Thermally stimulated depolarization current (*TSDC*) study of molecular motions in the glass-transition region of polyarylate (PAr)

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Dipolar relaxation processes in the glass-transition region of a commercial polyarylate (PAr) have been studied by means of the thermally stimulated depolarization current (*TSDC*) technique. Complementary differential scanning calorimetry (d.s.c.) and thermogravimetry (t.g.) measurements have also been carried out for comparison. The *TSDC* global spectrum obtained is resolved into two thermocurrent peaks. The elementary processes involved in these broad peaks were separated by application of the fractional polarization procedure. The Arrhenius-like kinetic parameters corresponding to the different elementary processes have been obtained fitting each elementary *TSDC* peak by a Debye-like expression. Empirical distribution function of activation energies has been also deduced. The origin of the different studied dipolar relaxation processes is discussed in relation to the molecular motions in the glass-transition region.

(Keywords: dielectric relaxation; glass transition; thermally stimulated depolarization current; polyarylate; amorphous polymer)

INTRODUCTION

Amorphous engineering thermoplastics have received considerable attention over recent years, both commercially and scientifically. The technological interest of these polymers is in general related to their high glass-transition temperature and exceptional levels of rigidity. Structurally, many of these materials, including polyarylate, polysulphone and polycarbonate, contain rigid aromatic rings in the backbone chain.

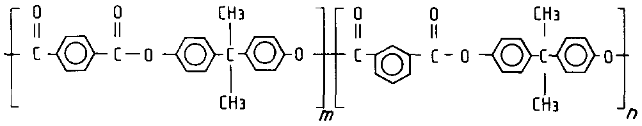
On the other hand, the mechanical and electrical properties of the amorphous polymers, which generally determine their principal applications, as well as their industrial processing, are closely dependent on the structural relaxation processes around the glass transition in these materials.

A previous paper[1] reported a complete characterization of the dielectric relaxation processes in the liquid-like equilibrium region ($T > T_g$) of a commercial polyarylate performed by means of a 'dielectric spectroscopy' technique. The aim of the present work is to perform a study of these relaxation processes in the glassy region ($T < T_g$) of this same polymer by means of the thermally stimulated depolarization current (*TSDC*) technique, which obtains the dielectric response of a nonequilibrium (glassy zone) polymer because of its very low equivalent frequency. The complementary techniques, differential scanning calorimetry (d.s.c.) and thermogravimetry (t.g.), have also been used for polymer characterization and for comparison with *TSDC* measurements.

EXPERIMENTAL

Samples

Polyarylate (PAr) is a commercial copolyester obtained by polycondensation of an equimolar mixture of isophthalic and terephthalic acids with bisphenol-A; the molecular formula is:



where the molar ratio of terephthalic and isophthalic acids (m/n) is close to 50:50 and the number average molecular weight and molecular weight determined by viscometry are respectively $\bar{M}_n = 21\,000$ and $\bar{M}_w = 51\,660$. Details of fabrication procedure, applications and general and physical properties can be found in refs. 2 and 3. Information about blending of PAr with other polymers is reported in refs. 4 and 5. Polyarylate used in this work (Arylef U-100) was kindly supplied by Solvay. Samples for dielectric measurements were prepared in different ways. Polymer films, 0.5 mm thick, were made by casting from solutions of about 10% PAr in chloroform and subsequently dried under vacuum at a temperature of 60°C for at least two days. Pellets of 12 mm diameter and 0.5–1.5 mm thickness were prepared under pressure of 200 kg cm^{-2} at room temperature from polymer that had been purified chemically by precipitation from chloroform solution and dried, as well as from as-received polymer.

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TSDC *measurements*

TSDC[6] has already evolved into a basic tool for studying relaxation processes in polar polymers.

The first to devise a consistent theory for *TSDC* applied to dipolar processes were Bucci and Fieschi[7]. This theory is based on the classical Debye treatment with a single relaxation time, τ, for polarizing and depolarizing processes in polar materials. In this framework, if the sample is polarized at a temperature T, the polarization would have a value P_0 after an infinite time; the decay of this polarization after removal of the polarizing field is given by:

$$P(t) = P_0 \exp[-t/\tau(T)] \tag{1}$$

The corresponding depolarization current is:

$$J(t) = -\frac{\mathrm{d}P(t)}{\mathrm{d}t} \tag{2}$$

so that

$$J(t) = \frac{P(t)}{\tau(T)} \tag{3}$$

In a *TSDC* experiment the polarization obtained at high temperature is quenched at a sufficiently low temperature, T_0, and then the sample is warmed up from T_0 with a linear temperature programme $T = T_0 + qt$, where q is the heating rate.

