polymer papers

The dipolar relaxation behaviour of a liquid-crystalline side-chain polymer as studied by thermally stimulated discharge currents

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The various dipolar relaxation mechanisms of a liquid-crystalline side-chain polymer have been studied in detail by the technique of thermally stimulated currents. The α relaxation, or glass transition relaxation, showed a compensation behaviour, i.e. a correlation between the activation enthalpy and the activation entropy of its components. Two sub-glass relaxations were observed. The lower-temperature one shows a small activation enthalpy (5–6 kcal mol^{-1}), and is attributed to slightly hindered internal rotations in the side group. The higher-temperature one, on the other hand, shows a higher activation enthalpy (23 kcal mol^{-1}) and a low positive activation entropy, and is attributed to restricted internal rotations of the side groups around bonds near the main chain, eventually in cooperation with the movements of the main-chain segments. An upper glass relaxation was also observed. This relaxation shows a Williams–Landel–Ferry or Vogel behaviour and high values of its mean activation enthalpy and entropy. The attribution of this discharge at the molecular level is discussed.

(Keywords: thermally stimulated current; dielectric relaxation; liquid-crystal polymer)

INTRODUCTION

Liquid-crystalline polymers (LCPs) are high-molecular-weight materials that exhibit mesomorphism, and the properties of these novel materials are clearly explained in a recent and excellent book[1]. An interesting point about LCPs is that they give rise to a very great deal of interest for both theoretical and applied scientists. From the theoretical point of view, the study of LCPs leads to the heart of interdisciplinary science. This subject area brings into interaction two well established and important areas of physical chemistry: the science of liquid crystals and polymer science. Further fundamental research is still required in order to make the bridge between these areas and that is why those materials are undoubtedly extremely interesting from an academic standpoint. Integrated research teams are carrying out, at the present time, research programmes on LCPs which include the synthesis of new molecules, the physical, chemical and microstructural characterization, the study of properties and applications. From the point of view of applied science, on the other hand, the study of LCPs constitutes one of the most rapidly growing areas of materials science. Different potential applications for LCPs have been considered[1,2]: new structural materials (fibres with good axial strength and stiffness, excellent mouldability, fire and solvent resistance) and new opto-electronic materials (optical data storage, optical elements and cladding, non-linear optics, photochromic behaviour, photoconductivity, etc.).

The side-chain liquid-crystalline polymers constitute a major class of LCPs in which the mesogenic units are attached laterally to the main chain via a flexible link (spacer), usually a methylene chain. The dielectric relaxation mechanisms in these materials were studied in the 1980s for a great number of substances, particularly polyacrylates and polysiloxanes, and the results reviewed up to 1988[3]. Various relaxation mechanisms have been detected and labelled α, β, γ in order of decreasing temperature. In low-molecular-weight (as well as in side-chain polymeric) liquid crystals, a further relaxation at lower frequency (labelled δ) was observed. The δ peak was attributed to the motions of the longitudinal component of the dipole moment of the mesogenic side

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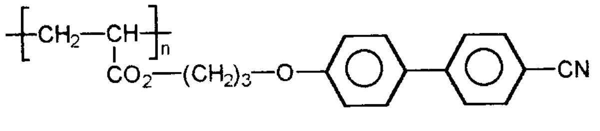
group, and corresponds to a process having nearly a single relaxation time, whereas the α peak is broader and is attributed to a combination of different processes. The β and γ peaks have been attributed to local motions involving the spacer unit.

The technique of thermally stimulated discharge currents (t.s.d.c.) is a suitable technique to study the dipolar relaxation mechanisms in polymers[4,5] and it shows a good capacity for resolving complex relaxation spectra as a function of temperature[6,7]. This high resolution power of the t.s.d.c. technique is a consequence of its low equivalent frequency. In fact, van Turnhout[8] showed that a t.s.d.c. experiment is equivalent to a low-frequency dielectric loss experiment and that the equivalent frequency is given by:

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

where E_a is the activation energy, r the heating rate ($r = dT/dt$), R the ideal gas constant and T_m the temperature at which the t.s.d.c. peak has its maximum. This low equivalent frequency of the t.s.d.c. technique leads to an enhancement of the resolution of the different relaxation processes or, otherwise stated, the separation of the t.s.d.c. peaks along the temperature axis is increased when compared with higher-frequency techniques such as dielectric relaxation spectroscopy. The t.s.d.c. studies on LCPs are nevertheless very scarce, and this scarcity is even more pronounced in the case of side-chain LCPs. The present work is part of a project whose objective is to understand the molecular dynamics in LCPs using the t.s.d.c. and other related techniques. In this paper we report the t.s.d.c. spectra obtained for polymer **1**, poly({3-[4-(4-cyanophenyl)phenoxy]propyloxycarbonyl}-ethylene), in a large temperature range and we analyse the different observed discharge peaks in order to understand the different relaxation mechanisms at the molecular level.



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EXPERIMENTAL

The studied side-chain LCP **1** was obtained from Merck (catalogue code LCP95); its glass transition temperature is reported to be $T_g = 46.7$°C and it shows a smectic A–isotropic transition at 82.9°C. The number-average molecular weight, M_n, is reported to be 3790 and the polydispersity index, M_w/M_n, is 1.58.

Thermally stimulated current experiments were carried out with a TSC/RMA Spectrometer (Solomat Instruments, Stamford, CT, USA) covering the range -165 to 400°C. A Faraday cage shields the sample, and prior to the experiments the sample is evacuated to 10^{-4} mbar and flushed several times with 1.1 bar of high-purity helium. Prior to use, the samples were degassed by heating at 85°C in a vacuum oven for several hours. This procedure prevents air bubble formation in the sample, particularly in experiments at higher temperatures, and warrants a good electrical contact between the sample and the electrodes. Sample thickness was approximately 0.8 mm, with an electrode contact area of ~ 38 mm^2.

