The low temperature relaxation mechanisms in poly(vinyl acetate): a thermally stimulated currents study

Ana B. Dias and Joaquim J. Moura Ramos*
Centro de Química-Física Molecular, Complexo I, IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

and Graham Williams
Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, UK
(Received 15 March 1993; revised 19 July 1993)

The dipolar relaxation behaviour of poly(vinyl acetate) has been studied extensively in the low temperature region from -160 to $-20°C$. It is shown that the observed relaxation peak does not correspond to a single relaxation process but to a continuous distribution of relaxation times. The components of this distribution show Arrhenius behaviour and the corresponding activation energies are low ($\sim 8\,\mathrm{kcal\,mol^{-1}}$), which suggests that the dipolar motions involved are local motions, probably internal rotations about single bonds in the acetate groups. A continuous increase of the Gibbs activation energy for higher temperature components is observed, which is a consequence of a lowering of the activation entropy (the higher temperature relaxation modes have more negative activation entropies).

(Keywords: thermally stimulated current; poly(vinyl acetate); dipolar relaxation)

INTRODUCTION

Thermally stimulated currents (t.s.c.) is a technique to measure the thermally stimulated discharge current resulting from release of the polarization that was frozen in during a previous electric field poling. This poling is carried out at an elevated temperature with subsequent cooling in the presence of the field. The t.s.c. analysis of polymers is increasingly recognized as a rich source of information about polymeric materials. The first t.s.c. experiment was performed in 1964 in the study of point defects in alkali halides, and the theoretical basis of the method was developed in 1966[1]. The t.s.c. technique has been applied to the study of transitions in polymers since 1971[2].

The t.s.c. technique presents some experimental difficulties. First, the currents measured are of very small intensity (10^{-8}–10^{-16} A) so the equipment used must have very good resolution power and, in particular, the sample should be shielded from external electrical interference. The temperature stability and control are also highly important, especially the linearity of the heating rate. The atmosphere of the sample is also important: since high vacuum may interfere with good thermal control, an inert gas atmosphere (helium, for example) at a pressure near atmospheric provides the best conditions for performing t.s.c. experiments. These experimental difficulties are overcome by commercial t.s.c. apparatus which provides very good experimental conditions.

The t.s.c. technique has an inherently high resolution and a low noise level[3]. van Turnhout[1] has shown that a t.s.c. experiment is equivalent to a low-frequency dielectric loss experiment and that the equivalent frequency is:

$$f=\frac{E_a r}{2\pi R T_m^2}$$

where E_a is the activation energy, r the heating rate, R the ideal gas constant and T_m the temperature at which the t.s.c. peak has its maximum. For a heating rate of $4°C\,\mathrm{min}^{-1}$, a peak with $E_a=60\,\mathrm{kcal\,mol^{-1}}$ occurring at $T_m=320$ K will have an equivalent frequency of 3×10^{-3} Hz. For relaxation processes occurring at cryogenic temperatures (with concomitant lower activation energies) the equivalent frequencies will be 10^{-5} Hz or lower. This low equivalent frequency of the t.s.c. technique leads to an enhancement of the resolution of the different relaxation processes. This means that the separation of the peaks along the temperature axis is greater in t.s.c. than in other higher frequency techniques such as dielectric relaxation spectroscopy.

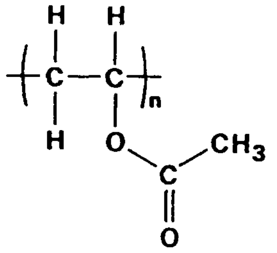
Poly(vinyl acetate) (PVAc) is an amorphous polymer whose glass transition is near room temperature. Many studies have been published concerning the relaxation behaviour of PVAc and it is often used as a standard for experimental measurements and to test the current theories of dielectric relaxation. From a chemical point

---

* To whom correspondence should be addressed

0032-3861/94/06/1253–05

of view it has a main chain formed by carbon–carbon single bonds at which polar acetate side groups are connected:



Two relaxation mechanisms have been identified in this polymer by dielectric relaxation spectroscopy: the main dispersion, the so-called α-process, which is associated with the glass transition and is attributed to the Brownian motion of the segments of the main chain; and a lower temperature mechanism, the β process, which is attributed to the movements of the side groups. The α relaxation of PVAc has been studied in great detail[4–6]. The log f_m (frequency of maximum loss) *versus* $1/T$ plot is well described by a Williams–Landel–Ferry type equation and the apparent activation energy was found to be near 55–60 kcal mol^{-1} at temperatures near 55°C. The β relaxation is a lower temperature process and the corresponding loss peak is of much smaller amplitude and broader than the α peak. It shows Arrhenius behaviour and the activation energy is 10 kcal mol^{-1} (ref. 4).

