The thermally stimulated current technique applied to side-chain liquid-crystal polymers

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The thermally stimulated current (t.s.c.) technique is applied to three side-chain liquid-crystal polymers (LCP) and an LCP that contains a highly dipolar dye. The t.s.c. trace is shown to be very sensitive to a number of LCP properties including glass transition, degree of mesogenic alignment and the amount of polarization that can be stored. A strong correlation between such properties and the results of high-frequency dielectric spectra is established. These parameters are directly relevant for the application of these materials as optical storage media and in non-linear optics. In particular, the technique is able to define the optimum conditions for poling these LCP systems. The technique can also be used to determine a number of fundamental molecular properties such as activation energy, molecular relaxation distribution and polymer flexibility and, as such, allows fundamental examination of the relationships between main-chain and mesogenic motions.

INTRODUCTION

Side-chain liquid-crystal polymers (LCP) are novel materials able to combine the properties of low-molar-mass mesogens with the properties of the polymer backbone to which they are attached via flexible spacer units. This allows ample scope for varying polymer properties by altering the molecular architecture. The mesogenic unit can be aligned in electric and magnetic fields. In low-molar-mass mesogens this orientation is lost upon removal of the driving field. In LCP samples the macromolecular backbone may afford sufficient viscosity to allow the orientation to remain upon the removal of the field, even if the sample is above T_g[1,2]. Many aspects of the behaviour of these materials have been examined and a number of summaries exist[3-5].

The correlation of the motions of the main chain and the pendant mesogenic unit are not well understood. Since liquid-crystal (LC) phenomena involve interaction between the polar, rigid moieties, there must exist organized regions of mesogenic groups within the LCP to allow behaviour such as alignment, yet these units must still be intimately mixed with the polymer main chains as the backbone is found to have a major effect on the motion of the mesogenic groups in terms of relaxation frequency[6] and activation energies[5], for example. In the LCP case the relaxation frequencies are much lower and the activation energies much higher than in the low-molar-mass material.

DeGennes has said that very little is understood of the dynamics of LCPs on a molecular scale[7]. Only a few studies of relaxation spectroscopy have been done from the LC phase into the T_g region. Dynamic mechanical results[8] indicate that the polymer backbone dominates the mechanical spectra, although the liquid-crystal/isotropic transition (at the clearing point, T_{cl}) also causes a noticeable disturbance on the dynamic mechanical trace. Clearly, then, the LC structure existing above T_g

does impose some sort of mechanically measurable constraint onto the polymer chain, analogous to a weak physical crosslink. It is of interest, therefore, to be able to determine the glass transition of an LCP and the interaction between main-chain and mesogenic alignment and motion. Finkelman and Rehage[4] showed that the local order parameter, S, remains constant below T_g. This implies that, once the glass transition region is reached, the mesogenic motion is not able to proceed.

The polar nature of the mesogenic units makes dielectric spectroscopy a potent technique for the study of these materials. A.c. dielectric measurements have been performed extensively in recent years[9-13]. The predominant relaxations observed appear to involve motion around the long and short axes of the mesogen. The frequency spectrum changes depending on the alignment of the units—either parallel (homeotropic alignment) or perpendicular (planar alignment) to the measuring field. Essentially, the spectrum is composed of a weighted sum of four basic relaxation modes. These are explained in detail and graphically illustrated elsewhere[14]. The magnitude of the weighting depends on the degree of alignment and the mesogen dipole moment.

There are essentially two ways to align these materials depending on the nature of the material. One involves cooling the sample with the alignment field applied at the required frequency from the isotropic region into the LC phase[15]. In other samples it is possible to align the sample by applying the field while the sample is in the LC phase[16]. Clearly this latter technique is more desirable since to achieve full alignment by cooling through the biphasic range requires very slow cooling rates[15] especially if the sample is pure and the transition region very narrow[17]. The nature of the alignment (homeotropic or planar) can be changed by varying the frequency of the aligning field. For an LCP with a mesogen with positive dielectric anisotropy[1,13-18] it has been shown that there

exists a critical frequency, v_c, which is temperature-dependent. If the aligning field is above this frequency then the sample is planar, and below it the sample is homeotropically aligned. There is a practical lower limit to frequencies that can be used since electrohydrodynamic instabilities, such as Williams domains, can possibly occur at frequencies less than about $300\,Hz$[19,20].

Measurement of the usual bulk properties of LCPs as a function of macroscopic alignment is difficult using techniques such as differential scanning calorimetry (d.s.c.) or dynamic mechanical measurements because the small size and geometry of the sample make it difficult to handle. With LCP samples of about 0.1 mm thickness, voltages of about 300 V are required. (Because it is not possible to determine sample thickness precisely in the experimental configuration used in this work, the magnitude of the aligning field is represented by the poling voltage.) The thermally stimulated current (t.s.c.) technique is a method in which a sample in a dielectric cell is formed into a charged polymer electret by cooling in the presence of an applied d.c. field. A thermal scan of the short-circuited electret yields peaks indicative of molecular motions including T_g. The sample geometry allows easy *in situ* alignment. Further, the charging process of the electret by a d.c. field can be used to assess ohmic conductivity at the electret-forming temperature (not presented in this paper). The basic theory and application of t.s.c. measurements to LCPs are presented below. A survey of the literature indicates that this technique has not been applied yet to LCP systems. We believe it will prove a useful technique for such materials in that it is sensitive to molecular mobilities, alignment and LCP poling properties—all crucial factors in fundamental understanding and technological use of LCPs.

MATERIALS

Four main LCP systems are presented in this work and these are discussed below.

