Thermally stimulated depolarization currents used in the study of chemical relaxation

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An equilibrium reaction between two species, A and B, which carry different dipole moments can give a specific peak in thermally stimulated depolarization current (TSDC) diagrams of solids if the orientation of B is slow with respect to the chemical reaction. The expression for the current is derived: dipole moments and the thermodynamic kinetic parameters can be obtained from the TSDC relative to the chemical reaction and that due to dipolar disorientation. An experimental illustration is given for an aromatic poly(sulphopropylbetaine) in which a thermally induced conformational change of the zwitterionic group is observed: using three approximations, the dipole moment $\mu \approx 12D$ in the low T curled conformation and $\mu \approx 23D$ in the extended conformation. The rate constants of the forward and back reactions are determined as a function of temperature.

(Keywords: thermally stimulated depolarization currents; chemical relaxation; polyzwitterions)

INTRODUCTION

The thermally stimulated depolarization technique is widely used to study dipole and space charge relaxation as well as charge injection and detrapping. Methods for extracting parameters from the heating curves are described in the literature[1]. However, for poly(4-vinyl-1-3-sulphopropylpyridiniumbetaine), experimental curves which could not be explained with classical concepts have been obtained. In this paper the curves are described and an interpretation is suggested.

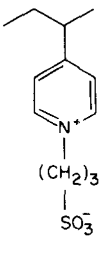
EXPERIMENTAL

The polymer studied was poly(4-vinyl-1-3-sulphopropylpyridiniumbetaine) which was prepared by Galin *et al.* as described in Reference 2. Each constitutive unit bears a dipolar ion in the side chain (see *Scheme 1*). The experiments aimed to determine the dielectric constant increment of this polyzwitterion, hereafter called B-3, by using thermally stimulated depolarization currents (TSDC).

The polymer is amorphous and is in the glassy state up to 220°C, above which it decomposes[3]. As it is hygroscopic, it was dried (60°C, 0.01 torr, 18 h) and immediately pressed at room temperature (40 MPa). The discs, diameter 12 mm, thickness $(e) \approx 1$ mm were silver coated by painting. They were further dried in the TSD device above 100°C for >6 h under 10^{-2} torr pressure after they had been set between stainless steel electrodes, which exerted a slight pressure through a weak spring, and put in a gas-tight chamber. Once it was filled with nitrogen, a voltage V_p was applied at high temperature for time t_p, after which the sample was quenched and then the field removed. Current was measured with a Keithley 617 electrometer and a linear heating scheme was used. The voltage of a thermocouple set in one of the electrodes, near the sample, and the current were recorded simultaneously.

Two typical TSDC diagrams are shown in *Figure 1*. They were obtained under the same conditions, except for the poling temperature which is 140°C (------) and 112°C (———). Above room temperature two maxima are observed on both curves, indicating two processes, but the faster, centred at 87°C, is more intense when a lower poling temperature is used. Classical theories of TSD processes cannot account for this. An interpretation is given below based on (1) a temperature dependent equilibrium occurring between two conformational isomers of the $-N^+-(CH_2)_3-SO_3^-$ groups and (2) dipole-dipole interactions between zwitterionic neighbours.

Scheme 1



B-3

THEORY

In an applied field E, the dipole contribution to the dielectric constant, $\Delta\varepsilon$, the dipolar part of the polarization P_μ, the dipole moment μ of the entities and concentration c (in mol m^{-3}) are related through:

$$\varepsilon_0 \Delta\varepsilon E = P_\mu = G_1 \mu^2 c \qquad \varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{F\,m^{-1}} \tag{1}$$

In condensed phase, it is impossible to give an exact expression for the parameter G_1. In what follows

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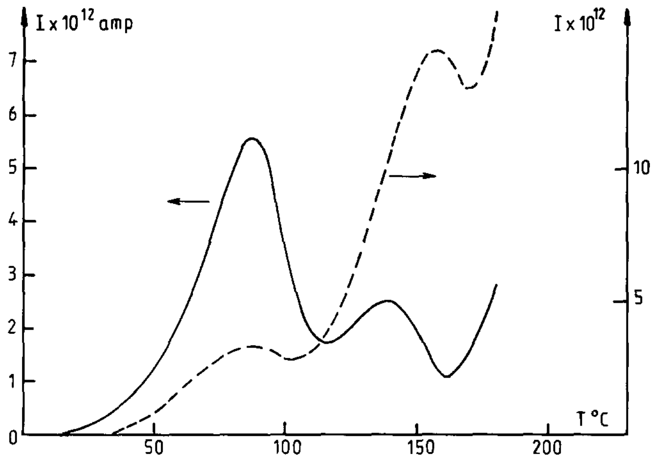