While the dielectric relaxation of amorphous polymers, including PVAc, is well documented in the literature[4], measurements made over wide ranges of frequency and temperature show that the dielectric α and β processes exhibit rather broad loss peaks, especially the β process, whose half-width for the ε'' *versus* $\log(f/\mathrm{Hz})$ plots may be as large as six decades of frequency. The t.s.c. technique may give information on the component processes of such loss peaks, since it is possible to polarize and depolarize a sample using different conditions, as described below. Therefore the present t.s.c. measurements for PVAc at low temperatures may aid our understanding of the processes that contribute to the overall β process in this polymer. PVAc is a model polymer whose dielectric properties, as a function of frequency and temperature, have been well documented[4], but t.s.c. studies of this polymer are scarce, particularly in the low temperature region. Vanderschueren[7] reports a low temperature relaxation in PVAc (~ -140°C), a β relaxation, which is attributed to local motions of dipolar groups, but this peak was not studied in detail. One aim of the present work is to make a systematic study of the low temperature dielectric relaxation mechanisms in PVAc using the t.s.c. method. This relaxation mechanism is studied in detail using different polarizing techniques and thermal treatments, namely the techniques of partial polarization, partial depolarization and thermal cleaning.

EXPERIMENTAL

The PVAc samples were of medium molecular weight, and were obtained from Aldrich (cat. no. 18,948-0). Prior to use, the samples were degassed by heating at 160°C in a vacuum oven for 8 h. This procedure prevents air bubble formation in the sample, particularly in experiments at higher temperatures, and warrants good electrical contact between the sample and the electrodes.

T.s.c. experiments were carried out with a TSC/RMA Spectrometer (Solomat Instruments, Stamford, CT, USA) covering the range -170 to $+400$°C. A Faraday cage shielded the sample and, prior to the experiments, the sample was evacuated to 10^{-4} mbar and flushed several times with 1.1 bar of high purity helium.

Different methods of polarizing the sample were used, in order to analyse the different peaks in the t.s.c. spectra.

Method 1. To obtain the global t.s.c. spectra of a given peak the sample was first polarized with a static field ($E \approx 10$–$500\ \mathrm{V\,mm^{-1}}$) at a temperature, T_p (polarization temperature), well above the peak maximum (T_m) during a certain time (2–10 min) and then quenched to the 'freezing temperature', T_0, in the presence of the field. The temperature T_0 is well below the temperature region where the peak appears, and the cooling to T_0 in the presence of the field enables the dipolar orientation to be frozen. With the field off and the sample short-circuited, the depolarization current due to dipolar reorientation was measured as the temperature was increased at a constant rate (4°C min^{-1}) from T_0 to a final temperature $T_f \geqslant T_p$. This method of polarizing the sample is termed t.s.c. global experiment.

Method 2. To analyse the components of a complex relaxation process we applied the polarization field ($E \approx 400$–$500\ \mathrm{V\,mm^{-1}}$) during the following thermal cycle: 5 min at T_p and quenching to $T_p - 5$°C. T_p is in the temperature range at which the peak appears. The field is then removed, the sample remains isothermal for 2 min and is then quenched to a temperature T_0 well below the peak's temperature region (~ 50°C below T_p). The depolarization current was then measured as the temperature was increased at a constant rate (4°C min^{-1}) from T_0 to a temperature T_f well above the peak maximum ($T_f \approx T_p + 40$°C). Different experiments with T_p varying in the peak's temperature range allow activation of fractions or segments of the global t.s.c. spectrum of the peak (narrow relaxation distributions). This technique of polarizing the sample is called thermal cleaning or thermal windowing, and enables the global peak to be separated into the individual relaxation modes.

Method 3. To check whether a dipolar peak is inhomogeneously broadened we performed a partial depolarization experiment. This is similar to the global t.s.c. experiment but has two discharge cycles: in the first the temperature T_f is in the peak temperature range ($T_f \approx T_m - 5$°C) and then lowered immediately to a temperature well below this range ($T_f - 50$°C). The sample is then heated again at constant rate (4°C min^{-1}) in the second discharge cycle and the depolarization current is measured until $T_f \approx T_m + 50$°C. In the first discharge cycle some of the lower temperature relaxation modes are allowed to relax and the peak obtained in the second discharge cycle contains only the higher temperature relaxation modes of the global peak.