The first is a siloxane-backbone side-chain liquid-crystal polymer (LCP6), which is of the form:

where $n = 50$ and $m = 6$ LCP6
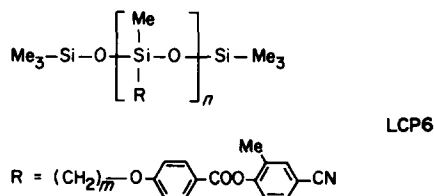
This material was provided by Professor G. Gray and Dr D. Lacey of Hull University. A d.s.c. scan of this material (scan rate $20°C\,min^{-1}$) has shown that it has a T_g of about 17°C and an approximate clearing point of 52°C. This sample has been examined by other methods of high- and ultra-low-frequency spectroscopy and the results reported[18,21–23]. It is nematic in the LC phase and is very pure (biphasic region only 0.5°C). Less pure samples of the materials had lower T_g values and biphasic regions of 5°C[18,21]. It is found that to align this material we needed to cool it through the biphasic region with the aligning field on. Voltages of about 250 V were required and aligning frequencies of about 700 Hz (homeotropic) and 10 kHz (planar) were used. We find that it

cannot be aligned directly by the application of an a.c. electric field while the sample is in the LC state.

The second material studied was a nitro-aromatic side-chain polyester liquid-crystal polymer (OI), which had the structure:
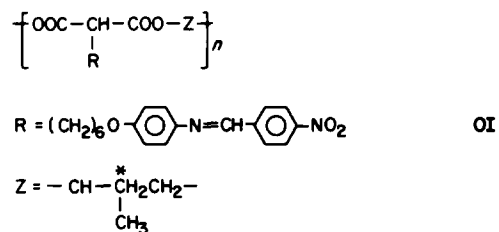
This material was synthesized by Professor A. Griffin of the University of Southern Mississippi[24]. The sample is chiral nematic in the LC phase and has approximate T_g and T_{cl} of 3°C and 48°C, respectively. It is very pure, with a biphasic range of less than 1°C from optical microscopy[24]. It is an interesting material since it can be aligned in the LC state. This and other dielectric properties have been reported previously[16]. Because of its ease of alignment in the LC phase, it is easy to switch between the homeotropic and planar alignments in this system, without the need for heat treatment. Further, this polymer is known to be useful for its second-order non-linear properties[24]. The criteria for such materials is that they are highly dipolar and non-centrosymmetric. Symmetry can be reduced by introducing a helical arrangement in the polymer backbone (as in OI). Also, by 'poling' the sample a highly dipolar sample has its symmetry destroyed[25]. Poling is essentially the process by which a polymer electret is prepared for t.s.c. and thus this technique is useful to determine both whether a sample can be poled and, if so, how well the polarization can be maintained with time. The t.s.c. thermogram allows the determination of sufficient and optimum conditions (of temperature and voltage) for this process. It should be noted that the poling of the polymer in the t.s.c. experiment is normally performed within the linear range (where current maximum is proportional to voltage) whereas much higher fields, such as obtained by corona discharge, are necessary to produce non-linearly active materials.

The third system is another LCP alignable in the LC state. It has already been reported to be useful for optical storage[2]. It is a copolymer with cyanobiphenyl and benzoic ester liquid-crystal side-chains randomly arranged along a siloxane main chain (PG 296). The chemical structure of PG 296 is schematically:

PG296
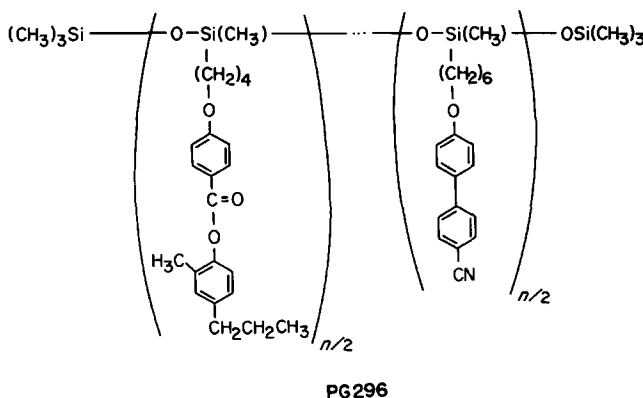
The sample was again provided by Professor G. Gray of Hull University. The T_g of this sample is 4°C and T_{cl} about 86°C. Its LC phase is smectic. It cannot be aligned planarly using conventional equipment, only homeotropically[26]. It was aligned in this work by application of 300 V at 78°C at a frequency of 1 kHz.

The fourth system examined also involves LCP6 but modified by the addition of a dye, 4-dimethylamino-4'-nitrostilbene (Stil) with a strong, permanent polarization. The use of dyes in LCPs (guest–host system) is another method of producing non-linear optical properties by altering existing polymer matrices. The structure of Stil is as follows and we see that the 'push–pull' nature the constituents confer on it results in a very large dipole moment and higher-order non-linear optical properties[25]:

$$(CH_3)_2 NC_6H_4CH \vdots CHC_6H_4NO_2 \qquad \text{Stil}$$

By poling these samples and destroying the centre of symmetry, second-order non-linear optical properties can be produced. The addition of solutes to the LCP changes the nature of the matrix and subsequent relaxations. These systems were examined by t.s.c., which can indicate optimum parameters for electret formation and poling. The dye concentrations used here were 0%, 1.15% and 3% Stil/LCP6 by weight. The samples were made by dissolving LCP6 and Stil in a mutual, water-free solvent, dichloromethane, removing the solvent under vacuum and thoroughly drying the remaining plasticized sample. The samples were examined in the unaligned state.

THEORY OF THERMALLY STIMULATED CURRENT MEASUREMENTS

The essence of the t.s.c. experiment is the formation of the polymer electret. This involves placing a thin layer of sample in a dielectric cell, raising the sample temperature to a level in excess of T_g and applying a d.c. voltage for a predetermined time, such as 1 h. This causes a degree of alignment of the dipoles and a drift of free charges to the electrodes. While maintaining the field the sample is cooled to below T_g to freeze-in molecular motions. The voltage source is then removed and the sample short-circuited across an electrometer, which is able to monitor low currents. The cell is heated at a constant rate and different molecular modes become activated at specific temperatures. This motion of the dipolar groups results in image charges being released and this is measured as the t.s.c. current peak on the thermogram at relaxations such as T_g and secondary motions. In this sample configuration (known as a 'heteroelectret'[27], where there are no air gaps between electrode and sample) a super-T_g peak is normally seen. This is known as the ρ peak and is due to the motion of excess charges.

