Dipolar relaxation mechanisms in the vitreous state, in the glass transition region and in the mesophase, of a side chain polysiloxane liquid crystal

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The dipolar relaxation mechanisms in a side chain liquid crystalline polysiloxane have been studied by Thermally Stimulated Discharge Currents (t.s.d.c.) and by Dielectric Relaxation Spectroscopy (d.r.s.). The study was carried out in a wide temperature range covering the vitreous phase, the glass transition region and the liquid crystalline phase. Different discharges were observed in the t.s.d.c. spectrum of this polymer which were attributed, in the order of increasing temperature, to local non-cooperative motions probably involving internal rotations in the spacer and in the alkyl group of the mesogenic moiety, to the Brownian motions of the main chain associated with the glass transition and to motions involving reorientations of the components of the dipole moment of the mesogenic side group in the liquid crystalline phase. The dielectric relaxation spectrum, on the other hand, is dominated by two relaxation processes both of which are above the measured glass transition temperature and shows also a much broader and less intense relaxation below the glass transition temperature which is attributable to local motions along the side groups. It is emphasized that the comparison between the d.r.s. and the t.s.d.c. results is not straightforward and that more research work is needed in order to enable a clear attribution of the relaxation processes at the molecular level, and an unambiguous interpretation of the results obtained by the two techniques.

1. Introduction

Side chain liquid crystalline polymers (LCPs) are hybrid systems since they exhibit the electro-optical properties of low molar mass liquid crystals and, at the same time, they show many physical properties of conventional polymers. This combination of properties confers upon these materials a versatility which can be used in different applications, namely in optical information storage, non-linear optics and chromatography [1].

The molecular motions in side chain LCPs have been extensively studied over the last fifteen years by Dielectric Relaxation Spectroscopy (d.r.s.) [2]. Two relaxation mechanisms, named δ and α, were identified in the liquid crystalline phase and attributed to complex modes of motion involving the longitudinal and the transverse components of the dipole moment of the mesogenic side groups. Nevertheless, one of the diffi-

culties encountered in the analysis of the dielectric relaxation spectra of LCPs is the fact that the different relaxation modes often occur closely spaced in the frequency domain, so that the dielectric loss peaks appear as partially superposed.

The technique of Thermally Stimulated Discharge Currents (t.s.d.c.) has been recently used to study the dipolar relaxation mechanisms in side chain liquid crystalline polymers [3–6]. The results obtained are very promising and seem to confirm the expected resolution power of the technique. In fact, van Turnhout [7] has shown that a t.s.d.c. experiment is equivalent to a low-frequency dielectric loss experiment and that the equivalent frequency is

$$f = \frac{E_a r}{2\pi R T_m^2} \qquad (1)$$

where E_a is the activation energy of the relaxation process, r is the heating rate used in the t.s.d.c. experi-
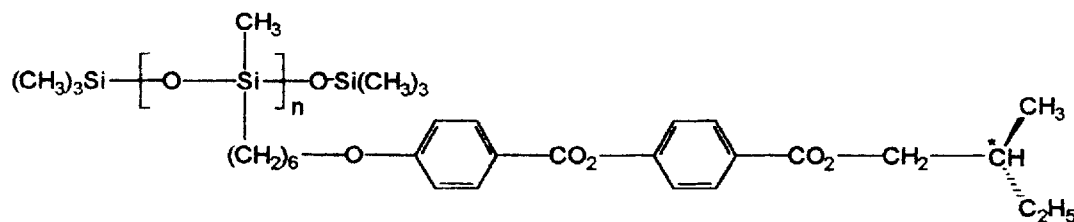
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ment, R is the ideal gas constant and T_m is the temperature at which the t.s.d.c. peak has its maximum. From equation (1) it can be concluded that, for a relaxation mechanism with $E_a = 60\,\text{kcal/mol}$ appearing at $T_m = 320\,\text{K}$, in a t.s.d.c. experiment performed with a heating rate $r = 4°\text{C}\,\text{min}^{-1}$, the equivalent frequency is $3 \times 10^{-3}\,\text{Hz}$. This is a low frequency when compared with the frequency range between $10\,\text{Hz}$ and $1\,\text{MHz}$ commonly used in dielectric relaxation studies. This low frequency of the t.s.d.c. technique is expected to lead to an enhancement of the resolution of the different relaxation processes, increasing the separation of the different peaks in the temperature axis. We thus expect a higher resolution power for the t.s.d.c. technique when compared with other higher frequency techniques such as dielectric relaxation spectroscopy, which means that we expect to be able to resolve, by the t.s.d.c. technique, relaxation mechanisms which appear as partially overlapped in d.r.s.. The results we obtained in previous t.s.d.c. studies of liquid crystalline polymers [3–6] confirm this expectation. On the other hand, the t.s.d.c. is a non-isothermal technique and this can be considered as a drawback of the technique. Moreover, it is well known that the t.s.d.c. spectrum sometimes presents peaks which do not arise from dipolar relaxations. It is thus interesting, from a physico-chemical point of view, to use both dielectric related techniques (d.r.s. and t.s.d.c.) in order to compare the results and to be able to ascribe the observed peaks to the motions at the molecular level.

In the present work we present a study by t.s.d.c. and by d.r.s. of the dipolar relaxation mechanisms in a side chain liquid crystalline polysiloxane. Different relaxation mechanisms were detected by both techniques in the vitreous state, in the glass transition region and in the liquid crystalline phase. The results obtained emphasize the need for further studies in order to enable a clear articulation of the results obtained by both techniques.

2. Experimental

The liquid crystalline polymer studied in this work is from Merck (catalogue no. LCP 1) and has the following structure
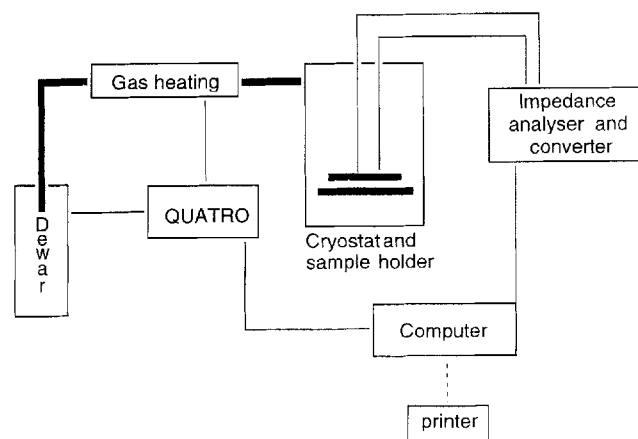

Figure 1. General overview of the apparatus used for the dielectric relaxation spectroscopy measurements.

Thermally Stimulated Depolarization Current (t.s.d.c.) experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, U.S.A.) covering the range -170 to $+400°\text{C}$. A Faraday cage shields the sample and prior to the experiments the sample is evacuated to $10^{-4}\,\text{mbar}$ and flushed several times with $1\cdot1\,\text{bar}$ of high-purity helium. Experimental details concerning the different techniques (thermal and electrical treatments) used for obtaining the t.s.d.c. spectra are explained in previous work [4,8].

Dielectric relaxation measurements were performed using a SOLARTRON SI1260 Schlumberger Impedance/Gain-phase Analyser with a Chelsea Dielectric Interface, enabling the a.c. frequency range 10^{-2} to $10^5\,\text{Hz}$ to be measured accurately. A full schematic of the apparatus is given in figure 1. Temperature control of the sample was achieved using a NOVOCONTROL QUATRO temperature controller unit that utilizes a liquid nitrogen cryostat system. This enables complete temperature control with N_2 gas in the experiment to an accuracy of $0\cdot1°\text{C}$. The dielectric instrumentation and QUATRO temperature controller system are connected to a central 486PC unit from where both are controlled by NOVOCONTROL's

According to the manufacturer, it has a glass transition temperature $T_g = -7\cdot2°\text{C}$ and a smectic C/isotropic transition at $76\cdot8°\text{C}$.

'WinDETA' software package. This is a Windows-based software package that enables the user to set up and carefully control a complete dielectric measurement.

The sample holder consists of two brass discs; the first is a flat circular disc of outside diameter 40 mm that acts as the bottom sample–electrode connection, and a smaller upper disc (30 mm) acts as the top sample–electrode connection. The two discs are separated from one another by a circular spacer of Teflon (70 µm thick) which acts to stop shorting between the two electrodes and ensures a constant sample thickness. This electrode sample holder is then centred in the NOVOCONTROL BDS1200 sample cell, where electrical contact is made to the brass discs via two more circular brass discs that form part of the BDS1200 holder. The BDS1200 discs consist of a height adjustable top disc of 30 mm diameter and a fixed bottom disc of 40 mm diameter that contains a small thermocouple that acts as the temperature sensor for the sample. Tight adjustment of the BDS1200 top disc ensures good electrical contact between corresponding discs and sample. The fact that corresponding discs have the same diameter ensures that there are no fringing field effects. The WinDETA software instructs the SOLARTRON SI1260 to measure the impedance of the parallel plate capacitor that is formed by the sample. From this, the capacitance (C) and resistance (R) of the sample cell are obtained directly. In order to calculate values of the dielectric constant, ε', and relative loss factor, ε'', of a sample, the software uses the following equations;

$$\varepsilon' = C_f/C_0 \qquad (2\,a)$$

$$\varepsilon'' = 1/R\omega C_0 \qquad (2\,b)$$

where C_f is the capacitance of the sample filled capacitor, ω is the angular frequency $(2\pi f)$ and C_0 is the empty cell capacitance given by

$$C_0 = \pi D^2 \varepsilon_0/4d \qquad (3)$$

where d is the perpendicular distance between the parallel electrodes, ε_0 is the permitivity of free space and D is the diameter of the top electrode. The value of C_0 is calculated by WinDETA after the parameters D and d are input by the operator.