If $\tau(T)$ can be approximated by an Arrhenius expression:

$$\tau(T) = \tau_0 \exp(E/k_B T) \tag{4}$$

where τ_0 is a preexponential factor, E an apparent activation energy, and k_B the Boltzmann constant, it is possible to write equation (1) as:

$$P(T) = P_0 \exp\left[-\frac{1}{q\tau_0}\int_{T_0}^{T} \exp(-E/k_B T')\,\mathrm{d}T'\right] \tag{5}$$

so that equation (3) becomes:

$$J(T) = \frac{P_0}{\tau_0}\exp(-E/k_B T)\exp\left[-\frac{1}{q\tau_0}\int_{T_0}^{T} \exp(-E/k_B T')\,\mathrm{d}T'\right] \tag{6}$$

At the temperature, T_m, of the maximum of $J(T)$, equation (6) leads to the condition:

$$\frac{q\tau_0 E}{k_B T_m^2}\exp(E/k_B T_m) = 1 \tag{7}$$

which relates E, τ_0 and T_m.

The single Debye relaxation model put forward by Bucci and Fieschi has been successfully applied to *TSDC* study of dipole reorientation in ionic crystals[8]. However, the occurrence of a single relaxation time is very unusual in glassy polymeric systems, so that broad *TSDC* peaks that correspond to a spectrum of relaxation times are commonly observed. However, *TSDC* can separate different elementary processes that contribute to a complex dielectric relaxation by use of several experimental methods known as 'peak cleaning', 'thermal sampling', 'fractional polarization', etc.[6,9], which allow separation of the elementary processes of a given broad *TSDC* peak as well as application of Bucci and Fieschi analysis to each of them.

The operating procedure for *TSDC* measurements used in this work is summarized in *Figure 1*. In the first case, A, the sample is heated at a rate of 10 K min^{-1} to a temperature of 500 K ($T_g = 470$ K) and, after about 3 min, cooled at a rate of 20 K min^{-1} to room temperature. The electrical polarizing field is set on at a temperature $T_{\mathrm{pon}} > T_g$ during cooling and set off when the sample reaches a temperature $T_{\mathrm{poff}} \ll T_g$, near room temperature, where any molecular motion is completely hindered, so that the polarization of the sample is now frozen-in. This procedure allows dipoles with a relaxation time smaller than the experimental relaxation time ($\sim 1/q$) at any temperature between T_{pon} and T_{poff} to orientate and contribute to the polarization of the sample. The sample is subsequently heated at a constant rate of 10 K min^{-1} so that the dipoles can return to random orientation. The corresponding depolarization current, I, as well as the temperature of the sample, T, are recorded *versus* time. In this case $T_{\mathrm{pon}} > T_g$ and $T_{\mathrm{pon}} - T_{\mathrm{poff}}$ is a large range of temperature; therefore the *TSDC* spectrum is a broad peak that corresponds to a wide distribution of relaxation times. This peak will be denoted the global *TSDC* spectrum associated with the glass transition.

In *Figure 1* the experimental procedure used in this work for applying the fractional polarization technique is shown at B. The thermal history is similar to case A. The electrical field is also applied during cooling but now