The main variables are the electret-forming conditions (temperature, rate of cooling and magnitude of the d.c. field applied) and the t.s.c. scan rate. The faster the scan rate, the higher is the current maximum peak and the higher is the temperature of the peak, similar to d.s.c. thermograms.

BASIC THERMALLY STIMULATED CURRENT EXPERIMENTS AND CALCULATIONS

The basic result of the t.s.c. experiment is the thermogram showing the position of maximum charge flow and this

is related to polymer relaxations. However, there are a number of other experiments that can be done.

One of these is that of 'thermal cleaning' or 'multistage' t.s.c. experiments. If a current maximum is composed of more than one relaxation or if there is a distribution of relaxations (of either relaxation frequency or activation energy) it is possible to separate the components[27]. This is achieved by scanning the polymer electret partially up the peak and then cooling and rescanning the sample again. The motions released during the initial, part scan are exhausted and the remaining peak is due to motions activated at higher temperatures. If this is done incrementally the peak can be broken down into multiple components. Van Turnhout[27] states that if there is a single Debye-like relaxation process then, if a t.s.c. peak is partially scanned and rescanned, the temperature position of the rescan is the same as if the electret had been fully scanned initially. If there is a distribution of relaxation times then the position of the two peaks will differ, with the latter pushed to high temperatures.

Activation energy is an important parameter calculable by the t.s.c. technique. It can be determined in two ways. It can be done by scanning the sample a number of times at different scan rates and observing the change of peak positions[27]. However, this is often not possible since it becomes difficult to control the uniform heating of the dielectric cell over a wide range of scan rates. A much more direct way is to use the initial slope of a single t.s.c. thermogram peak. The relationship is Arrhenius-like, modified by the breadth of the relaxation process. The latter is quantified by m, the distribution parameter of the Fuoss–Kirkwood fit. The method of obtaining this parameter from high-frequency spectra is described elsewhere[14]. The equation for activation energy is:

$$\ln(I/V) = -(mE/R)(1/T) \qquad (1)$$

where A is activation energy (J mol^{-1}), R is the gas constant, I/V is the current I (A) normalized by the voltage V (V). The m parameter is such that $0 < m < 1$. A value of $m = 1$ implies a single relaxation time. It is often found that a plot of $\ln(I/V)$ vs. $1/T$ is not linear, even for the initial current rise. An improvement is found by weighting I/V by the area under the t.s.c. thermogram[27]. The equation used is given below, and the parameters of the integral are illustrated in *Figure 1*:

$$\ln[(I/V)/P_s] = -(mE/R)(1/T) \qquad (2)$$

$$P_s = \int_{T_i}^{T} [I(T')/V] \, dT' \bigg/ \int_{T_i}^{T_0} [I(T')/V] dT' \qquad (3)$$

EXPERIMENTAL

The dielectric cell has been described previously[1], and the main points are summarized here. Samples are made as discs in a three-terminal cell using PTFE as a spacer to ensure constant sample thickness. The sample dimensions are normally 150 μm in thickness. The cells are spring-loaded to ensure good sample–electrode contact.

A Keithley 617 digital electrometer was used as the ammeter for short-circuit current measurement. This device has both a high sensitivity in the ranges used (about 10^{-14} A) and also conveniently supplies a d.c. voltage internally, which we used to pole the sample. This, and all measuring modes and ranges, were controlled by a Hewlett–Packard HP-85 computer to automate this technique.
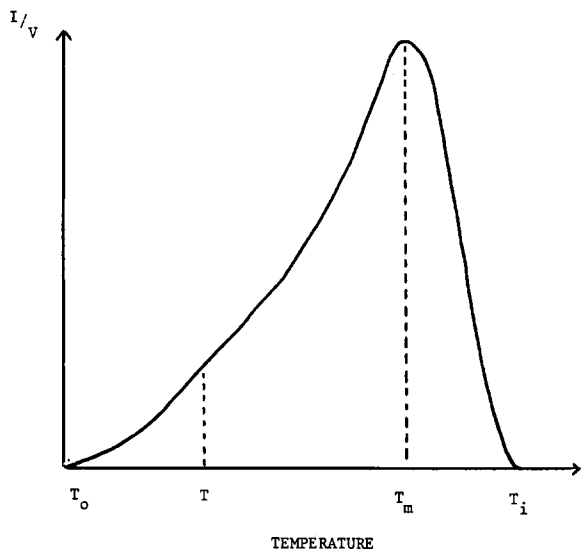
Figure 1 Parameters of t.s.c. curve used in equation (2)

Temperature control was maintained by immersing the cell in a methanol bath able to achieve super- and sub-ambient temperatures. The temperature scan was achieved using a Eurotherm 815P programmable temperature controller. The temperature was directly acquired by computer using a Keithley 195A digital electrometer/thermometer. Scan rates of between 1 and $3°C\,min^{-1}$ could be obtained.

The output currents were of the order of $10^{-11}\,A$ for poling voltages of 60–100 V. The thermograms are displayed with the y-axis being the normalized current (I/V) value. A t.s.c. current peak for a molecular dielectric relaxation is proportional to the electret-forming voltage (V) for the magnitude of voltages used in the t.s.c. experiment[27] and thus I/V is a useful scaled variable.

Mention is made in this work of the m parameter relating to relaxation broadness from a Fuoss–Kirkwood fit. This is obtained from high-frequency dielectric spectroscopy of the sample and the method for doing this is described elsewhere[1]. Essentially, the dielectric loss peaks can be modelled interactively on computer using Fuoss–Kirkwood equations to produce a satisfactory fit. The frequency spectrum for which this fit was performed was between 10^1 and 10^5 Hz.

RESULTS AND DISCUSSION

LCP6 system

Figure 2 shows the thermogram for LCP6 in its homeotropic, unaligned and planar states. The electret-forming conditions were 60 V at 40°C for 1 h followed by subsequent cooling to $-50°C$ and a temperature scan of $1.6°C\,min^{-1}$.

The unaligned LCP6 spectrum is initially examined. The resolution of I/V at temperatures below $-10°C$ was not sufficiently greater than noise to allow secondary relaxations to be observed. The two major peaks that occur are at 11°C and 29°C.