3. Results and discussion

3.1. *Thermally stimulated currents results*

In order to detect the different relaxation mechanisms present in the sample, we performed t.s.d.c. global experiments covering the available temperature range. Figures 2 and 3 show the results of such experiments. Figure 2 shows the relaxation mechanism in the lower temperature region (between $-160°C$ and $-60°C$), which is a broad and non-structured discharge. It is to be noted that the peak observed in the right hand side of figure 2 (at $\approx -40°C$) corresponds to the lower temperature part of peak 1 in figure 3.

Figure 3, on the other hand, shows the results in the glass transition temperature region and in the liquid crystalline phase. On that figure are shown three different and well separated discharges which seem to arise, as shown in a previous paper [3], from dipolar relaxation mechanisms. This statement was based on the fact that the intensity of those three peaks showed a linear dependence on the polarizing electric field [3].

The different discharges revealed by the t.s.d.c. global experiments were thus analysed in detail using the partial polarization (or thermal cleaning) technique. As explained before [8], the result of a partial polarization experiment is a single peak which was obtained after polarizing the sample in a narrow temperature range between the polarization temperature, T_p, and $T_p–\Delta T$, where ΔT is typically 2–5°C. Each thermally cleaned peak has a given location in the temperature axis, with maximum intensity at T_m, and it corresponds very approximately to a single relaxation mechanism whose activation parameters $(\Delta G^{\neq}, \Delta H^{\neq}, \Delta S^{\neq})$ can be obtained by integration of the peak's area according to the Bucci method [9]. Figure 4 shows the representation of the temperature of maximum intensity, T_m, of a large series of thermally cleaned peaks as a function of the polarization temperature, T_p, in the whole range of the t.s.d.c. spectrum, including the lower temperature region shown in figure 2, as well as the glass transition region and the mesophase shown in figure 3.

Four different regions can be clearly distinguished in this figure: (1) from $T_p = -150°C$ to $-40°C$ (region 0), which corresponds to the lower temperature discharge shown in figure 2, and where we observe a linear relationship between T_m and T_p; (2) from $-40°C$ to $-8°C$ (region 1), which is the temperature region where peak 1 of figure 3 appears; (3) from $-8°C$ to 7°C (region 2), corresponding to peak 2 of figure 3; and finally (4) from 7°C to 30°C (region 3), which is the temperature range where peak 3 of figure 3 appears.† It must be pointed out at this stage that the points in figure 4 (as well as in figures 5 and 6) were obtained from the analysis of the results of different sets of partial polarization experiments, which are partially shown in figures 7 and 8 and will be discussed further below. Our choice in presenting such results now has the objective of giving a global view of the behaviour of this side chain LCP over the whole temperature range. The four distinct temperature regions in the t.s.d.c. spectrum of this polymer, which are apparent from figure 4, are also clearly shown on

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†Note that the variable in the abcissa axis of figure 4 (and of figure 5) is the polarization temperature of the partial polarization experiments. This is the reason why the temperature intervals which emerge from these figures do not exactly coincide with the temperature regions in which the peaks appear in figure 3.
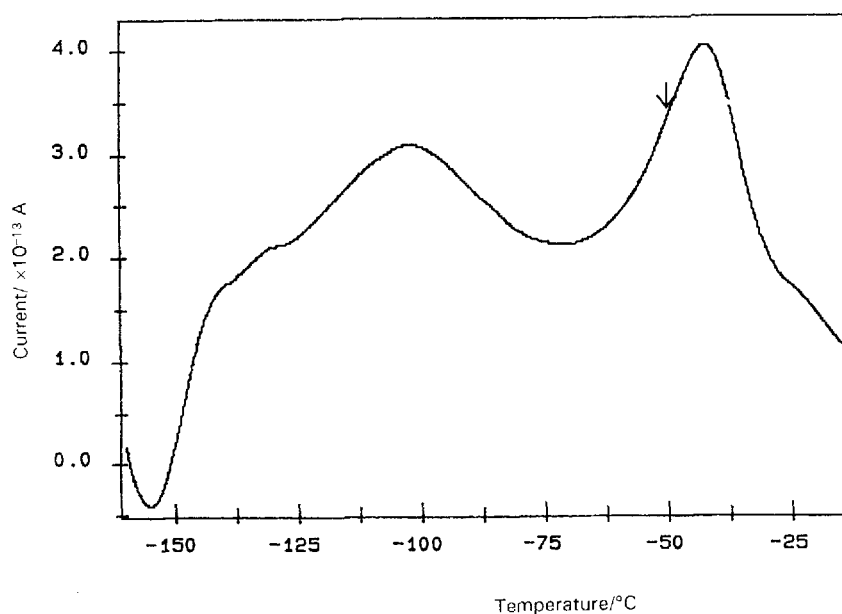
Figure 2. t.s.d.c. global spectrum in the lower temperature region obtained under the following experimental conditions: $T_p = -50°C$; $T_o = -160°C$; polarization field, $E = 600\,V\,mm^{-1}$; heating rate, $r = 8°C\,min^{-1}$.
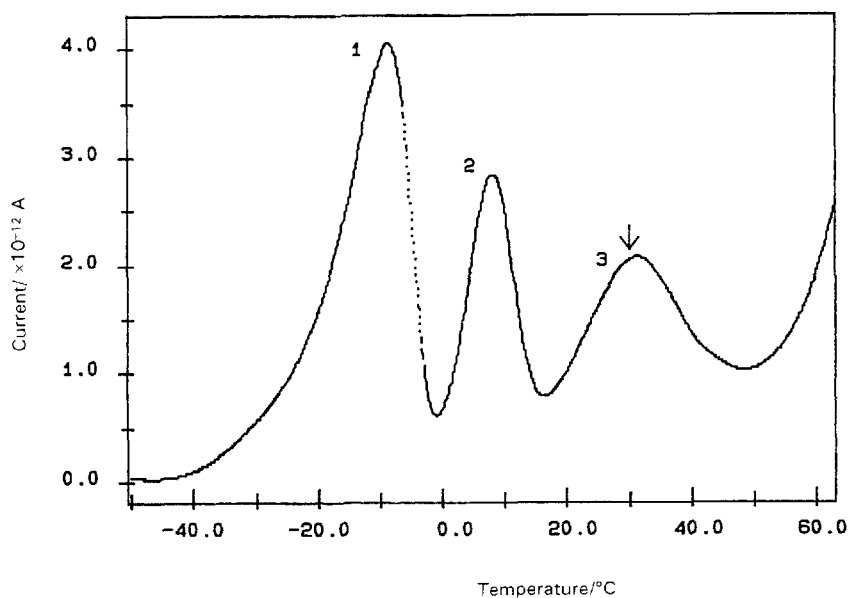

Figure 3. t.s.d.c. global spectrum in the glass transition region and in the mesophase obtained under the following experimental conditions: $T_p = 30°C$; $T_o = -50°C$; polarization field, $E = 900\,V\,mm^{-1}$; heating rate, $r = 8°C\,min^{-1}$.

figure 5 where the activation enthalpy, $\Delta H^{\neq}$, of the different thermally cleaned peaks is plotted as a function of T_p (the behaviour of the activation entropy, not shown, is similar).

Figure 6 shows, on the other hand, the Gibbs activation energy, $\Delta G^{\neq} = \Delta H^{\neq} - T_m \Delta S^{\neq}$, of the different thermally cleaned peaks as a function of its location in the t.s.d.c. spectrum, T_m.