Method 4. In contrast to method 3, this allows the lower temperature relaxation modes of the global peak to be isolated. The thermal cycle for this experiment is similar to that of method 1 but different experiments are performed at different polarization temperatures, T_p. These T_p are not, as in method 1, well above T_m but they are in the temperature range at which the peak appears.

These experiments allow polarization of only a part of the global peak (the lower temperature side) and thus we will call them partial polarization experiments.

RESULTS AND DISCUSSION

In our t.s.c. study of PVAc we observed one peak at low temperature ($T_m \approx -138°C$). *Figure 1* (curve 1) shows the result of a t.s.c. global experiment in this low temperature region. The shape of this curve indicates that we are in the presence of a rather complex mechanism where two regions can be distinguished: a lower temperature and more intense region, and a broader region of weaker intensity on the high temperature side of the peak. The most intense lower temperature component can be isolated by changing the polarization temperature, T_p, as shown by curve 2 in *Figure 1*.

A more careful inspection of this curve shows that the corresponding relaxation mechanism is itself a complex one, showing a shoulder on the lower temperature side. This lower temperature component can be isolated by carrying out partial polarization experiments with $T_p < T_m$, where T_m is the temperature at which the intensity of the peak is a maximum. The results of these experiments are shown in *Figure 2*. When we polarize at $-150°C$ (curve 1) we only excite the lower temperature relaxation mechanisms contained in this peak, and we can observe an increasing broadening as T_p increases. The analysis of this low temperature component ($T_m = -142°C$) by the Bucci method[8]* shows Arrhenius behaviour and its activation energy is $9.0\,\mathrm{kcal\,mol^{-1}}$. This value of the activation energy is of the same order of magnitude as that observed for barriers of internal rotation about single bonds in low molecular weight molecules[9], suggesting that this mechanism corresponds to a local motion involving the acetate side group. On the other hand, the Eyring activation entropy of this relaxation process is small and positive ($7\,\mathrm{cal\,K^{-1}\,mol^{-1}}$).

The high temperature component of this relaxation process, on the other hand, can be isolated experimentally by carrying out a partial depolarization experiment. *Figure 3* shows the results of such an experiment, where the global peak (curve 1) was depolarized until $-146°C$ in the first discharge cycle. Curve 2 is the high temperature component ($T_m = -133°C$) obtained in the second discharge cycle. Curve 2 shows Arrhenius behaviour and the corresponding activation energy is $8.0\,\mathrm{kcal\,mol^{-1}}$, similar to that obtained for the low temperature component. The Eyring activation entropy for this relaxation mechanism is negative ($-12\,\mathrm{cal\,K^{-1}\,mol^{-1}}$), indicating a more ordered or more symmetric activated state for this local motion. *Figure 4* shows the Arrhenius plots corresponding to two peaks of the lower temperature component obtained by partial polarization, and two peaks of the higher temperature component obtained by partial depolarization of the global peak.

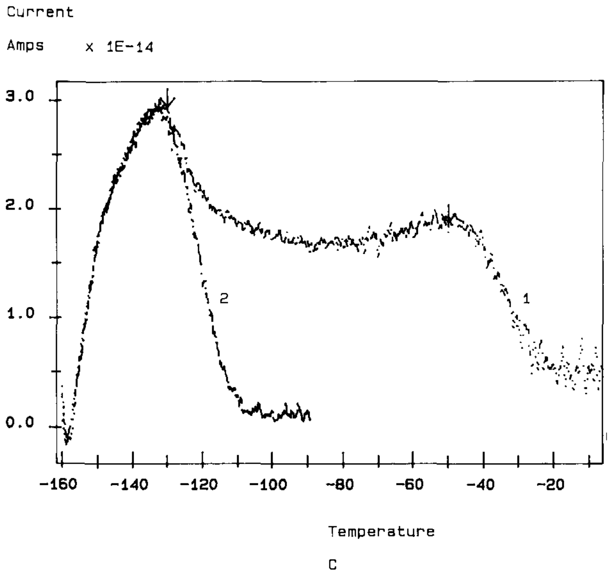


Figure 1 Low temperature relaxation peak of PVAc obtained from t.s.c. global experiments (method 1). Curve 1, $T_p = -50°C$; curve 2, $T_p = -130°C$