The d.s.c. thermograms of polymer **1** were obtained in a Setaram Differential Scanning Calorimeter DSC-121, in a heating mode run using a scanning rate of 5 K min^{-1}. Before each run, the sample was heated up to 115°C, annealed at this temperature for 5 min and then cooled down to 0°C at 5 K min^{-1}.

One of the advantages of the t.s.d.c. method is the possibility of using different polarizing techniques and thermal treatments. We will describe now three such experiments that were used in the present work and will be called (i) *t.s.d.c. global experiment*, (ii) *partial polarization experiment* and (iii) *thermal cleaning experiment* (also called *thermal windowing* or *thermal sampling*).

(i) In a t.s.d.c. global experiment the sample is polarized at a temperature T_p (polarization temperature) well above the temperature at which the peak has its maximum, T_m. The polarization time, t_p, is such that $t_p \gg \tau(T_p)$, where $\tau(T_p)$ is the relaxation time at T_p. The sample is then quenched to the 'freezing temperature', T_0, in the presence of the field. This temperature 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 polarization induced by the field to be frozen in. With the field off at T_0, the sample is then short-circuited and the discharge current due to dipolar reorientation is then measured as the temperature is increased at a constant rate (typically 4°C min^{-1}) from T_0 to a final temperature $T_f \geq T_p$. The result of a t.s.d.c. global experiment is a global spectrum that contains all dielectrically active relaxations excited by the field between T_0 and T_p.

(ii) A partial polarization experiment is quite similar to a t.s.d.c. global experiment but now T_p is a temperature situated in the temperature region in which the peak appears (in this case we do not have $T_p \gg T_m$ as was the case in the global experiment). This experiment allows one to polarize only a part of the global peak (its lower-temperature side).

(iii) A thermal cleaning experiment, on the other hand, is used in order to resolve the global peak into its individual relaxation modes. In this experiment the field is applied only in a narrow temperature range within the region where the peak appears in order to polarize a single segment of the global discharge spectrum. A typical thermal cleaning experiment may be described as follows: (1) field on at T_p for 5 min (T_p varies from experiment to experiment in the region of the peak); (2) quenching to $T_p - 5$°C in the presence of the field; (3) removal of the field and isothermal holding for 2 min; (4) quenching to a temperature T_0 well below the peak temperature region (say 50°C below T_p); and (5) short-circuiting and measuring the discharge current as the temperature increases at a constant rate from T_0 to a final temperature T_f well above the peak maximum (say 20°C above T_m). Performing different thermal cleaning experiments with T_p varying in the peak temperature range allows the selective activation of the different fractions or segments of the global peak or, otherwise stated, the separation of a broad distribution of relaxations into its narrowly distributed components.

T.s.d.c. data and relaxation parameters

When the sample is poled by a static electric field E at a temperature T_p for a time $t_p \gg \tau(T_p)$, an equilibrium polarization, P, is induced that is proportional to the field intensity and to the dielectric strength of the dipolar relaxation process:

$$P = \varepsilon_0 \Delta\varepsilon(T_p) E \tag{1}$$

where $\Delta\varepsilon$, the dielectric strength (which is proportional to the square of the relaxed dipole moment and to the dipole number density), is the difference between the relaxed and the unrelaxed dielectric constant and ε_0 is the permittivity of vacuum. When the temperature is decreased in the presence of the field, the relaxation time, τ, becomes longer than the timescale of the experiment and the polarization (the orientation of the dipoles) is frozen in. When the field is removed and the sample is heated at a constant rate, the measured current J is related to the polarization by:

$$P = \int_{t_0}^{\infty} J \, \mathrm{d}t \tag{2}$$

where J is the measured current and t_0 is the time at which the depolarization scan is started.

From (1) and (2), and considering that the heating rate, r, is given by $r = \mathrm{d}T/\mathrm{d}t$, we have:

$$\Delta\varepsilon(T_p) = \frac{1}{\varepsilon_0 E A} \int_{t_0}^{+\infty} J \, \mathrm{d}t = \frac{1}{\varepsilon_0 E A r} \int_{T_0}^{T_f} J \, \mathrm{d}t \tag{3}$$

which shows that the dielectric strength of a relaxation process can be obtained by integrating the area under the corresponding t.s.d.c. spectrum. In equation (3) T_0 and T_f are temperatures that are respectively well below and above the temperature range in which the peak appears.

During the discharging or charging process the polarization, for a single relaxation time, is given by the Debye equation[9]:

$$\frac{\mathrm{d}P(t)}{\mathrm{d}t} = -\alpha(T)P(t) + \varepsilon_0 \Delta\varepsilon \alpha(T) E \tag{4}$$

where $\alpha(T) = 1/\tau(T)$ is the dipole relaxation frequency. In the discharging process $E = 0$ and therefore:

$$P(T) = P_0 \exp\left(-\frac{1}{r}\int_{T_0}^{T} \frac{\mathrm{d}T'}{\tau(T')}\right) \tag{5}$$

where P_0 is the total polarization at $t = 0$. Since the measured current J is proportional to the change of the polarization, we have:

$$J(T) = -\frac{\mathrm{d}P(T)}{\mathrm{d}t} = \frac{P(T)}{\tau(T)} = \frac{P_0}{\tau(T)} \exp\left(-\frac{1}{r}\int_{T_0}^{T} \frac{\mathrm{d}T'}{\tau(T')}\right) \tag{6}$$

Since the relaxation time decreases strongly with increasing temperature, the t.s.d.c. peak shows a marked asymmetry with a slow rise on the low-temperature side. From equations (2) and (6), it comes out that:

$$\ln \tau(T) = \ln\left(\int_{t}^{\infty} J(T) \, \mathrm{d}t\right) - \ln[J(T)] \tag{7}$$