This figure shows that the $\Delta G^{\neq}$ function is an increas-

ing function of temperature or, otherwise stated, that the relaxation processes which appear at higher temperatures in the t.s.d.c. spectrum have a higher Gibbs activation energy. Nevertheless, as shown on figure 5, we can have relaxation mechanisms characterized by lower activation enthalpies which appear at higher temperatures (if they have lower activation entropies). On the other hand, figure 6 also shows clearly, as was the case for figures 4 and 5, that the whole t.s.d.c. spectrum
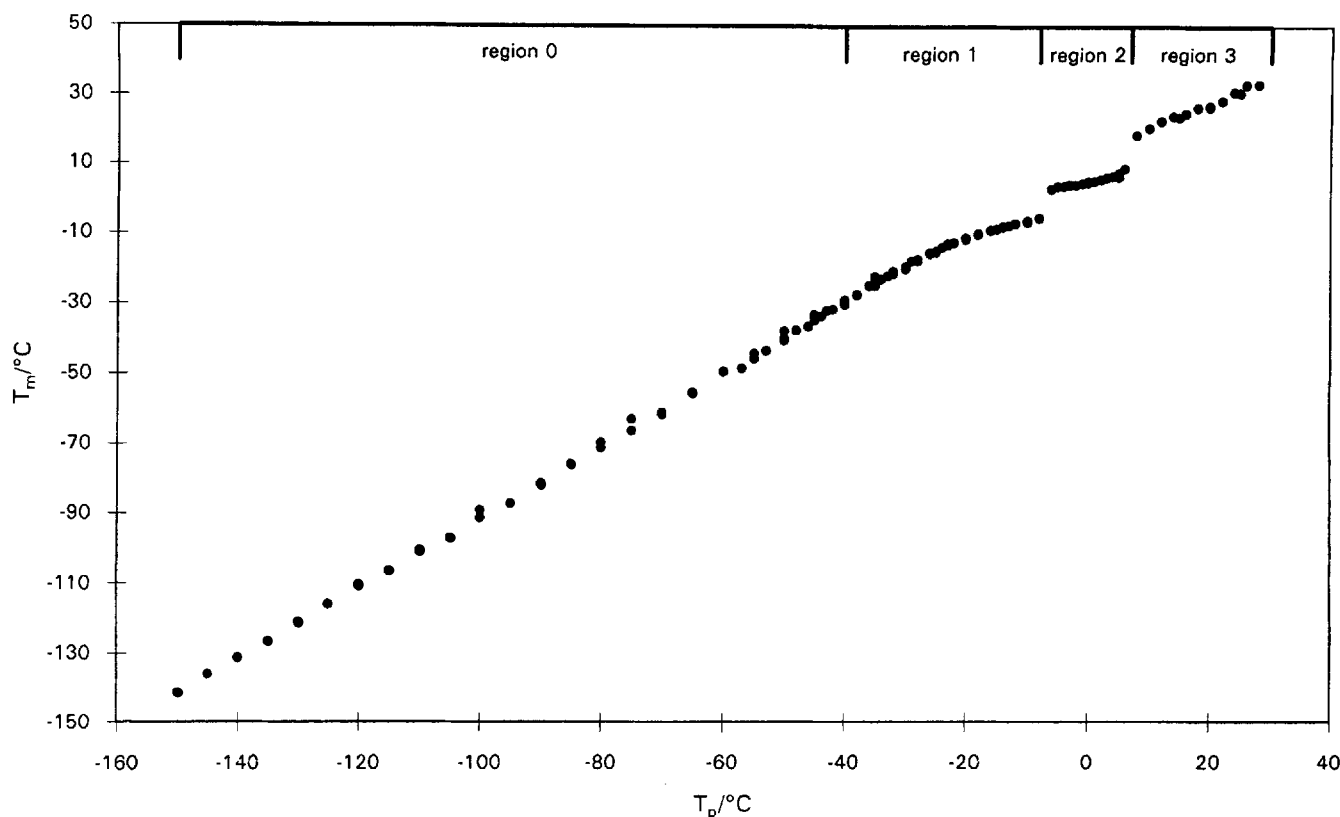
Figure 4. Temperature of maximum intensity, T_m, as a function of the polarization temperature, T_p, for different individual thermally cleaned components in the whole t.s.d.c. spectrum including the low temperature region below T_g (figure 2), and the glass transition region and the mesophase (figure 3). Some of the thermally cleaned peaks corresponding to points in this figure are shown later in figures 7 and 8.

of this side chain LCP is composed of four different regions, i.e. that we have at least four different relaxation mechanisms in this polymer. In the following, we will analyse those relaxation mechanisms in detail.

3.1.1. *The lower temperature relaxation (from* -160 *to* $-40°C$)

Figure 7 shows a series of thermally cleaned peaks obtained in this temperature region. From the analysis of these peaks it can be concluded that T_m is a linear function of T_p with slope equal to unity (see figure 4).

The shapes of the peaks do not change appreciably, and the corresponding activation enthalpies are low and increase slightly with temperature: $\approx 7\,\text{kcal mol}^{-1}$ ($29\,\text{kJ mol}^{-1}$) at $T_p = -140°C$, and $\approx 17\,\text{kcal mol}^{-1}$ ($71\,\text{kJ mol}^{-1}$) at $T_p = -60°C$ (see figure 4). The activation entropies, on the other hand, are negligible. Those values of the activation parameters of the components of this broad relaxation suggest that it corresponds to local and non-cooperative motions which arise from internal rotations of small molecular segments around single covalent bonds, and can consist in small amplitude motions involving the spacer or rotations in the alkyl

group of the mesogenic moiety. Even if those motions with zero activation entropy are called 'simple' and are considered to be local and non-cooperative [10,11], the fact that the corresponding discharge is broad reveals some degree of complexity. This broadness, which was observed for the side chain LCPs we studied before [4–6], suggests that this low temperature discharge is related with motions involving the spacer which links the mesogenic side group to the main chain. In fact, it is recognized that sequences of methylene groups with four or more units exhibit a relaxation similar to the γ relaxation of polyethylene and that this involves the motion of a spectrum of chain segment lengths [12]. These motions will be dielectrically active if they induce small amplitude motions of polar molecular segments and will give rise to a complex discharge containing eventually different components.

3.1.2. *The glass transition relaxation*

Figure 8 shows a large series of thermally cleaned peaks obtained in the temperature region between -40 and $50°C$. The peaks in the region 1 correspond to the glass transition ($T_g = -7\cdot2°C$) relaxation and show a
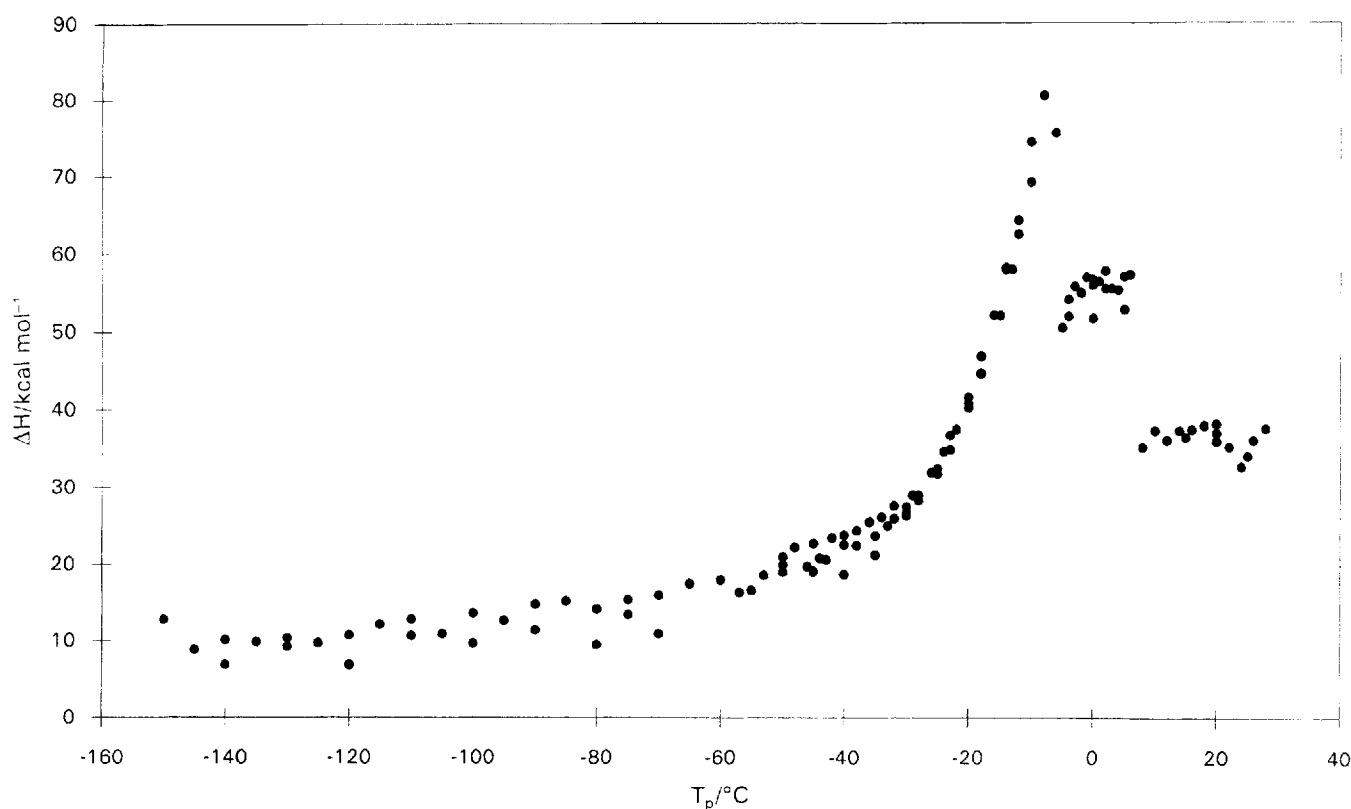
Figure 5.   Activation enthalpy, $\Delta H^{\neq}$, as a function of the polarization temperature, T_p, for different individual thermally cleaned components in the whole t.s.d.c. spectrum including the low temperature region below T_g (figure 2), and the glass transition region and the mesophase (figure 3). Some of these points correspond to thermally cleaned peaks shown in figures 7 and 8.

particular behaviour: the thermally cleaned components become narrower and steeper as the polarization temperature, T_p, increases.

This change of shape of the thermally cleaned components (the increase in the steepness of the higher temperature components) is a behaviour which is always observed for the T_g relaxation obtained by thermo-stimulated currents, and is found in amorphous polymers [8,13,14], as well as in side chain LCPs [4–6]. The fact that the peaks become steeper as T_p increases means that the activation enthalpy of the corresponding polarized segments also increases (see region between -30 and $-10°C$ in figure 5). Furthermore, this increase in the activation enthalpy is associated with a concomitant increase of the activation entropy and this behaviour is called the *compensation effect*. A consequence of the compensation effect is the apparent convergence to a single point, the compensation point, of the Arrhenius lines ($\log \tau(T)$ versus $1/T$) corresponding to the different components of the T_g peak (see figure 9).