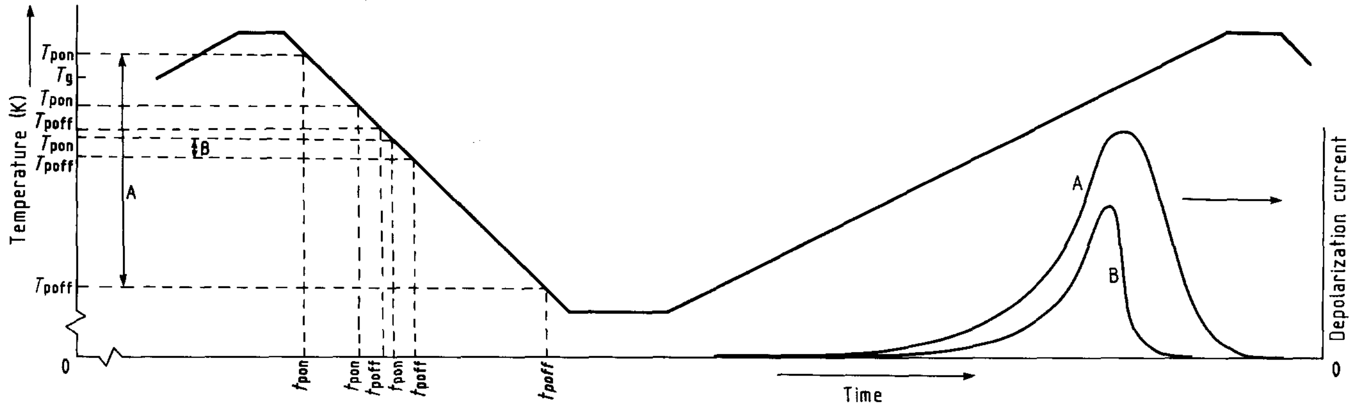

Figure 1 Sample temperature during polarizationand depolarization processes. (A) global polarization; (B) fractional polarization

$T_{pon} - T_{poff}$ is a narrow temperature window of 5–10 K. By varying the interval (T_{poff},T_{pon}) in the temperature range between $T > T_g$ and room temperature, where the thermoelectric currents appear, the global *TSDC* spectrum can be resolved into quasi-elementary peaks that can be associated approximately with a single Debye relaxation time $\tau_i(T)$. The apparent activation energy E_i and the preexponential factor τ_{0i} corresponding to each relaxation time can be obtained by fitting the corresponding experimental fractionated spectrum with equation (6) applying the condition (7).

In this work, *TSDC* measurements have been carried out in an experimental set-up similar to that described in refs. 9 and 10 but now improved with a data aquisition system (HP-3421A) linked to a HP-85 on-line desk computer. The experimental data, current and temperature are read by the system at a rate of one datum each five seconds; a typical *TSDC* curve is formed by 100 to 200 experimental points.

RESULTS

Figure 2 shows at A the first global *TSDC* spectrum of PAr obtained by the experimental procedure described in the previous section. The curve comprises a broad peak with a high temperature shoulder. This spectrum, however, is not stable and changes, after successive *TSDC* scans or any thermal treatment, to a double peak by enhancement of the shoulder and a continuous decrease of the first broad peak (see *Figure 2*). These changes can be systematically monitored by isothermal annealing, performed inside the *TSDC* cell, at temperatures above T_g before *TSDC* scanning. Results shown in *Figure 2* were obtained using an annealing temperature of 513 K; the *TSDC* global spectrum is nearly stable after an annealing time at this temperature of ~ 17 h. A similar result was obtained by plotting the polarization frozen in the sample during the *TSDC* experiment, ΔP (proportional to the area under the *TSDC* curve), *versus* the time of previous isothermal annealing at 513 K. *Figure 3* shows that ΔP decreases until a stable value is reached that corresponds to the *TSDC* curve of *Figure 2F*. Moreover, this behaviour also occurs, although more slowly, under annealing at temperatures below T_g.

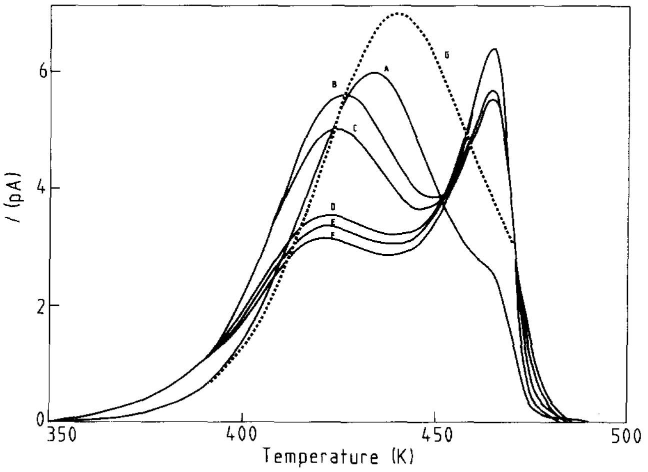

Figure 2 Global *TSDC* spectra for PAr, obtained at 10^6 V m^{-1} poling field before any thermal treatment (A) and after annealing for 1 h (B), 2 h (C), 5.2 h (D), 10.5 h (E) and 17 h (F) at 513 K. Curve G was obtained after exposing the sample to water vapour at 500 K