Figure 1 TSDC above room temperature for polyzwitterion B-3; $E_p = 720\ \mathrm{V\,cm^{-1}}$, $b = 4.6°\ \mathrm{min^{-1}}$. ———, $T_p = 112°\mathrm{C}$, $t_p = 5$ min; – – –, $T_p = 140°\mathrm{C}$, $t_p = 15$ min

Kirkwood's calculations[4] will be used in which

$$G_1 = NE/2kTg = Gg$$

where N is Avogadro's number and g a correlation factor which can be strongly temperature dependent.

The change in polarization will now be formulated when a thermally induced reversible reaction between two species, A and B, carrying different dipole moments μ_A and μ_B occurs in a small temperature interval. More explicitly, for B-3, it will be assumed that a low dipole moment bearing conformation of the zwitterionic group may expand into a high dipole moment bearing conformation as temperature increases. The two isomers would differ in distance between unlike charges.

At intermediate temperatures, in the electric field, the total polarization produced by A and B groups whose respective concentrations are A and B is not related simply to these quantities because the strong dipole and multipole interactions between the closely packed highly polar groups must be taken into account. It is not possible to calculate them and reference is made to Kirkwood's theory[4] to give a qualitative formulation. In a mixture of k molecules, the dielectric constant is expressed by equation (16) of Reference 4:

$$\varepsilon - 1 = \frac{9}{2} \sum_{k=1}^{\nu} C_K P_k$$

$$P_k = \frac{4\pi N}{3} (\alpha_K + \mu_K \cdot \bar{\mu}_K / 3kT)$$

By subtracting the optical contribution to the parameter P_k and using SI units, its dipolar part is given by

$$\Delta P_{k,\mathrm{dip}} = \frac{N}{3\varepsilon_0} \frac{\mu_K \cdot \bar{\mu}_K}{3kT}$$

where $\bar{\mu}_K$ is the total moment of a molecule and its neighbours in a region surrounding it where the local dielectric constant differs from the macroscopic one. In other words, $\bar{\mu}_k$ is the sum of the electric moment of a zwitterionic group and the moment which it induces in its neighbouring groups by hindering their rotation relative to itself.

Adapting this to the case considered here, the dipolar contribution of species A and B to the dielectric constant is

$$\Delta\varepsilon = \frac{N}{2kT\varepsilon_0} (A\mu_A \cdot \bar{\mu}_A + B\mu_B \cdot \bar{\mu}_B)$$

Both $\bar{\mu}_A$ and $\bar{\mu}_B$ are functions of μ_A, μ_B and concentrations.

The differential equation describing the equilibrium:

$$\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{B}$$

is

$$\frac{\mathrm{d}B}{\mathrm{d}t} = -k_r B + k_f A \tag{2}$$

where k_r and k_f are the rate constants for the reverse and forward reactions, respectively, which vary with temperature according to an Arrhenius law:

$$k_r = A_r \exp(-E_r/kT)$$

$$k_f = A_f \exp(-E_f/kT)$$

The equilibrium constant is defined as usual by

$$K = k_f/k_r = B/A$$

Furthermore,

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{\mathrm{d}B}{\mathrm{d}t}$$

and

$$A + B = C_0$$

where C_0 is the total concentration of the zwitterionic groups.

The TSD experiment consists of first heating the polymer to T_p. This temperature is supposed to be high enough to complete the reaction A → B and to allow for orientation of the highly polar dipolar ions when the electric field is applied. Subsequent quenching to T_0 while the field is maintained will freeze the polar B conformation in. The field is then withdrawn. If T_0 is low enough so that at T_0 the stable conformation is the less polar A form, then by heating the sample from T_0 to T_p depolarization will occur by two mechanisms: the B groups tend to adopt their less polar equilibrium conformation and they disorient. If the relaxation time characteristic of the equilibrium reaction is lower than that due to dipolar disorientation, as will be proposed below, two maxima will occur when recording the current while heating. The first, between T_0 and T_E, is due to the depolarization of the amount of B groups exceeding their equilibrium concentration B_E at T_E. The second, above T_E, is due to disorientation of the remaining dipoles. This is schematically shown in *Figure 2*. The sum of the areas of the two peaks is proportional to the polarization at T_p. By performing successive experiments with lower T_p's, one can, in principle, obtain the equilibrium $\Delta\varepsilon$ *versus* T curve provided the orientation is completed during the time of application of the field.