The peak at 11°C is associated with the motion of the strong dipolar mesogenic side-chain units in the LC phase. Since this motion occurs just above the apparent glass transition of the polymer (requiring main-chain motion to liberate it), this peak is associated with the glass transition temperature, T_g. It is important to realize

that the occurrence of a t.s.c. current maximum requires the motion of dipolar groups, releasing excess 'image' charges[27], which results in a current. The actual motion of the non-polar siloxane backbone would, on its own, not release many charges but it is the motion of the dipolar mesogens that does. Thus essentially the peak is classified 'T_g'. If anything, the true T_g value would be slightly below the position of the current maximum, since there may be a slight temperature lag between the main chains becoming mobile and the side-chains linked to them both becoming mobile. The value of T_g peak by t.s.c. (11°C) compares well with that of 17°C from d.s.c. That they are different depends on a number of factors including the fact that the scan rate of the t.s.c. experiment is much slower than that of the d.s.c. experiment $(20°C\,min^{-1})$. Further, the assignment of the actual T_g value from d.s.c. traces is somewhat arbitrary.

The other peak at 29°C is the ρ peak, due to excess charge motion. It is well separated from the T_g peak when compared with t.s.c. scans of other linear polymers[27]. It is found to depend on the electret-forming conditions. For instance, a t.s.c. scan of a sample formed with a higher voltage (100 V) results in the ρ peak changing in size and shape while leaving the T_g peak unchanged. This is consistent with the ρ peak being far more susceptible to forming conditions whereas the scaled T_g peak remains invariant (providing the electret has been properly formed at a temperature above T_g). Van Turnhout[27] proposes that the variability of the ρ peak arises due to variability of low concentrations of impurity charges arising from the electrodes and traces of water.

Further confirmation that the peak at 11°C can be associated with the glass transition comes from recent work[28] involving dynamic mechanical measurements of LCP6. The lowest-frequency spectrum at 0.1 Hz yielded a T_g of 21°C. To compare this with the t.s.c. experiment it is necessary to evaluate the frequency of the t.s.c. experiment. This can be calculated using the following relationship[29]:

$$f_m = \frac{0.133Es}{RT_m^2} \qquad (4)$$

where f_m is the effective frequency of the t.s.c. experiment, T_m is the peak temperature (K), s is the heating rate $(K\,s^{-1})$ and E is the activation energy $(J\,mol^{-1})$. Insertion
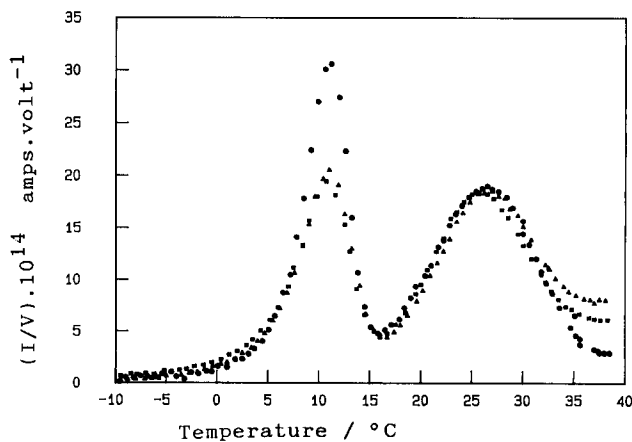

Figure 2 T.s.c. thermogram of LCP6 for various alignments. These are homeotropic (●), unaligned (▲) and planar (■). The electret-forming conditions were: 40°C, 60 V for 1 h. Scan rate was $1.6°C\,min^{-1}$

of the relevant parameters (calculation of E will be presented shortly) yields an f_m of about $10^{-3.1}$ Hz. When the t.s.c. value of T_g of 11°C is included in an Arrhenius plot with the dynamic mechanical results over a range of frequencies, this point fits in well in a linear relationship between $1/T$ and $\log(f_m)$.

A number of interesting comparisons can be made between the aligned (homeotropic and planar) and unaligned sample t.s.c. spectra in *Figure 2*.

(1) All of the alignments show a T_g and ρ peak and the T_g is similar in all cases although it was found that the homeotropically aligned sample was consistently [1] to 2 K higher than the planar and unaligned samples.

(2) The ρ peak was essentially the same although it varied in height when different conditions were used.

(3) The heights of the t.s.c. T_g were dependent on the macroscopic alignment, the homeotropic being the largest, about 1.5 times the height of the unaligned and planar phases. The unaligned peak height was just higher than that of the planar sample.

(4) The unaligned and planar samples show a broader peak than the homeotropic peak.

The similarity in the t.s.c. T_g for all three alignments is expected. Indeed, since mesogenic motion is negligible below T_g, it is probable that T_g is nearly the same in all three cases. The reason for the t.s.c. peak height differences is due to the activation of the mesogenic motions at super-T_g temperatures. It is possible to establish a correlation between the peak strength and broadness of the low-frequency t.s.c. technique with other high-frequency dielectric properties of these systems. The results for LCP6 are presented in *Table 1*. Data columns 1 and 4 of this table show the results obtained from the high-frequency dielectric spectra (h.f.d.s.) measured at 46°C: $\varepsilon_0 - \varepsilon_\infty$ is a measure of the relaxation strength of the sample, the difference between the static and high-frequency permittivities; the value m is related to peak broadness and obtained from the Fuoss–Kirkwood deconvolutions. There is a direct correlation between relaxation strengths of various alignments and the t.s.c. height and areas. Since relaxation strength is related to the strength of dipolar motion, the greater this value, the more image charges are released and the greater is the integrated charge, Q. The relaxation strength is greatest in the homeotropic sample and the t.s.c. technique is sensitive to this.

