

## Multiple and inter-related relaxation mechanisms in the mesophase of side-chain liquid crystalline polysiloxanes: a thermally stimulated currents study

João F. Mano and Joaquim J. Moura Ramos\*

*Centro de Química-Física Molecular, Complexo I, IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*

and David Lacey

*School of Chemistry, The University, Hull HU6 7RX, UK*

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The thermally stimulated discharge currents technique was used to study the relaxations above the glass transition temperature in two side-chain liquid crystalline polysiloxanes. Taking into account the molecular structure of the mesogenic side groups, the results seem to show that the observed relaxations are associated with reorientation of the transverse and longitudinal components of the mesogenic side groups. Moreover, the thermally stimulated spectrum obtained for one of the polymers shows interesting behaviour which can be ascribed to a coupling between the modes of motion associated with the relaxation processes observed in the liquid crystalline phase. Copyright © 1996 Elsevier Science Ltd.

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### Introduction

The molecular dynamics in side-chain liquid crystalline polymers (LCPs) has been studied by different techniques, but mostly and more extensively by dielectric relaxation spectroscopy (d.r.s.)<sup>1</sup>. From such studies it can be concluded that there are essentially two relaxations in the liquid crystalline phase of these polymers: the low-frequency relaxation, the so-called  $\delta$ -relaxation, which is believed to be caused mainly by rotation of the longitudinal ( $\mu_{\parallel}$ ) component of the dipole moment of the mesogenic side groups; and the higher frequency relaxation, the  $\alpha$ -relaxation, which shows a very broad absorption curve and is considered to arise from a combination of modes of motion which depend on both the transverse ( $\mu_{\perp}$ ) and longitudinal ( $\mu_{\parallel}$ ) components of the dipole moment of the mesogenic side groups<sup>1,2</sup>. The major difficulty encountered in the analysis and interpretation of the dielectric relaxation spectra of LCPs is that the loss curves observed experimentally are often broad, highly asymmetric, with coalescence of the different bands and without clearly resolvable features.

Recently, we carried out a systematic study of different side-chain LCPs using the dielectric-related technique of thermally stimulated discharge currents (t.s.d.c.)<sup>3–8</sup>. From our studies we can conclude that at least three relaxations are observed in the t.s.d.c. spectra of side-chain LCPs: (1) a broad relaxation in the vitreous state, characterized by low activation enthalpies and entropies which can be ascribed to local non-cooperative motions probably involving the spacer that links the main chain to the mesogenic side group; (2) the glass transition

relaxation which is characterized, in all the polymers studied, by the so-called compensation behaviour; and (3) relaxations in the liquid crystalline phase.

The molecular nature of the relaxations observed by t.s.d.c. above the glass transition temperature ( $T_g$ ) are the subject of some controversy, some authors considering that these relaxations arise from space charge effects<sup>9,10</sup>. Nevertheless, the d.r.s. studies clearly identify molecular motions in the liquid crystalline phase and these motions are, as stated before, attributed to reorientation of the components  $\mu_{\parallel}$  and  $\mu_{\perp}$  of the dipole moment of the mesogenic side groups. On the other hand, our t.s.d.c. results<sup>3–8</sup> show systematically the existence of reproducible discharges in the liquid crystalline phase of all the side-chain LCPs studied. Since the existence of relaxation mechanisms of the mesogenic moieties in the liquid crystalline phase is a natural feature of liquid crystalline materials, we tend to believe that the discharges observed by t.s.d.c. above the glass transition temperature in side-chain LCPs arise from dipolar motions and not from space charge effects. Moreover, in some cases the t.s.d.c. spectrum shows more than one relaxation in the liquid crystalline phase and this observation seems to be directly related to the molecular structure of the mesogenic side group<sup>3</sup>. In fact, our results seem to show that one single relaxation above  $T_g$  is observed when the side group only has a longitudinal component of the dipole moment,  $\mu_{\parallel}$  (as is the case for the cyanobiphenyl group), whereas multiple relaxations are observed when the mesogenic group has both  $\mu_{\parallel}$  and  $\mu_{\perp}$  (as is the case for aromatic ester groups like phenylbenzoate).