The coordinates of the compensation point for this particular LCP are $T_c = -0.7°C$ and $\tau_c = 2.04\,s$. The physical significance of the compensation behaviour is not yet clarified and there is some controversy about

the subject. Some authors consider that the compensation behaviour is in many cases an artifact which is a consequence of a statistical compensation pattern arising from experimental approximations and errors [15–17]. Others, on the other hand, believe that the compensation behaviour observed for the glass transition t.s.d.c. peak is a genuine behaviour characteristic of the amorphous phase of polymers [13,14,18]. Most of the criticism against the physical significance of the compensation law is based on the fact that a large covariance exists between the $\Delta S^{\neq}$ and the $\Delta H^{\neq}$ values. In this context, the propagation of experimental errors itself induces a linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$. Krug *et al.* [15] developed a hypothesis test to verify if the observed compensation behaviour corresponds to a true physico-chemical behaviour or if it is indistinguishable from a statistical pattern generated by random errors. It has been shown that, for a compensation phenomenon with a purely statistical origin, the representation of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ is linear with a slope equal to T_{hm}, the harmonic mean of the measurement temperatures, T_i.

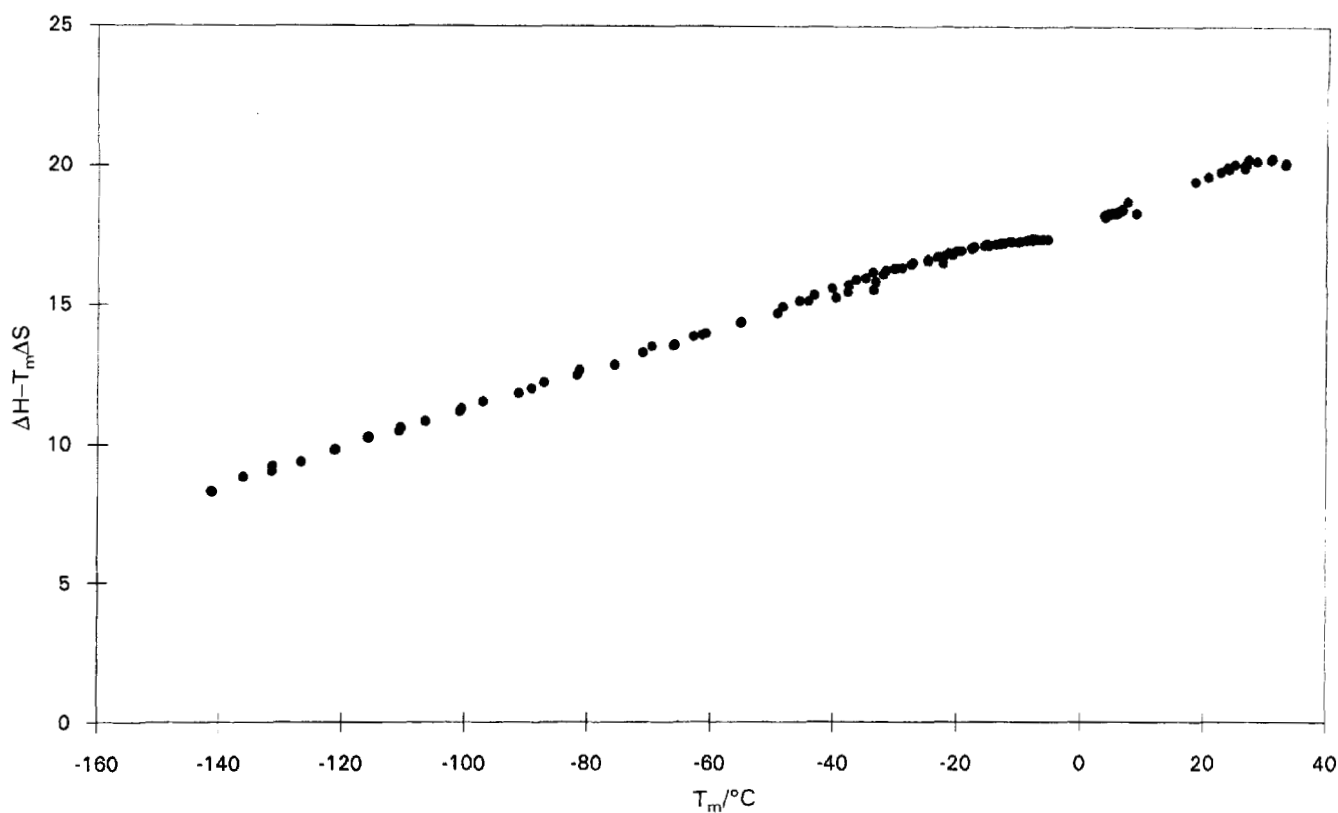$$T_{hm} = n \left(\sum_i \frac{1}{T_i} \right)^{-1} \tag{4}$$

Figure 6. Activation Gibbs energy, $\Delta G^{\neq}$, as a function of the temperature of maximum intensity, T_m, for different individual thermally cleaned components in the whole t.s.d.c. spectrum including the low temperature region below T_g (figure 2), and the glass transition region and the mesophase (figure 3). Some of the thermally cleaned peaks corresponding to points in this figure are shown later in figures 7 and 8.
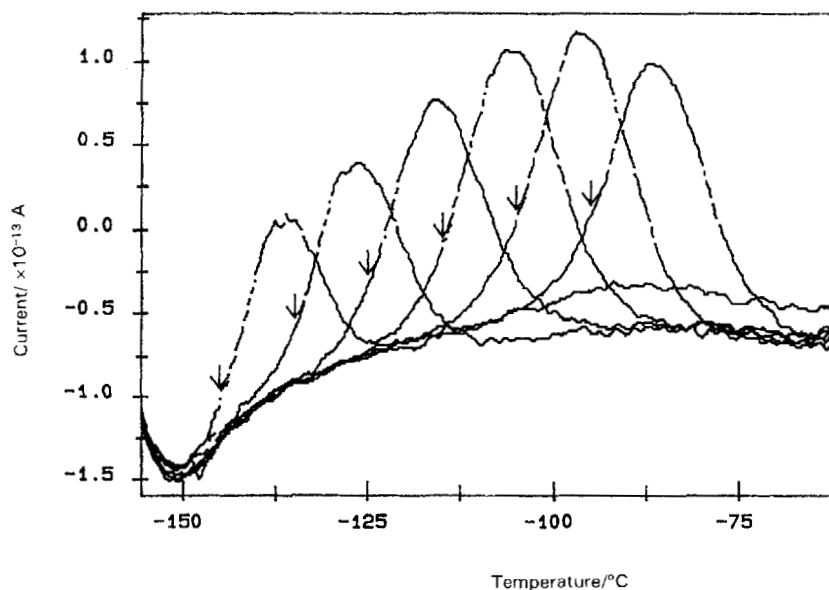

Figure 7. Thermally cleaned components of the lower temperature relaxation. The experimental conditions were: polarization field, $E = 600\,\mathrm{V\,mm^{-1}}$, heating rate, $r = 8^\circ\mathrm{C\,min^{-1}}$; window width, $\Delta T = 5^\circ\mathrm{C}$; $T_o = -160^\circ\mathrm{C}$; the polarization temperatures, indicated by the arrows, were -145, -135, -125, -115, -105 and $-95^\circ\mathrm{C}$.
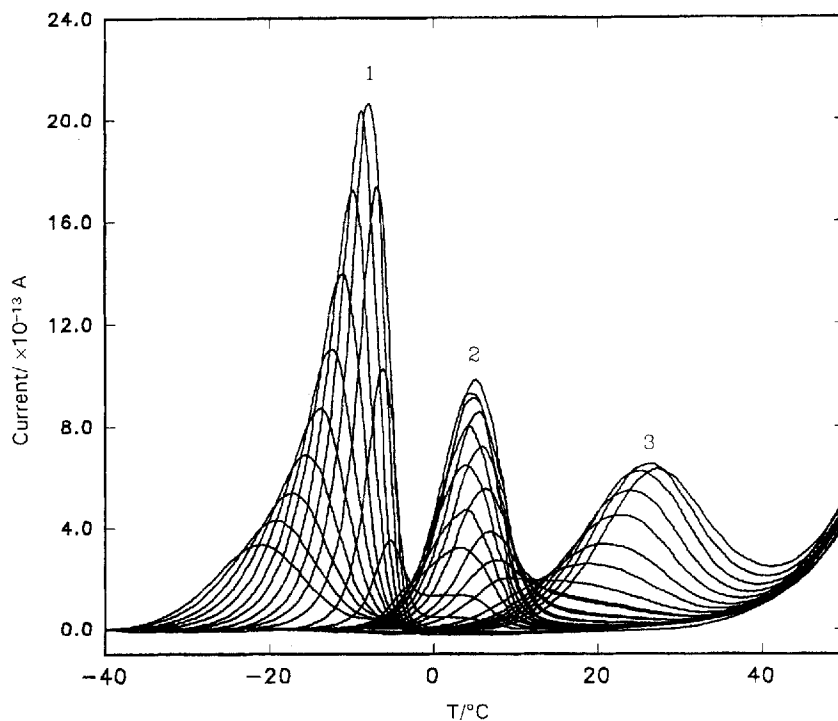
Figure 8. Thermally cleaned components of the t.s.d.c. spectrum in the glass transition region and in the mesophase. The experimental conditions were: polarization field, $E = 600 \, \text{V mm}^{-1}$, heating rate, $r = 4°C \, \text{min}^{-1}$; window width, $\Delta T = 2°C$.
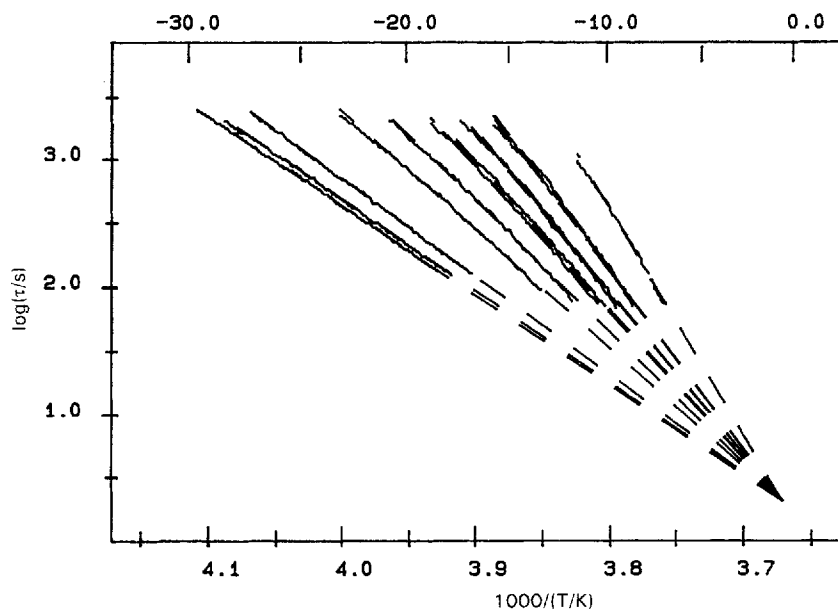