Since no field is present, the depolarization current density J due to the conformational change alone will be sensitive to the relative orientation of the dipole vector with respect to the molecular axis in the two conformations. If it is unchanged (case I), the expression for J is

$$J = -\frac{\mathrm{d}P}{\mathrm{d}t} = -G\left[\mu_A \cdot \frac{\mathrm{d}(A\bar{\mu}_A)}{\mathrm{d}t} + \mu_B \cdot \frac{\mathrm{d}(B\bar{\mu}_A)}{\mathrm{d}t}\right]$$

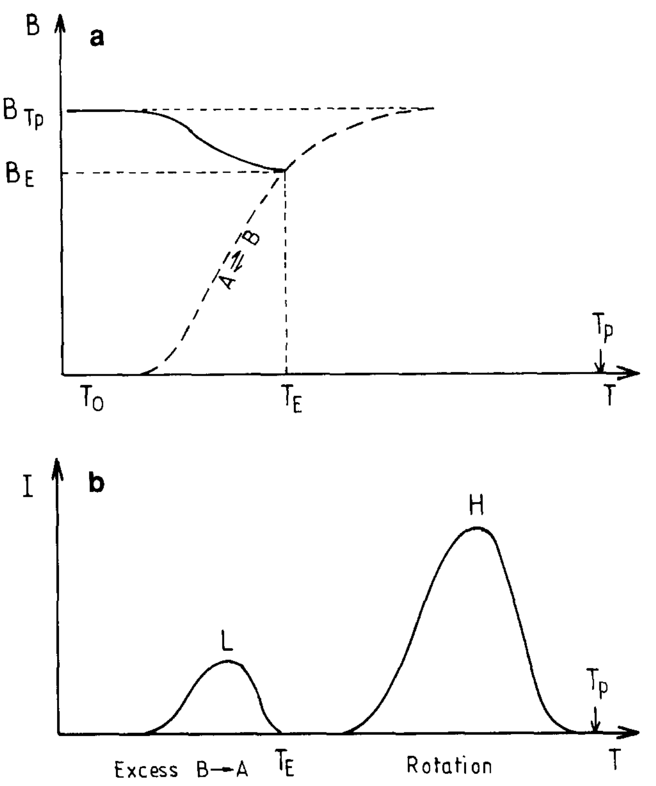


Figure 2 Schematic variation of: (a) concentration of species B with temperature; (b) depolarization current with temperature

It cannot be resolved in this general case. It cannot be resolved either if there is no correlation between the orientation of the A and B species while they react. The quantity $g_\infty \mu_B^2$ can be determined by adding the areas of the two peaks obtained for a high poling temperature T_p, such that $K_{T_p} \to \infty$. At such temperatures the parameter g is g_∞.

We introduce now the assumption $\mu_A = 0$ (case II). In this case, there is no need to know *a priori* whether the molecular axis carrying the dipole loses its field-induced orientation or not in the course of the conformational change. Equation (1) for $P = P_\mu$ is

$$P = Gg\mu_B^2 B$$

where g is the temperature dependent factor which describes the correlations between the polar B species. The variation of G with temperature will be neglected:

$$\frac{dP}{dt} = P\left[\frac{1}{g}\frac{dg}{dt} - (k_r + k_f)\right] + GC_0\mu_B^2 g k_f \qquad (3)$$

When linear heating rate is used in the experiments, $T = T_0 + bt$,

$$\frac{dP}{dt} = -Pf(T) + P_0\varphi(T) \qquad (4)$$

with

$$f(T) = \frac{1}{b}\left[(k_r + k_f) - \frac{1}{g}\frac{dg}{dT}\right]$$

$$\varphi(T) = \frac{1}{b} g k_f$$

$$P_0 = GC_0\mu_B^2$$

$$\frac{d\left\{P \exp\left[\int_{T_0}^{T_1} f(T')\,dT'\right]\right\}}{dT_1} = \varphi(T_1)P_0 \exp\left[\int_{T_0}^{T_1} f(T')\,dT'\right] dT_1$$

By integrating both members between T_0 and T and setting

$$Q(T) = \int_{T_0}^{T} \varphi(T_1) \exp\left[\int_{T_0}^{T_1} f(T')\,dT'\right] dT_1$$

$$P = [P_{T0} + P_0 Q(T)] \exp\left[-\int_{T_0}^{T_1} f(T')\,dT'\right]$$

$H(T)$ is defined as follows:

$$H(T) = \exp\left[-\int_{T_0}^{T} f(T')\,dT'\right]$$

By substituting $P = [P_{T_0} + P_0 Q(T)]H(T)$ into equation (4), the equation of the TSD curve is

$$-J = \frac{dP}{dT} = -[P_{T_0} + P_0 Q(T)]H(T)f(T) + P_0\varphi(T) \qquad (5)$$

The total area under this curve is equal to $P_{T_0} - P_{T_E}$.