There are different models to describe the temperature dependence of the relaxation times. According to the Arrhenius model, the relaxation time changes with T as:

$$\tau(T) = \tau_0 \exp(E_a/kT) \tag{8}$$

where τ_0 is the natural relaxation time of the considered relaxation mechanism and E_a is its apparent activation energy. The t.s.d.c. peaks observed in polymers are not generally described by a single relaxation time but by a distribution of relaxation times. This causes the peaks to be broadened and in this case equation (6) has to be modified to a summation over all the relaxation times assuming a given distribution function. On the other hand, some relaxation processes in polymers are not localized motions but cooperative relaxations involved in chain segment mobility. In these cases the empirical Williams–Landel–Ferry (WLF) or Vogel equations are more appropriate to describe the temperature dependence of the relaxation time. The Vogel equation, for example, can be written as:

$$\tau(T) = \tau_0 \exp[\alpha_f(T - T_\infty)]^{-1} \tag{9}$$

where α_f is the average thermal expansion coefficient of the free volume and T_∞ is a critical temperature. From the above, we have the basis for obtaining an analytical expression for the discharge current in a t.s.d.c. experiment. The substitution of equation (8) or (9) into equation (6) should give the desired expression. Nevertheless, some mathematical difficulties concerned with the integral calculation necessitate the use of some approximations. The equation:

$$J(T) = A \exp\left[-\frac{E_a}{kT} - \frac{B(kT)^2}{E_a} \exp\left(-\frac{E_a}{kT}\right)\right] \tag{10}$$

where A and B are adjustable parameters, is reported to reproduce the experimental t.s.d.c. peaks as well as those obtained from very different techniques such as thermoluminescence[4]. The first term in equation (10) is responsible for a slow increase of the function with increasing temperature on the low-temperature side of the t.s.d.c. peak. The second term, on the other hand, is a steeply decreasing function with increasing temperature and describes the high-temperature side of the t.s.d.c. peak. Equation (10) thus describes the asymmetry of the experimental t.s.d.c. peaks we mentioned before. Inspection of equation (10) also shows that in the early stages of the depolarization (when the second term is negligible) there should be a linear relationship between $\ln J(T)$ and $1/T$. On the low-temperature side of the peak (for $T \ll T_m$) equation (10) can be written as*:

$$\left.\frac{\mathrm{d}\ln J(T)}{\mathrm{d}(1/T)}\right|_{T \ll T_m} \cong -\frac{E_a}{k} \tag{11}$$

This corresponds to a method for obtaining the activation energy of a given relaxation process called the *initial-rise method*[4]. Other parameters associated with a given relaxation process can be obtained from the t.s.d.c. data. The activation enthalpy ($\Delta H^{\ddagger}$) and the activation entropy

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* For a distribution of relaxation times, equation (11) must be written as[9,10]:

$$\left.\frac{\mathrm{d}\ln J(T)}{\mathrm{d}(1/T)}\right|_{T \ll T_m} \cong -\frac{mE_a}{k}$$

where m is a distribution parameter such that $0 < m < 1$, with $m = 1$ for a single relaxation time

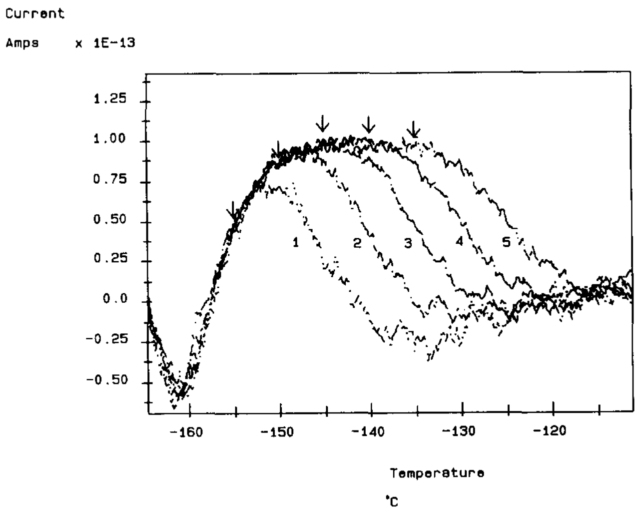

Figure 1 Partial polarization experiments on the low-temperature relaxation. The polarization temperatures, indicated by the arrows, are: (1) −155°C, (2) −150°C, (3) −145°C, (4) −140°C, (5) −135°C

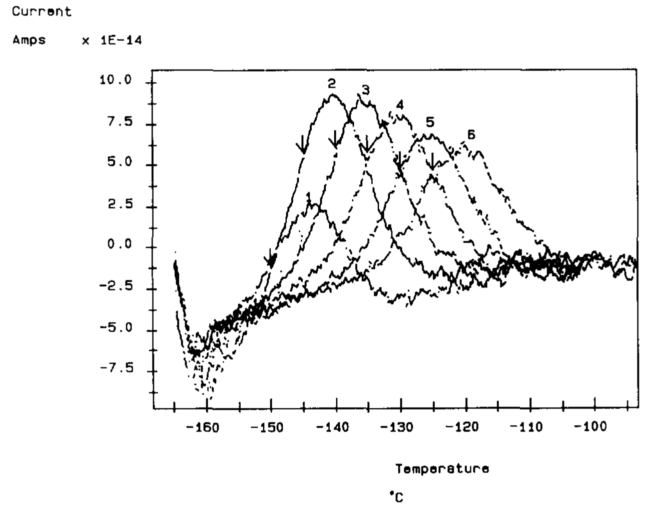

Figure 2 Thermally cleaned components of the lower-temperature broad relaxation. The window width is 5°C and the polarization temperatures are: (1) −150°C, (2) −145°C, (3) −140°C, (4) −135°C, (5) −130°C, (6) −125°C

