Dielectric properties of polyarylate (PAr) around the glass transition

A. Alegría, J. Colmenero and J. J. del Val
Departmento de Física, Facultad de C. Químicas, Universidad del Pais Vasco, San Sebastián, Spain

and J. M. Barandiarán
Departmento de Electricidad y Electrónica, Facultad de Ciencias, Universidad del Pais Vasco, Lejona, Vizcaya, Spain
(*Received 21 May 1984*)

Dielectric characterization of the α-relaxation in polyarylate (PAr) has been carried out by means of a dielectric spectroscopy technique in a frequency range of 10–30 kHz. Complementary thermally stimulated depolarization currents (*TSDC*) and differential scanning calorimetry d.s.c.) measurements have also been performed. The results are interpreted in terms of the standard Cole–Cole plot and Havriliak–Negami distribution for the dielectric relaxation times. Information about the temperature and frequency dependence of a.c. conductivity is also obtained from the experimental curves. However, the behaviour of the main dielectric relaxation time is deduced from the experimental data in a wide range of temperature around the glass transition. This behaviour results in close agreement with the theoretical predictions of a free-volume approach for the dielectric α-relaxation recently proposed by the authors.

(Keywords: dielectric relaxation; relaxation times distribution; glass transition; polyarylate(PAr); amorphous polymer)

INTRODUCTION

Polyarylate (PAr) is a commercial polar polymer obtained by polycondensation of an equimolar mixture of isophthalic and terephthalic acids and bisphenol-A.

Although some works concerning applications, general and physical properties of PAr[1], as well as its blends with other polymers[2], can be found in literature, up to now there has not been a detailed study of the dielectric relaxation in PAr.

Dielectric relaxation processes are, however, generally related to the characteristic transitions of polymers. In PAr the most prominent relaxation (α-relaxation) occurs at the glass transition owing to its amorphous character.

Standard characterization of the dielectric relaxation in polar polymers, like PAr, is usually done by measuring the real and imaginary parts of the dielectric constant as a function of frequency and temperature. The experimental data are generally interpreted in terms of empirical expressions like Cole–Cole, Cole–Davidson or the more general Havriliak–Negami one[3], which relate the complex dielectric constant to frequency at a given temperature. Moreover, the above mentioned procedure also allows us to obtain the variation with temperature of a main dielectric relaxation time, τ_D, a characteristic of the processes. The behaviour of this τ_D in a different temperature range can also be obtained by the standard thermally stimulated depolarization current (*TSDC*) technique.

In a recent study[4] we proposed a unified interpretation of the behaviour of the dielectric relaxation time below, around and above the glass transition temperature, supported by a free volume dependent relaxation time. A first check of this approach was also successfully carried out by dielectric measurements on PVC samples in the same study.

The aim of this paper is to present a complete dielectric characterization of PAr around the glass transition as well as to interpret results obtained in the framework of the free volume approach previously reported.

EXPERIMENTAL

Samples of PAr (Arylef U-100) have been supplied by SOLVAY. The isophthalatic and terephthalatic acids ratio given by n.m.r. analysis is close to 50:50 and the average number and viscous molecular weight are respectively: $\bar{M}_n = 21\,000$ and $\bar{M}_w = 51\,660$.[5]

Pellets 12 mm diameter, 0.5 mm thick were prepared by pressure of 200 kg cm^{-2} at 430 K. Two 8 mm diameter Al electrodes were evaporated on both sides.

For a.c. measurements the samples were introduced into a cryostat with coaxially disposed leads, carefully shielded so that stray capacitance was reduced to $\sim 10^{-14}$ F. Current through a standard 10^{-8} F capacitor in series with the sample was measured by means of a lock-in amplifier which allows the in-phase and quadrature components to be separated[6]. These two components are related to the real and imaginary parts of the dielectric constant ($\varepsilon^* = \varepsilon' - i.\varepsilon''$). At a given frequency, the temperature was raised at 0.1 K s^{-1} up to 530 K in nitrogen atmosphere. The range of frequencies used was 10 to 30 kHz, taking two frequencies in each decade. Moreover, the temperature at the maximum of the dielectric losses was determined at 100 and 300 kHz.

