Polymer Vol. 37 No. 14, pp. 2915–2923, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

On the interpretation of the TSDC results in the study of the α-relaxation of amorphous polymers

A. Alegría*, L. Goitiandía and J. Colmenero
Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Facultad de Química, Apartado 1072, 20080 San Sebastián, Spain

(Received 30 December 1994; revised 26 June 1995)

The α-relaxation around the glass transition of poly(vinyl acetate) (PVAc) is investigated by combining several dielectric techniques, namely frequency and time domain dielectric spectroscopies, as well as thermally stimulated depolarization current (TSDC). The results obtained by means of both the isothermal methods and the TSDC technique are interpreted on the basis of a Kohlrausch–Williams–Watts functional form of the time decay function. Both isothermal and TSDC measurements show that the dynamics of the α-relaxation in the glassy state has a non-Debye character which is similar to the one observed in the supercooled melt. From the comparison between the obtained results, a new way of analysis and interpretation of the TSDC results in the α-relaxation range is proposed. Moreover, from a set of TSDC spectra obtained at different heating rates, both $\beta(T)$ and $\tau(T)$ are calculated in the whole temperature range covered by TSDC, i.e. below and across the glass transition. Copyright © 1996 Elsevier Science Ltd.

(Keywords: glass transition; dielectric relaxation; thermally stimulated techniques)

INTRODUCTION

The dynamics of the α-relaxation of glass-forming liquids, and in particular of polymer melts, has been extensively studied for a long time[1–6]. Nowadays, it is well established that the α-relaxation shows several universal features regardless of the type of glass-forming system considered[1–3] (ionic, low molecular weight organic, inorganic, polymeric, etc.). The two main common features are: (i) the non-Debye behaviour of the frequency, or time, dependence of the corresponding susceptibility; and (ii) the non-Arrhenius temperature dependence of the characteristic relaxation time, which is often described by the Vogel–Fulcher (VF) law, $\tau \propto \exp[B/(T-T_0)]$. The VF-type temperature behaviour of the α-relaxation is evidenced as a strong slowing down of the relaxation rate during cooling when the liquid–glass transition is approached from the liquid side. The liquid to glass transition phenomenon is commonly characterized by a temperature T_g, which, in fact, defines a temperature range where the supercooled melt falls out of the equilibrium-like state and therefore a glassy material is obtained. Below T_g, a very slow dynamics, which is evidenced by the so-called structural recovery and physical aging processes[7,8], is still present. Most of the investigations on the glassy state dynamics have been focused on observing the time evolution of static properties such as volume or enthalpy[9,10]. However, there are a few dielectric studies where experimental information about the isothermal behaviour of the α-relaxation across the T_g range is reported[11–13]. In these studies, it seems that the non-Debye character of the α-relaxation remains almost unaffected through the glass transition. However, a clear crossover of the temperature behaviour of the characteristic time from the VF law above T_g to an Arrhenius-like one below T_g is observed. A main difficulty of the isothermal studies below T_g is that, due to the low mobility of the system, these experiments are very time consuming and, as a consequence, the structural recovery, which is also going on during the time of measurement, will affect to some extent the state of the system under observation[8,11,12]. In addition to this problem, the isothermal measurements below T_g are in practice limited to the temperature range where the characteristic time of the system is shorter than 10^5 s.

On the other hand, there are an important number of works studying the α-relaxation around T_g by means of thermally stimulated techniques[14] like the Thermally Stimulated Depolarization Current (TSDC) one[14,15]. TSDC is a dielectric technique in which the dynamics of the system are observed through the trend of the previously aligned structural dipoles to orientate at random as the mobility of the system increases during the continuous heating from temperatures far below T_g. This non-isothermal method has similarities with the well known differential scanning calorimetry (d.s.c.). Both techniques monitor the dynamics of the system during the transformation from the glassy state to the supercooled melt one. For this reason the response observed depends on the thermal history and, in particular, on the heating rate, which, in fact, determines the observation time. The main advantage of the TSDC technique is that it provides simultaneously a high resolution

---

* To whom correspondence should be addressed

(neighbouring processes are well resolved) and very high sensitivity. This high sensitivity allows to detect the onset of the segmental motions responsible of the α-relaxation at temperatures well below T_g, i.e. in the actual glassy state. A review of the work performed before 1986 using the TSDC technique can be found in ref. 16, whereas more recent studies using this technique around T_g can be found in refs 17–20.

The TSDC results, contrary to the conventional dielectric spectroscopy ones, are generally interpreted in terms of a distribution of parallel (uncoupled) activated Debye-like processes. On the basis of such interpretation, different experimental methods like the thermal sampling or the fractional polarization are usually applied[14]. However, the non-exponential character of the α-relaxation does not seem to be a simple consequence of the presence of a distribution of parallel Debye-like process[21]. Moreover, the non-Debye nature of the α-relaxation, regardless of its origin, produces memory effects[9,22] which makes the interpretation of the thermal sampling and fractional polarization methods unclear. Besides, the quite complicated thermal histories often involved in these experimental procedures make the analysis of the results even more intricate. In view of these problems, the results usually obtained from TSDC measurements are hardly comparable with those obtained from isothermal methods.

The aim of this work is to find a new method of analysis for the TSDC spectra in such a way that the results obtained below and around T_g might be compared with the ones obtained above and around T_g, using conventional techniques. To do this, we have studied the dielectric α-relaxation around the glass transition on poly(vinyl acetate) (PVAc) by combining several dielectric techniques. First of all, the isothermal dynamic behaviour of supercooled and glassy PVAc has been characterized by means of dielectric spectroscopy, both in the frequency and the time domain. Secondly, the thermally stimulated depolarization current technique has been used to investigate the dynamic behaviour of the α-relaxation around and below T_g. The results obtained by means of this technique, using different heating rates, are interpreted on the same grounds used in the interpretation of the isothermal experiments. From the comparison between the results obtained, a new way of analysis and interpretation of the TSDC results in the α-relaxation range is proposed.