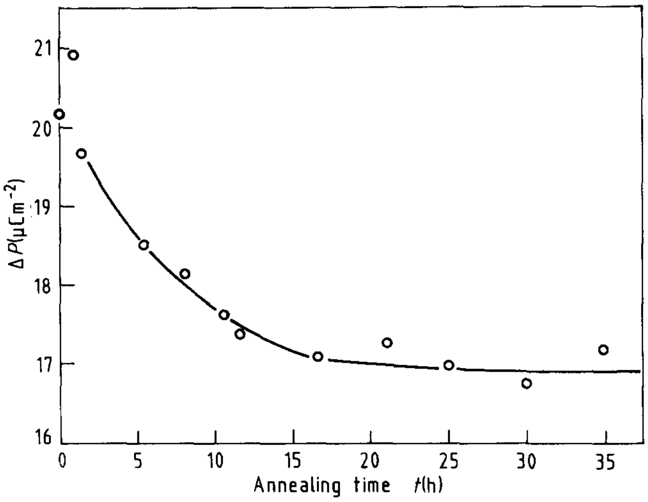

Figure 3 Change of the equilibrium polarization with annealing time at 513 K

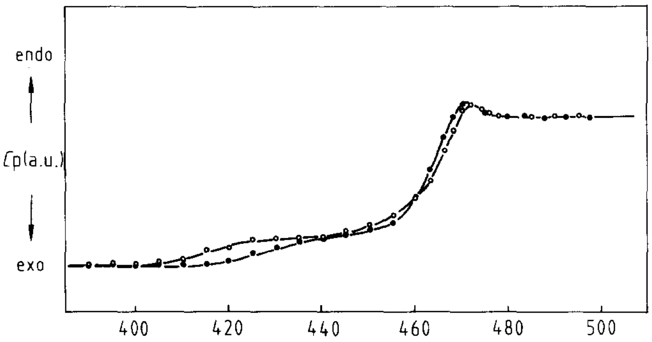

Figure 4 D.s.c. scans of PAr obtained at a heating rate of 10 K min^{-1} after cooling at 20 K min^{-1} corresponding to sample as prepared (●) and to the sample in the dielectrically stable state of *Figure 1F* (○)

The behaviour of the samples shown by the changes of the *TSDC* curves can also be observed by means of standard d.s.c. *Figure 4* shows two d.s.c. scans performed on a sample as prepared for a first *TSDC* experiment and after annealing at 513 K for 17 h. As can be seen, although less marked than in the *TSDC* case, the changes in the specific heat curves are qualitatively similar.

On the other hand, changes in the *TSDC* and d.s.c. curves shown in *Figures 2*, *3* and *4* correspond to an actual weight decrease, as can be verified by standard thermogravimetry. *Figure 5*, curve A, shows a t.g. scan of a sample of PAr performed in a Du Pont 951 balance. A decrease of about 1 wt% is detected in the temperature range at which the *TSDC* peaks appear. In *Figure 5*, curve B corresponds to a sample previously annealed at 513 K for 17 h. No decrease in the sample weight is detected before thermal decomposition starts (400°C).

Effects on *TSDC*, d.s.c. and t.g. due to residual polar solvent (chloroform) in the samples can be disregarded as this behaviour appears even in samples prepared from as-received polymer, i.e. not treated with any solvent (see Experimental section). We ascribe the change of sample response with thermal treatment to the loss of water present in PAr samples. To confirm this assumption a *TSDC* scan was carried out on the *TSDC* 'stable' sample annealed at 513 K for 17 h after exposure to water vapour at high temperature (500 K). The result of this experiment is shown in *Figure 2*, curve G. The *TSDC* spectrum obtained is similar to that corresponding to curve A