The in-phase and quadrature signals were automati-

0032-3861/85/060913-05$03.00

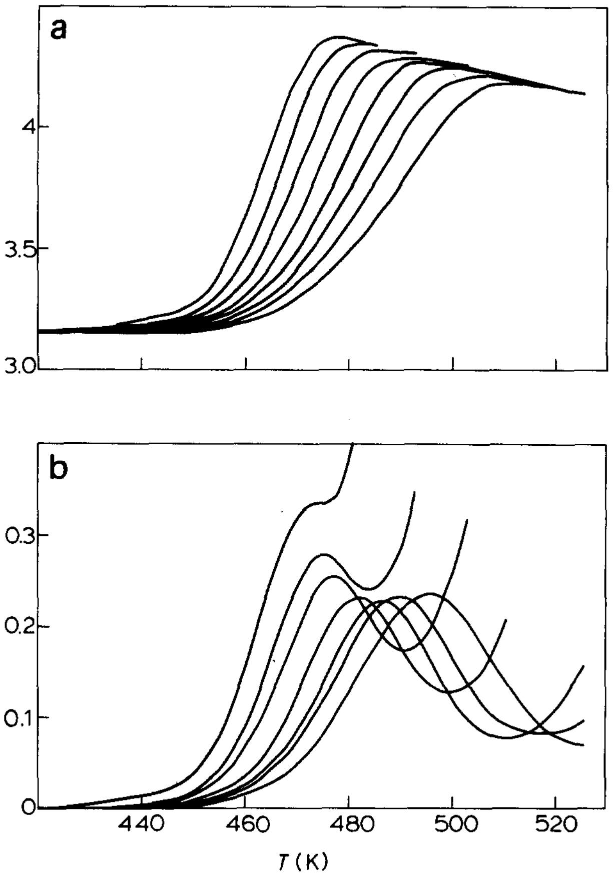

Figure 1 Experimental curves showing the temperature variation of (a) real part ε' and (b) imaginary part ε' of the dielectric constant. The used frequencies are: 30, 100, 300, 1000, 3000, 10000 and 30000 Hz

cally chopped at 10 s intervals so that both were determined in a single temperature scan.

Standard *TSDC* measurements were also performed on the samples. The experimental set up and the procedure used by us are extensively described in Ref 7.

Complementary d.s.c. measurements have also been carried out by means of a Perkin Elmer DSC-2 calorimeter.

RESULTS

The ε' and ε'' variation for the used frequencies directly obtained from the recorder are plotted in *Figure 1*. As can be seen in *Figure 2*, the ε' step, Δε', obtained from *Figure 1a*, follows a Curie–Weiss law given by:

$$\Delta\varepsilon' = \varepsilon_s - \varepsilon_\infty = \frac{240}{T-283} \qquad (1)$$

where ε_s and ε_∞ are the low and high frequency limits of the dielectric constant and T is the absolute temperature. However, the Curie temperature obtained ($T_c = 283$ K) is always below the glass transition temperature, T_g. In this range of temperatures the material is out of equilibrium and so the expression (1) cannot be extended. Therefore this T_c value should be considered as the temperature of an ideal ferroelectric transition.

However, in *Figure 1b*, a high temperature experimental tail associated with the a.c. conductivity is observed. From this tail one can obtain the temperature dependence of conductivity. For all the used frequencies, an Arrhenius behaviour has been found with an activation energy of about 1.5 eV, similar to the one observed by d.c. conductivity measurements, 1.7 eV.

For a given temperature the frequency dependence of the a.c. conductivity is easily obtained giving:

$$\sigma_{ac} \propto \omega^{-0.88} \qquad (2)$$

where ω is the angular frequency. This bahaviour is characteristic of a Jonscher law[8] $\sigma \propto \omega^{n-1}$, with $n = 0.12$ in our case. This low value indicates a low contribution of a the hopping charge carriers between neighbour sites to the a.c. conductivity.