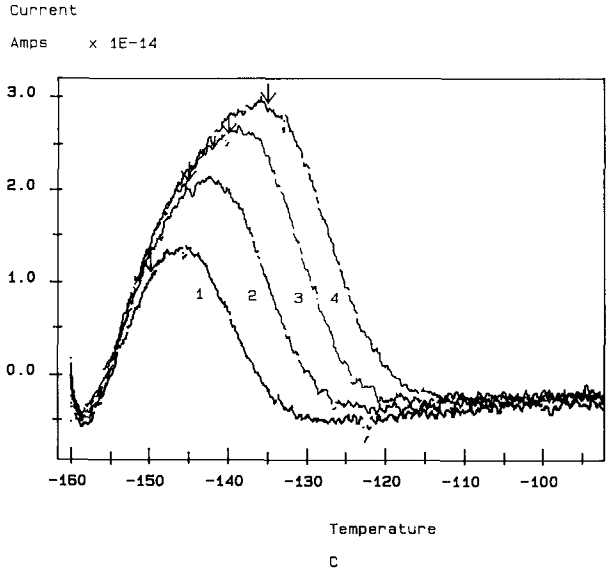


Figure 2 Partial polarization of the low temperature peak of PVAc. Curve 1, $T_p = -150°C$; curve 2, $T_p = -145°C$; curve 3, $T_p = -140°C$; curve 4, $T_p = -135°C$

The fine structure of this complex relaxation process has also been studied by the technique of thermal cleaning (method 2). *Figure 5* shows the results of four such experiments in which different segments of the global peak are polarized (different polarization windows). The Arrhenius plots corresponding to these experiments are shown in *Figure 6*, which confirms the Arrhenius behaviour of these relaxation processes. The treatment of these results also confirms that the high temperature component of this peak has a negative activation entropy.

The dipolar nature of the relaxation processes discussed before is confirmed by the fact that the intensity of the peak, as well as the relaxed charge (the area under

---

*The Bucci method for obtaining the kinetic parameters of the t.s.c. relaxation peaks assumes the Debye equation:

$$J(t) = \frac{\mathrm{d}P(t)}{\mathrm{d}t} = -\frac{1}{\tau(T)}P(t)$$

according to which the rate of change of the polarization at any time of the depolarization process, $J(t) = \mathrm{d}P(t)/\mathrm{d}t$, is proportional to the remaining polarization, $P(t)$; the proportionality constant is the inverse of the relaxation time at the corresponding temperature, $\tau(T)$, and this relaxation time is thus obtained from the quotient $J(T)/P(T)$, where $J(T)$ is the measured current at temperature T and $P(T)$ is the surface area of the discharge peak from T to infinity. The activation parameters of the corresponding process are thus obtained from the fitting of $\tau(T)$ *versus* $1/T$ using an Arrhenius or Eyring type equation

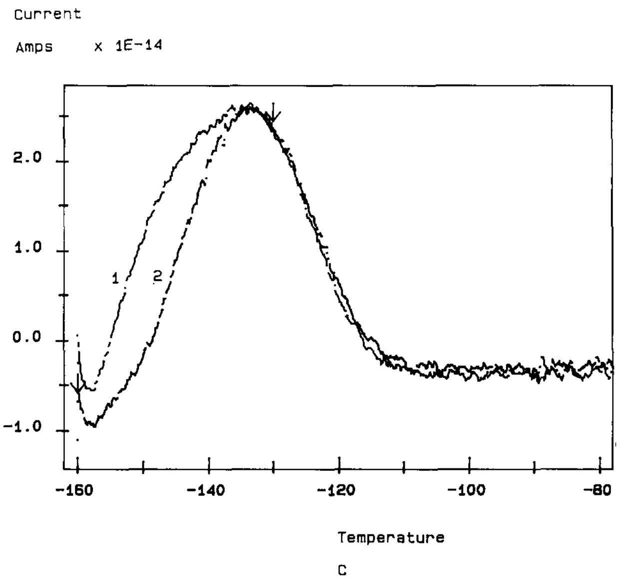


Figure 3 Partial depolarization of the low temperature peak of PVAc. Curve 1, same as curve 2 in *Figure 1*; curve 2, $T_p = -130°C$, depolarized until $-146°C$ in the first discharge cycle

