Electric relaxation study in poly(*trans* 1-octenylene) by the thermally stimulated discharge technique

J. Fraile, A. Torres, J. Jiménez and J. A. de Saja
Departamento de Fisica de la Materia Condensada, Facultad de Ciencias,
47011 Valladolid, Spain

(Received 29 July 1988; revised 24 February 1989; accepted 7 March 1989)

The thermally stimulated depolarization currents (TSDC) spectrum of the poly(*trans* 1-octenylene) has been analysed by means of the thermal sampling technique over the 150–320 K temperature range. Three relaxation zones are defined. In the first zone, up to some degrees above T_g ($\simeq 208$ K) the relaxation is mainly dipolar, associated with motions in the amorphous phase, and the analysis reveals dipole–dipole interactions. In the second zone, above T_g the relaxation takes place in the crystalline–amorphous interface. In the third zone, a relaxation at the crystalline phase is identified in the high temperature region. In addition, a shoulder localized in a narrow temperature interval (220–240 K) of the TSDC spectrum between the first and second zones is observed. It was found to be correlated with a change in the slope of the microhardness (Vickers) vs. T plot. This suggests a relation between the anomalous relaxation and the motion of the polymer chains bound to the crystalline–amorphous interface.

(Keywords: poly (*trans* 1-octenylene); electric relaxation; thermally stimulated process; general order kinetic; interaction parameter)

INTRODUCTION

The study of the dielectric relaxation processes in amorphous and semicrystalline polymers constitutes a useful tool for the characterization of these materials. The experimental method usually employed for this analysis is thermally stimulated depolarization currents (TSDC). It was initially used for the characterization of doped alkali halides and was previously called ionic thermocurrents (ITC)[1]. These currents were associated with dipolar-like motions in these crystals, however they may be extended to other kinds of electric relaxations. Therefore, we will refer to the method in a more general form as thermally stimulated discharge currents[2]. This term covers any kind of electric relaxation, for example, dipolar, space charges or trapped charges.

This method has been largely used because of its high sensitivity and the experimental simplicity. Generally, the TSDC spectra of polymers are complex and are usually resolved in single peaks by means of either peak cleaning or thermal sampling techniques, which will be described later.

The single peaks associated with dipolar motions, are generally observed below the glass temperature. The calculation of their relaxation parameters is done by assuming a Debye-like behaviour, for which is known that the associated relaxation time fits to an Arrhenius law. Generally, the experimental peaks deviate from a pure Debye plot. In these cases, the mathematical analysis is made by means of distribution functions of the relaxation parameters, i.e. the activation energy and/or the pre-exponential factor[3].

In the last few years, the idea of many-body cooperative phenomena has been incorporated in order to understand the dipolar relaxation which is assumed to be influenced by such interactive processes[4]. With this in mind, several materials were studied. The analysis of the TSDC spectra was done using the rate equation for general order kinetics[5–7]. In order to fit our experimental plots to the deduced electric current equation a third parameter, the kinetics order, is required in addition to the activation energy and the pre-exponential factor. We refer to this as the interaction parameter, because all the materials for which the electric relaxation arises from dipolar motion exhibit a high coherence between these fitting parameters and the dipolar unities accounting for the relaxation[8–10].

In polymers, the analysis of the elementary TSDC peaks by means of the general order kinetics equation makes it possible to obtain a reliable definition of the different relaxations taking place in the temperature range scanned, no matter what the origin of such relaxations. The origin of the relaxations must be studied separately, using other techniques.

This paper deals with the study of the electric relaxation of poly(*trans* 1-octenylene) (following the IUPAC nomenclature), which is usually known as *trans*-polyoctenamer or P8. The TSDC spectrum of this material extends from 150 K to 320 K and presents two broad bands centred around 180 K and 283 K, respectively. A first analysis of this spectrum reveals the existence of three relaxation zones in the temperature margin considered. These have been ascribed, in increasing temperature order, to dipolar relaxations, relaxations at the crystalline–amorphous interface and relaxations at the crystalline region, respectively.

Poly(*trans* 1-octenylene) is a relatively new material. This is why most of the literature about it refers to the characterization of its structure by spectroscopic analysis[11–15].

0032–3861/89/111977–07$03.00

The only data available in relation with the transition temperatures is the glass transition temperature (T_g = 208 K)[15]. It should be noted that the viscosity is strongly temperature dependent, especially above the melting temperature ($T \simeq 324$ K). Also, a high mechanical and chemical stability has been reported, which would be due to the practical absence of branches observed in this polymer[16]. TSDC curves analysis is therefore shown to be useful for study the relaxations mentioned above, which are normally expected in these compounds. Our method will also allow the resolution of an electric relaxation associated with a thermoelastic transition that was observed earlier from microhardness measurements.

EXPERIMENTAL

Samples

The poly(*trans* 1-octenylene), for which the chemical formula is $[\text{-CH=CH-(CH}_2)_6\text{-}]_n$, was synthesized by Montecatini–Edison[17]. The *trans* double bond percent is 70–80%. The fusion temperature is found around 324 K as deduced from d.s.c.[18]. The samples used for measurements were prepared by heating molten polymer at 373 K for 5 min at 4 MPa, cooling down to 293 K and then annealing it for 24 h at 315 K. The samples so obtained were 65 μm thick. The typical area of the specimens used for TSDC measurements was $5 \times 5\,\text{mm}^2$.