($\Delta S^{\ddagger}$) can be obtained by fitting the Eyring equation to the data obtained from equation (7). On the other hand, the total relaxed charge, Q, due to the overall depolarization process is calculated from the area bounded by the t.s.d.c. peak and the abscissa[11]:

$$Q=\frac{A}{r}\int_{T_0}^{T_f} J(T)\,\mathrm{d}t \qquad (12)$$

where A is the electrode area and r the heating rate. Since Q/A is the total polarization, P, we can conclude from equation (1) that there is a linear relationship between the relaxed charge and the field strength, E. On the other hand, a linear relationship is commonly observed between Q and I_m, the intensity of the peak maximum, and therefore a linear dependence is also often observed between I_m and the field intensity. This linear behaviour is often considered as an indication of the dipolar nature of the relaxation process.

RESULTS AND DISCUSSION

The t.s.d.c. spectrum of this LCP polymer obtained from t.s.d.c. experiments shows four depolarization peaks at −140, 59, 70°C and a huge one beginning at ~75°C, whose maximum intensity appears at $T_m > 120$°C and which corresponds to a charge release due to melting. This higher-temperature discharge is not relevant to the study of the dipolar relaxation mechanisms in this polymer and it will not be analysed here. In the following text we will discuss separately the other three observed peaks.

The peak at −140°C

This peak is a broad relaxation in the temperature axis, as seen in *Figure 1*, which shows the results of different partial polarization experiments. When the polarization temperature, T_p, increases in these experiments, the peak becomes broader, suggesting that the relaxation segment that is polarized is larger. Analysis of the different components of this complex relaxation mechanism has been carried out by performing a series of thermal windowing experiments. The results of some of those experiments are shown in *Figure 2*. This figure shows that the maximum intensity, I_m, of the different components decreases as the T_p increases and that those peaks vanish for T_p values near −110°C. On the other hand, the peak position changes continuously with T_p and a linear relationship is observed between the temperature of the maximum, T_m, and the polarizing temperature, T_p. Each thermal cleaned peak, or otherwise stated each individual component of the broad peak, shows an Arrhenius behaviour as shown in the Arrhenius plots of *Figure 3*.

The activation enthalpy of the different segments is constant and equal to 5.5 kcal mol^{-1} and the entropy is negative (−20 to −30 cal K^{-1} mol^{-1}) and becomes more negative as T_p increases. This behaviour is the same as we observed in the low-temperature relaxation of poly(vinyl acetate)[12], and indicates that the transition state of this process is more ordered or more symmetric than the initial state. Since the pre-exponential factor, τ_0, increases with T_p and the activation energy is constant,

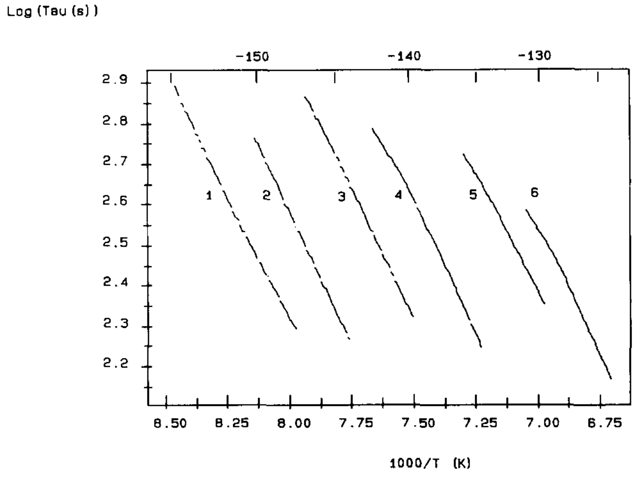

Figure 3 Arrhenius plots (log τ *versus* $1/T$) for the different thermally cleaned segments of the global relaxation at lower temperatures. The numbers indicate the correspondence between the Arrhenius lines and the peaks in *Figure 2*

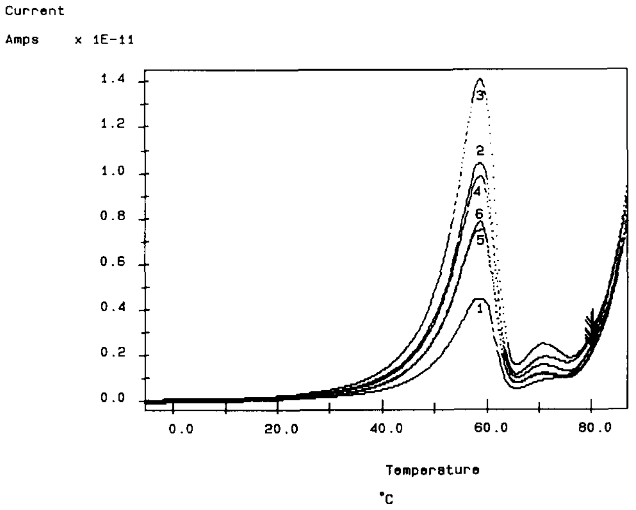

Figure 4 Effect of polarization voltage on the relaxation peaks at 59 and 70°C. The experiments were t.s.d.c. global with $T_p = 80°C$. Polarization voltages are: (1) 100 V mm^{-1}, (2) 200 V mm^{-1}, (3) 250 V mm^{-1}, (4) 300 V mm^{-1}, (5) 350 V mm^{-1}, (6) 370 V mm^{-1}

the Gibbs activation energy increases continuously with increasing T_p. The low value of the activation enthalpy obtained for all the segments of this complex relaxation process suggests that it is related to local motions in the side chain, probably slightly hindered internal rotations in the spacer $-(CH_2)-$ and around the CO bond of the ether group. On the other hand, the distribution of the pre-exponential factor indicates that the local groups move in a variety of local environments. These motions can lead to rigid excursions of the bond dipoles in the side chain, and the small site-energy differences for these motions can be at the origin of the low strength of this mechanism when compared with the other relaxations observed in this polymer. Nevertheless we must acknowledge that the previous comments are somewhat speculative since the sub-glass relaxation processes in polymers are not well understood in terms of molecular mechanisms[13,14]. The dipolar nature of these motions, however, seems to be confirmed by the fact that the relaxed charge (and the intensity of the peak maximum) shows a linear dependence on the polarization voltage.