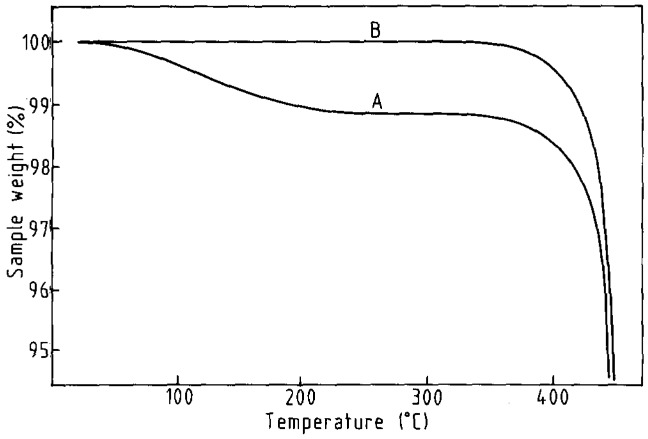

Figure 5 T.g. scans of PAr before any thermal treatment (A) and after annealing at 513 K for 17 h (B) obtained at a heating rate of 10 K min^{-1}

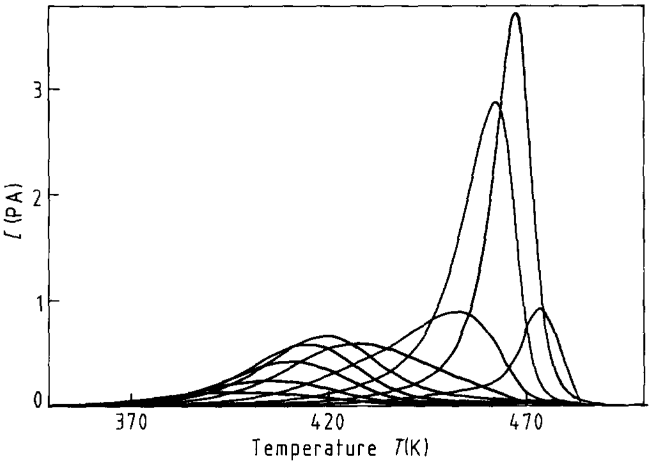

Figure 6 Fractional polarization of PAr obtained by applying a poling field of 1 MV m^{-1}

(*Figure 2*) but it is more intense, which corresponds to a greater water content. An approximate estimate of the water removed from the sample by the annealing previously described can be obtained from the decrease of the area under the *TSDC* curve (*Figure 3*) on the assumption that all water in the sample is free. This amount, ~0.3 wt%, is similar in order of magnitude to that reported in ref. 2.

Following these ideas, fractional polarization was applied only to samples previously annealed at ~510 K until the *TSDC* global spectrum was stable, repeatable and similar to that in curve F of *Figure 2*. Thus, ten elementary peaks were obtained by varying the polarization window ($T_{pon} - T_{poff} = 10$ K) from 393 to 483 K (*Figure 6*). In addition, a temperature window of only 5 K was used more accurately to resolve the high temperature narrow peak. *Figure 7* shows the temperature of the maximum of fractionated peaks *versus* the corresponding mean polarization temperature; the peaks are located around the two temperature maxima of the whole *TSDC* spectrum. Moreover, two kinds of linear behaviour are observed, which enable the fractional polarized peaks to be classified into two groups related to the different processes that correspond to the two maxima of the *TSDC* global spectrum.

On the other hand, above T_g, many polymers show in their *TSDC* spectrum a peak that is commonly attributed to the motion of space-charge stored in the material[6]. This non-dipolar peak is commonly known as the ρ-peak. Although the high temperature maximum in the *TSDC* global curve F of *Figure 2* is centred close to the calorimetric T_g, an assurance of their dipolar origin is needed. This can be obtained first by studying the behaviour of the area of a *TSDC* peak in relation to the electrical polarization field. If a *TSDC* peak has a dipolar origin, a linear relationship between the polarization stored in the sample, ΔP, and the poling field is expected from the elementary theory of dielectrics. *Figure 8* shows the behaviour of ΔP *versus* the poling field, E_p, for the most intense high temperature fractional polarized peak; ΔP is proportional to E_p throughout the measurement range.