By subtracting the conductivity losses, a pure dipolar contribution for ε'' is obtained. This contribution is generally related to a distribution of dielectric relaxation times. Information about its characteristics is usually obtained by means of Cole–Cole like representations. *Figure 3* shows a Cole–Cole plot obtained from the pure dipolar contribution to the dielectric relaxation at several temperatures above the glass transition. This data shows the observed dielectric relaxation is in agreement with the well known Havriliak–Negami equation for the dielectric constant,ε*:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{(1+(i\cdot\omega\tau)^\beta)^\alpha} \qquad (3)$$

where τ is the relaxation time and α and β are parameters describing the distribution of relaxation times. This

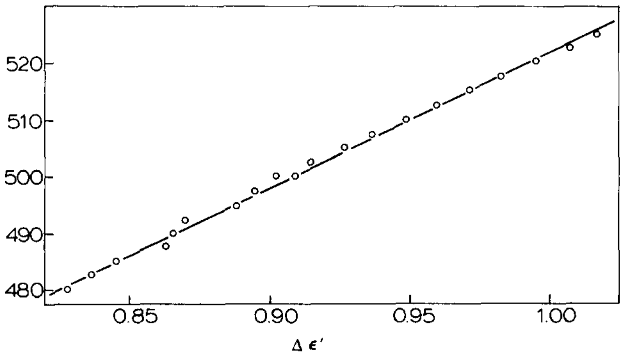

Figure 2 Temperature variation of the difference between the low frequency limit, ε_s and the high frequency limit, ε_∞, of the dielectric constant

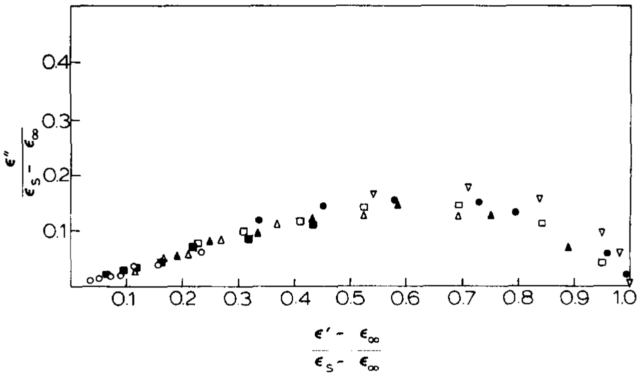

Figure 3 Cole–Cole plot at: (△) 490 K; (●) 482.5 K; (□) 477.5 K; (▲) 475 K; (▽) 470 K; (■) 465 K and (○) 460 K, for the dipolar contribution to the dielectric relaxation

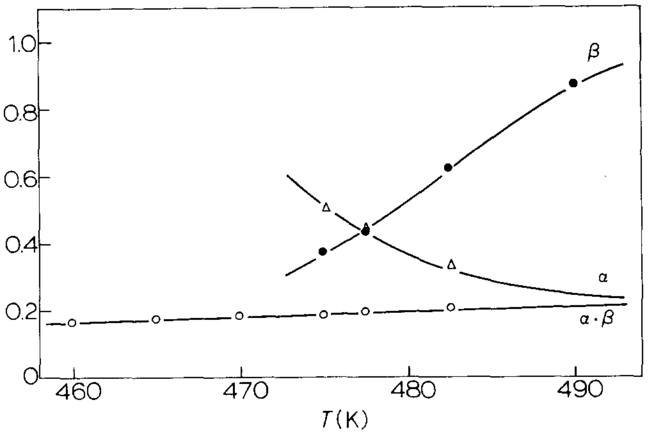

Figure 4 Temperature variation of empirical distribution parameters α and β obtained from *Figure 3*