Experimental technique

TSDC measurements were carried out in a classical experimental configuration, which has been largely described elsewhere[6,19]. Basically, the experimental set-up consists of a small cryostat, which is characterized by a weak thermal inertia. The sample is mounted on the cold-finger of this cryostat and electrically isolated by BeO platelets. The system operates under vacuum (10^{-5} torr). The sample is polarized with a high voltage power supply. The temperature is measured by a chromel–alumel thermocouple and regulated to ± 0.5 K in the scanned range. The electric current is measured with a digital electrometer (Keithley no. 616), which has an accuracy better than 5% of the full range in the ranges used. The input impedance is higher than $2 \times 10^{14}\,\Omega$.

Different electrodes were used for measurements. The best signal/noise ratio was obtained with coated copper platelets, which were mechanically pressed on the surfaces of the sample by means of a holder specially designed for this purpose.

Once the TSDC was obtained, its resolution in single peaks was carried out by the thermal sampling technique[6,20]. This is a procedure largely used in thermally stimulated discharge measurements and basically consists of the stages schematically represented in *Figure 1*.

The sample is biased at a temperature T_p (polarization temperature) for a time t_p. The sample is then cooled down a few degrees, θ, below T_p and thereafter is short circuited. The temperature is kept at $T_s = T_p - \theta$ for a time t_s, and then is quickly cooled down to liquid nitrogen temperature. The sample is next warmed in short circuit, and a single glow peak, labelled TS (thermal sampled) peak, is recorded.

It is essential to have a good definition of the $(T_p - T_s)$ temperature margin for this procedure. This is achieved by an accurate regulation of the temperature. The fluctuations of T_s and T_p were measured and thermal sampled peaks for which these fluctuations exceeded the accuracy of our regulation temperature system were excluded.

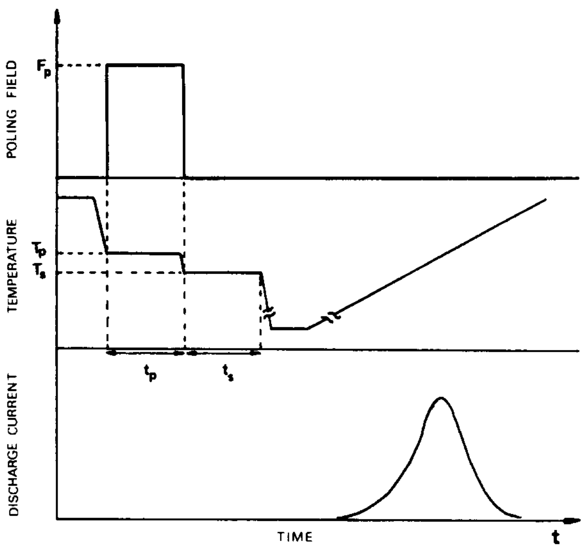

Figure 1 Sketch of the thermal sampling technique. The bias field, F_p, the temperature and the current density are schematically represented as a function of time. The thermal sampled peak corresponds to the T_p–T_s thermal margin, where T_p is the polarization temperature and T_s is the short-circuit temperature

RESULTS

A typical TSDC spectrum of P8 is shown in *Figure 2*. The experimental polarization parameters for which this spectrum is obtained are indicated in the caption. The average heating rate was 0.1 K/s in the temperature range scanned. This spectrum exhibited two well defined broad bands. The temperature of the maxima are 180 K and 283 K respectively. A shoulder is also observed in the high temperature side of the 283 K band. Taking the nomenclature used in dielectric loss measurements[21,22], these bands will be associated with β and α relaxations, respectively. It is well known that β-type relaxations occur below T_g; α relaxations are normally observed above this temperature.

The resolution of the spectrum by the thermal sampling technique was made in the 158–313 K temperature range. The polarization temperature was sampled every 5 K. Therefore 32 single peaks were obtained (*Figure 3*). The relaxation parameters for every single TSDC peak are obtained from the expression originally deduced by Bucci, Fieschi and Guidi (BFG)[23]

$$\tau(T) = \frac{P(T)}{J(T)} \tag{1}$$

where $P(T)$ and $J(T)$ are the remanent polarization and the electric current density at a temperature T, respectively. The relaxation time deduced in this way does not follow an Arrhenius law. Instead it obeys a more complex law dependent on $P(T)$, which is given by the following expression:

$$\tau(T) = \left(\frac{P_0}{P}\right)^{q-1} \tau_0 \exp(E/kT) \tag{2}$$

τ_0 is a pre-exponential factor with time dimensions; P_0 is the polarization at $t = 0$, before the relaxation starts;