Another method for distinguishing between dipolar and space-charge peaks is based on the variation of the temperature at the peak maximum with sample thickness. A ρ-peak appears at lower temperatures for thinner samples while a dipolar one always occurs at the same

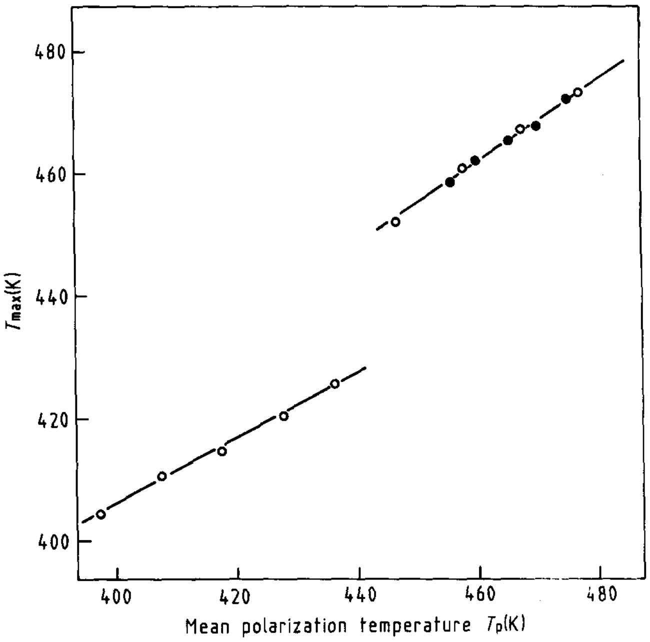

Figure 7 Change of temperature of the maximum of *TSDC* fractional polarization spectra with mean polarization temperature. Polarization window (●) 5 K; (○) 10 K

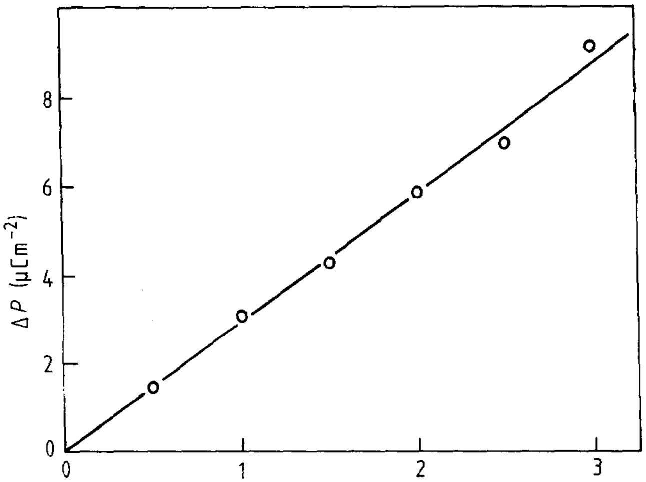

Figure 8 Field dependence of the polarization remaining in the sample after fractional polarization between 473–463 K

temperature. Samples of PAr with thickness 0.5–1.5 mm were measured and the temperature of the *TSDC* peaks was the same in all cases.

On the other hand, the dipolar relaxation strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, where ε_s and ε_∞ are the low and high frequency limits of the dielectric constant, can be evaluated easily by integrating the current density corresponding to the *TSDC* global curve[6]. If the total *TSDC* curve has only a dipolar origin, the calculated value of $\Delta\varepsilon$ would be close to that obtained from standard dielectric measurements. The variation of $\Delta\varepsilon$ with absolute temperature, *T*, for PAr[1] is given by

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = 240/(T-283) \qquad (8)$$

The $\Delta\varepsilon$ value obtained from the area of *TSDC* curve ($\Delta\varepsilon = 1.7$) agrees with that obtained through equation (8) for a temperature of 424 K, which is close to the maximum of the first peak of the *TSDC* global spectrum.

These considerations support the idea of considering the two *TSDC* peaks of PAr as corresponding to dipolar processes.

Each quasi-elementary *TSDC* peak obtained by fractional polarization can be fitted by an expression like (6) by making the assumption of a single relaxation time $\tau_i(T)$. The values obtained for the apparent activation energy and preexponential factor by this procedure are listed in *Table 1*.