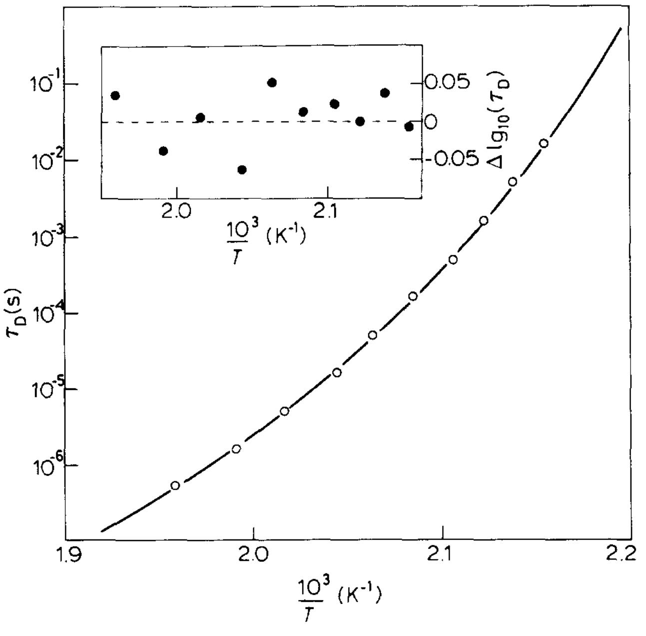

Figure 5 Temperature behaviour of the main dielectric relaxation time obtained from the a.c. measurements. The inset shows the deviation of the experimental points from the fitting curve

expression includes both Cole–Cole ($\alpha = 1$) and Cole–Davidson ($\beta = 1$) empirical distribution functions widely found in the literature for the α-relaxation in polymers[9]. As can be seen in *Figure 3*, the shape of the Cole–Cole plot at high temperature is in accordance with the Cole–Davidson distribution of relaxation times, whereas at lower temperatures it spreads to a Cole–Cole distribution. The parameters of the distribution, α and β, obtained from *Figure 3* are plotted against the temperature in *Figure 4*. The low frequency behaviour, described by β, depends strongly on the temperature; however, the changes in the high frequency behaviour, described by $\alpha \cdot \beta$, are moderate.

The above mentioned results indicate a distribution of relaxation times variable with the temperature as is commonly reported in the literature for other polymers[9]. At low temperature, the distribution is broad and symmetrical. When the temperature increases, the high relaxation times tail begins to vanish, and then, the distribution becomes strongly asymmetrical.

Although a distribution of relaxation times is clear, the condition $\omega\tau_D = 1$ at the temperature of the maximum of dipolar contribution to ε'' gives a main value of the relaxation time τ_D. By so doing, the evolution of τ_D with the temperature can be followed. *Figure 5* shows a plot of log τ_D *versus* the inverse temperature. The curvature in the plot suggests a Williams, Landel and Ferry[10] or the equivalent Vogel–Fulcher[11,12] behaviour given by:

$$\tau_D = A \exp\left(\frac{B}{T - T_0}\right) \tag{4}$$

where A, B and T_0 are empirical constants.

A computer program similar to that used in Ref. 13 was employed to obtain the values: $A = 2.4\ 10^{-14}$ s, $B = 2040$ K and $T_0 = 389$ K. These values are in the range of the usual ones found in the literature for amorphous polymers. The difference between the experimental points and the fitting curve is plotted in the inset of *Figure 5* and shows a random deviation.

On the other hand, *TSDC* measurements allow the dielectric relaxation time to be evaluated from the Debye equation for a single dielectric relaxation time τ_D:

$$\frac{dP}{dt} = \frac{P_0 - P}{\tau_D} \tag{5}$$

where P is the polarization of the sample and P_0 is the equilibrium polarization for a given electric field E_0 ($P_0 = \varepsilon_0 \chi E_0$).

The occurrence of a single relaxation time is very unusual in the α-relaxation of polymers; *TSDC*, however, has the possibility of separate different elementary processes contributing to a complex dielectric relaxation[14]. This possibility arises from the low equivalent frequency (10^{-2} to 10^{-3} Hz) and from the use of the thermal sampling technique[15], which allows the elementary processes to be separated.