The peak at 59°C

On *Figure 4* are shown the results obtained in t.s.d.c. global experiments ($T_p = 80°C$) at different polarization voltages. Two peaks are observed in this figure: a higher-intensity one whose temperature of maximum intensity, T_m, is 59°C and a lower-intensity one with $T_m = 70°C$.

It is apparent from *Figure 4* that the intensity of both peaks is not a monotonically increasing function of the polarization voltage. The variation of the maximum intensity, I_m, as a function of the polarization voltage shows a behaviour that is not very common: for low polarization voltage, I_m increases linearly with V; but for high polarization voltages, there is a decrease of the intensity (and strength) of the peak. This anomalous behaviour could be ascribed to the detrapping of ionic impurities and/or homocharges at higher voltages, with the consequence that the motion of those charges through the sample would make difficult the dipolar orientation induced by the electric field in the liquid-crystalline phase. This reduction of the dipolar orientation power of the field due to the motion of space charges through the sample would be a phenomenon somewhat similar to that of the 'dynamic dispersion' that was used in the first generation of liquid-crystal displays. This behaviour, which is common to both peaks (at 59°C and 70°C), will be discussed later.

The peak at 59°C was studied in detail by the technique of thermal cleaning. Different components of the whole peak, obtained with polarizing windows of 5°C at different polarization temperatures, are shown on *Figure 5*. It is apparent from that figure that there is a strong modification of the peaks as T_p varies.

In *Figure 6* are shown the ln τ *versus* $1/T$ plots for different 'individual' components of this peak, and it can be seen that they show an Arrhenius behaviour. On the other hand, one can distinguish two different groups of Arrhenius lines: those corresponding to segments of low polarization temperature, which are parallel to each other, and those corresponding to higher-polarization-

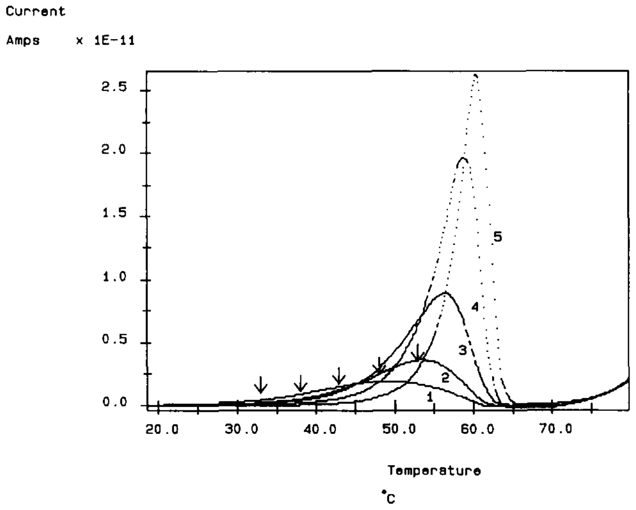

Figure 5 Thermally cleaned components of the peak at 59°C. The window width was 5°C and the polarization temperatures, indicated by the arrows, were: (1) 33°C, (2) 38°C, (3) 43°C, (4) 48°C, (5) 53°C

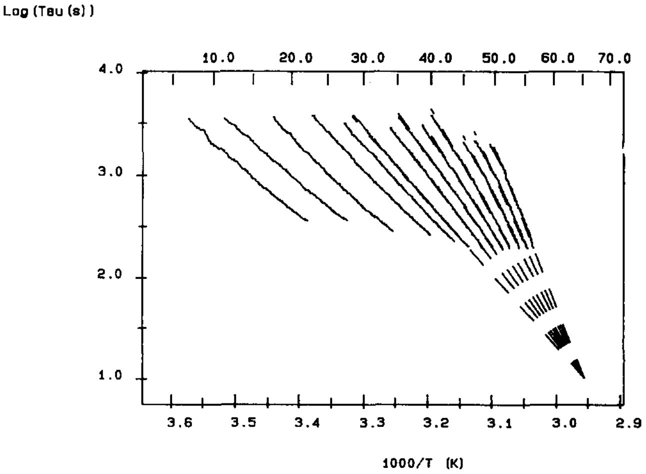

Figure 6 Arrhenius plots (log τ *versus* $1/T$) for different thermally cleaned components of the peak at 59°C. The coordinates of the compensation point are log $\tau_c = 1.02$, $T_c = 65.1°C$