To account for experimental observations in which this area increases when T_p decreases it is interesting to determine the conditions under which its derivative is zero. This is done by stating that $P(T_0) = P(T_p)$ if the cooling process is fast enough, that at T_E $J = 0$ and also that $B(T = T_E)$ is an equilibrium concentration B_E whose expression as a function of T is

$$B_E = \frac{KC_0}{1 + K}$$

Setting

$$R(T_E) = \frac{bf(T_E)}{k_{f,T_E} + k_{r,T_E}} = 1 - \frac{b}{g_{T_E}(k_{f,T_E} + k_{r,T_E})}\left(\frac{dg}{dt}\right)_{T=T_E}$$

the derivative is

$$\left(\frac{dP}{dT}\right)_{T=T_p} [1 - H(T_E)R(T_E)] - \frac{P_0\varphi(T_E)R'(T_E)}{f(T_E)} \qquad (6)$$

In this expression $R'(T_E)$ is the derivative of R at $T = T_E$. Note that, if the dipolar interaction parameter g does not vary with T, i.e. $R = 1$, the derivative cannot be zero. Thus, an increasing amount of depolarization with decreasing poling temperature can only occur when g varies with T.

Note also that $k_r(T)$ can be determined by using a further approximation. From equation (3) it is obvious that the beginning of the TSD curve (when $B/A \gg K$) can be expressed simply if $(b/g)(dg/dT) \ll k_r$. This will be detailed later; $k_f(T)$ can then also be determined.

The next three cases (III, IV and V) concern materials for which $g = 1$ (no dipole interactions) and $\mu_A \neq 0$. The amount of depolarization due to excess polar species reacting toward their equilibrium concentration during the heating stage in the absence of field will depend on the orientation of the molecular axis bearing dipole μ_A with respect to that carrying μ_B. First consider case III in which the component μ'_A of dipole μ_A is projected onto the axis carrying μ_B (the last remained oriented in the low T range under concern):

$$P = G[\mu_B^2 B + \mu_A'^2(B_{T_p} - B) + \mu_A^2(C_0 - B_{T_p})]$$

$$= G[B(\mu_B^2 - \mu_A'^2) + \mu_A'^2 B_{T_p} + (C_0 - B_{T_p})\mu_A^2]$$

$$\frac{dP}{dt} = G(\mu_B^2 - \mu_A'^2)\frac{dB}{dt}$$

With the help of equation (2) and using a similar procedure to that for case II, the expression of the depolarization current is

$$J = -G(\mu_B^2 - \mu_A'^2)\Big\{[B_{T_0} + C_0 Q(T)] \times \exp\left[-\int_{T_0}^{T} f(T')\,dT'\right] f(T) + C_0\varphi(T)\Big\} \qquad (7)$$

where

$$f(T) = \frac{1}{b}(k_r + k_f)$$

$$\varphi(T) = \frac{1}{b}k_f$$

$$Q(T) = \int_{T_0}^{T} \varphi(T_1)\exp\left[\int_{T_0}^{T_1} f(T')\,dT'\right] dT_1$$

Note that $B_{T_0} = B_{T_p}$ and that J does not depend on μ_A. The second, high temperature depolarization process depends on μ_A. At T_p, the total polarization is

$$P_{T_p} = G[B_{T_p}\mu_B^2 + (C_0 - B_{T_p})\mu_A^2] \qquad (8)$$

The area of the low T peak is:

$$P_L = G(B_{T_p} - B_E)(\mu_B^2 - \mu_A'^2) \qquad (9)$$

The area of the high T peak is:

$$P_H = G[B_E\mu_B^2 + (C_0 - B_{T_p})\mu_A^2 + (B_{T_p} - B_E)\mu_A'^2] \qquad (10)$$

To determine k_r, it is useful to note that in the general equation

$$\frac{dB}{dt} = -k_r B + k_f(C_0 - B)$$

if the second term of the right-hand side is negligible, which occurs in the low T part of the rising portion of the TSDC curve, the expression for J is the well known first order kinetics equation common to a variety of thermally stimulated phenomena

$$\frac{dP}{dt} = -Pk_r$$

The determination of k_r is straightforward from this equation: on the recording of J *versus* time, k_r is obtained by dividing the current density by the retained polarization, which is the area of the peak above time t. By relating temperature T and time t, a plot of $\ln k_r$ *versus* $1/T$ allows the determination of A_r and E_r. This is analogous to the Bucci–Fieschi–Guidi (BFG) plot for relaxation times[15].