The mean *TSDC* dielectric relaxation time was obtained, as in previous works[4], from the maximum intensity isolated *TSDC* peak. Its temperature variation is plotted in *Figure 6* showing an Arrhenius like, $\tau_D = C\exp(E/K_BT)$, behaviour up to a given temperature, which is close to the temperature of the maximum of the

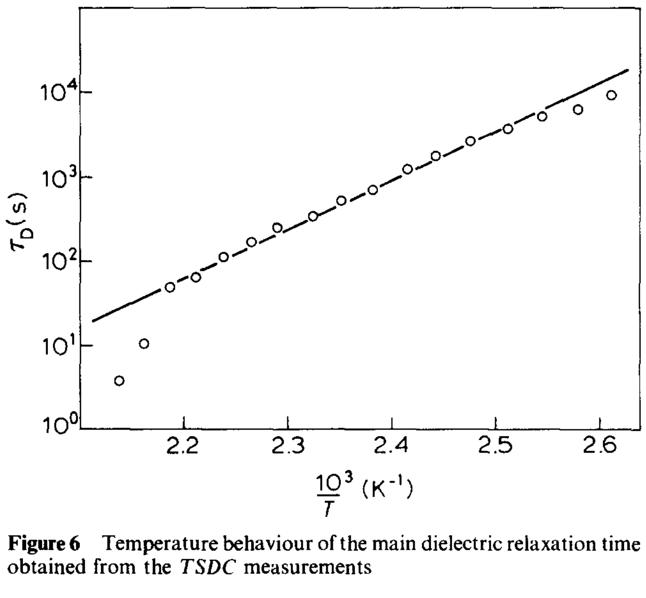

Figure 6 Temperature behaviour of the main dielectric relaxation time obtained from the *TSDC* measurements

peak. The values of C and E obtained fitting the experimental points are $1.3\ 10^{-11}$ s and 1.15 eV respectively.

FREE VOLUME INTERPRETATION

The empirical expression (4) is to be expected on the basis of the Debye theory relating the relaxation time to the viscosity, and the well known equation given by Doolittle for the latter[16]:

$$\eta = \eta_0 \exp\left(\frac{b}{f}\right) \tag{6}$$

where b is a factor close to unity and f is the fractional free volume of the liquid at equilibrium, which usually behaves close to $f = \alpha_f(T - T_0)$ at high temperatures. Here α_f is an expansion coefficient characteristic of the free volume and T_0 is the temperature at which the free volume vanishes. Hence the expression (4) can be written as:

$$\tau_D = \tau_0 \exp\frac{1}{\alpha_f(T - T_0)} \tag{7}$$

The empirical values A and B above obtained correspond to τ_0 and $1/\alpha_f$ respectively ($\alpha_f = 4.9\ 10^{-4}\ \text{K}^{-1}$).

In temperature varying a.c. measurements at a constant frequency ω in the experimental range used, the condition $\omega\tau = 1$ implies relaxation times between 10^{-2} and 10^{-7} s. Such relaxation times lie in the liquid at equilibrium, ($T > T_g$) at least for the heating rate employed by us. Doolittle behaviour is characteristic of the structural relaxation times in this liquid state. If the dielectric relaxation times are identified with the structural ones, similar Doolittle behaviour is found for the dielectric relaxation time. This identification is not ridiculous because, in polymers, dielectric α-relaxation is related to the motion of the structural dipole moments of the main chain. Such a process is closely related to the structural relaxation and this supports the above idea.

In marked contrast to a.c. measurements, *TSDC* technique allows us to obtain the dielectric response of polymer out of equilibrium, 'glassy zone' ($T < T_g$), because of its very low equivalent frequency.

The liquid to glassy transformation is the well known glass transition, characteristic of the glasses. Although the T_0 parameter can be seen as an ideal thermodynamic glass transition temperature, the actual glass transition takes place at $T_g > T_0$ when the structural relaxation time becomes greater than the experimental time of cooling. The configurational changes, characteristic of the liquid state, can no longer take place and a free volume is frozen-in in the material which is now in the glassy state. Below T_g, the out of equilibrium state of the glass can be described, at a given temperature, by means of a fractional excess free volume, δ, first introduced by Kovacs[17] as:

$$\delta = \frac{V - V_\infty}{V_\infty}$$

where V is the actual specific volume of the glass and V_∞ is that corresponding to the thermodynamic equilibrium at the same temperature.

Upon heating, the glass will try to return to equilibrium by elimination of excess free volume. This glass to liquid transformation, seen as a recovery of the equilibrium state, can be kinetically described by means of an equation for δ proposed by Kovacs[17]:

$$\frac{d\delta}{dt} = -\Delta\alpha . q - \frac{\delta}{\tau} \tag{9}$$

where $\Delta\alpha$ is the difference between the expansion coefficients of the liquid and the glassy zones, q is the rate constant of temperature variation and τ is the relaxation time which drives the return to equilibrium.