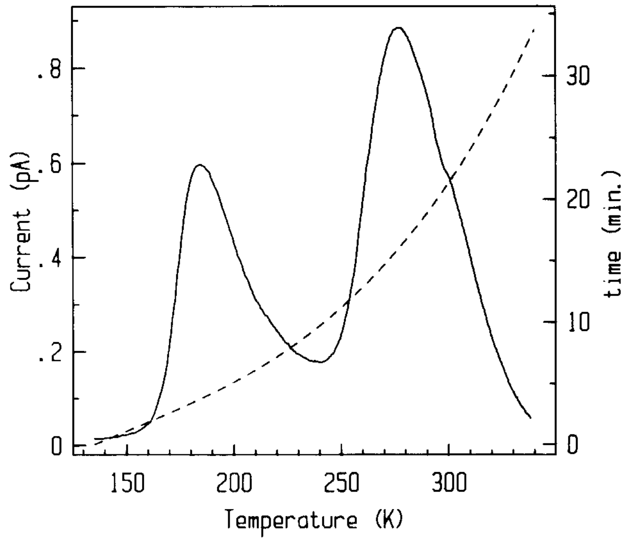

Figure 2 The TSDC spectrum of P8, as obtained by polarizing with $F_p=3.8\times10^6$ V/m, for 5 min at 314 K. The dotted line corresponds to the time vs. temperature plot. The average heating rate is 0.1 K/s. According to the classical nomenclature the two broad bands of the spectrum are labelled β and α, respectively

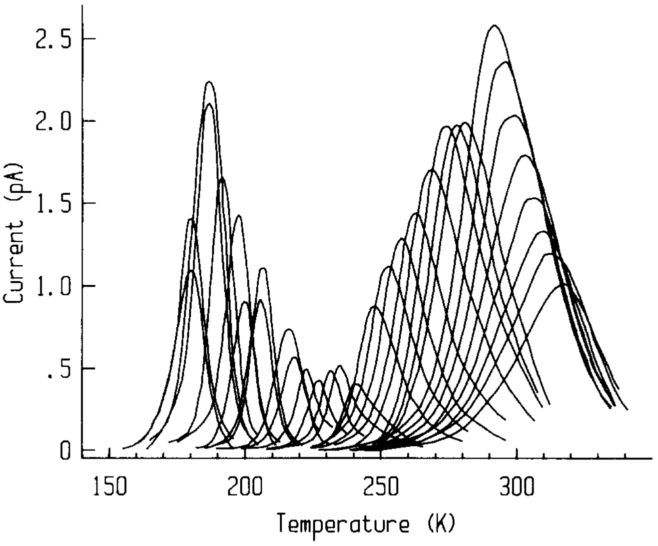

Figure 3 Single peaks obtained by the thermal sampling technique, with T_p–$T_s=5$ K, $t_p=t_s=5$ min and $F_p=3.8\times10^6$ V/m

E is the activation energy and k is the Boltzmann constant. There is an additional parameter, q, which is called the interaction parameter[10], because the relaxation defined when $q>1$ corresponds to an interacting process when the relaxation is dipolar-like. By extrapolating this idea we label it as for any other discharge case. This parameter corresponds, in fact, to the kinetics order, which takes a value greater than unity when a general order kinetics is considered[24].

From equation (1) with τ given by equation (2) and the fact that $J=-\mathrm{d}P/\mathrm{d}t$ we deduce the following expression for the electric current density:

$$J(T)=P_0\tau^{-1}(T)$$
$$\times\left[1+(q-1)\int_{T_0}^{T}\tau^{-1}(T')f'(T')\,\mathrm{d}T'\right]^{-q/(q-1)} \qquad (3)$$

where $f'(T')$ is the derivative of the time variation with temperature, or in other words, the inverse of the heating rate at each instant.

The adequate choice of τ_0, E and q makes it possible to fit equation (3) to the single peaks obtained by thermal sampling. Two peaks and their corresponding fits are represented in *Figure 4*. They correspond to different relaxation regions, peak (a) deals with β region and peak (b) corresponds to the α region.

The area enclosed by a single peak is proportional to the polarization associated with such a peak. Taking this into account the global TSDC spectrum can be reproduced from the polarization calculated for every thermal sampled peak. *Figure 5* represents a histogram of the area enclosed by every single peak, the rectangle is centred either in the temperature of the peak maximum (narrow, full rectangle) or the polarization temperature (wide, unfilled rectangle). The envelope of this histogram

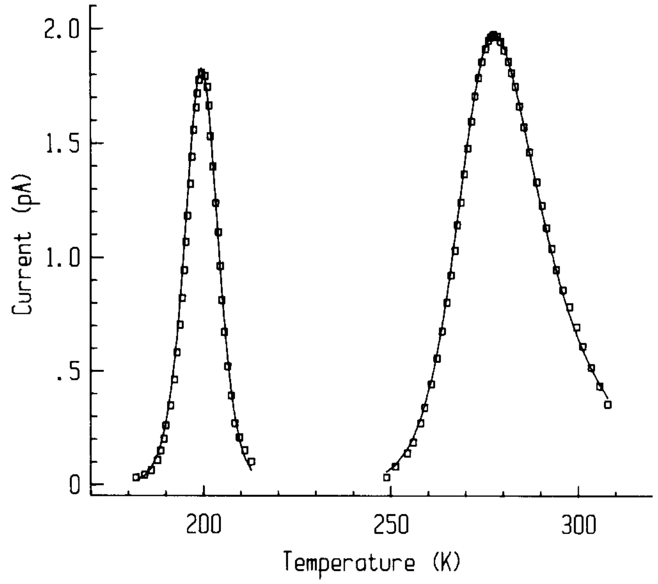

Figure 4 Some examples of the fitting of thermal sampled TSDC peaks to equation (3). (a) peak of the β phase with $T_p=188$ K; $q=1.8$, $E=1.04$ eV, $\tau_0=2.2\times10^{-25}$ s. (b) peak of the α phase with $T_p=268$ K; $q=4.4$; $E=1.02$ eV, $\tau_0=7.4\times10^{-17}$ s. Squares are the experimental points, the line shows the fit using equation (3)