The parameters A_f, E_f and $(\mu_B^2 - \mu_A'^2)$ can be obtained by curve fitting, using the TSD curve after one experiment at T_p such that $K \rightarrow \infty$ since $B_{T_p} = C_0$ is then known. The temperature T_E at which $J = 0$ allows the determination of $B_E = C_0 K_E/(1 + K_E)$ and equation (9) leads to μ_A', whereas equation (10) leads to the value of μ_A by using the experimental areas of the two peaks.

An alternative method to obtain A_f and E_f which avoids the curve fitting procedure is to perform two additional TSD experiments at T_{p2} and T_{p3} where the equilibrium constants are K_2 and K_3 and the concentrations of the B species are $B_{T_{p2}}$ and $B_{T_{p3}}$. Making use of the following expression for J for $k_f(C_0 - B_{T_p}) \ll k_r B$, which imposes the condition that T_{p2} and T_{p3} are high,

$$J = -G(\mu_B^2 - \mu_A'^2)k_r(T)B_{T_p}\exp\left[-\frac{A_r}{b}\int_{T_0}^{T}\exp -\frac{E_r}{kT}\,dT'\right] \qquad (11)$$

$B_{T_{p2}}$ and $B_{T_{p3}}$ can be obtained from the ratio of J in experiments 2 and 3 to that in experiment 1; the exponential in brackets is negligible with respect to that in k_r at low T. The constants K_2 and K_3, and thus $k_f(T)$ are then determined.

In case IV, the direction of μ_A is unchanged with respect to that of μ_B during the reaction. Equations (9)–(11) with $\mu_A' = \mu_A$ will hold.

In case V the A species is oriented at random through the chemical reaction in absence of field. Equations (9)–(11) with $\mu_A' = 0$ can be used. In the last two cases, $k_r(T)$, $k_f(T)$ and μ_A can, of course, be determined.

Case VI deals with $g = 1$ and $\mu_A = 0$. There is then no need for another postulate. Equation (7) with $\mu_A' = 0$ is used, and all the parameters are determined from the TSD curves. The various cases are summarized in *Table 1*.

Results for B-3

There are two pieces of evidence that B-3 possesses strong dipole correlations which vary with temperature. The first, already mentioned, is that P_L can be stronger for lower T_p. The second appears when the equilibrium $\Delta\varepsilon$ *versus* T_p curve, shown in *Figure 3*, is examined. $\Delta\varepsilon$ is obtained from $\Delta\varepsilon = P_{T_p}/\varepsilon_0 E$. Since the orientational relaxation is slower than the chemical relaxation it is

Table 1 Determination of unknowns in various cases

			Orientation of dipole A while B → A, $E=0$			Determination of:			
Case	μ_A	dg/dT	No correlation	Correlated	Expression for J (equation no.)	μ_B	μ_A	k_r	k_f
I	$\neq 0$	$\neq 0$	×	×	None	Yes	–	–	–
II	$=0$	$\neq 0$	–	–	(5)	Yes	0	Yes[a]	Yes
III	$\neq 0$	$=0$		$\mu_A' < \mu_A$	(7)	Yes	Yes and μ_A'	Yes	Yes
IV	$\neq 0$	$=0$		$\mu_A' = \mu_A$	(7)	Yes	Yes	Yes	Yes
V	$\neq 0$	$=0$	×		(7) with $\mu_A' = 0$	Yes	Yes	Yes	Yes
VI	$=0$	$=0$	–	–	(7) with $\mu_A' = 0$	Yes	0	Yes	Yes