Figure 9. Arrhenius plots for the thermally cleaned components in the glass transition region. The convergence of the lines to a single point is a manifestation of the compensation behaviour.

where n is the number of experiments. The null hypothesis of Krug *et al.* [15] is then

$$\hat{\beta} = T_{hm} \qquad (5)$$

where $\hat{\beta}$ is the slope observed for the representation of the $\Delta H/\Delta S$ pairs. To test this hypothesis, the observed slope should be compared with T_{hm}. A confidence interval for $\hat{\beta}$ of $(1 - \alpha) \times 100$ per cent is thus defined as

$$\hat{\beta} \pm t_{n-2, \alpha/2}[V(\hat{\beta})]^{1/2} \qquad (6)$$

where t is the parameter of the Student's distribution and

$$\hat{\beta} = \frac{\sum (\Delta H - \overline{\Delta H})(\Delta S - \overline{\Delta S})}{\sum (\Delta S - \overline{\Delta S})^2} \qquad (7\,a)$$

$$V(\hat{\beta}) = \frac{\sum (\Delta H - \hat{\beta}\Delta S - \overline{\Delta G_\beta})^2}{(n-2)\sum (\Delta S - \overline{\Delta S})^2} \qquad (7\,b)$$

With $\overline{\Delta G_\beta} = \overline{\Delta H} - \hat{\beta}\,\overline{\Delta S}$. In the previous equations the bar denotes the mean value, e.g. $\overline{\Delta H}$ is the mean of the observed ΔH values.

From our data on the glass transition relaxation of this side chain LCP we obtained the confidence interval of 95 per cent for $\hat{\beta}$ of [272·16 K; 272·75 K]. On the other hand, the harmonic mean (equation (4)) of the temperature location, T_m, of the thermally cleaned peaks is 262·56 K. We conclude that T_{hm} is very different from the values of the 95 per cent confidence interval for $\hat{\beta}$ and thus that the null hypothesis (equation (5)) can be rejected at the 5 per cent level of significance. This means that the observed compensation behaviour of the glass transition relaxation corresponds to a real extra-thermodynamic relationship. A similar conclusion was reached before for the α relaxation in poly(methyl methacrylate) [19]. On the other hand, we must point out that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are not independent variables, since any change in $\Delta H^{\neq}$ is deterministically accompanied by a corresponding change in $\Delta S^{\neq}$ (the trend in $\Delta S^{\neq}$ mimics $\Delta H^{\neq}$). In fact, since

$$\Delta G^{\neq} = RT \ln\left(\frac{\tau kT}{h}\right) = RT[21\cdot92 + \ln T - \ln f] \qquad (8)$$

where the relaxation time, τ is given by $\tau = 1/(2\pi f)$, where f is the frequency, and

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (9)$$

and since, on the other hand, the variations of $\ln(f)$ have little influence on the results obtained from equation (8), it comes out that $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are not independent variables. The consequence is that the activation Gibbs energy, $\Delta G^{\neq}$, of a t.s.d.c. peak is a quantity which depends only on the temperature and not on the sample properties, so that the representation

shown in figure 6 is essentially the same for all polymers (the function $\Delta G^{\neq}(T)$ is the same).

3.1.3. *The first relaxation above* T_g

This peak shows a maximum intensity at 8°C (see figure 3), a temperature which is situated in the liquid crystalline range ($T_g = -7\cdot2$°C). A series of thermally cleaned components of this relaxation is shown in the region 2 of figure 8. It can be observed from that figure (and from figure 4) that the temperature location of the peak's maximum, T_m, changes very slightly with the polarization temperature, T_p. The integration of the peaks by the Bucci method gives the Arrhenius lines which are shown on figure 10.

We can conclude from that figure that no compensation is observed for this discharge, and that the Arrhenius lines show a WLF behaviour (the activation energy, proportional to the slope at each point, decreases with increasing temperature). The mean activation parameters are 55 kcal mol^{-1} (231 kJ mol^{-1}) for the enthalpy (figure 5) and 130 cal (K mol)$^{-1}$ (546 J (K mol)$^{-1}$) for the entropy.

3.1.4. *The higher temperature relaxation*

The region 3 of figure 8 shows a series of thermally cleaned components of this relaxation. Figure 11, on the other hand, presents the results of three t.s.d.c. global experiments in this temperature range, and clearly shows that this discharge is complex and does not correspond to a single relaxation mechanism.

In fact, from that figure and from figure 8 it can be concluded that this discharge contains at least two components, one whose maximum intensity is at ≈ 25–30°C and the other at ≈ 45°C. The thermally cleaned peaks obtained in the low temperature side of this complex discharge (region 3 of figure 8) do not show any compensation and the corresponding Arrhenius lines show a WLF behaviour, as was the case for the relaxation at 8°C. Nevertheless, the mean activation parameters for this relaxation are lower when compared to those corresponding to the peak at 8°C. From figure 5 we have ≈ 35 kcal mol^{-1} (147 kJ mol^{-1}) for the activation enthalpy. For the activation entropy we obtained ≈ 50 cal (K mol)$^{-1}$ (210 J (K mol)$^{-1}$). The higher temperature component of this complex discharge, on the other hand, has activation parameters which are even lower than those of the lower temperature component.

The side chain LCP studied in this work shows thus a complex pattern of relaxation mechanisms in the liquid crystalline phase. In some of the side chain LC polymers we studied before by t.s.d.c. [4–6], we observed only one discharge in the mesophase and we believe that the reason for this result is that the mesogenic side group in those polymers was a cyanobiphenyl group which
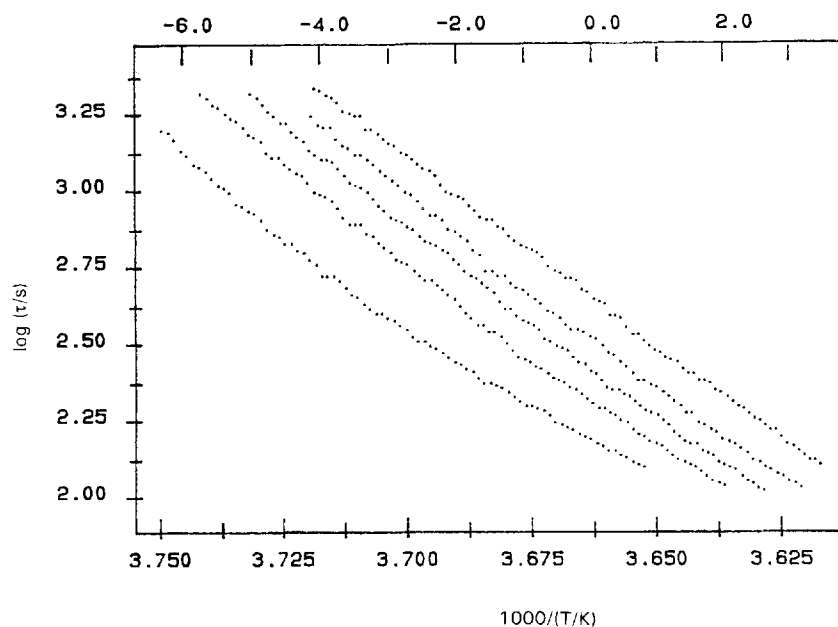
Figure 10. Arrhenius plots for the thermally cleaned components of the relaxation at 8°C. The curvature of the Arrhenius lines indicates a WLF behaviour.
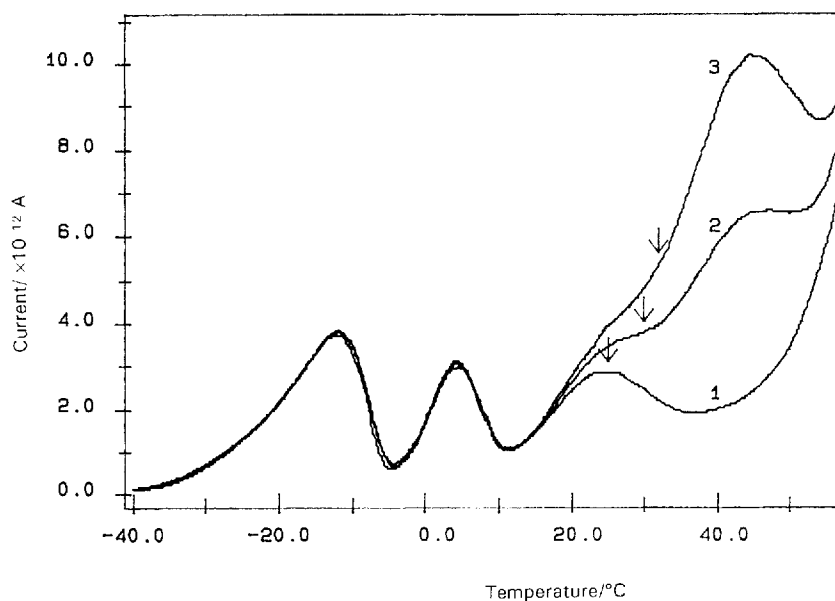