EXPERIMENTAL

Samples

The poly(vinyl acetate) used in this work was supplied by Aldrich-Chemie (cat. no. 18,949-9). The number average and weight average molecular weights were determined by means of gel permeation chromatography using polystyrene as a reference yielding $\bar{M}_n = 22\,470\,\mathrm{g\,mol^{-1}}$ and $\bar{M}_w = 98\,080\,\mathrm{g\,mol^{-1}}$, respectively. The glass transition temperature, $T_g = 315\,\mathrm{K}$, was determined from differential scanning calorimetry (d.s.c.) at $10\,\mathrm{K\,min^{-1}}$ from the mid-point of the heat capacity increment. Samples for dielectric experiments were prepared by melting the 'as-received' product directly on the electrodes in a vacuum furnace at 100°C. After degassing the sample, the upper electrode was placed on the sample with a light pressure. The so formed parallel plate capacitor was cooled down to room temperature also under vacuum.

Frequency domain dielectric spectroscopy

The dielectric measurements in the frequency domain were performed following standard procedures. The experimental set up, which was supplied by Novocontrol GmbH, consisted of a Solarton-Schlumberger frequency response analyzer SI 1260, which was supplemented by using a high impedance preamplifier of a variable gain. A frequency range from 10^{-2} to 10^6 Hz was covered. The sample was kept between two condenser plates (gold-plated stainless steel electrodes) that were maintained at a fixed distance (about 0.2 mm). Frequency scans were performed at constant temperature, which was decreased in steps. The temperature was controlled by means of a nitrogen gas jet system allowing a temperature stability better than 0.1 K.

Time domain dielectric measurements

The set-up used for these measurements consists of a cylindrical stainless steel cryostat which contains the sample cell. The cell was formed by two aluminium electrodes isolated by Teflon in the upper part, so the temperature of the Teflon insulator remained constant. The sample, placed between the two electrodes, forms a parallel plate capacitor (thickness about 0.5 mm). The cryostat with the sample cell was first evacuated and, after 30 min, filled with high purity helium slightly above atmospheric pressure. The temperature of the sample was controlled by a Cerbere temperature controller which provided a temperature stability better than 0.1 K in isothermal experiments. A Kepco APH 2000 M power supply was used to apply a constant d.c. voltage of 400 V in order to polarize the sample. The depolarization current was measured by means of a Keithley 642 electrometer with a resolution of 10^{-16} A.

The isothermal depolarization (ID) method. The experimental procedure followed, which is described in *Figure 1*, is based on the transient current method[6], i.e. a box-type excitation was applied during a given polarization time t_p and the corresponding depolarization current was recorded as a function of the time[11,12].

Two different experiments were conducted. First, ID measurements were performed on well equilibrated samples, i.e. annealed at the measurement temperature for a time long enough to ensure reproducible behaviour (independent of the prior thermal history). In a second set of experiments, the glassy sample was measured in a non-equilibrium state as follows: The sample was first heated up to $T_g + 30\,\mathrm{K}$ in order to remove the effects of prior thermal history and then cooled at a constant rate ($10\,\mathrm{K\,min^{-1}}$) down to the measurement temperature. At this temperature, the transient current experiment was performed. The t_p values used in these measurements ranged from a few to several thousand seconds depending on the temperature. Both experimental procedures can be used in the range where the characteristic time of the depolarization process of the sample is greater than the time characteristic of the electrometer response, about 0.1 s, but is short enough to provide measurable values of the depolarization current. These limitations allow us to obtain the dielectric response in the time range from 1 to 10^6 s.

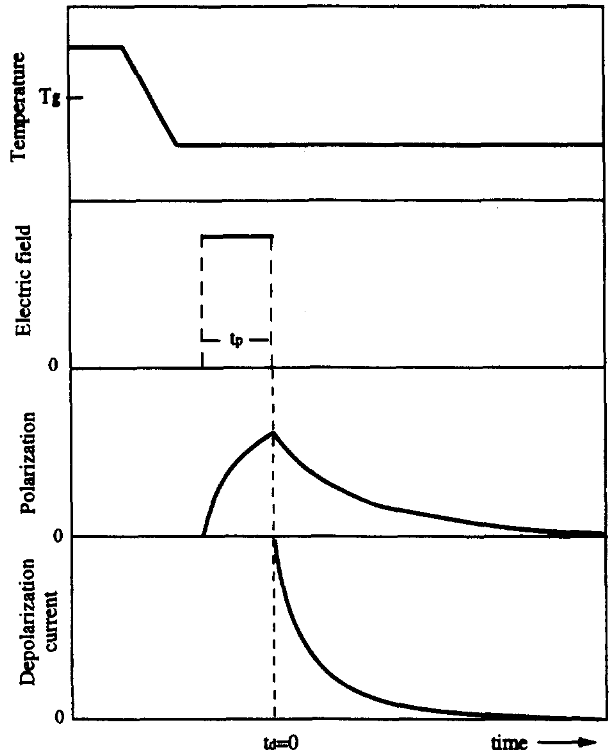

Figure 1 Schematic time evolution of the different quantities involved in a ID time domain experiment

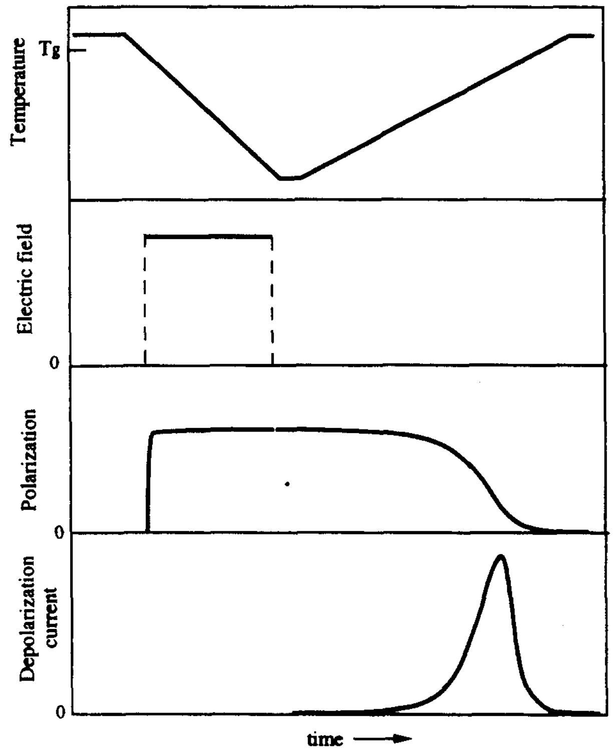

Figure 2 Schematic time evolution of the different quantities involved in a TSDC experiment

