case of windowing polarized electrets, the results obtained from
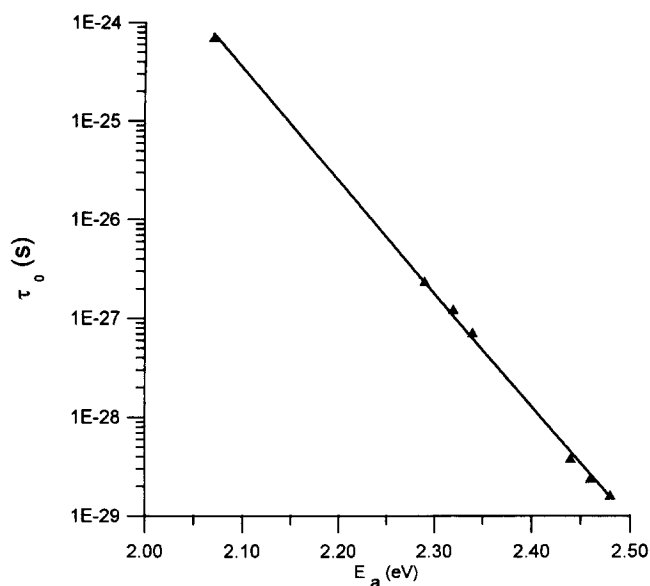
Figure 11 Variation of the pre-exponential factor of relaxation time τ_0 vs. the activation energy E_a for the TSDC discharges of PMMA WP electrets

their stimulated depolarization are more readily explained, as a direct relation can be found between relevant parameters of the trapping process (trapping depth, number of carriers involved) with parameters easily obtained from the TSDC spectra.

We have plotted the magnitudes that have appeared to be representative of the available trapping states at a determined energy level, which are the peak areas, the initial trapped charge and I_m, as a function of the activation energy (*Figure 10*). This plot suggests some properties of the trapping levels distribution function.

The distribution function seems to be asymmetrical; the number of available levels increases smoothly with the trapping depth up to a maximum value which corresponds to a trapping depth of approximately 2.35 eV. It can be seen that this value agrees with the one obtained by Vanderschueren[23] for space charge polarization mechanism in PMMA. For deeper levels, the available states decrease sharply in number, and eventually the distribution tends to vanish for trapping levels deeper than 2.50 eV. These results indicate that T_{po} corresponds to that polarization temperature at which the carriers activated during the WP process became trapped in the trapping level for which there is the maximum number of trapping states available.

On the other hand, the pre-exponential frequency factor values found do not agree with the classical Debye frequency ($10^{13}-10^{14}\,s^{-1}$). This result has also been obtained by del Val *et al.*[22] in the case of α relaxation in PVC. In the case of the α relaxation in amorphous polymers, this fact is interpreted as a result of the cooperative character of the molecular motions associated with the glass transition. As the temperatures involved in the polarization depolarization processes in our case are higher than the glass transition temperature, we conclude that molecular motions may also greatly affect the space charge relaxation processes in polymers. The fact that the plot of $\log(\tau_0)$ vs. the activation energy fits a compensation law, defined by the compensation parameters $T_c = 439.5\,K$; $\tau_c = 0.424\,s$ (*Figure 11*) seems to confirm the importance of molecular

motion on space charge relaxation in polymers at temperatures above the glass transition.

CONCLUSIONS

The thermally stimulated current spectrum of PMMA electrets in the temperature range that corresponds to space charge relaxation can be resolved if the electrets are formed by windowing polarization. In the case of windowing polarized electrets, there is a polarization temperature (T_{po}) for which there is a maximum activated charge. The current spectra obtained from windowing polarized electrets can be interpreted from correlations that have been found between the parameters that characterize the TSDC curves (I_m, T_m, the peak area) and parameters that characterize the trapping process (initial trapped charge, trapping depth). The intensity of the maxima and the temperature at which they appear are reliable indicators of the effect of poling temperature on the number of trapped carriers and their trapping depth respectively.

The combination of WP technique to form electrets and the subsequent fitting of TSDC discharge processes to the general kinetic order model allows a qualitative description of the trapping energy level distribution in PMMA. Using this distribution the optimal polarization phenomenon can be explained. Finally, the high values of the relaxation time pre-exponential factors and their fitting to a compensation law let us conclude that molecular motion in polymers at temperatures above the glass transition is a significant factor in space charge relaxation.

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