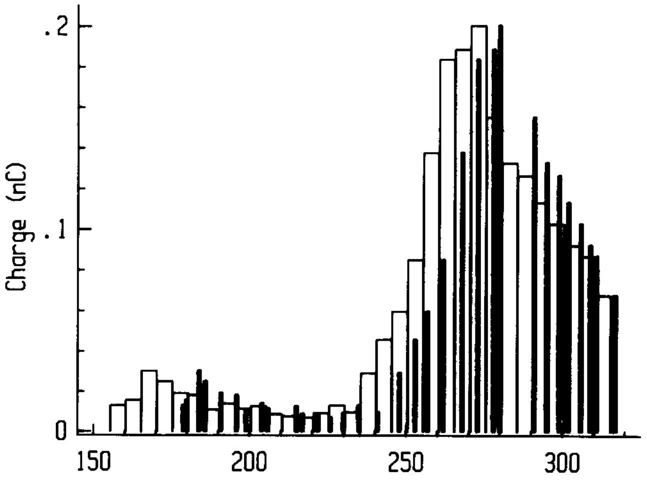

Figure 5 Plot of the charge enclosed by every elementary thermal sampled peak (nC) as a function of either the polarization temperature T_p (wide, vacuum rectangles) or the temperature of the maximum T_M (narrow, full rectangles). Because the charge is proportional to the polarization, the envelope of this representation must be the global spectrum of P8. Indeed this is verified by comparison with *Figure 2*. The lower intensity of the β region is due to the non uniform heating rate in *Figure 2*

is quite similar to TSDC spectrum of *Figure 2*, especially in the high temperature range.

The β relaxation, low temperature range, deviates slightly from such a correlation, and shows a lower relative intensity in the histogram than in the TSDC spectrum. This is due to a progressive decrease of the heating rate as the temperature increases (*Figure 2*), inherent in our experimental arrangement, which uses a small cryostat of weak thermal inertia and which results in a decrease of the heating rate as the system approaches room temperature. Recording the TSDC spectrum of the P8 at uniform heating rate over the temperature range of the spectrum would result in a spectrum similar to that deduced from these areas (*Figure 5*). In fact, the global spectrum obtained from the contribution of the individual peaks presents that shape (*Figure 6*). This should be the characteristic TSD spectrum of the P8 corresponding to the polarization conditions described above.

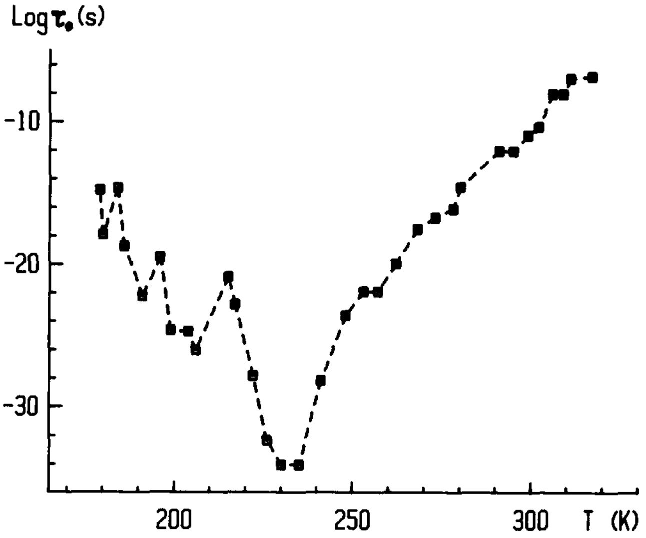

Figure 7 Plot of $\log \tau_0$ (pre-exponential factor) vs. T_M (temperature at the maximum intensity), as deduced from equation (3)

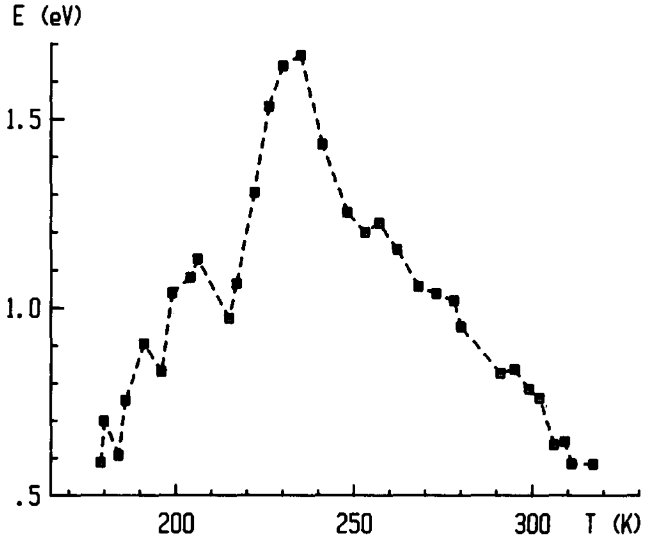

Figure 8 Plot of E (activation energy) vs. T_M, as deduced from equation (3)

DISCUSSION

The different temperature zones of relaxation can be determined from the temperature dependence of the relaxation parameters. In fact, sharp variations of these parameters should indicate transition temperatures, and therefore changes in the mechanisms accounting for the electric relaxation. This technique constitutes a useful tool for the characterization of these types of materials. It should also be valuable for correlation with other techniques. We usually followed this procedure in our previous work when we studied other materials[6]. Unfortunately, experimental knowledge for P8 is rather poor. This is why our present determination of the relaxation zones is mainly supported by the TSDC experimental results. However, we believe they are reliable because of the high sensitivity of the method.