DISCUSSION

As can be seen in *Table 1*, values of both activation energy, *E*, and preexponential factor, τ_0, that correspond to the low temperature processes are relatively close. Moreover, these values ($E \sim 1$ eV and $\tau_0 \sim 10^{-13}$ s) lie in the expected range for thermally activated localized motions. In marked contrast, values of *E* and τ_0 for the high temperature processes are more widely scattered. Besides, the high values of *E* as well as the exceptionally low values of τ_0 cannot be associated with thermally activated molecular site changes between two equilibrium positions separated by a true molecular energy barrier. These values of both *E* and τ_0 can be explained[11] only in terms of cooperative motions corresponding to conformational changes characteristic of the α-relaxation (glass transition) in amorphous polymers. Hence, both *E* and τ_0 should be considered as apparent kinetic parameters.

Table 1 Data obtained from the *TSDC* fractional polarization spectra of PAr

T_{pon} (K)	T_{poff} (K)	ΔT_p (K)	T_{max} (K)	E (eV)	τ_0 (s)
402	392	10	405.6	0.99	4.34×10^{-11}
412	402	10	410.9	1.10	1.12×10^{-13}
422	412	10	414.9	1.22	1.12×10^{-13}
432	422	10	419.3	1.24	9.27×10^{-14}
442	432	10	426.0	1.18	8.83×10^{-13}
452	442	10	452.2	1.5	1.37×10^{-15}
463	453	10	461.5	2.9	8.37×10^{-31}
473	463	10	466.7	4.3	1.00×10^{-45}
483	473	10	472.9	5.0	1.26×10^{-52}
458	453	5	458.7	2.75	2.48×10^{-29}
463	458	5	462.8	3.2	5.08×10^{-34}
468	463	5	465.3	4.0	1.38×10^{-42}
473	468	5	468.6	4.6	8.69×10^{-49}
478	473	5	473.2	4.7	2.26×10^{-49}

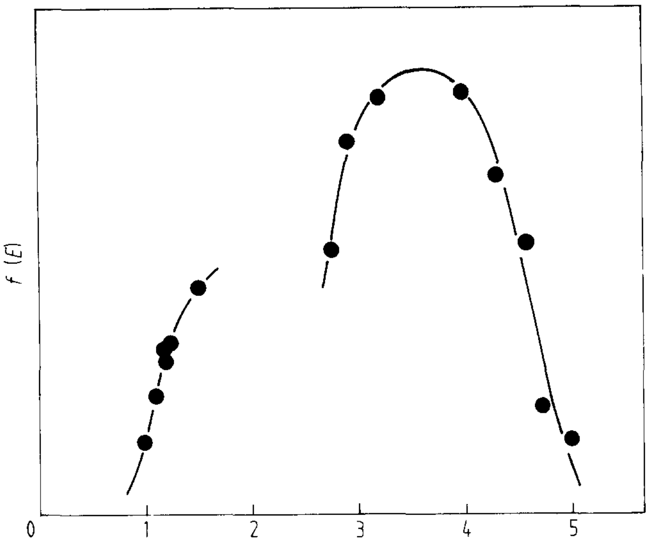

Figure 9 Empirical 'distribution function', *f*(*E*) (arbitrary units), of the different dipolar processes in the activation energy range

On the other hand, a measure of the distribution of the different processes in the energy range can be estimated from the 'distribution function' *f*(*E*), which is obtained by plotting the area of the theoretical Debye peak used to fit each fractional polarized spectrum *versus* the corresponding energy, *E*. *f*(*E*) is thereby proportional to the number of dipolar structural units that need activation energy values *E* to move. *f*(*E*), expressed as arbitrary units of area, is shown in *Figure 9*. As expected, *f*(*E*) comprises to distribution functions that correspond to the two different kinds of processes noted above. The origin of these two kinds of dipolar processes is now considered.

High temperature processes. The temperature of the *TSDC* peak maxima is close to the temperature range of the calorimetric glass transition as observed by d.s.c. In addition the high values of the corresponding apparent activation energies are in good agreement with the cooperative nature of the molecular motions in the glass transition region. These facts allow assignment of these processes to the cooperative motions of the large segments of the polymeric chain associated with the α-dielectric relaxation or glass transition.