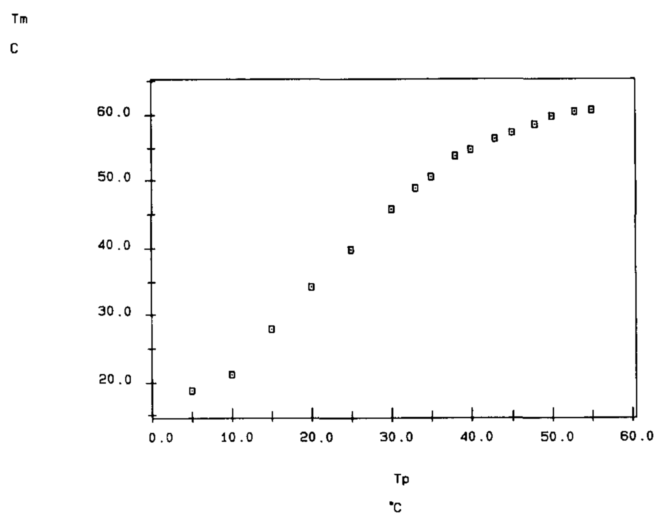

Figure 7 Temperature of maximum intensity, T_m, as a function of the polarization temperature, T_p, for the different thermally cleaned components of the peak at 59°C

temperature components, which converge to a point showing the so-called compensation behaviour. The different behaviour of those two groups of individual components of this complex discharge is also observed in the plot of the temperature of maximum intensity, T_m, as a function of the polarization temperature, T_p (*Figure 7*): for the components with $T_p \leqslant 30°C$ the dependence is linear, but for $T_p \geqslant 35°C$ a distinct behaviour is observed.

The different behaviour of the lower-temperature components of this complex discharge, on the one hand, and that of the higher-temperature components, on the other, is also explicit on the representations of the peak maximum intensity, I_m, or of the activation enthalpy or entropy as a function of T_p. For $T_p < 30°C$, I_m changes very slightly with T_p, whereas for the higher-temperature components a strong variation is observed. In the representation of the activation enthalpy and entropy as a function of T_p, two different behaviours are again observed as expected: the low-temperature components have activation enthalpies and entropies that do not change with T_p (Arrhenius lines parallel in *Figure 6*), whereas the high-temperature components show a strong and concomitant increase of both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with increasing T_p. This concomitancy leads to a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and this linearity corresponds to the so-called compensation phenomenon that is observed for the glass transition relaxation of many amorphous polymers[6,7,15].

The above observations suggest the presence of a lower-activation-energy process below T_g or, otherwise stated, that the peak at 59°C contains two superimposed relaxation mechanisms that can be resolved by thermal cleaning experiments. The low-temperature and low-intensity mechanism of that peak, on the one hand, has an activation enthalpy of 23 kcal mol^{-1} and an activation entropy that is low and positive ($\sim$10 cal K^{-1} mol^{-1}). These values of the activation parameters, as well as the location of this relaxation in the temperature scale, suggest that we are in the presence of a β process, which can be ascribed to the hindered internal rotations of the side groups around the CO bonds. The high-temperature and higher-intensity mechanisms, on the other hand, which show a compensation behaviour, can be ascribed to the glass transition. This compensation phenomenon, also sometimes called the isokinetic effect, is often observed in different areas of physical chemistry[16]. Nevertheless, strong reasons have been advanced to show that, in most cases, the linear dependence of enthalpy vs. entropy is a consequence of a statistical compensation pattern that arises solely from experimental errors[17]. The compensation effect we are dealing with in this context of the glass transition relaxation peak is nevertheless believed to be a genuine behaviour, and it is recognized that this behaviour is characteristic of many amorphous polymers or of the amorphous regions of semicrystalline polymers at T_g (ref. 15). The observed compensation effect would be a consequence of the coupling between the different relaxation modes at the glass transition and it has been suggested that, at the compensation point, T_c, all relaxations occur at a single relaxation time. This claim of a unique relaxation at T_c has nevertheless been refuted by Read[18] on the basis of the analysis of the width of the relaxation-time distribution. Alternatively, the increase of both activation enthalpy and activation entropy was attributed to a structural change towards equilibrium with increasing temperature.

We pointed out before that the variation of the strength of this peak with the polarization voltage, obtained from t.s.d.c. global experiments, showed a behaviour that is not very common since the intensity decreases at higher voltages. From the detailed analysis of this peak, we suggested that it is composed of two different relaxation mechanisms, and so it should be interesting to analyse how the strength of those two relaxation mechanisms changes with the polarization voltage. *Figure 8* shows the influence of the polarization voltage, *V*, of a thermally cleaned component on the low-temperature side of the global peak at 59°C. The peak maximum intensity shows a linear variation with the polarization voltage, which is an indication of the dipolar nature of this relaxation mechanism.

Figure 9 is equivalent to *Figure 8* but it corresponds now to a thermally cleaned component on the

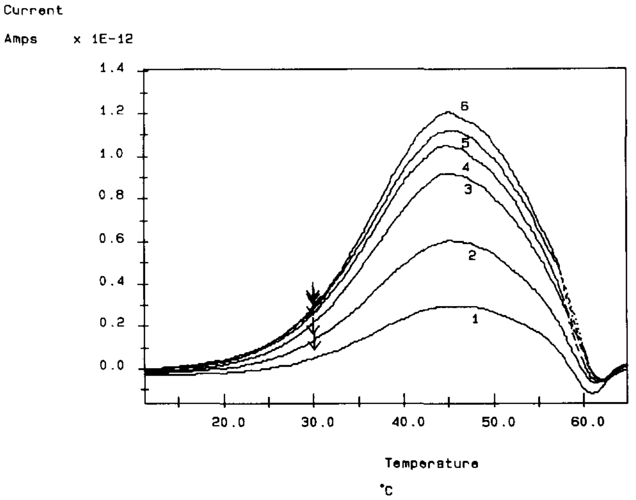

Figure 8 Effect of polarization voltage on the low-temperature thermally cleaned component of the peak at 59°C. The polarization temperature was $T_p = 30°C$, the window width was 5°C and the polarization voltages were: (1) 100 V mm^{-1}, (2) 200 V mm^{-1}, (3) 300 V mm^{-1}, (4) 350 V mm^{-1}, (5) 370 V mm^{-1}, (6) 400 V mm^{-1}