The broadness of a t.s.c. peak is related to activation energy, temperature of the peak and the parameter, m (ref. 27). These can be related by the formula:

$$mE/RT = 0.572/h \qquad (5)$$

where h is the width at half-height of the t.s.c. peak. Since the temperature of the peak, T_m, and the activation energy, E, are similar for all alignments (demonstrated shortly), the broadness is essentially related to m, which is a measure of the range of dielectric environments present. *Table 1* shows that there is a good correlation between the broadness of the t.s.c. peak and parameter m. It has been shown in other work[14] that the homeotropic sample relaxation is essentially composed of the 00 motion, with a linewidth of $10^{1.34}$ Hz, which is narrow and close to the single, Debye linewidth of $10^{1.14}$ (ref. 30). Both the unaligned and planar samples are composed of constituent modes of greater linewidth. The fact that this detail of mesogenic relaxation is reflected in the t.s.c. data indicates that although the t.s.c. peak is related to main-chain glass transition motions its characteristics are also determined by the mesogenic head groups. This corresponds to the theory of Plate *et al.*[31], who have deduced that the motion and alignment of mesogens leads to a subsequent change in main-chain motion.

The apparent activation energy for a molecular process is an important quantity and can be calculated from a single t.s.c. scan. The activation energy of each alignment has been calculated from equation (3) using the thermograms and values of m in *Table 1*. A plot of $\ln[(I/V)/P_s]$ vs. $1/T$ for each alignment is presented in *Figure 3*. The normalizing of the I/V values by the area under the curves is successful to some degree in linearizing the curves, especially on the low-temperature side, from which the activation energy is calculated. The overall non-linearity
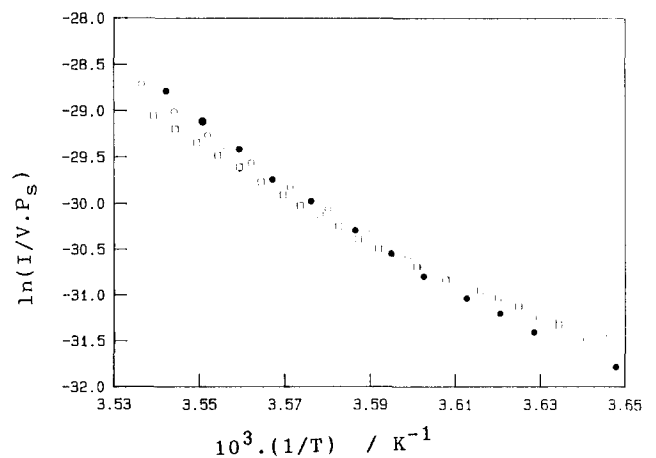

Figure 3 Activation energy plots of the unaligned (○), planar (□) and homeotropic (■) LCP6 systems. The I/V values are weighted by the area under the curve (as defined by equation (1) and *Figure 2*)

Table 1 Correlation of dielectric parameters from thermally stimulated current (t.s.c.) techniques and high-frequency dielectric spectroscopy (h.f.d.s.) in LCP6. C_a is the geometric capacitance of the cell; $\varepsilon_0 - \varepsilon_\infty$ is the dielectric relaxation strength. For a single relaxation time $m = 1$ ($0 < m < 1$)

	Relaxation strength[a], $C_a (\varepsilon_0 - \varepsilon_\infty)$ (pF)	T.s.c. peak height[b]	T.s.c. peak area[b], Q	$m^{a,c}$	T.s.c. peak half-width[d] (°C)
Homeotropic (H)	88.9	31	25	0.70	5
Planar (P)	58.49	20.8	18	0.40	6.5
Unaligned (U)	59.23	22	20	0.50	6
Ratio (H/U)	1.5	1.41	1.3	–	–
Ratio (P/U)	0.98	0.94	0.9	–	–

[a] From h.f.d.s. measurements, $T = 48$°C
[b] Arbitrary units
[c] Obtained from Fuoss–Kirkwood fit
[d] Width at half-height

can be ascribed to a number of factors such as experimental error, the fact that equation (3) is an approximation and the difficulty in determining the area ratios from the thermogram due to the overlapping T_g and ρ peaks. The resulting activation energies are shown in Table 2. They are compared with the activation energies calculated for the motion of the mesogenic head groups using Arrhenius-type plots of high-frequency spectra. There is good agreement between the two values. Mechanical relaxation work mentioned previously[28] also produced an activation energy of $291\,kJ\,mol^{-1}$ for this system. A number of interesting points arise from Table 2.

(a) The activation energy for the planar specimen is greater than that of unaligned or homeotropic specimens. This was seen in both the t.s.c. and high-frequency activation energy data.

(b) The t.s.c. values all tend to be a little greater than their high-frequency dielectric counterparts. This is probably because of the strong temperature dependence of activation energy near T_g and because equation (3) is only approximate.

(c) The strong similarity in activation energy from both methods confirms that the motion of the mesogenic groups is strongly related to (coupled with) that of the main chains.

(d) As expected, the activation energy of LCPs is greater than that of low-molar-mass mesogens, which is about $90\,kJ\,mol^{-1}$ (ref. 32). This is due to the restriction in motion imposed by the viscous macromolecular backbone.

OI system

Figure 4 shows the t.s.c. results for the second LCP system mentioned—OI. They are the homeotropic and planar samples for electrets formed at 25°C for 15 min and 30 V prior to cooling and scanning at $1.6°C\,min^{-1}$. The conditions of electret formation are much less extreme than those for the LCP6 system because care had to be taken in the OI system that the application of a d.c. field to form the electret does not change the alignment of the unaligned sample (since it is possible to align OI in the liquid-crystal state with d.c. fields[34]) and cause it to be partially aligned. The kinetics of such a d.c. alignment in this system has been investigated[33]. If such alignment occurred this would alter the unaligned

sample *in situ* to slightly homeotropic and give an incorrect thermogram for that specimen.

It is expected that this system would give good spectra because the OI side-groups are highly dipolar. The fact that they pole well is important in being able to optimize the second-order non-linear optical properties of these systems. The t.s.c. work clearly shows that these samples can be poled and t.s.c. can be used to determine factors such as the stability of polymerization upon field removal.

Once again the major peaks at 2.5°C and 4°C for the planar and homeotropic samples, respectively, are close to the measured values of $T_g = 4°C$ from d.s.c. measurements, although unlike LCP6 there is a slight difference of about 1°C between them.

As in the LCP6 system the homeotropic peak is higher and narrower than that of planar alignment. Likewise, the t.s.c. parameters of this sample correlate well with high-frequency dielectric parameters measured at 45°C (*Table 3*). Table 4 shows the activation energies for OI from both t.s.c. and high-frequency dielectric experiments. Like LCP6 the t.s.c. activation energy values are greater than the high-frequency values and in each technique the planar sample is higher than the homeotropic value.