Low temperature processes. The presence of a second 'α-relaxation' peak in a *TSDC* scan could be first associated with a second glass transition corresponding to a separate amorphous phase in the material. This is expected to occur in amorphous incompatible blends and even in some kinds of block copolymers, but not in a random copolymer, such as PAr. On the other hand, the small values of apparent activation energies corresponding to these low temperature processes suggest that they should be considered as sub-T_g processes that arise from the localized molecular motions similar to those associated with β-relaxation processes. The intensity of the low temperature *TSDC* peaks is affected hardly by the water content of the samples (see *Figure 2*), as is reported for the β-relaxation in many polymers[12]. This kind of sub-T_g process also has been found by dielectric measurements on polycarbonate based on bisphenol-A[13], a polymer structurally related to PAr. It is suggested that, for this polymer, motions in the sub-T_g region are of the same kind as at T_g but involve fewer consecutive structural units. In this sense, these processes (known as 'intermediate processes') could be viewed as some kind of precursor of the α-relaxation. This idea is supported in the case of PAr by the results obtained from a compensation analysis of the kinetic data of *Table 1*. If the logarithm of the preexponential factor, τ_0, varies linearly with the activation energy, E, a compensation law is observed:

$$\tau = \tau_c \exp(E/k_B[(1/T) - (1/T_c)]) \qquad (9)$$

where τ_c and T_c are the phenomenological parameters compensation time and compensation temperature respectively. The physical significance of these parameters is not yet clear but in the most general interpretation they are taken as characteristics of processes that arise from the same molecular mechanism[14,15]. One of the most usual assumptions for the compensation law in polymers is based on the possibility of a process where chain segments of increasing length contribute at increasing temperature until a maximum size is reached at the compensation temperature[16]. *Figure 10* shows a compensation plot for the high and low temperature processes present in the α-region of PAr; both the points corresponding to the high temperature processes (glass transition) and those corresponding to the low temperature (sub-T_g) processes fit only one compensation law defined by the parameters $T_c = 493.7$ K and $\tau_c = 0.37$ s. This suggests a similar origin on the molecular level for the two kinds of dipolar relaxation process and hence enables the low temperature processes to be considered as some β-like precursor of the high temperature (glass-transition) processes.

Finally, a comparative *TSDC* study of other polymers structurally related to PAr, such as polycarbonate, phenoxy and polysulphone, should provide a deeper explanation of the sub-T_g processes at the molecular level. This study is now in progress.

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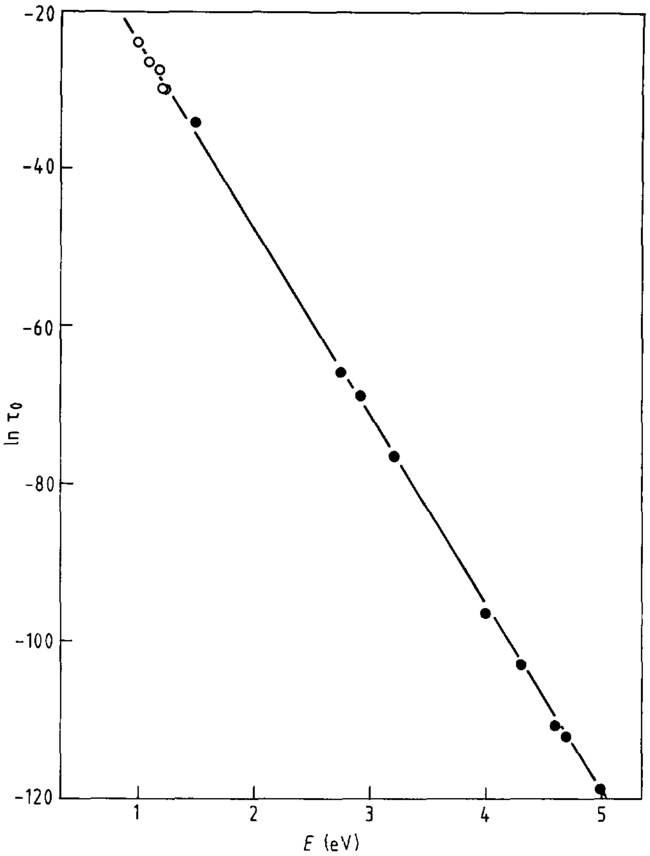

Figure 10 Compensation plot for the glass-transition (●) and sub-T_g (○) processes obtained by *TSDC* on PAr

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