Next we studied the evolution with the temperature of the three fitting parameters, $\log \tau_0$, E and q. An inspection of *Figure 7* shows that the pre-exponential factor monotonously decreases with temperature up to 200 K. Then, it increases 10^4 times its value at 200 K, and finally sharply decreases, reaching its minimum value at $T = 232$ K ($1E-35$). A new enhancement is observed, $\tau_0 = 1E-21$ at 250 K. Finally the pre-exponential factor slightly and monotonously increases, showing a change in the slope around 290 K.

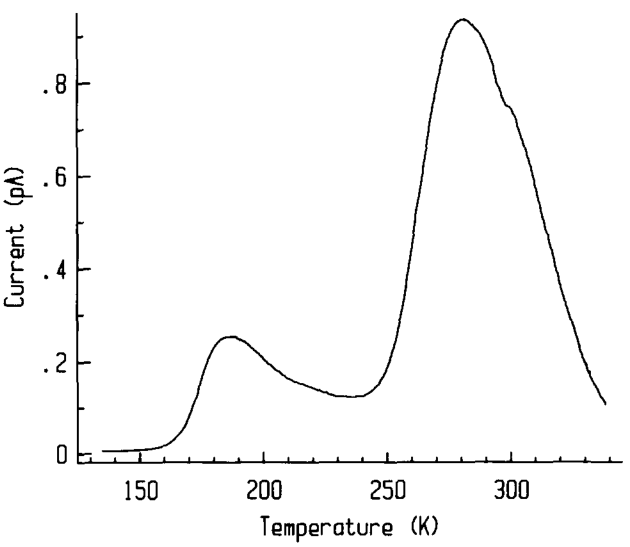

Figure 6 Reconstruction of the TSDC spectrum of P8 from the areas enclosed by the single peaks corrected for a uniform heating rate. The current associated with β relaxation is weak, compared to the rest of the spectrum

The activation energy (*Figure 8*) exhibits a similar temperature dependence to that of the pre-exponential factor and shows similar changes to those reported for τ_0. It should be noted that both values are anticorrelated. This is confirmed by the plot of E vs. $\log \tau_0$, which obeys to a compensation law $\tau_0 = \tau_\infty \exp(E/kTc)$. It is found (*Figure 9*) that τ_∞ and T_c (the compensation temperature) take characteristic values for every temperature range considered. This relation between E and τ_0 is frequently observed in thermally activated processes, no matter what the relaxation mechanism. The physical meaning of these values lies in the particular relaxation mechanism accounting for it[25,26]. There is an abundant literature on this subject. We believe this behaviour is a useful method to separate different relaxation regions.

The information obtained from E and τ_0 is used for characterizing the relaxation. However an inspection of the evolution of the third parameter, q, allows a more

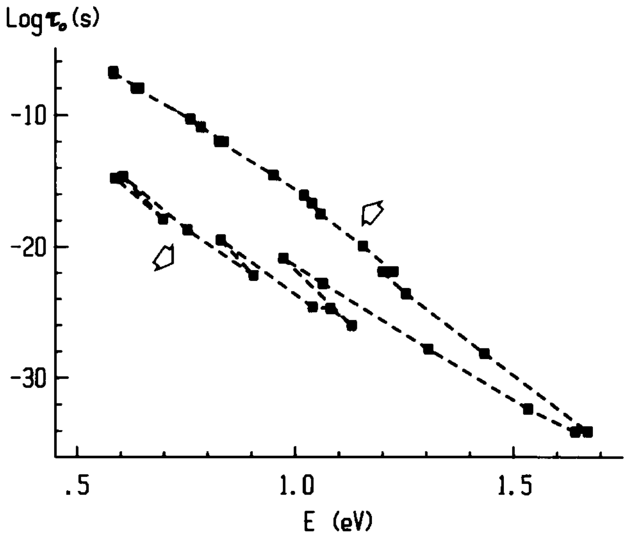

Figure 9 Plot of $\log \tau_0$ vs. E. The linear relation between both is observed over the entire temperature range considered. The arrows show the increasing temperature direction

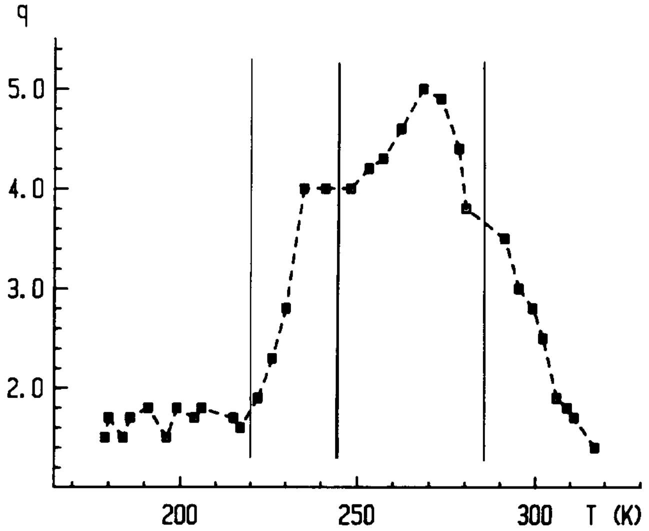

Figure 10 Plot of q (interaction or general order kinetic parameter) vs. T_M, as deduced from equation (3). The study of the evolution on q, E and $\log \tau_0$ over the thermal range scanned allows the determination of four relaxation zones, which are conveniently shown in the figure and discussed in the text