Figure 5 is an example of 'thermal cleaning' of sections of the planar t.s.c. thermogram. The sample was scanned to 10°C, thus exhausting the peak associated with the glass transition, cooled and scanned to 17°C, just past a
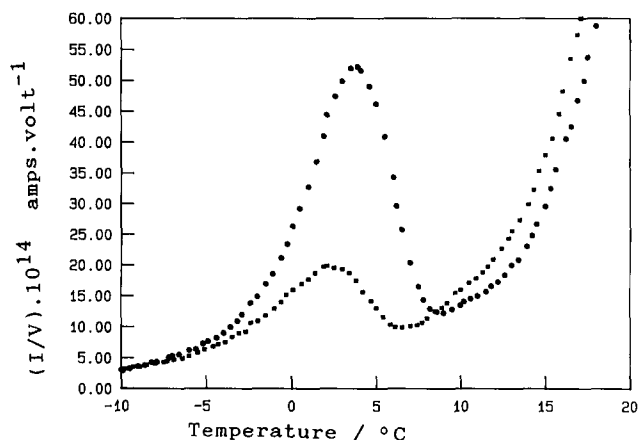

Figure 4 T.s.c. thermogram of OI material. The various alignments are homeotropic (●) and planar (■). Electret-forming conditions were: 25°C, 30 V for 15 min. Scan rate was $1.6°C\,min^{-1}$

Table 2 Activation energies of LCP6 using t.s.c. or h.f.d.s. for various alignments $(kJ\,mol^{-1})$

Alignment	Activation energy (h.f.d.s.)	Activation energy (t.s.c.)
Homeotropic	200	260
Unaligned	195	254
Planar	240	320

Table 4 As *Table 2*, but for OI

Alignment	Activation energy (h.f.d.s.)	Activation energy (t.s.c.)
Homeotropic	154	171
Planar	173	220

Table 3 As *Table 1*, but for OI

	Relaxation strength[a], $C_a\,(\varepsilon_0 - \varepsilon_\infty)$ (pF)	T.s.c. peak height[b]	T.s.c. peak area[b], Q	$m^{a,c}$	T.s.c. peak half-width[d] (°C)
Homeotropic (H)	54.1	53	4.56	0.73	6.4
Planar (P)	28.55	20	2.08	0.34	8.8
Ratio (H/P)	1.89	2.65	2.19	–	–

[a,b,c,d] See *Table 1*

slight peak seen on the ρ peak. The sample was cooled and scanned once again to yield the final part of the ρ peak. This demonstrated that thermal cleaning is able to break down the thermogram into its constituent components (it should be noted that the scan rate is somewhat larger than the 1.6°C min⁻¹ of *Figure 4*). This resulted in a slightly greater temperature maximum as well as a higher t.s.c. T_g peak height, as predicted earlier.

PG 296 system

As with the OI sample, PG 296 is also alignable in the LC phase, although only homeotropic and unaligned samples are possible with conventional equipment. *Figure 6* shows the t.s.c. thermograms for the unaligned

Figure 5 Thermal cleaning of sections of planar t.s.c. thermograms, thus breaking down the trace into its constituents. First scanned to 10°C (▲), cooled, rescanned to 17°C (○), cooled, and rescanned to 25°C (●)

Figure 6 T.s.c. thermogram of both homeotropic (●) and unaligned (▲) PG 296. Electret-forming conditions were: 30°C, 100 V for 1 h. Scan rate was 1°C min⁻¹

and homeotropic samples. The electret-forming conditions were 100 V at 30°C for 1 h. Once again, the value of the t.s.c. maximum compares well with the value previously determined by d.s.c. ($T_g = 4°C$)[35]. The t.s.c. peak maximum occurred at 3.5°C for the unaligned and at 4°C for the homeotropic sample. The planar specimen gives a broader, smaller peak than the homeotropic trace. The peak is well resolved in the case of the homeotropic sample, although it looks markedly different in the unaligned case. *Table 5* shows the previously described t.s.c./high-frequency dielectric parameter correlations for this system. The close correlation is continued for this system. The activation energies of both techniques are likewise similar (*Table 6*). Clearly t.s.c. is an appropriate technique in elucidating properties such as T_g and alignment in this LCP, which is being actively developed for optical storage[2,35].

LCP6 with Stil

Figure 7 shows the t.s.c. thermogram for the fourth system, the LCP6 polymer with the Stil dye incorporated at different concentrations. All t.s.c. scans are for samples in the unaligned state. The electret-forming conditions, prior to cooling and scanning were 60 V at 40°C for 1 h.
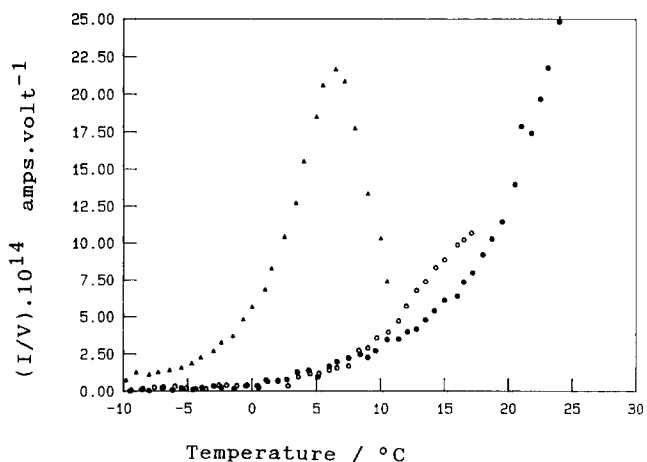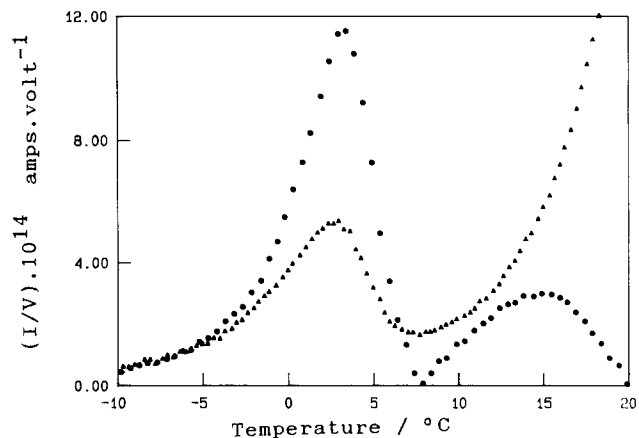
Table 6 As *Table 2*, but for PG 296