Figure 11. Three t.s.d.c. global spectra obtained with different polarization temperatures: curve 1, $T_p = 25°C$; curve 2, $T_p = 30°C$; curve 3, $T_p = 32°C$. The other experimental conditions were: polarization field, $E = 600 \, \text{V mm}^{-1}$, $T_o = -40°C$; heating rate, $r = 4°C \, \text{min}^{-1}$. These results clearly show that the higher temperature relaxation is composed of two different mechanisms.

only presents a longitudinal component of the dipole moment. In the polymer studied in this work the side group is a phenyl benzoate where the ester group between the two phenyl rings allows internal rotation of one of those rings relative to the other and the reorientation of the transverse dipole moment of the ester group. Moreover, a second ester group is present in the meso-

genic moiety of this polymer. In the phenyl benzoate side group we have thus both longitudinal ($\mu_\parallel$) and transverse ($\mu_\perp$) components of the dipole moment and the spatial direction of the transverse component can be changed by internal rotation around the ester carbon/ phenyl carbon bonds. The fact that the t.s.d.c. spectrum of side chain LCPs always presents discharges above T_g,

associated with the new observation that there are two separated discharges above T_g when the side group presents both $\mu_\parallel$ and $\mu_\perp$, whereas a single discharge is observed when the side group only has $\mu_\parallel$, leads us to believe that those discharges occurring in the liquid crystalline phase of side chain LCPs arise from molecular motions and not to space charge effects. It is to be recalled that the intensity of all three peaks shown in figure 3 showed a linear dependence on the polarizing electric field [3], behaviour which is often considered as an indication of the dipolar nature of the corresponding relaxation mechanisms. In the t.s.d.c. spectra of side chain LCPs with cyanobiphenyl side groups, only one upper T_g relaxation is observed, which should thus be attributed to the motions of $\mu_\parallel$ (δ process).

In the polymer studied in the present work, two well separated peaks are observed in the liquid crystalline phase (peaks 2 and 3 of figure 3), and one hypothesis is to consider that these peaks correspond to the α and δ processes observed by d.r.s. According to the d.r.s. results [2,20], the α-process appears at higher frequencies when compared with the δ-process and thus the α process is faster than the δ process. Consequently it should appear at lower temperatures in the t.s.d.c. spectrum. In this context, peaks 2 and 3 of figure 3 should correspond respectively to the α and δ processes observed by d.r.s. This hypothesis is strengthened if we consider the location of the different peaks in the t.s.d.c. spectrum. On table 1 are shown the positions (temperature of maximum intensity) in the t.s.d.c. global spectrum of the T_g peak, as well as of the peaks observed in the liquid crystalline phase for different side chain polysiloxanes previously studied in our laboratory. It can be seen from table 1 that the distance in the temperature axis, ΔT, between the glass transition relaxation and the higher temperature discharge observed in the liquid crystalline phase (whose location is labelled as T_2 in table 1) is 30–40°C for all the polymers studied. It seems reasonable, then, to consider that the relaxations at T_2 correspond to the δ-process. On the other hand, we can see from table 1 that the relaxations at T_1 observed in polymers 1, 3 and 4 are absent from the t.s.d.c. thermogram of the LCPs with cyanobiphenyl side groups (polymers 2, 5 and 6) and they must thus be attributed to the α process. It is to be noted that a side chain polysiloxane very similar to polymer 3 in table 1 was previously studied by t.s.d.c. [23]. One single relaxation above T_g was reported in this study and it was attributed to space charge effects. According to this study, the T_g peak occurred at 11°C and the peak in the liquid crystalline phase had its maximum intensity at 29°C so that the distance, in the temperature axis, between those peaks is only 18°C. The peak at 29°C in [23] has thus a location in the t.s.d.c. spectrum which is similar to

those at T_1 presented on table 1, and it seems thus reasonable to consider that it corresponds to the α-process. We must note that the temperature scans in the t.s.d.c. experiments of [23] seem to have been carried out only up to a maximum temperature of 40°C and this can be the reason why no more relaxations were detected in the liquid crystalline phase.

We can thus conclude from the preceding discussion that the relaxations observed in the mesophase of the side chain polysiloxane studied in this work can be attributed to the α and δ processes in the order of increasing temperature. This attribution is also reinforced by the observation by d.r.s. [20] that the α-process has an apparent activation energy higher than the δ-process at a given temperature. According to our t.s.d.c. results, the peak at 8°C has in fact an activation enthalpy which is higher than that of the peak at 33°C (see figure 5). Nevertheless, we would like to point out that we are aware of the fact that the attribution of the relaxations observed above T_g in the t.s.d.c. spectrum of polymeric materials is a controversial subject, and we are aware that more research work is needed in order to clarify this problem.

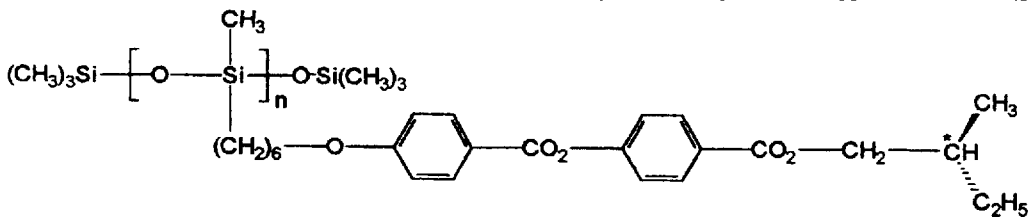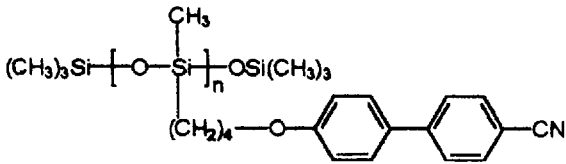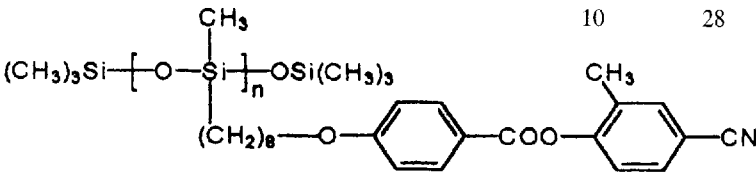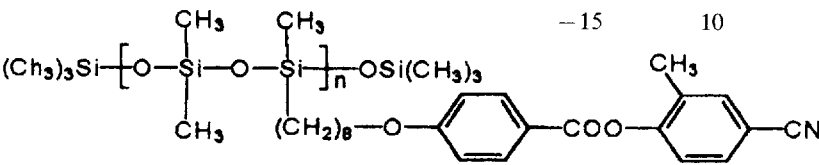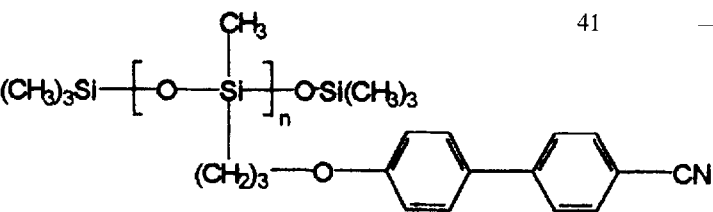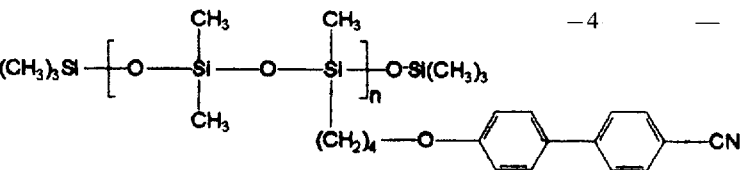### 3.2. *Dielectric relaxation spectroscopy results*

Figure 12 shows the dielectric loss factor measured at a frequency of 1 kHz over a wide temperature range. It can be seen that there are two processes that dominate the dielectric spectrum, both of which occur above the measured glass transition temperature of the polymer ($-7.2°C$). The first, at about 10°C at 1 kHz, is close to the glass transition of the polymer and is probably due to the main α-relaxation process, whilst the second at higher temperature is probably due to the dipolar relaxation occurring for the mesogenic side groups along the main polymer chain. This is found to be the case for many side chain liquid crystalline polymers. There is also a much broader and less intense relaxation process occurring in the dielectric spectrum at a temperature well below the glass transition, and this is attributable to local dipolar relaxations along the side groups. In order to characterize the three processes observed, each needs to be studied in more detail.