In a recent study[4] we proposed a free volume dependence for τ, even out of equilibrium, given by:

$$\tau(T,\delta) = \tau_0 \exp\left(\frac{1}{f + \delta}\right) \tag{10}$$

where $f + \delta$ is now the total fractional free volume. When the material is at equilibrium, 'liquid zone', δ vanishes and we recover the Doolittle behaviour for τ (7).

In the same study we also extended this picture to the dielectric α-relaxation of amorphous polymers with the above mentioned assumption of equivalence between the structural and dielectric relaxation times. One of the results reported there, is a relationship between q and T_g given by:

$$\ln q = \text{Const.} - \frac{1}{\alpha_f(T_g - T_0)} \tag{11}$$

where T_g is here defined as the temperature at which:

$$\frac{d\tau}{dT} = -1/q \tag{12}$$

Relation (11) can be seen as a generalization of the Ozawa expression:

$$\ln q = \text{Const.} - E/k_B T_g \tag{13}$$

commonly used to obtain kinetic parameters in many thermally stimulated processes[18].

Figure 7 shows the results obtained by standard d.s.c. measurements on PAr samples at different heating rates.

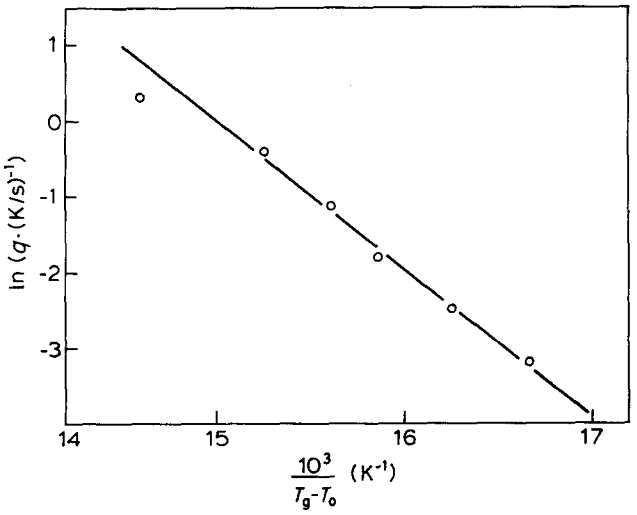

Figure 7 Kinetic variation of the calorimetric T_g of PAr. The cooling rate was $1.3\ \text{K s}^{-1}$ in all cases. The full line corresponds to the expression (11) with $\alpha_f = 4.9 \times 10^{-4}\ \text{K}^{-1}$ and $T_0 = 389\ \text{K}$

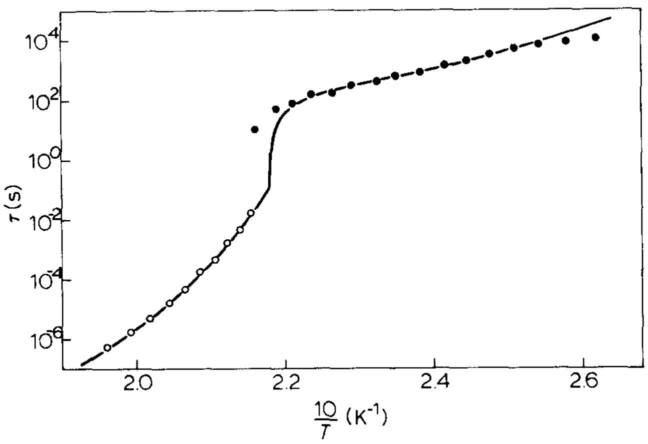

Figure 8 Experimental evolution of the main dielectric relaxation time τ_D: (○) from *TSDC* and (●) from a.c. measurements. The full line shows the behaviour described by the used model

T_g is obtained from the experimental scan as the temperature corresponding to the inflection point of the change in specific heat. This can be considered as a similar condition to that in expression (12) for a mean structural relaxation time[19]. As seen in *Figure 7* the experimental points follow an expression similar to expression (11) with the same values of empirical parameters, α_f and T_0, found in the preceding section of the dielectric relaxation time at equilibrium. This result conforms perfectly to the idea worked out by us of developed equivalence between the structural and dielectric relaxation times. For heating rates higher than the previous cooling rate the approximations made to draw the expression (11) are no longer valid and the evolution of T_g deviates from (11). This deviation can also be observed in the Figure for the heating rate of 80 K min^{-1} similar to the cooling rate employed between successive scans in d.s.c. measurements.