accurate estimation of the electric relaxation regions. Indeed the evolution of τ_0 and E shown in *Figures 7* and *8* does not clarify the identification of the different electric relaxation regions in an unambiguous way. This is the reason why most of our discussion will be centred around the observed features of the q parameter. This information allows us to reconsider the results about τ_0 and E for the interpretation of the electric relaxation in this material.

The parameter q follows an evolution with temperature different to that reported for τ_0 and E (*Figure 10*). Thus, in the low temperature range, q takes a constant value 1.7. Above 220 K the value of q increases quickly reaching a value near 4 only in a narrow temperature margin of 15 K. Then it remains constant over a 15 K interval. Above 250 K, it increases again to a maximum value $q = 5$ at 270 K and then monotonously falls to $q = 1.6$ at 315 K. Around 290 K a change in the slope of the q vs. T plot is observed.

The q parameter is associated with an interaction parameter in dipolar relaxation. Values of q higher than unity lead to non-monomolecular kinetics for the relaxation. This was interpreted on the basis of dipole–dipole interactions during relaxation. Values of q as high as 2–2.5 have been found in fitting TSDC peaks of the β relaxation zone, which is mainly dipolar, in some other polymers[6,7]. Moreover, inorganic solids with clearly identified structural dipoles showed q values[4] settling up to 3 (ref. 5).

The value of q remains practically constant for temperatures below T_g (*Figure 10*). This makes it possible to define a relaxation region associated with the low temperature, $T < 215$ K, of the TSDC spectrum. This relaxation is dipolar-like and, taking into account the structure of this material, is probably related to dipolar motions in the amorphous phase of P8. The contribution of this relaxation to the total electric current observed by TSDC is rather weak (*Figure 6*). Indeed, though the crystalline composition percentage is low, the low concentration of branches in the amorphous region results in a small amount of dipolar relaxation. On the other hand, cycles of TSPC–TSDC (thermally stimulated polarization currents–thermally stimulated discharge currents) confirm the dipolar nature of the discharge current observed in this temperature range[5,27]. In *Figure 11*, a TSPC–TSDC cycle is shown. It should be noted that below 220 K both curves are symmetric, whereas above 240 K, the TSPC spectrum exhibits a typical equilibrium associated with the formation of space charge.

In the high temperature region, the q vs. T plot exhibits a change of slope at 290 K ($q = 3.5$). In addition, E and $\log \tau_0$ show a significant discontinuity at this temperature. Above 290 K, q monotonously falls to 1.6 at 315 K. These values of q were obtained from the high temperature peaks in *Figure 3*, which are slightly shifted relative to the remainder peaks associated with the α phase. One can also see a step in the high temperature side of the global TSDC spectrum (*Figure 2*). Because of this it is possible to define the limit temperature of the relaxation at 290 K. The relaxation occurring beween 290 and 320 K

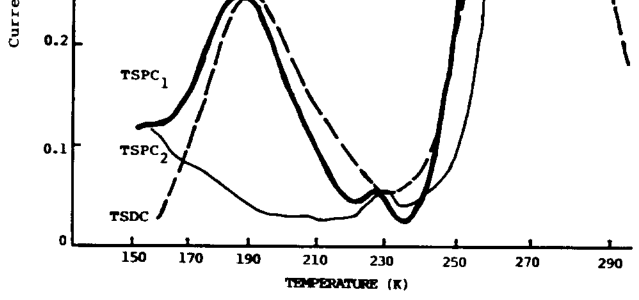

Figure 11 Thermal cycles of P8, showing TSPC, (thick line), $TSPC_2$ (thin line) and TSDC (broken line) spectra, $TSPC_1$, and TSDC are practically symmetrical below 220 K, this implies a dipolar relaxation origin on this part of the spectrum. Above 240 K, TSPC exhibits an equilibrium current, which overshadows the α peak

is related to the α phase. It should be noted that this temperature range is just below the fusion temperature ($T=330$ K), which suggests it is an electric relaxation associated with the liquid–liquid transition and related to the crystalline phase. Indeed, for temperature regions close to the fusion temperature, the relaxation mechanisms are usually ascribed to the formation of free volume, which is required for the expansion and ulterior motion of the polymeric chains[28]. This mechanism results, from an electrical point of view, in the formation of a charge distribution, which raises an internal electrostatic field. Other authors assume that the electric currents are due to the trapping and subsequent detrapping of electrons[29]. In our opinion, this relaxation might be due to the existence of dipoles bounded to the crystalline phase. This is supported by the calculated value of q, which lies within the limits usually calculated for crystals with structural dipoles[8]. Moreover, it is observed that q decreases as T increases. This is understandable on the basis of interacting dipoles. In fact, as temperature grows the mobility of dipoles becomes higher, and the influence of the surrounding strain field becomes more and more negligible, which should explain the decrease of the q value.