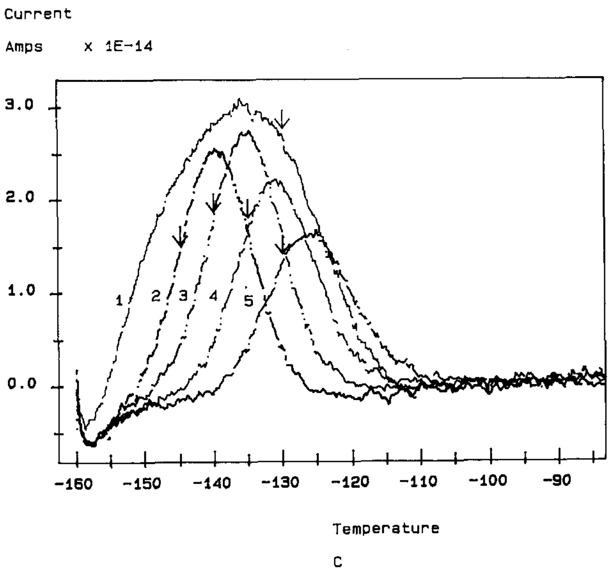


Figure 5 Thermal cleaning of the global peak (curve 1). Curve 2, $T_p = -145°C$; curve 3, $T_p = -140°C$; curve 4, $T_p = -135°C$; curve 5, $T_p = -130°C$; polarization windows of 5°C

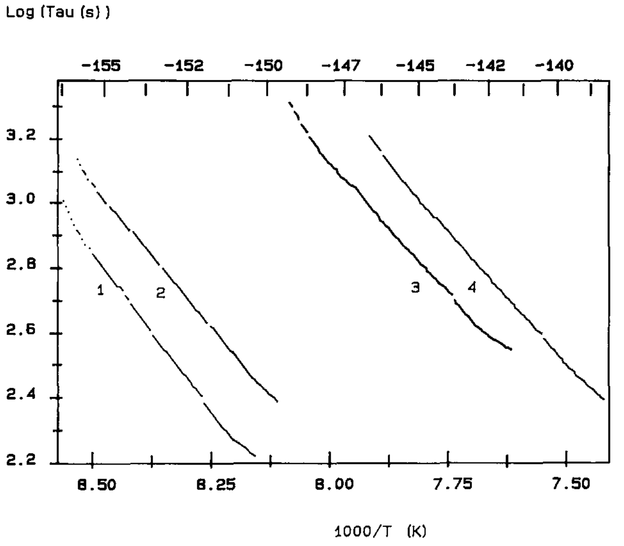


Figure 4 Bucci plot of the calculated relaxation time, τ, *versus* $1/T$ for the lower temperature component obtained from partial polarization experiments (curves 1 and 2) and for the higher temperature component obtained from partial depolarization experiments (curves 3 and 4)

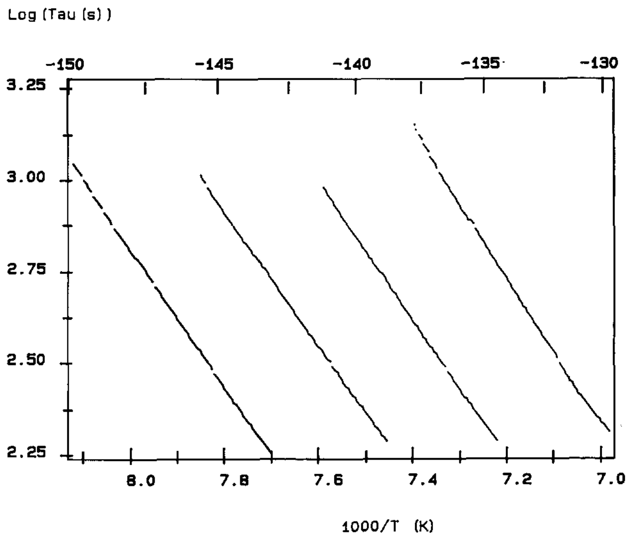


Figure 6 Bucci plots of the calculated relaxation time, τ, *versus* $1/T$ for the thermally cleaned segments of the global peak. The activation energy calculated from the fitting of these lines is 8.5 kcal mol^{-1}

the peak), shows a linear variation with the polarization voltage. *Figure 7* shows the variation of the peak's maximum intensity (and of the peak's area) as a function of the polarization voltage. The linearity of this variation is shown without any ambiguity.