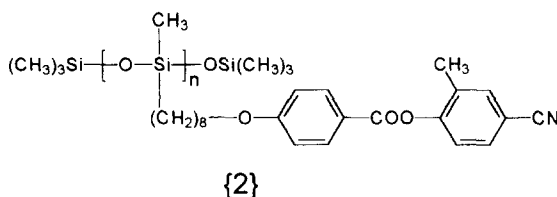
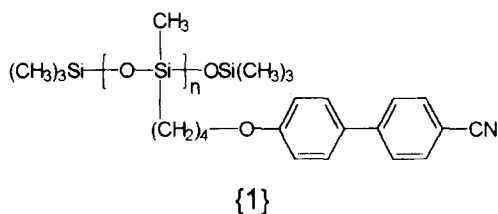
In the present work we wish to report the results obtained with a side-chain LCP where two relaxations above  $T_g$  are observed, and to compare these results with

\* To whom correspondence should be addressed

those obtained with a different side-chain LCP where a single relaxation above  $T_g$  is observed. Moreover, we want to point out a behaviour, which has not previously been reported in the literature, that can arise from a coupling or inter-relation between the modes of motion associated with the two relaxation processes observed in the liquid crystalline phase. These results seem to confirm that the t.s.d.c. technique is eminently suitable for the study of dipolar relaxation mechanisms in this kind of material.

### Experimental

One of the side-chain LCPs studied in this work (structure 1) is from Merck (catalogue number LCP18). As supplied, LCP18 has the transition temperatures  $g$  20 S<sub>A</sub> 129°C I.



The other side-chain LCP (structure 2) was synthesized at the University of Hull.

The material is smectic with an apparent glass transition temperature of about 1°C and a clearing point of about 87°C, and has been extensively studied by d.r.s. previously<sup>2,11-14</sup>.

The t.s.d.c. experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, USA) covering the range -170 to 400°C. A Faraday cage shielded the sample, and prior to the experiments the sample was evacuated to 10<sup>-4</sup> mbar and flushed several times with 1.1 bar of high-purity helium.

### Results and discussion

The results reported in the present work are for t.s.d.c. global experiments which can be described as follows. The sample is submitted to a polarization voltage  $V_p$  at a temperature  $T_p$  (the polarization temperature), during a time  $t_p$ ; the sample is then cooled down in the presence of the electric field to a temperature  $T_0$  such that  $T_0 \ll T_p$ . With the field off, the sample is then heated up at a constant rate to a temperature  $T_f > T_p$  and the depolarization current is recorded as a function of temperature. The result of each experiment is a curve of current intensity as a function of temperature, as shown in Figures 1, 2 and 3, which reveals different discharges corresponding to different relaxation mechanisms.

Figure 1 shows the results of different t.s.d.c. global experiments performed on polymer 1 with different

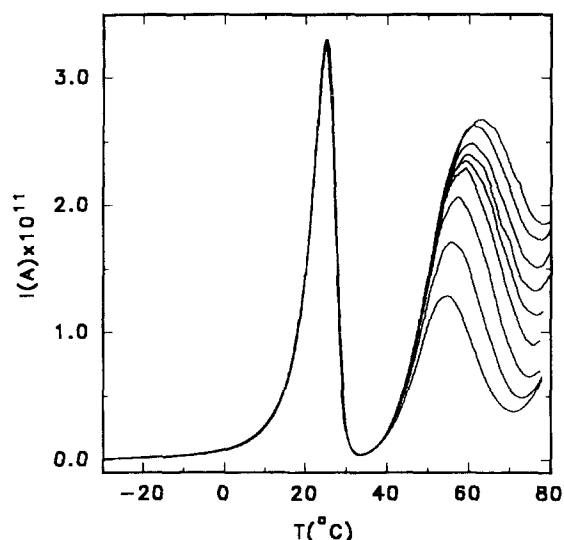
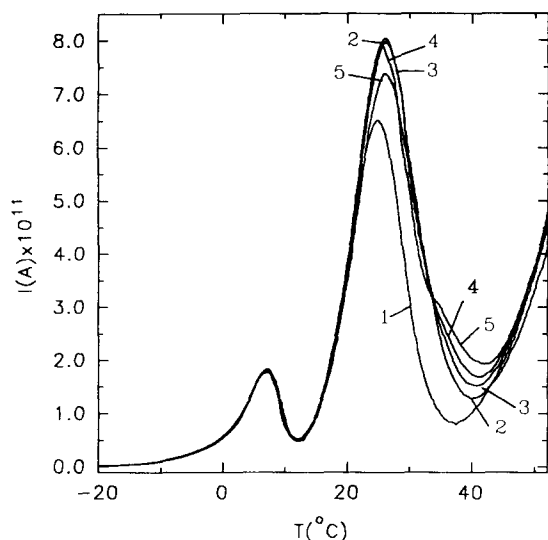