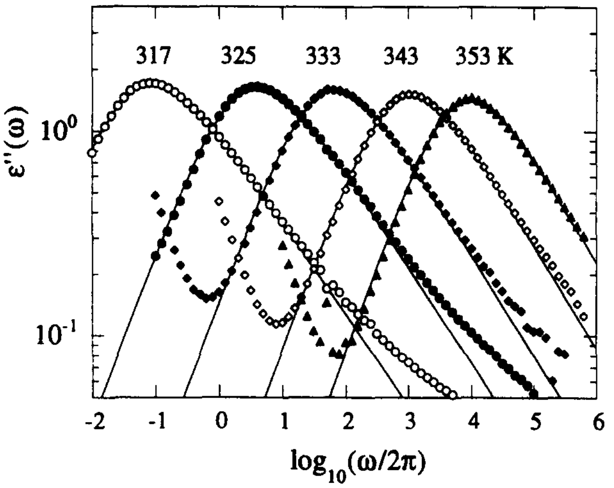

Figure 3 Experimental dielectric losses of PVAc at several temperatures in the range $T > T_g$. The lines through the data show the fitting curves corresponding to a KWW function for $\phi(t)$

The TSDC method. Standard TSDC measurements[14] were performed by using different heating rates ranging from 0.06 K min^{-1} to 16 K min^{-1}. The experimental procedure followed, which is described in *Figure 2*, consists of an initial voltage applied at high temperature where dipoles are able to orientate quickly, followed by cooling at 10 K min^{-1} to a low temperature where dipoles can be considered frozen. At this low temperature the field is removed and the current due to the depolarization is detected during the subsequent heating.

RESULTS

PVAc is a typical amorphous polymer whose dynamics have been long and extensively studied by using most of the available experimental techniques. This polymer shows two well defined relaxation ranges[6]: (i) the α-relaxation which is detectable at a few degrees above room temperature; and (ii) the β-relaxation which is active below −100°C, i.e. far below T_g. The much higher strength of the dielectric α-relaxation and the very different time scales of both processes justified the common use of PVAc as a standard in the experimental investigations of the polymer segmental dynamics (recent publications concerning the segmental dynamics of PVAc can be found in refs 23–25). Although studies on the dielectric α-relaxation of PVAc by means of conventional dielectric spectroscopy have been widely reported in the literature[6, 23,26], we have performed this kind of measurement on the samples used in this work to avoid any ambiguity in the further comparison among the results obtained by means of the different dielectric techniques.

Frequency domain

The frequency dependence of the imaginary part of the permittivity $\varepsilon''(\omega)$ of the PVAc samples studied by us is shown in *Figure 3* at several temperatures. The behaviour observed is in agreement with the above mentioned non-Debye character of the α-relaxation process in glass-forming polymers. The non-Debye character of the normalized relaxation decay function in time domain $\phi(t)$, is usually well described by means of the Kohlrausch–Williams–Watts (KWW) formula[27]:

$$\phi(t) = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where β is the parameter characterizing the non-Debye nature of the time decay, and τ is a characteristic relaxation time. The method followed to fit the $\varepsilon''(\omega)$ behaviour according to equation (1) has been previously described in refs 12 and 28. As can be observed in *Figure 3*,

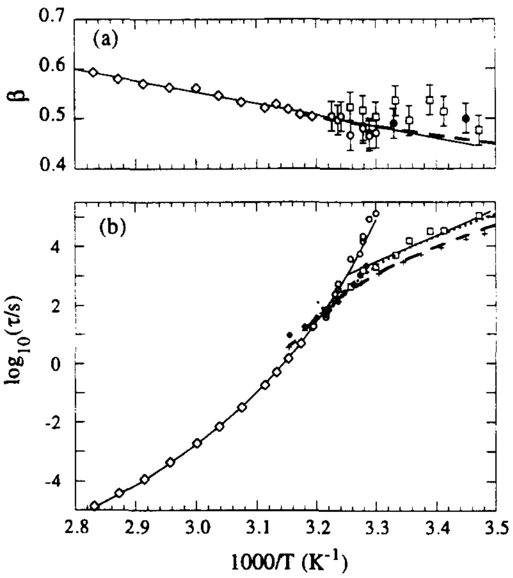

Figure 4 (a) $\beta(T)$ behaviour through the glass transition range. Open diamonds (frequency domain) and circles (time domain) correspond to the supercooled melt, whereas open squares represent the glassy state behaviour. Filled circles and the thick dashed line were obtained from TSDC measurements by following different methods. (b) $\tau(T)$ characterizing the KWW time scale of the dynamics of the dielectric α-relaxation around T_g. Filled diamonds refer to the characteristic times obtained from the maximum of the TSDC spectra on the basis of a Debye process and crosses represent the $\tau(T)$ behaviour deduced from TSDC experiments at $8\,\mathrm{K\,min^{-1}}$ with $\beta(T) = 0.50$. The other symbols have the same meaning as above. Solid lines stand for VF and Arrhenius fits. The $\tau(T)$ behaviour deduced from TSDC experiments following the way of analysis proposed in this work, with β depending on temperature, is shown as a dotted line for $q = 0.125\,\mathrm{K\,min^{-1}}$ and as a dashed line for $q = 8\,\mathrm{K\,min^{-1}}$

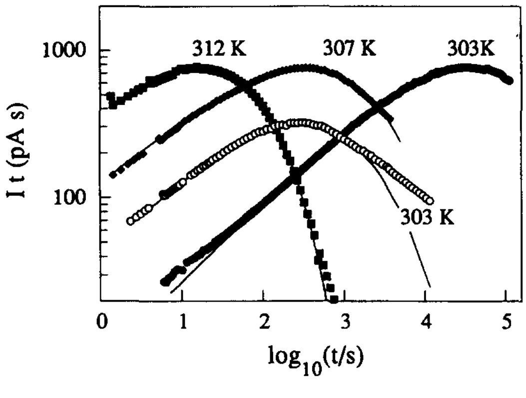

Figure 5 Representative experimental results obtained by means of the ID time domain dielectric measurements both at equilibrium (solid symbols) and on the non-equilibrated sample (empty symbols). Solid lines stand for KWW fits

equation (1) allows a good description of the main part of the α-relaxation although, as usually reported, an extra conductivity contribution is present at low frequencies and small deviations are apparent on the high frequency side. From these fittings the temperature dependence of the KWW parameters τ and β, which will be used to characterize the dynamics of the α-relaxation, were extracted. It is found that the shape parameter β increases systematically with temperature (see *Figure 4a*), in good agreement with previously reported results[23,26]. On the other hand, $\tau(T)$ displays the usual non-Arrhenius temperature dependence which can be well parametrized by means of the VF equation,

$$\tau(T) = \tau_0 \exp\frac{B}{T - T_0} = \tau_0 \exp\frac{DT_0}{T - T_0} \qquad (2)$$

Here, T_0 is a temperature below the experimental range at which the extrapolated relaxation time would diverge, $D = T_0/B$ is a dimensionless parameter which can be related to the fragility concept, first introduced by Angell[29], and τ_0 is the reciprocal of an attempt frequency. By fitting the $\tau(t)$ data by means of equation (2) the following VF parameters were obtained: $\tau_0 = 10^{-12}\,\mathrm{s}$, $T_0 = 266\,\mathrm{K}$ and $D = 5.40$, which are close to typical values reported in the literature for this polymer.