The broader and lower intensity high temperature region of this complex discharge mechanism (curve 1 of *Figure 1*) has been studied by the technique of thermal cleaning. Different segments of this relaxation process have been polarized (temperature windows of 5°C) at different polarization temperatures. The results of some of the experiments are shown in *Figure 8*, which shows that the amplitude of the peaks does not change significantly for polarization temperatures in the range from -110 to $-40°C$ and that the peak location (its temperature of maximum intensity, T_m) changes continuously with the polarization temperature. This variation of T_m with T_p is linear, as shown in *Figure 9*,

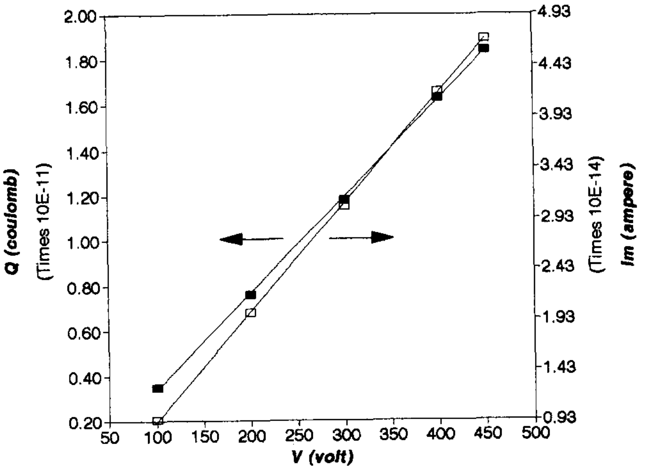


Figure 7 Maximum intensity, I_m, (and relaxed charge, Q) *versus* polarization voltage

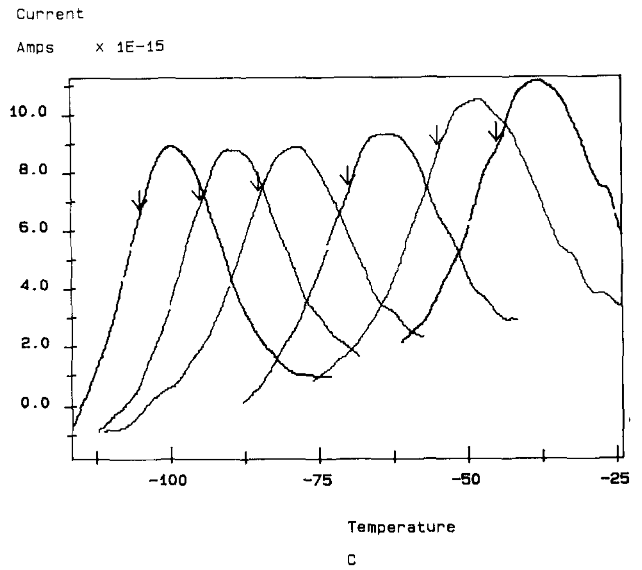


Figure 8 Elementary components of the broad, higher temperature side of the global peak obtained from thermal cleaning experiments (polarization windows of 5°C) at different polarization temperatures. The arrows indicate the polarization temperature for each experiment

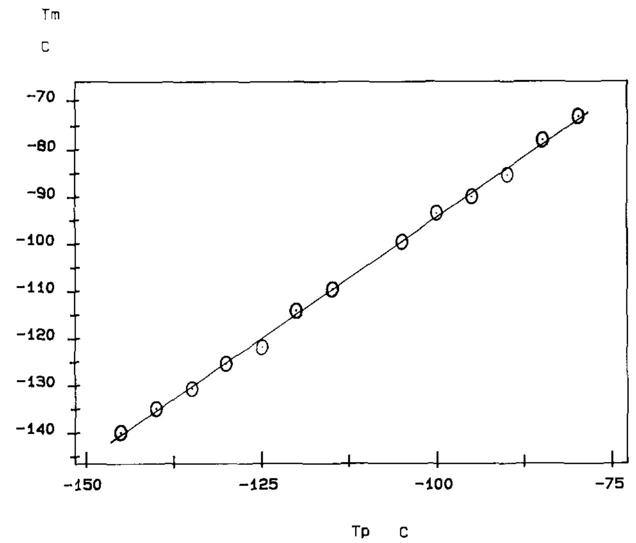


Figure 9 Temperature of maximum intensity, T_m, *versus* polarization temperature, T_p, for the different thermally cleaned components of the whole relaxation process

even for the higher intensity and lower temperature part of the peak, and suggests the presence of a continuous distribution of relaxation times[10,11].