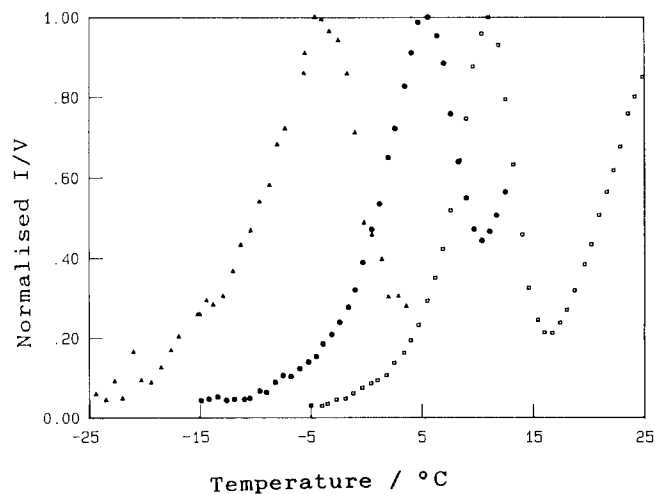| Alignment	Activation energy (h.f.d.s.)	Activation energy (t.s.c.)
Homeotropic	168	169
Unaligned	168	162

Figure 7 T.s.c. thermogram of Stil dye in LCP6 matrix. The different concentrations of dye are 0% (□), 1.15% (●) and 3% (▲). All concentrations are by weight. Electret-forming conditions were: 40°C, 60 V for 1 h. Scan rate was 1.4°C min⁻¹. All peaks were normalized to unity

Table 5 As *Table 1*, but for PG 296

	Relaxation strength[a], $C_a (\varepsilon_0 - \varepsilon_\infty)$ (pF)	T.s.c. peak height[b]	T.s.c. peak area[b], Q	$m^{a,c}$	T.s.c. peak half-width[d] (°C)
Homeotropic (H)	33.5	11.4	31	0.82	5.6
Unaligned (U)	16.1	5.36	19.4	0.72	6.7
Ratio (H/U)	2.08	2.12	1.6	–	–

[a,b,c,d] See *Table 1*

The scan rate was $1.4°C \, min^{-1}$. Since different samples of varying thickness (which could not be accurately determined) were used, the peaks were all normalized to unit height. The t.s.c. peaks associated with T_g are all shown. The fact that these systems are able to form electrets and are amenable to the t.s.c. technique is important with regard to possible second-order non-linear optical applications of these materials.

Relatively small amounts of Stil (1.15% and 3%) were found to be sufficient to reduce the T_g values substantially. This is important since the mobility that the dyes impart can be valuable in decreasing the response time (such as to a switched electric field) of the mesogens[2]. Slow response times are often a hindrance to LCP switching properties. Coles *et al.*[2] find that even with such concentrations of dye the LCP is still readily alignable. The dye may also be used to change the colour of the LCP–dye system by absorbing or transmitting light differentially, depending on its orientation, which is itself determined by the LC alignment.

The increase in mobility and reduced main-chain viscosity can be seen by calculation of the activation energy from these traces. The Arrhenius plots for these systems are shown in *Figure 8* and the values presented in *Table 7*. As the concentration of dye increases, so the activation energy decreases. Examination of *Figure 7* also shows a broadening of the peak with addition of dye. Such a plasticization broadening process is also seen in high-frequency spectra in polymer systems and is due to the range of mobility environments that the plasticizing dye produces[30].

An experiment was undertaken to determine the ability of the t.s.c. technique to establish the distribution of relaxation frequency in LCP systems using the 'multi-stage technique' in which the t.s.c. peak is broken down into its components. As stated earlier, Van Turnhout[27] proposed that, if there is a distribution of relaxation environments, the rescanned peak should occur at a different temperature to the fully scanned thermogram position. The experiment illustrated here is with PG 296
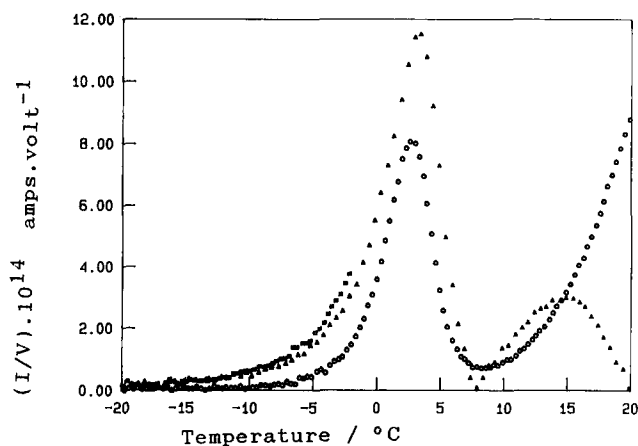

Figure 9 Multistage t.s.c. experiment on homeotropic PG 296. Electret-forming conditions were: 30°C, 100 V for 1 h. Scan rate was $1°C \, min^{-1}$. The sample is scanned through the whole temperature range initially (▲), repoled, cooled and scanned to $-1°C$ (□), cooled and rescanned through the whole temperature range (○)
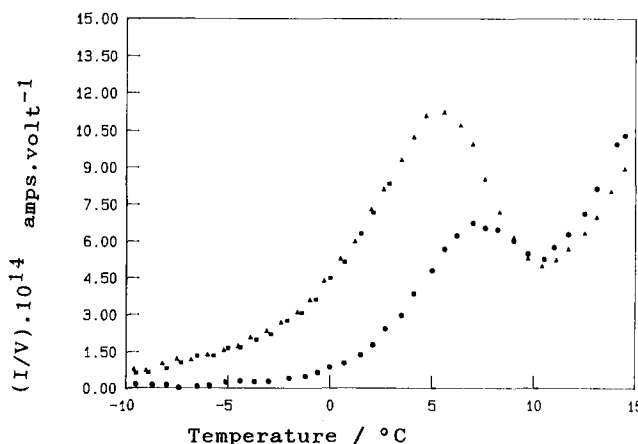