Between 235 and 290 K, q takes very high values. In the low temperature zone of this interval ($T \leqslant 250$) q is practically valued in single figures. For increasing temperature q increases up to 270 K. Above this temperature q slowly decreases. The existence of such high values for q suggests that in these cases it would be more suitable to interpret q in relation to dipolar motion on the basis of an order kinetics parameter rather than an interacting parameter. The fact that this relaxation region is observed in the proximity of the liquid–liquid temperature transition leads us to consider that the observed electric relaxation could deal with motions at the crystalline–amorphous interface. By analogy with the mechanism leading to the α relaxation in other better known polymers[7,30] space charge bound at this interface would probably be liberated by the motion of molecular chains linked at the interface, which should transfer the energy to the trapped charges.

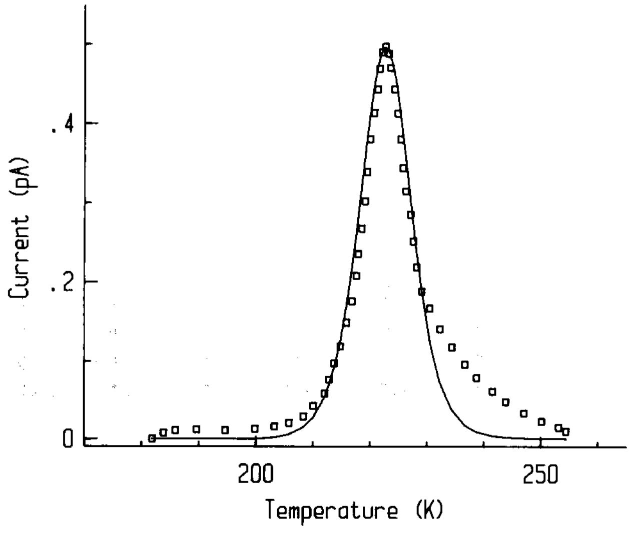

Figure 12 Fitting (continuous line) to equation (3) of a thermal sampled peak (squares) in the 220–245 K temperature range, with $T_p=213$ K; $T_M=222$ K, and parameter values given by $q=1.9$, $E=1.30$ eV, $\tau_0=1.4\times10^{-28}$. This fitting is not satisfactory above T_M, as is explained in the text

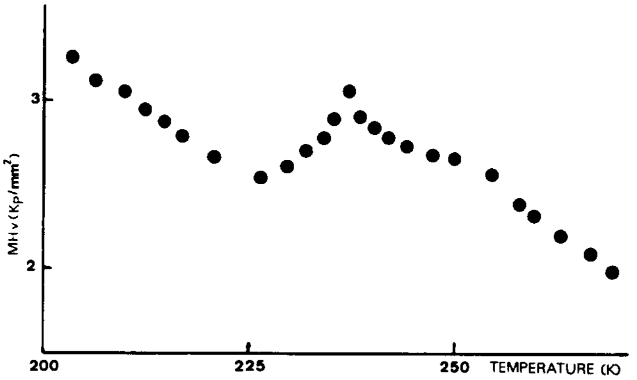

Figure 13 Microhardness (Vickers) vs. T plot of P8. The transition temperature regions occurs between 220 and 250 K

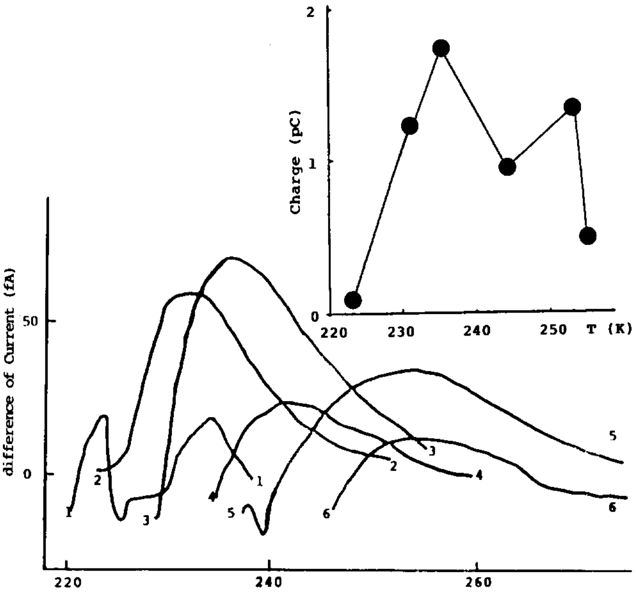

Figure 14 Plot of the differences between experimental and theoretical currents deduced from equation (3), of the thermal sampled peaks vs. T in the 220–270 K range. The curves are labelled with numbers from 1 to 6, corresponding to $T_p=203$ K up to $T_p=228$ K. The maximum difference is found near 235 K, the same temperature where the microhardness transition is observed. The insert shows the plot of the areas enclosed by the peaks vs. T_p