ID method

As mentioned above, two different types of experiments have been done. The equilibrium like state was characterized by measuring on well annealed samples. The glassy state was characterized by performing the ID experiments immediately after cooling the sample down to the desired temperature. In the former case the response obtained depends only on the temperature, but in the latter, the response depends on both the temperature and the prior thermal history of the sample. However, in this latter case, the experimental conditions were selected to ensure that the state of the sample characterized at each temperature is the same, i.e. the enthalpy of the state characterized differs in a constant value from the corresponding one to the glassy polymer obtained by cooling the supercooled melt at $10\,\mathrm{K\,min^{-1}}$. A detailed report of this procedure can be found elsewhere[12].

The response obtained in an ID experiment can be expressed as the first derivative of the response corresponding to a block shape excitation[30]:

$$-I(t) \propto \frac{\mathrm{d}}{\mathrm{d}t}[\phi(t) - \phi(t + t_p)] \qquad (3)$$

where $\phi(t)$ is the relaxation decay function corresponding to a fully polarized sample. Although measurements performed on equilibrated samples can be perfectly fitted by a KWW form for $\phi(t)$, the glass-like behaviour is not well described by this function over the whole time range (see *Figure 5*). This can be immediately attributed to the fact that, in the glassy state, the sample is approaching the equilibrium state during the measurement, which should induce non-linear effects. However, the description using the KWW form for $\phi(t)$ is still good enough to fit the faster part of the depolarization current behaviour. In fact, in this time range the enthalpy of the sample is nearly constant, thus the parameters obtained characterize the dynamics of the sample in the initial state (just after removing the electric field). A deeper discussion of this point can be found elsewhere[11,12]. Therefore, by fitting the experimental $I(t)$ behaviour, in the whole range for equilibrium measurements and up to the maximum of $I \cdot t$ for the measurements in the glassy state, the values of τ and β characterizing the dynamics of the dielectric α-relaxation around and below T_g were deduced. The results obtained are shown in *Figure 4*. As can be seen, the values deduced for the β parameter at equilibrium are in agreement with the temperature dependence obtained from the frequency domain measurements. Moreover, the values of τ obtained at equilibrium conform to the

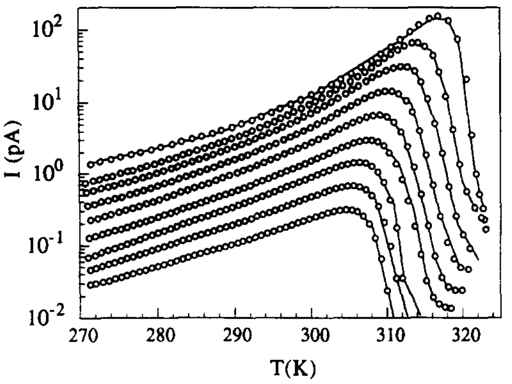

Figure 6 TSDC spectra of PVAc polarized during cooling at $10\,\mathrm{K\,min^{-1}}$ between 325 and 250 K. The heating rates used were 16, 8, 4, 2, 1, 0.5, 0.25, 0.125 and $0.0625\,\mathrm{K\,min^{-1}}$

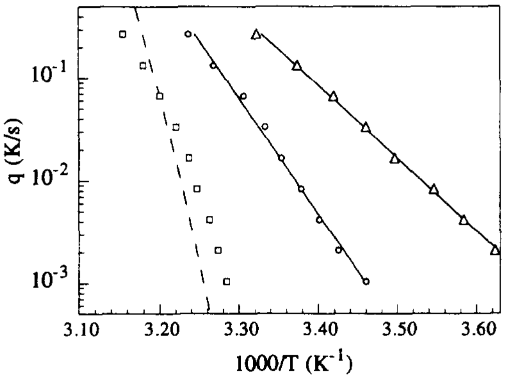

Figure 7 Heating rate dependence of the temperature at the maximum of the TSDC spectra (squares), the temperature where the intensity is 1/3 of the maximum intensity I_m (circles), and the temperature where the intensity is $I_m/10$ (triangles). Solid lines stand for Arrhenius fits and the dashed line stands for the VF supercooled melt behaviour

VF curve deduced from the fitting of the frequency domain data. Concerning the glassy state behaviour, we found that $\tau(T)$ is no longer described by the VF law but tends towards an Arrhenius law:

$$\tau(T) = \tau_\infty \exp\left(\frac{E}{k_B T}\right) \tag{4}$$

τ_∞ being a prefactor and E an apparent activation energy. The values of the fitting parameters obtained in the range $285\,\mathrm{K} < T < 310\,\mathrm{K}$ are $\tau_\infty = 2\,10^{-31}$ s and $E = 46\,\mathrm{kcal\,mol^{-1}}$. Obviously, these values cannot be interpreted to be associated to a simple activated process. An interpretation of such a behaviour in the framework of the Adams and Gibbs theory[31] can be found elsewhere[12].

On the other hand, we find that near T_g the values of β obtained in the glassy state are slightly higher than the values deduced from the $\beta(T)$ in the supercooled melt (at equilibrium). However, the difference, although systematic, is barely outside the estimated uncertainty in β.

The above reported behaviour, which is in qualitative agreement with the one reported using a different analysis of the time domain measurements[13], seems to be an universal feature of the glassy dynamics of polymer melts[11–13,32].