3.2.1. *δ process*

Figure 13 shows the plot of loss factor against log frequency for this smectic C polymer. This arises from the rotational fluctuations of the mesogenic groups around the short axis.

Initial loss results exhibited a high conductivity tail at lower frequencies, which made it difficult to examine the loss spectra for this process at lower temperatures, and thereby obscured any important data to indicate the change in the loss peaks during this alignment

Table 1. Location in the t.s.d.c. spectrum, of the glass transition relaxation and of the relaxations observed in the liquid crystalline phase. T_g, T_1 and T_2 are the temperatures of maximum intensity of the different discharges obtained from t.s.d.c. global experiments at a heating rate of 8°C min^{-1}

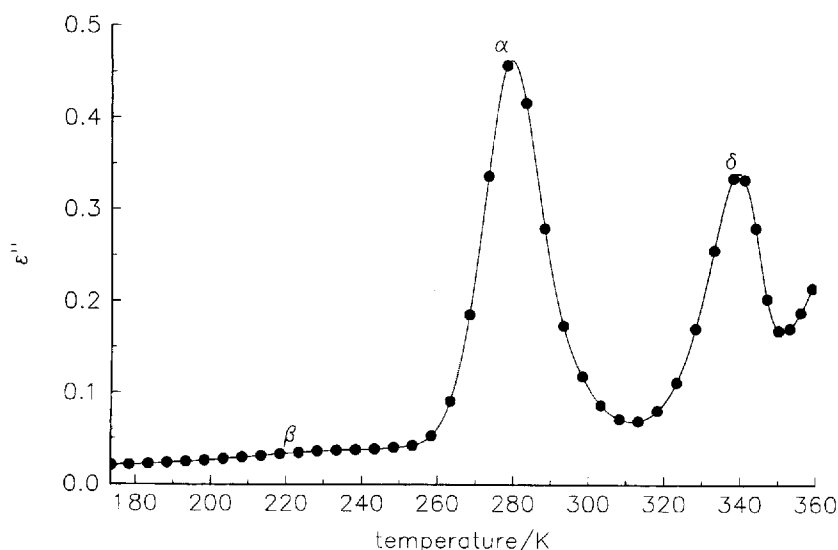| Structure	$T_g/°C$	$T_1/°C$	$T_2/°C$	$\Delta T = T_2 - T_g$	Ref.
1	-10	8	33	43	this work and [3]
2	25	—	61	36	[21]
3	10	28	40	30	[21]
4	-15	10	16	31	[22]
5	41	—	84	43	[5]
6	-4	—	39	43	[5,6]

Figure 12. Loss factor at 1 kHz as a function of the temperature showing the α and δ processes in the liquid crystalline state and the low temperature β relaxation process in the glassy state.
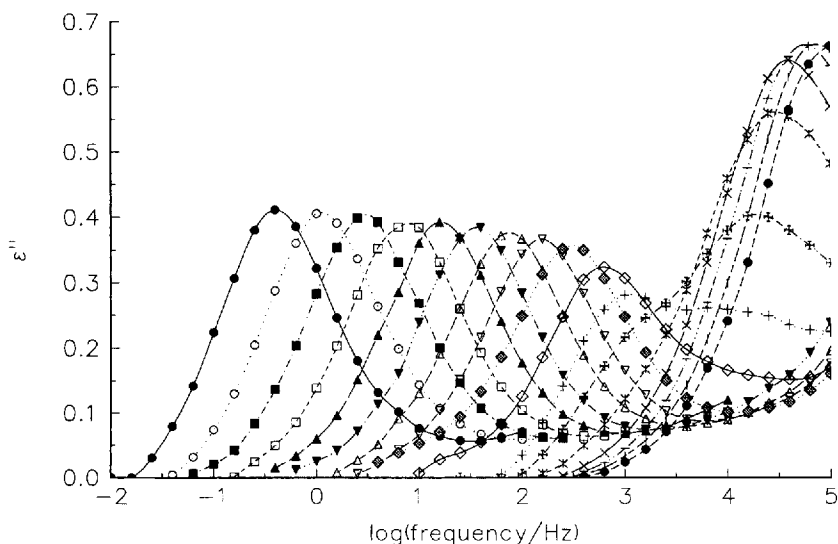

Figure 13. The δ relaxation process shown from 20 to 86°C. The data have been conductivity subtracted and show the change that occurs on heating to the clearing temperature.

process. In order to remove this low frequency conductivity process from the loss spectra, a mathematical procedure of conductivity subtraction was undertaken. This takes advantage of the fact that at high temperatures the conductivity process dominates at low frequencies. The functional behaviour of this can be calculated over the frequency range and the theoretical curve subtracted from the original data to reveal a 'cleaned' loss spectrum. For a true d.c. conductivity process, the loss factor should be proportional to $1/f$. However, it is usually found for organic solids that a $1/f^n$ law applies. The low frequency conductivity process

can be represented by

$$\log(\varepsilon'') = A - n\log(f) \tag{10}$$

If a plot of $\log(\varepsilon'')$ versus $\log f$ is made, values of A and n can be found from the interception and slope of the resulting linear equation. Table 2 gives the values of n and A determined this way. Values of A seem to have a linear relationship over the temperature range; this shows that the conductivity increases with a simple Arrhenius relation as temperature is increased, whilst values of n near 1·0 indicate a pure conductivity process with little dispersive transport of ions.

Table 2. Values of n and A calculated for the conductivity subtraction process in equation 10

Temperature/$^\circ$C	n	A
20	0·8966	−1·4440
25	0·9144	−1·0985
30	0·9287	−0·7747
35	0·9344	−0·4578
40	0·9440	−0·1669
45	0·9480	0·1070
50	0·9509	0·3694
55	0·9530	0·6128
60	0·9558	0·8467
65	0·8694	1·0617
68	0·8414	1·2535
71	0·9000	1·5160
74	0·9309	1·7075
77	0·9471	1·8518
80	0·9533	1·9636
83	0·9607	2·0742
86	0·9619	2·1695

The curves in the liquid crystalline state, up to 333 K, are well defined with a $\Delta \log f$ (the width of the loss curve at half height) of about 1·2 which is close to that of a single-relaxation-time process ($\Delta \log f = 1·14$) and is typical for a pure δ-process. From 338 K until the clearing temperature, the peaks are much broader with evidence of bimodal structure. Above the clearing temperature, the loss curves have increased in intensity and sharpened, becoming of constant intensity. These data show that the polymer goes from the smectic C state to the isotropic state via a fairly broad biphasic region. A convenient representation of part of these data is given

in figure 14 which shows a plot of the value of maximum loss against temperature. This shows more clearly the changes that occur in the δ relaxation process as the sample changes phase. Once the clearing temperature is reached (349 K), then there is no further change occurring.

Figure 15 shows a plot of the frequency of maximum loss factor versus reciprocal temperature for the data shown in figure 12. In the limited range of frequency covered in the isotropic range and in the smectic C range, the plots are approximately linear (the data are shown more clearly in the inset in figure 15) giving apparent activation energies of 110·5 and 159·2 kJ mol^{-1}, respectively. The activation energy for the liquid crystalline phase is typical of an activation energy associated with the relaxation of mesogenic groups within a side chain liquid crystalline polymer and compares very well with the value of 147 kJ mol^{-1} obtained by t.s.d.c. for peak 3 of figure 3.

3.2.2. α process

Figure 16 shows the α relaxation process plotted in the frequency plane at temperatures from 258 K to 288 K which is associated with the main glass transition of the polymer. This is confirmed by the activation energy plot (see figure 15) which shows the WLF dependence of the process with temperature with a considerable slowing down of the process as the glass transition is approached, and an activation energy that is much higher (estimated from a linear regression at lower frequencies to be about 380 kJ mol^{-1} at $\log f \sim 0$) than that of the δ relaxation process and typical of the main α process. In order to
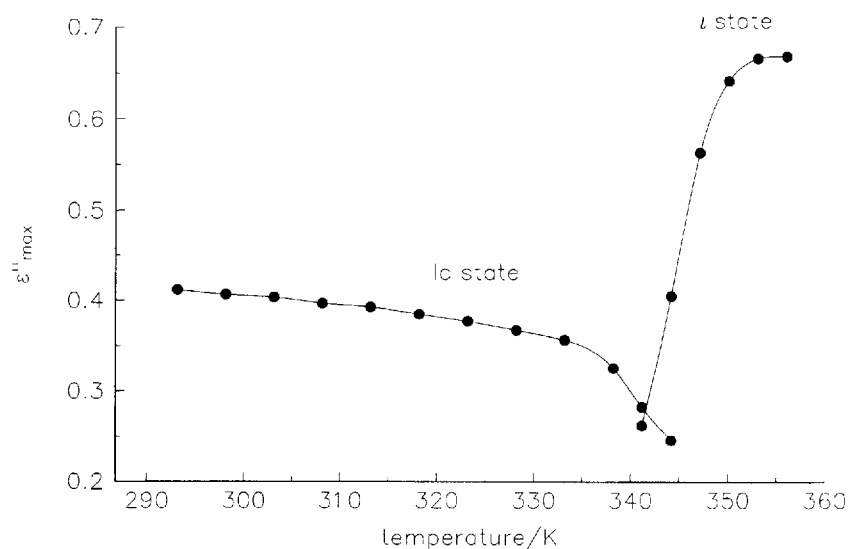