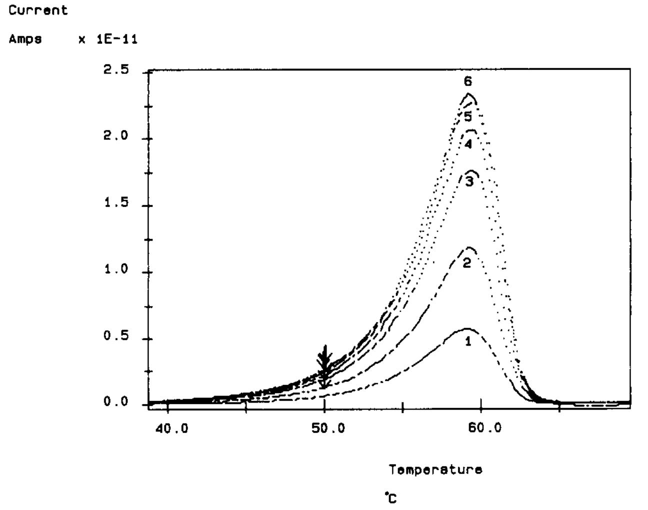

Figure 9 Effect of polarization voltage on the high-temperature thermally cleaned component of the peak at 59°C. The polarization temperature was $T_p = 50°C$, the window width was 5°C and the polarization voltages were: (1) 100 V mm^{-1}, (2) 200 V mm^{-1}, (3) 300 V mm^{-1}, (4) 350 V mm^{-1}, (5) 400 V mm^{-1}, (6) 420 V mm^{-1}

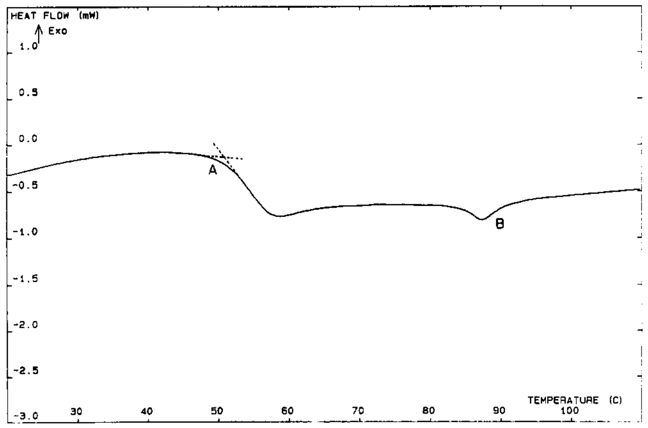

Figure 10 D.s.c. thermogram showing the glass transition, A, and the melting of the liquid-crystalline phase, B

high-temperature side of the global peak (glass transition relaxation). A slight departure from linearity is observed in this case for higher voltages. The explanation for this behaviour is not straightforward. On the one hand, it can be ascribed to the influence of the proximity, in the temperature scale, to the discharge at higher temperature, which begins at ~75°C and is due to the detrapping of heterocharges associated with melting. On the other hand, some experiments seem to point to the existence of a discharge, near 60°C, whose polarity is opposite to that of the dipolar relaxation peaks. This discharge, which can be seen on *Figure 8*, was disguised by the glass transition peak obtained in the experimental conditions of *Figure 9*. It can be ascribed to macroscopic motions of homocharges, and can be at the origin of the departure from linearity that we pointed out before. It must be noted here that a similar behaviour was reported in the context of a t.s.d.c. study of a side-chain LCP[19] and that this behaviour was interpreted in terms of a screening effect of space charges on blocking electrodes due to the migration of charge carriers under the influence of the electric field.

The glass transition temperature, T_g, of this polymer, obtained from our t.s.d.c. results, is $T_g = 57°C$, which corresponds to the temperature of maximum intensity of the component for which the activation enthalpy is maximum. This value is considerably higher than the value of 47°C reported in the Merck catalogue. This finding led us to study our polymer by differential scanning calorimetry (d.s.c.). *Figure 10* shows one of the thermograms obtained in different thermal cycles. From that figure we calculated T_g as the onset temperature and obtained a value of 51°C, which is not very far from our t.s.d.c. value. *Figure 10*, on the other hand, shows the endothermic peak corresponding to the melting of the liquid-crystalline phase (at 84°C) and the melting enthalpy obtained from the peak area was 0.13 cal g^{-1}.

The peak at 70°C

As shown on *Figure 4*, a relaxation peak above the glass transition relaxation was observed, having a maximum intensity at ~70°C. As previously pointed out, the strength dependence of this relaxation on the polarization voltage (when it was obtained by t.s.d.c. global experiments) showed a non-common behaviour similar to that observed for the peak at 59°C. Nevertheless, if we isolate this discharge by a thermally cleaned experiment (*Figure 11*), we observe that its maximum intensity, I_m, is linearly proportional to the polarization voltage.

The fact that the intensity of this thermally cleaned peak varies linearly with the polarization voltage may arise from the fact that, in those experiments, the temperature range in which the electric field is applied is higher than the temperature of ~60°C at which the homocharge discharge was observed. This would mean that, under these experimental conditions, the discharge at 60°C is relaxed and does not interfere with the molecular motions associated with the relaxation at 70°C. If this is the case, we could say that the non-linearity observed in *Figure 9* for the high-temperature component of this peak at 59°C is not a consequence of the influence of the high-temperature conductivity tail