TSDC measurements

The dielectric behaviour of PVAc, as observed by means of TSDC has been well characterized during the last years (see refs 19 and 33 and references therein). It is well established that the TSDC spectra of PVAc show several maxima in the temperature range from −160 to 200°C. The peaks appearing above 60°C seem to be due to the relaxation of space charge and conductivity, whereas the two peaks around 40°C and −140°C are attributed to the dipolar α- and β-relaxations, respectively. Since in this work we have focused our attention in the α-relaxation range, all the results below refer only to this relaxation process.

Figure 6 shows the TSDC spectra obtained at different heating rates for PVAc samples polarized during cooling at $10\,\mathrm{K\,min^{-1}}$ in the temperature range between $T = 325$ and 250 K. The most straightforward information we can get out of these spectra is the temperature, T_m, at the maximum of the depolarization peak. First of all, it is apparent that T_m is not strongly affected by the heating rate used, which in the usual interpretation, is attributed to the fact that the responsible process has a high apparent activation energy. The dependence of T_m on the heating rate is shown in *Figure 7*. This representation does not yield a straight line, as expected from an Arrhenius temperature dependence of the characteristic times, but shows a slope which increases with decreasing temperature. This is the behaviour expected according to a VF law for the temperature dependence of the characteristic time. A rough estimate of the α-relaxation characteristic time can be calculated from the TSDC spectra as follows[14]:

$$\tau_D(T_m) = \frac{kT_m^2}{qE} \tag{5}$$

where E is the apparent activation energy and the subscript D refers to the fact that equation (5) is obtained on the basis of a Debye-like relaxation process[34]. From the TSDC spectra, values of τ_D were calculated assuming a mean value of the apparent activation energy in the experimental temperature range ($E \cong 115\,\mathrm{kcal\,mol^{-1}}$). These values are located around the VF line fitting the equilibrium $\tau(T)$ behaviour (see *Figure 4b*), although apparent deviations are observed.

However, contrary to the grounds of equation (5), the α-relaxation is not a Debye process but, as shown above, is described by the KWW law for $\phi(t)$ both above and below T_g. On this basis the stored charge time decay is given by:

$$Q(t) = Q_0\phi(t) = Q_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{6}$$

Q_0 being the initial Q value. From equation (6) the depolarization current can be expressed as:

$$I(t) = -\frac{\mathrm{d}Q(t)}{\mathrm{d}t} = \beta\frac{Q(t)}{\tau}\left(\ln\frac{Q_0}{Q(t)}\right)^{[1-1/\beta]} \tag{7}$$

Contrary to the isothermal experiments described by equation (7), in non-isothermal measurements both τ and β would depend on temperature. For this case, equation (7) can be rewritten with the temperature as a variable in the following way:

$$I(T) = -\frac{\mathrm{d}Q(T)}{\mathrm{d}T}\,\frac{\mathrm{d}T(t)}{\mathrm{d}t} = \beta(T)\frac{Q(T)}{\tau(T)}\left[\ln\frac{Q_0}{Q(T)}\right]^{[1-1/\beta(T)]} \tag{8}$$

An analytical solution of equation (8) is not possible in general. However, if β is temperature independent one finds the following solution:

$$I(T) = \beta \frac{Q_0}{\tau(T)} \left[\frac{1}{q}\int_{T_i}^{T}\frac{\mathrm{d}T'}{\tau(T')}\right]^{\beta-1} \exp\left\{-\left[\frac{1}{q}\int_{T_i}^{T}\frac{\mathrm{d}T'}{\tau(T')}\right]^{\beta}\right\} \tag{9}$$

where, according to the TSDC experiments, it has been considered that the heating rate, q, is a constant, i.e. $t = (T - T_i)/q$, T_i being a temperature low enough to fulfil the condition $I(T_i) \cong 0$. Therefore, once β and $\tau(T)$ are known, it is possible to calculate the TSDC spectra by means of equation (9).

On the other hand, starting from equation (9), an estimate of the dependence of T_m on q can be deduced assuming a VF form for $\tau(T)$ (the Arrhenius case is recovered with $T_0 = 0$):

$$\ln q = -\frac{B}{T_m - T_0} + \ln\left(1 - 2\frac{T_m - T_0}{B}\right) + \ln\left[\frac{(T_m - T_0)^2}{\tau_0 B}\right] - \frac{1}{\beta}\ln\left\{\ln\left[\frac{Q_0}{Q(T_m)}\right]\right\} \tag{10}$$

It should be noted that with the current assumptions the rate $Q(T_m)/Q_0$ is about 0.33, independent of q. Therefore, the value of T_m for a given q value is mainly determined by the $\tau(T)$ equilibrium behaviour. The dashed line in *Figure 7* represents the behaviour deduced from equation (10) with $\beta = 0.5$ (the value of β around T_g) and the $\tau(T)$ behaviour found above in the range $T > T_g$. The obtained curve follows the experimental points within ±2 K. This agreement between the TSDC behaviour deduced from the supercooled melt dynamics and the experimental one seems to suggest that, at least around the maximum of the TSDC spectra, they are monitoring the behaviour of the α-relaxation close to the equilibrium-like state rather than to the glassy one. In order to test this idea, several spectra corresponding to different heating rates were calculated using equation (9). In *Figure 8*, it is shown that, once properly normalized, the simulated TSDC spectra fit approximately the experimental ones around and above T_m. However, clear disagreements are apparent in the low temperature range. A comparison of the TSDC spectra with a d.s.c. scan (see *Figure 8*) shows that the temperature range where these deviations are clear coincides with the temperature range where the polymer is in the glassy state. Therefore, the disagreements should be attributed to the fact that in the part of the spectra below T_m the sample is out of the equilibrium-like state corresponding to the supercooled melt. This evidences that, in TSDC measurements, the information concerning the glassy state is mainly confined in the $T < T_m$ range.

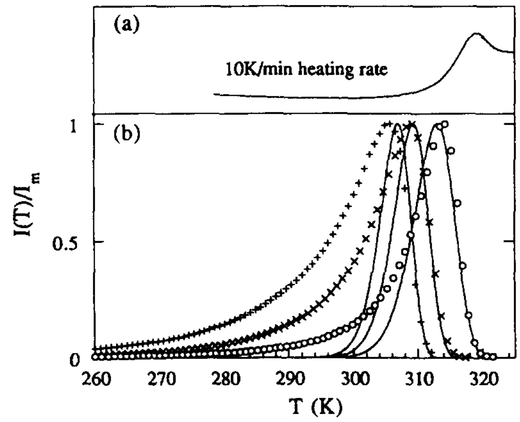

Figure 8 (a) Typical d.s.c. scan of PVAc at $10\,\mathrm{K\,min^{-1}}$. (b) Comparison between experimental and simulated TSDC spectra corresponding to different heating rates

From simple inspection of *Figure 6*, it is clear that the temperature shift of the spectra obtained at different heating rates is not uniform but is higher in the tail than around the peak (note the difference in the shape of the spectra). Although this fact has often been attributed to the presence of a distribution of activation energies, we will show below that it can be interpreted as a direct consequence of the above mentioned cross-over of $\tau(T)$ from the VF to the Arrhenius behaviour when the polymer is frozen out of the supercooled melt equilibrium-like state (see *Figure 4b*).