[a] If $(b/g)(dg/dT) \ll k_r$

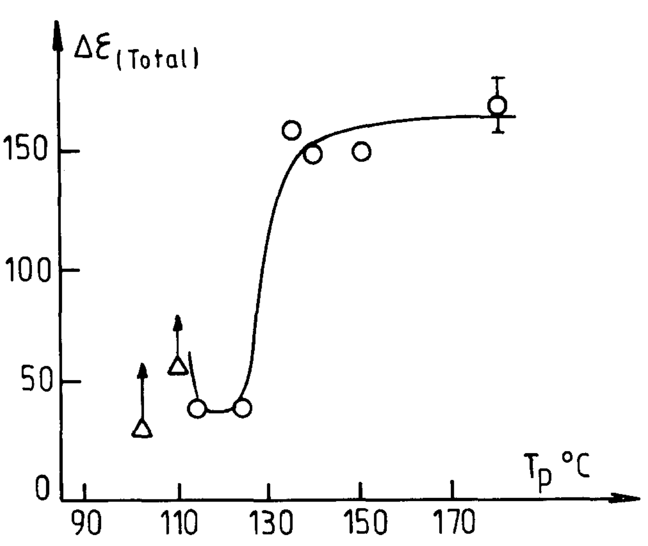


Figure 3 Total dielectric constant increment at T_p, obtained from the sum of the areas of the two peaks

obvious that the low T part of the curve does not reflect saturation of dipole orientation if reasonable poling times are used ($t_p = 15$ min, unless otherwise stated). The main feature is the appearance of a minimum around 118–120°C. The longer poling time $t_p = 2$ h at $T_p = 114$°C compared to $t_p = 5$ min at $T_p = 112$°C, which is insufficient to obtain the true value of Δε, makes the change of slope in dP_{T_p}/dT clear. In this figure the two low T values of Δε are lower limits. From the high temperature limit, $\Delta\varepsilon \approx 160$, and using $C_0 = 4.4 \times 10^3$ mol m^{-3} a value of $g_\infty^{1/2}\mu_B = 23D$ is found.

The hypothesis $\mu_A = 0$ is not expected to hold for B-3. We are thus faced with case I for which no other quantity can be obtained. However, it will be assumed first that the dipole interaction parameter does not change appreciably with T in the rising part of the curve, i.e. $(b/g)(dg/dT) \ll k_r$. If, furthermore, T_p is high so that $K \rightarrow \infty$, equation (11) may be used for the initial rising portion of the low T peak. For B-3, the BFG plot obtained therefrom is linear in the range 55–87°C, leading to $A_r = 9.3 \times 10^5$ s^{-1} and $E_r = 58$ kJ mol^{-1} (0.6 eV). Up to 87°C, the depolarization amounts to 10% of the total polarization. At peak maximum, $T_M = 87$°C, the classical condition $kT_M^2 = k_{rM}E_r b$ is satisfied, which seems to show that k_r is not distributed. The gradual departure from linearity above T_M may arise from the two conditions $B \gg B_{\text{equil}}$ and $dg/dT = 0$, which no longer hold.

To estimate the other parameters, a second TSD experiment will be performed in which T_{p2} is not lower than that at which $(P_1 - P_2)/P_1 < 10\%$. Then the first assumption made above leads to $g_\infty = g(T_{p2})$. It is further assumed that: $\mu'_A = 0$ (complete loss of orientational correlation or negligible mean value); at low concentrations of A, $\boldsymbol{\mu}_A \cdot \bar{\boldsymbol{\mu}}_A = \mu_A^2$ and $\boldsymbol{\mu}_B \cdot \bar{\boldsymbol{\mu}}_B = g\mu_B^2$; and $g_\infty = g(T_{p2}) = g(T_{E1}) = g(T_{p1})$.

For $T_{p1} = 185$°C, $\Delta\varepsilon_H = 134$, $\Delta\varepsilon_L = 26$, $B_{T_{p1}} = C_0$ and $T_E = 120$°C are found.

For $T_{p2} = 138$°C, $\Delta\varepsilon_H = 121$, $\Delta\varepsilon_L = 24$ and $B_{T_{p2}} = 0.87C_0$ is calculated from J_2/J_1 at low T. Equation (9), in which μ_B^2 is replaced by $g_\infty\mu_B^2$ and applied to results for T_{p1}, leads to $B_{120} = 0.8375C_0$ and thus $K_{120} = 5.15$. Since $K_{138} = 6.69$, the parameters in the Arrhenius equation

$$K = A_K \exp(-E_K/kT)$$

are $A_K = 2 \times 10^3$ and $E_K = 19$ kJ mol^{-1} (0.20 eV). From equation (8) applied at T_{p2} the apparent dipole moment $\mu_A = 12D$.