As shown in Ref. 4 the apparent activation energy E_a for τ_D obtained from *TSDC* measurements is related to the excess free volume kinetic parameters by:

$$E_a = k_B T^2 \left(\ln\frac{\tau}{\tau_0}\right)^2 (\alpha_f - \Delta\alpha) \qquad (14)$$

at low temperature where τ is high. When this expression is applied to the experimental values obtained in the preceding section we obtain $\Delta\alpha = 4.3\ 10^{-4}\ \mathrm{K}^{-1}$.

Experimental values of τ_0, T_0, α_f and $\Delta\alpha$ together with equations (10) and (9) allows us to obtain a computer simulation of the mean dielectric relaxation time behaviour around T_g. As seen in *Figure 8*, this simulated behaviour is in good agreement with the experimental points over a wide range of temperatures around the glass transition for PAr.

However, the use of a mean relaxation time gives only an approximate account of the complex α-dielectric relaxation observed in PAr. A more complete interpretation of the experimental aspect related to the distribution of the relaxation time is now in progress in the framework of a generalized free volume model[20].

ACKNOWLEDGEMENTS

The authors wish to thank Mr J. I. Equiazabal and Dr J. J. Iruin for performing d.s.c. measurements and providing the PAr samples respectively.

REFERENCES

1 Hazama, K. *Jpn. Plastics* 1974, **8**, 6
2 Dickinson, B. L., Eur. Pat. EP58,404(8/25/82) and Maresa, L. M., Markus, M. and See, B., Eur. Pat. EP48,493(3/31/82) assigned to Union Carbide Corporation
3 Böttcher, C. J. F. and Bordewicijck, P. 'Theory of Electric Polarization', Vol. II, Elsevier, Amsterdam, 1978, p. 72
4 Alegria, A., Barandiarán, J. M. and Colmenero, J. *Phys. Stat. Solidi(b)* 1983, **120**, 349
5 Equiazabal, J. I., Calahorra, E., Cortazar, M. and Iruin, J. J. *Polym. Eng. Sci.* (in press)
6 Abkowitz, M. and Pfister, G. *J. Appl. Phys.* 1975, **46**, 2559
7 Barandiarán, J. M., del Val, J. J., Colmenero, J., Lacabanne, C., Chatain, D., Millan, J. and Martinez, G. *J. Macromol. Sci.-Phys.* 1983, **B22**, 645
8 Jonscher, A. K. *J. Mater. Sci.* 1981, **16**, 2037
9 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967
10 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 4701
11 Vogel, H. *Phys. Z.* 1921, **22**, 645
12 Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, **6**, 339
13 Barandiarán, J. M., Telleria, I., Rivacoba, A. and Colmenero, J. *Thermochim. Acta* 1983, **63**, 255
14 Chatain, D., Lacabanne, C., Maitrot, M., Seytre, G. and May, J. F. *Phys. Stat. Solidi* (*a*) 1973, **16**, 225
15 Hino, T. *J. Appl. Phys.* 1975, **46**, 1956
16 Doolittle, A. K. *J. Appl. Phys.* 1951, **21**, 1471
17 Hutchinson, J. M. and Kovacs, A. J. *J. Polym. Sci.* 1976, **14**, 1575
18 Chen, R. and Kirsh, Y. 'Analysis of Thermally Stimulated Processes', Int. Ser. Sci. Solid State, Vol. 15, Pergamon Press, New York, 1981
19 Chow, T. S. *Polymer* 1983, **24** (*Commun.*), 77
20 Alegria, A., Barandiarán, J. M. and Colmenero, J., submitted to *Phys. Stat. Solidi* (*b*), 1984