In order to have an estimate of the apparent activation energy in the $T < T_m$ range, we have studied the heating rate dependence of the temperatures at which the depolarization current is $I_m/3$ and $I_m/10$, I_m being the current intensity at the maximum of the TSDC peak. For these characteristic temperatures below T_m, we found Arrhenius-like behaviours with apparent activation energies $E = 48\,\mathrm{kcal\,mol^{-1}}$ $(290 < T < 310\,\mathrm{K})$ and $E = 32\,\mathrm{kcal\,mol^{-1}}$ $(300 < T < 280\,\mathrm{K})$, respectively (see *Figure 7*). The former value is close to the activation energy obtained by means of isothermal measurements in the same temperature range. On the other hand, the lack of enough isothermal experimental data in the low temperature range makes any comparison with the latter value difficult. The above results support the interpretation of the non-uniform shift of the TSDC spectra when changing the heating rate as associated to the crossover of $\tau(T)$ from the supercooled melt to the glassy behaviour.

The ID measurements presented above showed that the α-relaxation below T_g was still well described by a KWW form for $\phi(t)$ with a nearly constant value of β. Thus, equation (9) can also be used in the glassy state. Moreover, in the glassy state $\tau(T)$ shows a nearly Arrhenius behaviour [equation (4)]. In the temperature range corresponding to the glassy state the condition $E/k_BT \gg 1$ is verified and the integral appearing in equation (9) can be approximated[35] to obtain the $I(T)$ behaviour in the range $T < T_m$:

$$I(T) \cong \beta \frac{Q(T)}{\tau_\infty \exp\left(\frac{E}{k_BT}\right)} \left[\left(\frac{k_BT^2}{q\tau_\infty E}\right)\exp\left(-\frac{E}{k_BT}\right)\right]^{(\beta-1)} \tag{11}$$

Taking the usual approximation $Q(T) \cong Q_0$ for the low temperature range of the TSDC spectra, equation (11) becomes:

$$I(T) = \beta\frac{Q_0}{\tau_\infty}\exp\left(-\frac{\beta E}{k_BT}\right)\left(\frac{k_BT^2}{q\tau_\infty E}\right)^{(\beta-1)} \tag{12}$$

Although an equation similar to equation (12) had been proposed for TSDC experiments many years ago without a justification, only recently has it been deduced in this field[36]. However, if the current intensity is replaced by the first derivative of the crystallization enthalpy, equation (12) becomes a widely used formula in the field of the non-isothermal crystallization[37] for systems whose isothermal crystallization follows the Avrami equation[38], which is formally equivalent to equation (1).

By using equation (12), once E has previously been determined in a given temperature range, the value of β can be estimated. The values of β calculated from the experimental TSDC spectra ($q = 1\,\mathrm{K\,min^{-1}}$) at 300 and 290 K (mid-points of the temperature ranges where E was previously determined) are $\beta = 0.48$ and $\beta = 0.50$, respectively. In *Figure 4a*, it can be observed that these values are in agreement with the values obtained from isothermal measurements in the same temperature range, which supports the validity of the KWW form for the TSDC interpretation.

DISCUSSION

All the above TSDC results show that the behaviour deduced from the TSDC spectra might be consistent with those obtained by isothermal methods, i.e. a nearly constant value of $\beta = 0.5$ around and below T_g and a crossover of $\tau(T)$ from a VF law around T_g towards an Arrhenius one below T_g. The main interest of this finding is that, whereas TSDC is a quite routine technique, isothermal measurements below T_g are very time consuming and require a simultaneous structural relaxation study to know the actual state of the sample during the ID experiment[11,12]. Concerning this latter problem, in the case of TSDC experiments the state of the sample is well determined because the thermal treatment involves only cooling and heating at constant rates. In spite of these advantages, up to this point only estimates of the apparent activation energy in the glassy state have been extracted by means of the TSDC technique. However, the complete information about $\tau(T)$ below the glass-transition range has not yet been obtained. A different method of evaluation of the TSDC spectra in order to obtain the $\tau(T)$, without previous assumptions, is presented below.

Once the validity of the KWW form for the description of the supercooled melt and glass dynamics has been established, equation (8) can be transformed to obtain the following expression for $\tau(T)$:

$$\tau(T) = \beta(T)\frac{Q(T)}{I(T)}\left[\ln\frac{Q_0}{Q(T)}\right]^{[1-1/\beta(T)]} \qquad (13)$$

If $\beta = 1$, i.e. for a Debye-like response, equation (13) reduces to the well known Bucci and Fieschi[39] formula

$$\tau(T) = \frac{Q(T)}{I(T)}$$

which is normally used for the evaluation of the fractional polarization experiments on the basis of the Debye interpretation. When equation (13) is used for evaluating $\tau(T)$ from experimental data, $Q(T)$ should be calculated directly from the TSDC spectra as:

$$Q(T) = \frac{1}{q}\int_T^{T_f} I(T')\mathrm{d}T' \qquad (14)$$

where T_f is a temperature above T_m high enough to fulfil the condition $I(T_f \cong 0)$. By using equation (13), the $\tau(T)$ behaviour can be extracted directly from the TSDC spectra provided $\beta(T)$ is known. In a first step, we have calculated the $\tau(T)$ behaviour from three TSDC spectra at different heating rates assuming constant values of β. The results obtained for $\beta = 0.40$ and $\beta = 0.50$ are presented in *Figures 9a* and *9b*, respectively.