Figure 1 Results of different t.s.d.c. global experiments performed on polymer 1 at different polarization temperatures,  $T_p = 45, 50, 55, 60, 65, 70, 75, 80$  and  $90^\circ\text{C}$  in the order of increasing intensity of the peak in the right-hand side of the figure. The other experimental conditions were:  $V_p = 400\text{ V}$ ;  $T_0 = -40^\circ\text{C}$ ; heating rate =  $8^\circ\text{C min}^{-1}$

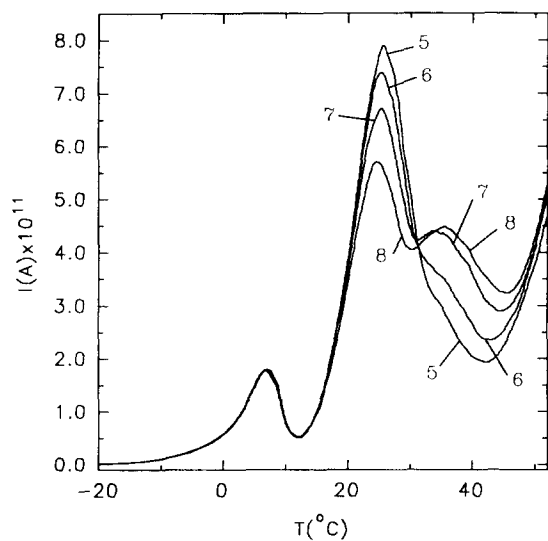
polarization temperatures,  $T_p$ . The peak on the left-hand side of the figure, the maximum of which occurs at  $\sim 25^\circ\text{C}$ , is the glass transition peak and the extremely good reproducibility of this peak from experiment to experiment should be noted.

A relaxation mechanism above  $T_g$  is also observed from Figure 1, with maximum intensity near  $61^\circ\text{C}$ , and the shape of this discharge suggests that it corresponds to a single mechanism. It can be observed that the intensity of the peak at  $\sim 61^\circ\text{C}$  increases as  $T_p$  increases; this is the expected behaviour since the corresponding relaxation mechanism is activated more efficiently when the polarization temperature increases from  $45^\circ\text{C}$  to higher temperatures. For example, for  $T_p = 45^\circ\text{C}$  (the experiment corresponding to the lower intensity of the peak at  $61^\circ\text{C}$ ) the electric field is applied in a temperature range significantly below the temperature of maximum intensity of the peak, so that only the lower temperature side of the whole discharge is polarized. For polarization temperatures significantly higher than the temperature of maximum intensity of the peak (as in the case for experiments with  $T_p = 65, 70, 75, 80$  and  $90^\circ\text{C}$ ), the relaxation mechanisms should be fully polarized and we would expect to obtain similar curves for all these experiments (as we obtain for the glass transition peak in the left-hand side of the figure). Nevertheless, the behaviour we observe in Figure 1 shows a slight increase with  $T_p$  of the intensity of the peak at  $61^\circ\text{C}$ . This behaviour is a consequence of the presence in the t.s.d.c. spectrum of this side-chain LCP of a huge conductivity tail associated with melting of the material, which begins in the liquid crystalline phase well below the clearing temperature (the beginning of this tail is shown in the extreme right-hand side of Figure 1). Since the intensity of the conductivity tail is increased as  $T_p$  increases, we have, for the higher  $T_p$  experiments, an increasing superposition between the peak at  $61^\circ\text{C}$  and the conductivity tail.

We can conclude, from the results presented in Figure 1, that polymer 1 (which has a cyanobiphenyl side



**Figure 2** Results of different t.s.d.c. global experiments performed on polymer 2. The polarization temperatures,  $T_p$ , were: 1, 25°C; 2, 30°C; 3, 33°C; 4, 37°C; 5, 40°C. The other experimental conditions were:  $V_p = 400$  V;  $T_0 = -20^\circ\text{C}$ ;  $T_f = 70^\circ\text{C}$ ; heating rate =  $4^\circ\text{C min}^{-1}$



**Figure 3** Results of different t.s.d.c. global experiments performed on polymer 2. The polarization temperatures,  $T_p$ , were: 5, 40°C; 6, 43°C; 7, 47°C; 8, 50°C. The other experimental conditions were:  $V_p = 400$  V;  $T_0 = -20^\circ\text{C}$ ;  $T_f = 70^\circ\text{C}$ ; heating rate =  $4^\circ\text{C min}^{-1}$

group) shows a single relaxation mechanism in the liquid crystalline phase.