The relaxation parameters between 220 and 250 K present a rather complex evolution with temperature. This is due in part to the rather weak electric current detected in TSDC for this temperature range (*Figure 6*). On the other hand, the fitting by equation (3) is not quite reliable, mainly in the high temperature side of the peaks (*Figure 12*). It is observed that an optimal choice of E, τ_0 and q does not provide a satisfactory fitting of the experimental peaks for such a temperature region. In relation to this, an unexpected behaviour of the microhardness vs. T plot[31] was observed at these temperatures (*Figure 13*). In order to confirm the relation between this thermoplastic transition and the anomalous relaxation observed in TSDC, the area of the theoretical peaks obtained according to equation (3) for the best set of E, q and τ_0 values was subtracted from the area of the experimental peaks. These areas are represented in *Figure 14*. They represent a measurement of remanent charge density associated with every single peak. Indeed, the maximum temperature of the peak enclosing the largest area corresponds to the temperature of the microhardness transition. This observation leads us to assume a tight relation between the thermoplastic transition and the observed remanent discharge in this temperature range. Because the variations in the microhardness value are associated with the bonds at the crystalline–amorphous interface, the existence of such relaxation could be related to changes in the strength of links at this interface.

CONCLUSIONS

In summary, equation (3), deduced from a general order kinetics analysis, satisfactorily fits the elementary peaks in which the TSDC spectrum of P8 is decomposed. This analysis makes it possible to separate the different electric relaxation zones associated with characteristic transitions of the material. This procedure is a useful tool for determining the different temperature relaxation zones with great accuracy in these kinds of materials.

The meaning of the different parameters, mainly q, requires additional information, especially above T_g. Below T_g the relaxation mechanism is dipolar and the value of q is coherent with that found for other solids, for which the dipolar-like relaxation was unambiguously identified.

ACKNOWLEDGEMENTS

The plot in *Figure 13* was kindly provided by Professor J. M. Pastor of the Faculty of Sciences, University of Valladolid, Spain.

REFERENCES

1 Bucci, C. and Fieschi, R. *Phys. Rev. Lett.* 1964, **12**, 16
2 Van Turnhout, J. 'Thermally Stimulated Discharge of Polymer Electrets', Elsevier, Amsterdam (1975)
3 Chen, R. and Kirsh, Y. 'Analysis of Thermally Stimulated Processes', Pergamon, Oxford (1980)
4 Jonscher, A. K. 'Dielectric Relaxation in Solids', Chelsea Dielectric Press, London (1983)
5 Torres, A., Jiménez, J. and de Saja, J. A. *Phys. Chem. Solids* 1985, **46**, 733
6 Torres, A., Jiménez, J., Vega, B. and de Saja, J. A. *J. Mater. Sci.* 1987, **22**, 1623
7 Fraile, J., Torres, A. and Jiménez, J. *J. Mater. Sci.* 1989, **24**, 1323
8 Torres, A., Jiménez, J., Sobrón, F., Merino, J. C. and de Saja, J. A. *J. Phys. Chem. Solids* 1985, **46**, 665
9 Torres, A., Jiménez, J., Vega, B. and de Saja, J. A. *IEEE Trans. EI*, 1986, **21**, 395
10 Torres, A., Jiménez, J. and de Saja, J. A. *Cryst. Latt. Def. Amorph. Mat.* 1987, **15**, 369
11 Natta, G., Bassi, I. W. and Fagherazzi, G. *Eur. Polym. J.* 1969, **5**, 239
12 Tosi, C., Ciampelli, F. and Dall'Asta, G. *J. Poly. Sci.* 1973, **11**, 529
13 Fraser, G. V., Keller, A., Pastor, J. M., de Saja, J. A. and Martuscelli, E. *Polymer* 1975, **20**, 780
14 Van Werden, K. and Holland-Moritz, K. *Colloid and Polymer Sci.* 1981, **259**, 731
15 Drâxler, A. *Kautsch Gummi, Kunstst* 1981, **34**, 185
16 Facioni, E. and Martuscelli, E. *Polym. Lett.* 1972, **10**, 423
17 Keller, A. and Martuscelli, E. *Macromol. Chem.* 1971, **141**, 189
18 Giannotti, G. and Capizzi, A. *Eur. Polym. J.* 1970, **6**, 743
19 Torres, A., Jiménez, J., Carbayo, V. and de Saja, J. A. *Phys. Status Solidi* (*a*) 1983, **78**, 671
20 Guillet, J., Seytre, G., Chatain, D., Lacabanne, C. and Monpagens, J. C. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 541
21 Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. *Poly. J.* 1982, **3**, 600
22 Lamure, A., Hitmi, N., Lacabanne, C., Hardmand, M. F. and Herbage, D., *IEEE Trans. EI* 1986, **21**, 443
23 Bucci, C., Fieschi, R. and Guidi, G. *Phys. Rev.* 1966, **148**, 816
24 Chen, R. *J. Electrochem. Soc.* 1969, **116**, 1254
25 Stuke, J. *J. Non-Cryst. Solids* 1970, **4**, 1
26 Jonscher, A. K. in 'Thermally Stimulated Processes in Solids' (Eds J. P. Fillard and J. Van Turnhout) Elsevier, Amsterdam, 1977, p. 53
27 McKeever, S. W. S. and Hughes, D. M. *J. Phys. Chem. Solids* 1978, **39**, 211
28 Takahashi, Y. and Miyaji, K. *Macromolecules* 1983, **16**, 1978
29 Suzuoki, Y., Mizutani, J. and Ieda, M. *Jpn. J. Appl. Phys.* 1976, **15**, 929
30 Mizutani, T., Suzuoki, Y. and Ieda, M. *J. Appl. Phys.* 1977, **48**, 2408