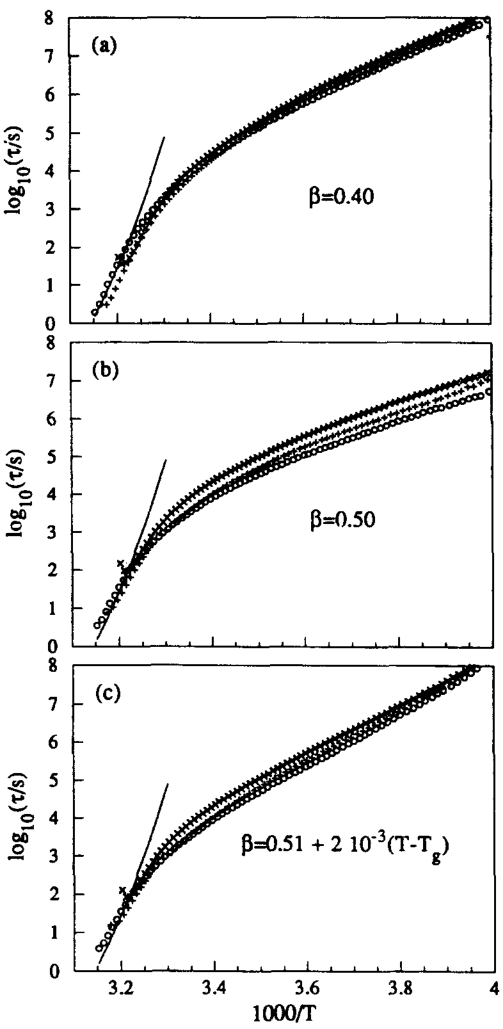

Figure 9 $\tau(T)$ behaviour obtained using equation (13) from the TSDC spectra at (O) 8, (+) 1 and (×) 0.125 K min^{-1} with the $\beta(T)$ behaviour indicated

As mentioned above, the thermal history involved in a TSDC experiment is simple. In the experiments performed by us, the sample was always cooled down to the same temperature at the same rate. Thus the initial state for the depolarization process is always the same. Based on this fact, one should expect that the values of $\tau(T)$ in the low temperature range do not depend on the heating rate used. This is what we found approximately for $\beta = 0.40$ but clearly not for $\beta = 0.50$. On the other hand, we have shown that the TSDC spectra above T_m monitors the dynamics of the supercooled melt in an equilibrium-like state. Therefore, in this high temperature range the $\tau(T)$ behaviour should also be independent of the heating rate. This condition is verified for $\beta = 0.50$ but not for $\beta = 0.40$ (see *Figure 9a*). These results appear to suggest that β cannot be taken as a constant in the whole temperature range covered by the TSDC spectra (70 K) but should increase from values close to 0.4 at low temperatures to values near 0.5 close T_g.

Equation (8) is a general one that can be used even when β is temperature dependent. Therefore, in a second step a linear $\beta(T)$ behaviour was assumed and the corresponding $\tau(T)$ behaviour was calculated. *Figure 9c* shows the result obtained for $\beta(T) = 0.51 + 2 \cdot 10^{-3} (T - T_g)$. It is apparent that in this case, the $\tau(T)$ behaviour obtained at the different rates coincides in both the low and high temperature ranges. On the contrary, in the intermediate temperature range $\tau(T)$ depends clearly on the heating rate, being higher as the heating rate is smaller. This trend is in agreement with what one expects taking into account that, at small heating rates, the glassy polymer is able to relax towards the equilibrium-like behaviour during the heating process easier than when the heating rate is high. This structural relaxation leads to the slowing down of the relaxation rate. The thick dashed lines in *Figures 4a* and *4b* stand from the $\beta(T)$ and $\tau(T)$ values corresponding to this calculation. In *Figure 4b*, it is apparent that the glassy $\beta(T)$ behaviour deduced in this very different way is also in agreement with the behaviour obtained above by means of both ID and TSDC measurements.

However, although assuming a linear increase of β with temperature results in an improvement of the $\tau(T)$ behaviour at very low temperatures, in the temperature range covered by the ID experiments equation (13) with $\beta = 0.50$ yields a near indistinguishable $\tau(T)$ behaviour (see *Figure 4b*). Therefore, it seems that the temperature dependence of β in the glassy state could only be addressed by means of the TSDC technique because it allows a very wide temperature range in the glassy state to be covered. However, several difficulties appear. (i) The $\beta(T)$ behaviour can only be addressed taking into account the very low temperature tail of the TSDC spectra which can be strongly influenced by the contributions to the TSDC spectra of secondary relaxations and/or experimental noise. (ii) Even in the best experimental conditions, such as those shown above for PVAc, the $\beta(T)$ deduced far below the maximum could be very dependent on the assumption that the KWW is able to describe the whole relaxation response. However, systematic deviations from the KWW law in the high frequency side, such as those we observed in the frequency domain experiments of PVAc (see *Figure 3*) are widely reported[23,40].

On the other hand, in *Figure 4b*, it is apparent that the times deduced from TSDC measurements are shorter than those obtained from the ID technique. The reason for this is that whereas the isothermal methods involve the annealing of the sample at the measurement temperature, which induces structural changes, the TSDC experiments are performed during continuous heating. Therefore, the structural relaxation effects in the TSDC experiments (provided that the heating and cooling rates are close to each other) are less important than those produced during isothermal measurements. However, when the heating rate is much smaller than the cooling rate, as mentioned above, one could expect that during the TSDC scan the sample evolves towards the equilibrium-like state and as a consequence the relaxation time would increase (see *Figure 9c*). In *Figure 4b* it is shown how the $\tau(T)$ behaviour deduced from the TSDC scan at $0.125\,\mathrm{K\,min^{-1}}$ fits the data points obtained from isothermal measurements. This would indicate that both TSDC at $0.125\,\mathrm{K\,min^{-1}}$ heating rate and the ID measurements characterize the sample in a similar structural state.

CONCLUSIONS

We have proved that, following an adequate analysis procedure, the TSDC spectra allow us to characterize the dielectric relaxation around and below T_g, the results obtained being perfectly consistent with those obtained from isothermal experiments. A comparison of the TSDC and isothermal experiments results shows that the behaviour around and above the maximum of the TSDC spectra is mainly controlled by the dynamical behaviour of the supercooled melt in an equilibrium-like state. In contrast, the low temperature part of the TSDC spectra is determined by the dynamics of the glassy polymer. Both isothermal and TSDC measurements also show that the dynamics of the α-relaxation in the glassy state has a non-Debye character which is similar to the one observed in the supercooled melt. Moreover, from a set of TSDC spectra obtained at different heating rates, it is even possible to determine both $\beta(T)$ and $\tau(T)$ in the whole temperature range below and across the glass transition. In this way, the influence of the glass transition on the dynamical behaviour of the system is clearly evidenced.