The activation energy of the different polarized segments is nearly constant (8 kcal mol^{-1}) but the Eyring activation entropy becomes more negative as the polarization temperature increases (the pre-exponential factor, τ_0, increases with increasing T_p). As a consequence, the Gibbs activation energy increases continuously with the increase of T_p, as shown in *Figure 10*.

CONCLUSIONS

We conclude that this low temperature relaxation mechanism in PVAc is a complex one in which at least two regions can be distinguished: a higher intensity and lower temperature ($T < -120°C$) region, and a

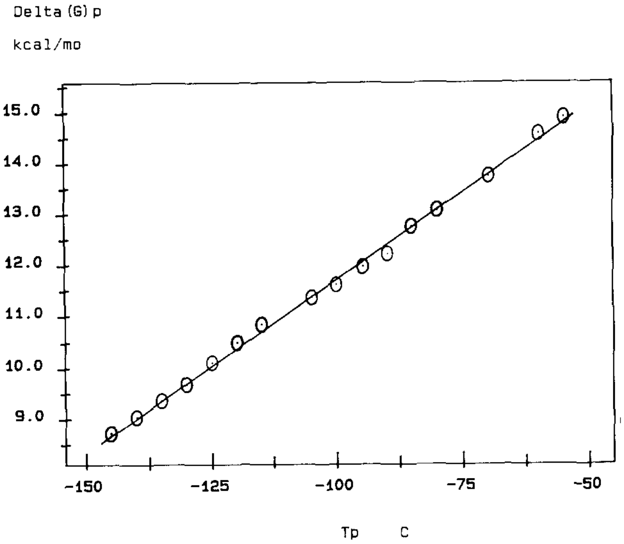


Figure 10 Variation of the Gibbs activation energy with the polarization temperature for the different thermally cleaned components of the whole relaxation process

broader, lower intensity, higher temperature region ($-120°C < T < -30°C$). The low values of the activation energies obtained for all segments of this complex mechanism suggest that it is related to local motions involving the acetate side groups. These motions may be associated with the internal rotation about the carbonyl carbon–oxygen single bond, which leads to a change of orientation of the dipoles of the carbonyl group, of the methyl group, as well as of the smaller dipole of the carbon(sp^3)–carbon(sp^2) single bond. A more detailed attribution of those motions would require the use of more microscopic techniques. Nevertheless, our results constitute a demonstration of the high resolution power of the t.s.c. technique.

ACKNOWLEDGEMENT

This work was carried out under the auspices of the Unidade de Química e Física de Materiais (Instituto de Ciência e Engenharia de Materiais e Superfícies, ICEMS).

REFERENCES

1 van Turnhout, J. *Polym. J.* 1971, **2**, 173
2 Ibar, J. P., Denning, P., Thomas, T., Bernes, A., de Goys, C., Saffell, J. R., Jones, P. and Lacabanne, C. in 'Polymer Characterisation: Physical Property, Spectroscopy and Chromatographic Methods' (Eds C. D. Craver and T. Provder), Advances in Chemistry Series no. 227, American Chemical Society, Washington, DC, 1990
3 Carr, S. H. in 'Electrical Properties of Polymers' (Ed. D. A. Seanor), Academic Press, New York, 1982
4 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids' 2nd Edn, Dover Publications, New York, 1991
5 Mashimo, S., Nozaki, R., Yagihara, S. and Takeishi, S. *J. Chem. Phys.* 1982, **77**, 6259
6 Nozaki, R. and Mashimo, S. *J. Chem. Phys.* 1987, **87**, 2271
7 Vanderschuren, J. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 873
8 Bucci, C., Fieschi, R. and Guidi, G. *Phys. Rev.* 1966, **148**, 816
9 Orville-Thomas, W. J. (Ed.) 'Internal Rotation in Molecules' John Wiley, London, 1974
10 Berticat, P., Chatain, D., Monpagens, J. C. and Lacabanne, C. *J. Macromol. Sci. — Phys.* 1978, **B15**, 549
11 Gourari, A., Bendaoud, M., Lacabanne, C. and Boyer, R. F. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 889