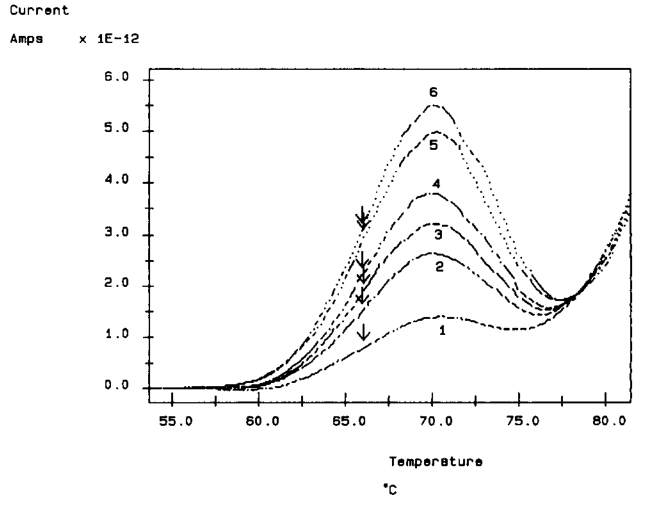

Figure 11 Effect of polarization voltage, *V*, on the intensity of the peak at 70°C. The polarization temperature was $T_p = 66°C$, the window width was 3°C and the polarization voltages were: (1) 100 V mm^{-1}, (2) 200 V mm^{-1}, (3) 250 V mm^{-1}, (4) 300 V mm^{-1}, (5) 400 V mm^{-1}, (6) 450 V mm^{-1}

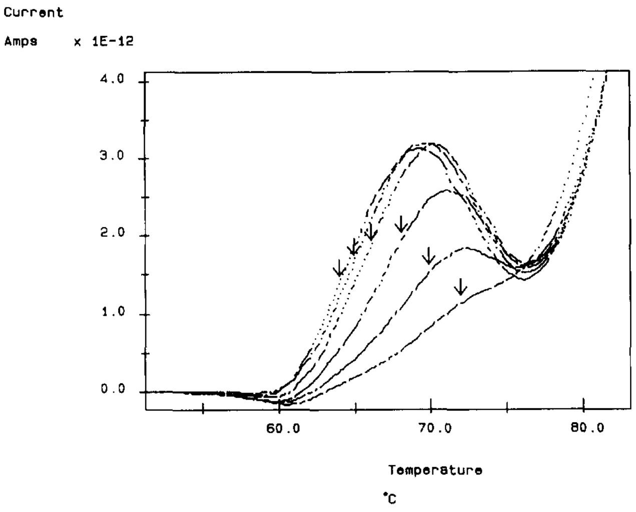

Figure 12 Thermally cleaned components of the peak at 70°C. The polarization voltage was $V = 250$ V mm^{-1}, the window width was 3°C and the polarization temperatures (indicated by the arrows) were 64, 65, 66, 68, 70 and 72°C

(which is nearer to the relaxation at 70°C but seems not to interfere with it) but is due to the homocharge discharge at ~60°C. The linearity observed in *Figure 11* is probably sufficient to dismiss any attribution that considers this peak as a discharge due to spatial charges (a ρ peak for instance). In an interesting t.s.d.c. study of LCPs by Williams *et al.*[19], the observed relaxation above T_g was considered as a ρ relaxation. The arguments given to support this assignment were the facts that the decay of the second harmonic generation signal with increasing temperature, which follows the α relaxation peak, was completely gone at the temperature of this peak and above, and also that this peak did not show a systematic behaviour for different experimental conditions, varying from sample to sample and even for the same sample depending on the sample age. We must note that, in the case of LCP95, we did not observe any change of this relaxation during the hundreds of thermal cycles to which the samples were subjected.

The analysis of this peak by thermal windowing experiments is shown on *Figure 12*. The slight variation of the temperature of maximum intensity, T_m, is certainly due to the influence of the high-temperature conductivity tail. The Arrhenius plots corresponding to the peaks of *Figure 12* show a slight curvature characteristic of WLF behaviour. On the other hand, the mean activation energies are high (96–97 kcal mol^{-1}) as well as the corresponding activation entropies (~210 cal K^{-1} mol^{-1}).

As stated before, the upper glass transitions observed by t.s.d.c. in polymers are frequently ascribed to the release of space charges. Nevertheless, some authors claim the existence of a genuine relaxation process in polymers above T_g and this relaxation is called liquid–liquid transition, T_{ll} (ref. 20). This type of relaxation process, which was reported in the literature 40 years ago[21,22], was considered for a long time as an artefact[23]. Some authors consider the T_{ll} transition as a precursor of T_g on cooling and the T_{ll} temperature is that at which the amorphous polymers and copolymers are free from some local structure. This process could be ascribed to global motions of the segments of the polymeric chains between successive entanglements. The stability of our peak at 70°C as a function of time and experimental conditions, its WLF behaviour, as well as the high values of its activation parameters could be compatible with such an attribution. Nevertheless, this is a somewhat speculative statement and we must acknowledge that we have not, at the present moment, all the information needed in order to make a non-ambiguous attribution of this discharge.

CONCLUSIONS

The dielectric relaxation of the side-chain liquid-crystalline polymer **1** was systematically and intensively studied over a wide temperature range from −160 to 120°C by the technique of thermally stimulated discharge current. Four different relaxations have been detected and studied in detail:

(1) a low-temperature relaxation (~ −140°C), which is broad, has a low activation enthalpy (5.5 kcal mol^{-1}) and was attributed to local motions in the mesogenic side group;

(2) a relaxation in the temperature range of 20–30°C, which has an activation enthalpy of 23 kcal mol^{-1} and a low activation entropy and was attributed to hindered internal rotations of the side groups around bonds near the connection to the main chain;

(3) the glass transition relaxation, which shows distributed enthalpies and entropies of activation and an enthalpy–entropy compensation effect; and

(4) an upper glass transition relaxation whose maximum is at 70°C, which shows high values for the enthalpy and for the entropy of activation and whose origin was not elucidated without ambiguity.

The obtained results undoubtedly show that the t.s.d.c. technique is a powerful method to study the dipolar relaxation mechanisms in liquid-crystalline polymers. Nevertheless, more work is needed on other LCPs in order to understand those mechanisms at the molecular level.

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