Recently, Brédas *et al.*[5] have applied molecular mechanics and quantum-chemical calculations to the [(dimethylhexylammonio)-propyl] sulphonate molecule and found two stable conformations differing in dipole moment: the curled one, $\mu = 20.7D$, which is the stable one at low T, and the extended one, $\mu = 27.7D$. The stability difference (7.9 kcal mol^{-1}) is found to be small. Comparison of these values for a small molecule with those found from TSD for B-3 bearing the same sulphopropyl groups reinforces the assumption that a conformational equilibrium is operative. The approximations used, electrode polarization at high T and proximity in position of the two peaks limit the precision of the parameters calculated from the above experiments.

Another argument in favour of a conformational change occurring during heating may be obtained by examining the effect of added salt using broad line nuclear magnetic resonance (n.m.r.) spectroscopy. *Figure 4* reproduces the second moment M_2 values reported by Monroy Soto[6] for B-3 and its blend with stoichiometric amounts of $LiClO_4$ ([salt]/[zwitterion] = 1). A sharp decrease of the second moment is observed for B-3 + $LiClO_4$ at the same temperatures as those at which the low T TSD peak reported above is observed. This can be interpreted as a change in solvation of the salt as the conformation of the zwitterionic group is changed: in the extended (high T) conformation the approach to the charged groups by the salt is easier; the dipole–dipole inter-polymer interactions are weakened in favor of zwitterion–salt interactions, which results in a decrease of the chain rigidity, as evidenced by the drop in M_2 ($\approx 4G^2$) when the conformational change occurs.

The second, high T peak observed for B-3 by TSD is due to randomization of the polar species which remained oriented at T_E during heating. The BFG plot is linear in the range 109–151°C, leading to an activation energy E_D of 78 kJ mol^{-1} (0.81 eV) for that process. At peak maximum, $T_M = 155$°C, $\tau_M = 365$ s.

Other poly(zwitterions)

In a previous publication[3] properties of four other polymers bearing the same zwitterionic group were reported. By using the above results, it is now possible

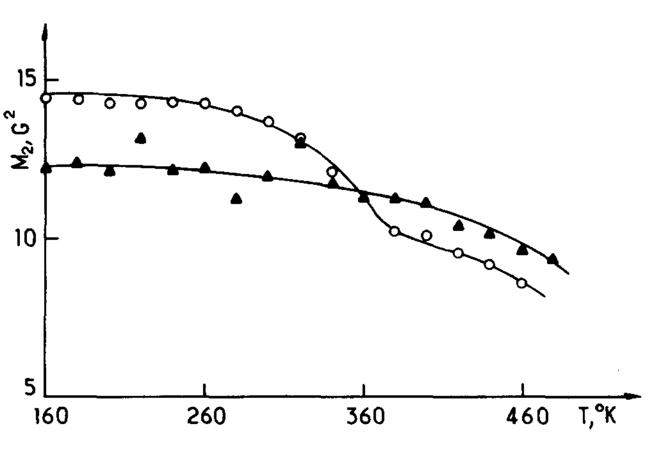
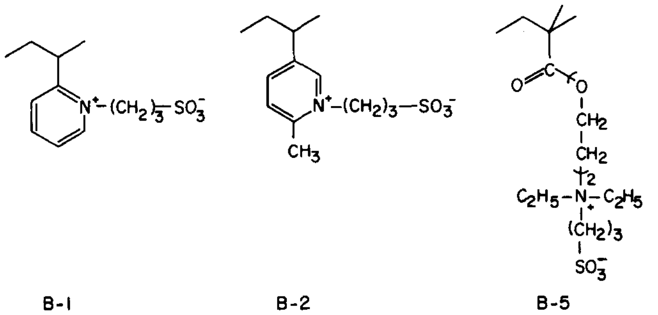


Figure 4 Results from broad line n.m.r. spectra of polymer B-3 (reproduced from Reference 6): ▲, without salt; ○, with stoichiometric amount of $LiClO_4$

Scheme 2



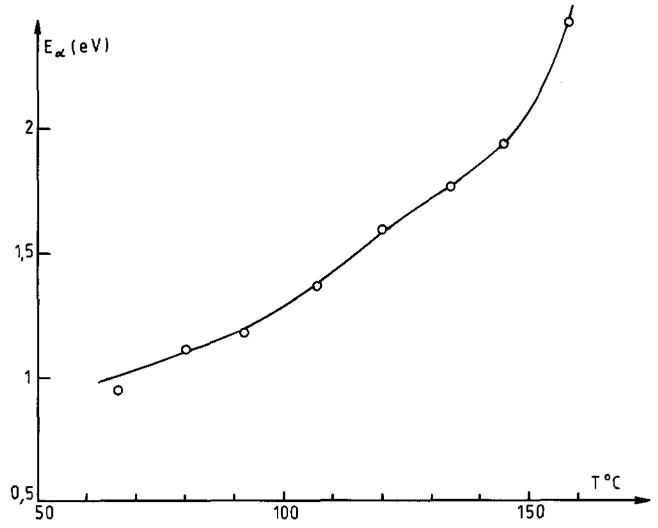


Figure 5 Activation energy of the α peak of polymer B-5 obtained by multistage heating *versus* the final temperature reached in each heating step