Figure 10 Multistage t.s.c. experiment on LCP6 with 1.15% Stil. Electret-forming conditions were: 40°C, 100 V for 1 h. Scan rate was $1.4°C \, min^{-1}$. Sample scanned through the whole temperature range (△), repoled, cooled and scanned to 2°C (■), cooled and rescanned over the whole temperature range (●)

in the homeotropic state. The electret-forming conditions were 100 V for 1 h at 30°C and cooling and scanning at $1°C \, min^{-1}$. The resultant thermograms are shown in *Figure 9*. A number of scans were done. First the full t.s.c. thermogram was run to show the position of the t.s.c. peak. Then the electret was repoled and scanned at the same heating rate to $-1°C$ (about half-way up the leading edge of the thermogram). Upon rescanning, the major t.s.c. peak manifested itself at the same position as the temperature of the original, complete scan. Thus t.s.c. predicts in this system that the mesogenic motion is essentially that of a single Debye relaxation. This is confirmed by other work[38] where the high-frequency dielectric spectrum of homeotropic PG 296 was fitted by Fuoss–Kirkwood equations and an almost single-relaxation-time peak obtained. This motion is related to the motion of the mesogenic group around the short axis[14].

In contrast to this, a sample of LCP6 with 1.15% Stil was also examined with the thermal cleaning technique. Electret-forming conditions were 100 V at 40°C for 1 h. The scanning rate was $1.4°C \, min^{-1}$. The same experimental procedure as described in the previous paragraph was done, the sample being scanned up to 2°C and then rescanned. The thermogram is shown in *Figure 10*. The

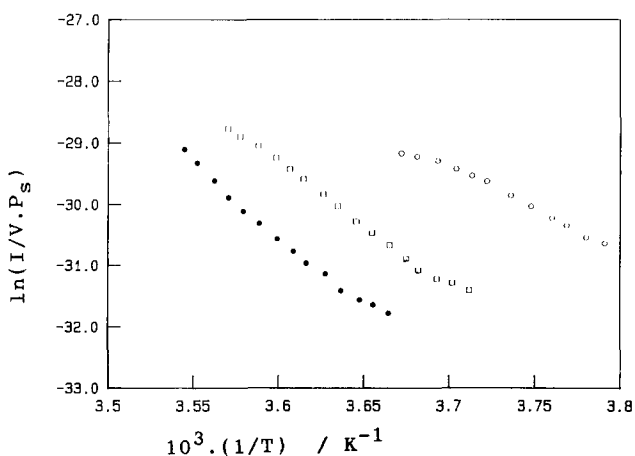**Figure 8** Activation energy plots for Stil dye in LCP6 matrix. The different concentrations of dye are 0% (●), 1.15% (□) and 3% (○)

Table 7 As *Table 2*, but for LCP6 with Stil dye

Dye (wt%)	Activation energy (h.f.d.s.)	Activation energy (t.s.c.)
0	195	254
1.15	191	197
3	147	173

peak maximum increased from 5°C to 7.5°C. This indicates that the relaxation time of this system is not that of a single Debye relaxation. Previous Fuoss–Kirkwood deconvolutions of LCP6[17] have shown that, as with PG 296, the major low-frequency peak in LCP6 is close to a single relaxation time. However, the addition of Stil causes a distribution of different relaxation environments, thus broadening the relaxation process. As can be seen in *Figure 10* the t.s.c. technique is sensitive to this.

CONCLUSIONS

It has been shown that t.s.c. is a useful dielectric technique that can be applied to a range of LCP systems, both in their original state and containing dyes. The modification of these materials by dyes that can be poled offers second-harmonic generation possibilities as well as reduced polymer viscosity and decreased response time. In addition to determining whether a sample can be poled, it is an excellent experiment for determining necessary and sufficient conditions for electret formation and can also be used to ascertain electret stability (ability of the system to maintain dipole polarization).

The technique has shown that it can measure a number of important dielectric and relaxation parameters. It can determine T_g, a key processing variable if these materials are to be cast into optical information storage media. Factors such as the height, area and broadness of the t.s.c. thermogram peaks correlate well with data from other conventional a.c. frequency-scan dielectric techniques. Likewise the activation energy can readily be determined for a single t.s.c. scan and yield information on molecular mobilities.

The t.s.c. technique also has the advantage of being a temperature scanning technique and it can be used in 'thermal cleaning' of a spectrum to reduce it into its constituent components.

The use of t.s.c. (which is largely related to T_g and its correlation with dielectric frequency spectra that examine mesogenic group motion) raises theoretical questions about the fundamental nature of the mesogenic motion above and below T_g and its relationship with the main-chain motion of the polymer (whose motion is required to be activated prior to the LC phase occurring). Clearly, since the LC state occurs above the glass transition the main chains are mobile and the LC domains attached to them become mobile on a larger scale than in the glassy state, depending on the flexibility of the spacer group. While this motion would involve some movement of the domains in space, the predominant motion is that of the mesogens around the local director within a LC domain. Indeed, this motion above T_g is not sufficient to destroy either macroscopic or inter-domain alignment to any degree since the alignment remains once the field is removed, even at super-T_g temperatures. Thus the glass transition allows sufficient main-chain motion for the mesogens to exist in the LC state and yet also is sufficiently restrictive and intimately mixed with the mesogens to restrain them from becoming unaligned, should the aligning field be removed. The current peak seen in t.s.c. at T_g is a combination of both the restricted motion of the mesogenic side-groups around the main chain (giving a measure of T_g) in addition to motions within the LC domains themselves (giving relaxation

parameters such as broadness, relaxation strength) and thus t.s.c. could be a useful, hybrid technique in developing molecular understanding of these systems.

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