Figure 14. Plot of the peak maximum versus temperature for the δ relaxation process in the liquid crystalline and isotropic phases, showing clearly the clearing transition.
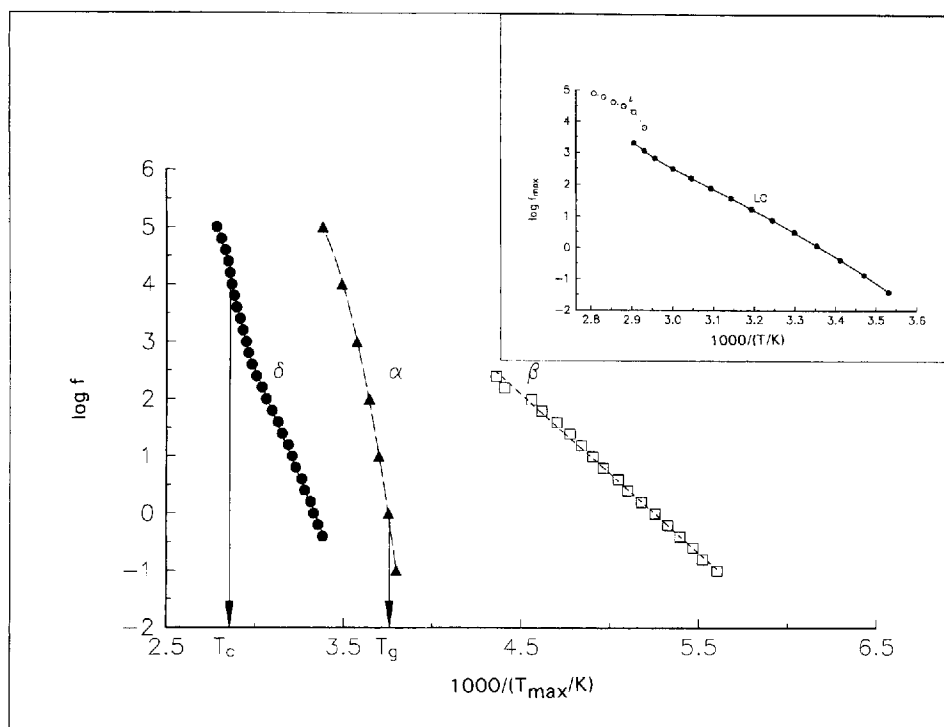
Figure 15. Arrhenius plots for the three dielectric relaxation processes; the α relaxation process shows WLF behaviour. The inset shows more clearly the change in the δ process as the sample clears.
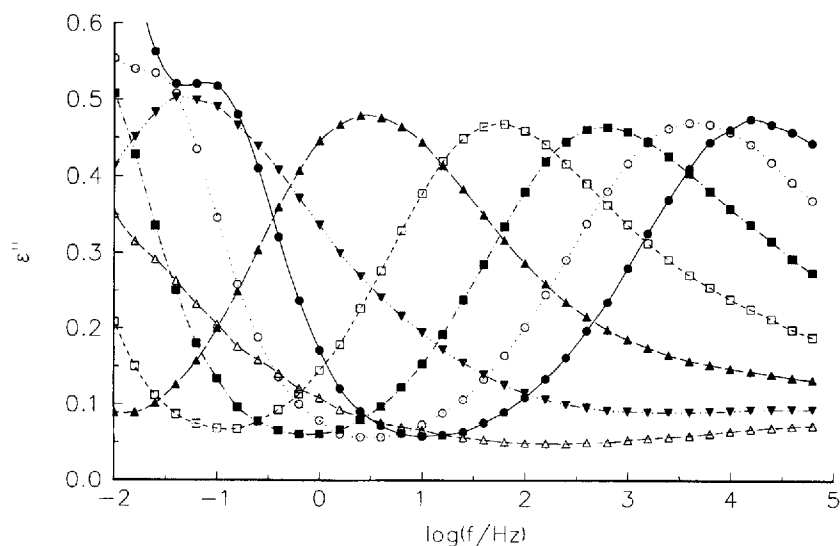

Figure 16. The α relaxation process measured with frequency from −15 to 15°C every 5°C. The figure shows the large half width of the transition.

compare with the activation energies obtained from t.s.d.c. experiments, we must note that the maximum activation enthalpy of the motions associated with peak 1 of figure 3 is $\sim 340\,kJ\,mol^{-1}$ which compares

well with the value previously reported, whereas that associated with peak 2 is substantially lower ($\sim 230\,kJ\,mol^{-1}$).

The half-width of 3·2 (giving a KWW β value of 0·36)

is much greater than the δ process and is typical of a loss process associated with the main glass transition which does not obey the single–relaxation–time model.

3.2.3. *β process*

Figure 17 shows the sub-T_g or β relaxation process that occurs well below the glass transition temperature of the polymer.

These data are shown in the temperature plane only since in the frequency domain they are unusually broad and loss peaks are not observed over the frequency range in the present study. Even so the process has a very low activation energy; a plot of log*f* against reciprocal temperature (see figure 15) exhibits a linear relationship expressing an independence of the dipolar motions with changes in temperature. The slope gives an apparent activation energy of 56 kJ mol^{-1} which is typical of a sub-T_g relaxation and is due to the rotational fluctuations of the mesogenic groups around their long axes. This value compares also very well with those (from 29 to 71 kJ mol^{-1}) obtained by t.s.d.c. for the sub-glass transition relaxation.

Comparison with figure 3 suggests that peaks 1 and 2 correspond to the α and δ processes observed dielectrically, since their positions correspond fairly closely in the temperature plane and the intensities are very similar. Extrapolation of the results of figure 15 to a frequency of 10^{-3} Hz (as with t.s.d.c.) gives estimated dielectric peak positions of $-114°C$ (β), $-14°C$ (α) and $1.3°C$ (δ).

According to this alternative proposal, the peak 3 in figure 3 would not correspond to a dipolar relaxation process and would probably correspond to a space charge peak (*ρ*-peak). On the other hand, comparing the

activation energies obtained by d.r.s. and t.s.d.c. we could be tempted to suggest that the peak 3 in figure 3 should correspond to the δ process. We must nevertheless emphasize that the attribution, at the molecular level, of the relaxations observed in the liquid crystalline phase of the t.s.d.c. spectrum is a controversial problem and that more research work is needed in order to clarify this problem and to enable an unambiguous comparison between the d.r.s. and the t.s.d.c. results.

4. Conclusions

From the results reported in this work we can draw the following conclusions:

(i) The t.s.d.c. spectra of the studied side chain LCP shows four different regions corresponding to four relaxation mechanisms.

(ii) The dielectric relaxation spectrum is dominated by two relaxations labeled α and δ in the order of increasing temperature and shows also a broad and low intensity relaxation below the glass transition temperature.

(iii) The values of activation energy of the lower temperature relaxation obtained by t.s.d.c. and by d.r.s. are similar and this relaxation was attributed to local motions along the mesogenic groups.

(iv) The glass transition relaxation studied by t.s.d.c. shows a compensation behaviour. It was demonstrated that this compensation effect corresponds to a true extra-thermodynamic relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and not to a propagation of experimental errors.

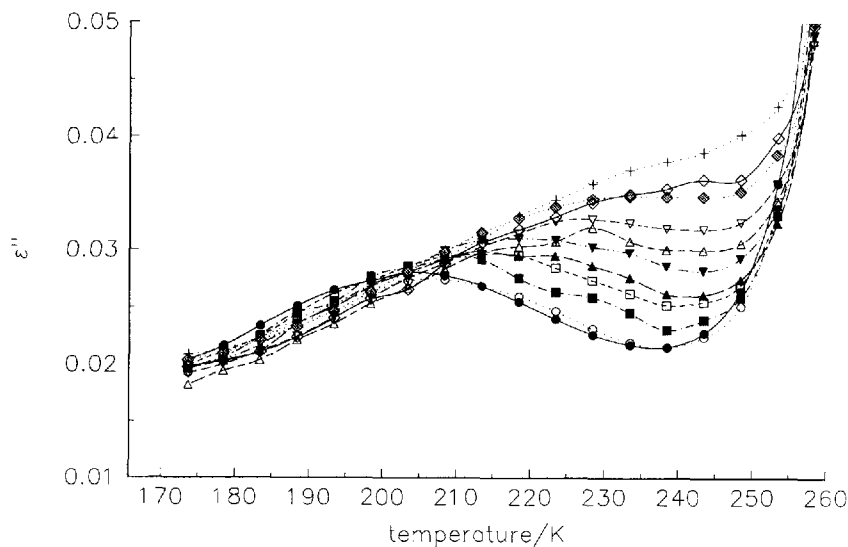(v) The α peak obtained by d.r.s. shows a WLF behaviour and the activation energy obtained in the

Figure 17.   The β relaxation process measured with temperature every 0·2 log Hz from 10 to 1 kHz. The transition is very weak and is obscured by the α relaxation process at higher frequencies.

lower frequency region is similar to that obtained by t.s.d.c. at the glass transition temperature.

(vi) Two relaxations were observed by t.s.d.c. above the glass transition temperature (with maximum intensities at 8 and 30°C). The activation energy of the relaxation at 30°C is similar to that of the δ process observed by d.r.s.

It was emphasized that the attribution of the different relaxations at the molecular level is a problem under study and that more research work is needed in order to allow a clear comparison between the results obtained by the two dielectric related techniques (d.r.s. and t.s.d.c.).

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