to give further interpretations of the TSDC results for B-1, B-2 and B-5 (see *Scheme 2*), where only one peak is observed in TSDC above room temperature.

For B-1 it was mentioned in Reference 3 that a TSDC peak is observed at 108°C. The BFG plot derived therefrom leads to an activation energy of 72 kJ mol^{-1} (0.75 eV), τ(108°C) = 241 s. The value of E_D found for the high T peak of B-3 is close to this value and from this as well as the high value of $\Delta\varepsilon$ it seems that disorientation of the extended conformation is the underlying process.

For B-2 the reported relaxation observed by TSDC is centred at 105°C, $\Delta\varepsilon = 5.7$. The activation energy and pre-exponential factor found for this process are 59 kJ mol^{-1} (0.61 eV) and 6×10^5 s^{-1}, respectively. In this case, the origin seems to be the chemical reaction, as invoked for the low T peak of B-3 with similar values of k_r. The low value of $\Delta\varepsilon$ could originate from incomplete polarization at the poling temperature. Above 108°C, a stronger decrease of M_2 is apparent in Figure 2 of Reference 3 (in which the two symbols have been inadvertently exchanged), in favour of this interpretation.

For B-5 the peak whose maximum lies at $T_M = 134$°C is attributed to main chain, so called α relaxation related to the glass transition. Through multistage heating, the activation energy is determined as a function of the temperature at which each partial depolarization is stopped. The result is shown in *Figure 5*. From the variation of T_M with heating rate, $E_\alpha = 135$ kJ mol^{-1} (1.4 eV) is found, whereas the method in which peak width at half height[1] is used leads to $E_\alpha = 140$ kJ mol^{-1} (1.45 ± 0.05 eV). Thus the activation energy related to this process is >97 kJ mol^{-1} (1 eV).

When a stoichiometric amount of $LiClO_4$ is dissolved, the TSD diagram shows a peak at 70°C and a shoulder at 145°C. From the BFG plot of the first, an activation energy of 73 kJ mol^{-1} (0.75 eV) is found and $\Delta\varepsilon = 62$. This would correspond to orientational relaxation of the extended form, whereas at 145°C the α process is effective, as already mentioned in Reference 3. In Figure 2 of Reference 3, two dips in M_2 are apparent, above 70°C and above 140°C. Although the n.m.r. results show the dips in both M-5 and M-5 + salt, no peak is detected below 100°C by TSD for B-5: it may be hidden by the strong nearby α peak. For B-5 as well as B-1 there is thus no proof that a conformational change is taking place.

Finally, it is interesting to note that several authors have predicted a dispersion in the dielectric constant due to a chemical equilibrium reaction when time-dependent fields are applied[7-11] and for the case of hydrogen bond donors and acceptors in equilibrium with the complex formed[12].

In these theories the molecular axis of the two species, A and B, is assumed to be preserved in the chemical reaction, whereas this is not a necessary condition for the appearance of the TSDC signal.

The possibility of having detected chemically induced dielectric relaxation in zwitterion solutions by dielectric absorption is discussed in Reference 13 but clear experimental evidence is absent for small molecules and has led to a controversy in the case of a macromolecule in solution[14].

CONCLUSION

Thermally stimulated depolarization measurements can be used to detect a chemical equilibrium reaction between species differing in dipole moments, provided that the orientational relaxation time is higher than that related to the chemical reaction. The change in dielectric constant may be induced by temperature, through electromagnetic radiation (ultraviolet or visible) or eventually by applying an electric field. In this work experimental support is obtained from TSD diagrams of poly(4-vinyl-1-sulphopropylpyridiniumbetaine) below its glass transition: it seems that an equilibrium reaction between a low dipole moment bearing zwitterionic group and its conformational isomer of higher polarity takes place in a small temperature interval. The dipole moments and thermodynamic kinetic parameters were determined, using the theoretical support developed and three approximations.

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