Therefore, TSDC measurements are shown to be an invaluable technique to study the α-relaxation in the actual glass-transition, i.e. during the cross-over from the glassy state to the equilibrium-like state characteristic of the polymer melt. Possible extensions of this work to the study of more complex systems, like polymer blends, LC polymers, etc. are now in progress. The implications of our results with regard to fractional polarization experiments are also being investigated.

ACKNOWLEDGEMENTS

This work has been supported by CICyT (project: MEC MAT92-0355) and the University of the Basque Country (project: UPV 206.215-EC020/93) The authors also thank Gipuzkoako Foru Aldundia for partial financial support.

REFERENCES

1 Ngai, K.L. and Wright, G.R. (Eds) 'Relaxation in Complex Systems (I)', North Holland, Amsterdam, 1991, *J. Non-Cryst. Solids* 1994, 172

2 Richter, D., Dianoux, A.J., Petry, W. and Teixeira, J. (Eds) 'Dynamics of Disordered Materials', Springer Verlag, Berlin, 1989

3 Colmenero, J. and Alegría, A. (Eds) 'Basic Features of the Glassy State', World Scientific, Singapore, 1990

4 Götze, W. in 'Liquids, Freezing and the Glass-Transition', Les Houches Summer School, Course LI, July 1989, (Eds J. P. Hansen, D. Levesque and J. Zinn-Justin), North-Holland, Amsterdam, 1991, p. 289

5 Ferry J. D. 'Viscoelastic Properties of Solid Polymers', John Wiley and Sons, New York, 1979

6 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967

7 Kovacs, A. J. *Fortschr. Hochpolym. Forschung* 1963, **3**, 394

8 Struik, L. C. E. 'Physical Aging in Amorphouse Polymers and Other Materials', Elsevier, Amsterdam, 1978

9 Hodge, I. M. *J. Non-Cryst. Solids* 1994, **169**, 211

10 Lee, H. H. and McGarry, F. J. *Polymer* 1993, **34**, 4267. Monserrat S. *J. Polym. Sci. B* 1994, **32**, 509

11 Alegría, A., Guerrica-Echevarria, E., Tellería, I. and Colmenero, J. *Phys. Rev. B* 1993, **47**, 14857

12 Alegría, A., Guerrica-Echevarria, E., Goitiandia, L., Tellería, I. and Colmenero, J. *Macromolecules* 1995, **28**, 1516

13 Schlosser, E. and Schönhals, A. *Polymer* 1991, **32**, 2135

14 Braünlich, P. (Ed.) 'Thermally Stimulated Relaxations in Solids, Topics in Applied Physics', Vol. 37, Springer Verlag, New York, 1979

15 van Turnhout, J. in 'Electrets, Topics in Applied Physics' (Ed. G. M. Sessler), Vol. 33, Springer Verlag, New York, 1980, pp. 81–201.

16 Bernes, A., Boyer, R. F., Chatain, D., Lacabanne, C. and Ibar, J. P. in 'Order in Amorphous State of Polymers' (Ed. S. E. Keinath), Plenum Press, London, 1987, p. 305

17 Sauer, B. B. and Avakian, P. *Polymer* 1992, **33**, 4128

18 Topic, M. and Veksli, Z. *Polymer* 1993, **34**, 2118

19 Dias, A. B., Correia, N. T., Moura-Ramos, J. J. and Fernandes, A. C. *Polym. Int.* 1994, **33**, 293

20 Teyssedre, C., Bernes, A. and Lacabanne, C. *J. Polym. Sci. B* 1993, **31**, 2027

21 Colmenero, J., Alegría, A., Arbe, A. and Frick, B. *Phys. Rev. Lett.* 1992, **69**, 478

22 Ferreira, G. F. L. and Gross, B. *J. Appl. Phys.* 1990, **68**, 2526

23 Schönhals, A., Kremer, F. and Schlosser, E. *Phys. Rev. Lett.* 1991, **67**, 999

24 Li, J. L. and Gelerinter, E. *Polymer* 1992, **33**, 963. Royal, J. S. and Torkelson, J. M. *Macromolecules* 1992, **25**, 1705

25 Krishnan, P., Le, H., Lee, S. H. and Gelerinter, E. *J. Polym. Sci. B-Polym. Phys.* 1993, **31**, 1885

26 Nozaki, R. and Mashimo, S. *J. Chem. Phys.* 1987, **57**, 2271

27 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1970, **66**, 80

28 Alvarez, F., Alegría, A. and Colmenero, J. *Phys. Rev. B* 1991, **44**, 7306. Alvarez, F., Alegría, A. and Colmenero, J. *Phys. Rev. B* 1993, **47**, 125

29 Angell, C. A. *J. Non-Cryst. Solids* 1991, **131–133**, 13

30 Böttcher, C. J. F., van Belle, O. C., Bordewijk, J. and Rip, A. 'Theory of Electric Polarization', Elsevier Scientific, Amsterdam, 1973

31 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1958, **43**, 139

32 Colmenero, J. *J. Non-Cryst. Solids* 1991, **131–133**, 860

33 Dias, A. B., Moura-Ramos, J. and Williams, G. *Polymer* 1994, **35**, 1253

34 This formula can be considered to be equivalent to the usual calculation of the characteristic time in fixed frequency experiments from the maximum of the $\varepsilon''(\omega_0, T)$ curve as $\tau(T_m) = 1/\omega_0$.

35 Abramowitz, M. and Stegun, I. A. 'Handbook of Mathematical Functions', Dover Publications, New York, 1970

36 Halpern, V. *J. Phys. D-Appl. Phys.* 1993, **26**, 307

37 Colmenero, J., Ilarraz, J. and Barandiarán, J. M. *Thermochim. Acta* 1980, **35**, 381, Colmenero, J., Barandiarán, J. M. and Criado, J. M. *Thermochim. Acta* 1982, **55**, 367

38 Avrami, M. J. *Chem. Phys.* 1941, **9**, 177

39 Bucci, C. and Fieschi, R. *Phys. Rev. Lett.* 1964, **12**, 16

40 Dixon, P. K., Wu, L., Nagel, S. R., Williams, B. D. and Carini, J. P. *Phys. Rev. Lett.* 1990, **56**, 1108