Figures 2 and 3 show the results of t.s.d.c. global experiments performed on polymer 2. Figure 2 corresponds to t.s.d.c. global experiments with lower polarization temperatures whereas Figure 3 shows the results of the same type of experiments with higher polarization temperatures.

The peak on the left-hand side of both figures, with maximum intensity at  $\sim 10^\circ\text{C}$ , corresponds to the glass transition relaxation and it is to be noted again the extremely good reproducibility of this discharge from experiment to experiment. From Figure 2 we observe clearly the existence of an upper  $T_g$  peak with a maximum intensity at  $28^\circ\text{C}$ . It can also be seen from that figure that the intensity of the peak increases from curve 1 to curve 2, which corresponds to the behaviour

described for polymer 1. Nevertheless, with further increases of  $T_p$ , a very distinct behaviour is observed. In fact, with increasing  $T_p$  a new peak appears: this peak is shown in curve 5 (Figures 2 and 3) as a small shoulder in the right-hand side of the peak and is clearly present on curve 8 (Figure 3), with a maximum intensity at  $\sim 37^\circ\text{C}$ . We are thus in the presence, in the case of polymer 2, of two relaxation mechanisms in the liquid crystalline phase, and this fact can be attributed to the particular features of the molecular structure of the mesogenic side group<sup>3,8</sup>. Polymer 2 has a phenylbenzoate type side chain where the ester group is responsible for a significant transverse component of the dipole moment and allows internal rotations, enabling reorientation of this transverse component. The same situation was observed by d.r.s.<sup>15</sup> and it seems reasonable to attribute the two relaxations observed by t.s.d.c. above  $T_g$  to the  $\delta$ - and  $\alpha$ -processes observed by d.r.s. in the liquid crystalline phase\*. It is to be noted that the proposed attribution is just a suggestion which seems to be reasonable in the context of the relationship we observed between the features of the t.s.d.c. spectrum and the molecular structure of the side groups. Nevertheless, as pointed out before, the attribution of the upper  $T_g$  relaxations observed in the t.s.d.c. spectrum is the subject of controversy. In order to clarify this problem more research work is needed, particularly a careful dielectric relaxation study in the very low frequency range.

Finally, we want to emphasize a new and interesting behaviour that can be observed from Figure 3: the intensity of the peak at  $28^\circ\text{C}$  decreases as  $T_p$  increases, i.e. as the relaxation at  $37^\circ\text{C}$  is activated more efficiently. This is the first time such behaviour is reported in the literature concerning the t.s.d.c. technique, and we have preliminary results on other LCPs with side groups of similar structure where this kind of behaviour is also apparent. More research work is needed in order to understand and interpret such behaviour. Nevertheless, it seems reasonable to consider that it can be ascribed to the existence of one or more common, or inter-related, modes of motion in both relaxation processes and to the possibility of transference of these modes from one process to another. The observed behaviour could be described as a decrease of the intensity of the  $\alpha$ -process as the  $\delta$ -relaxation becomes active and could be attributed to the transference of the  $\mu_{\parallel}$  mode from the  $\alpha$ - to the  $\delta$ -process. This interpretation is not unreasonable in the context of molecular theory, which suggests that the  $\delta$ -process is due to motions of  $\mu_{\parallel}$  whereas the  $\alpha$ -process contains contributions from both  $\mu_{\parallel}$  and  $\mu_{\perp}$ <sup>2,13,14</sup>. This would mean that the  $\mu_{\parallel}$  mode is operating essentially in the  $\delta$ -process when both the  $\alpha$ - and  $\delta$ -processes are polarized.

### Conclusions

Our previous studies of the molecular motions in

\* It is to be noted that, in the case of amorphous polymers, the  $\alpha$ -process is considered to arise from the cooperative micro-Brownian motions of the main chain ( $T_g$  peak). In the context of side-chain LCPs the nomenclature is somewhat different: the  $\alpha$ - and  $\delta$ -processes are ascribed to motions of the mesogenic side groups in the liquid crystalline phase such that the  $\delta$ -process (slower) is attributed essentially to motions of  $\mu_{\parallel}$  and the  $\alpha$ -process (faster) is attributed to modes of motions where the contribution of  $\mu_{\perp}$  is significant. The  $\alpha$ - and  $\delta$ -processes give thus rise to upper  $T_g$  relaxations

side-chain liquid crystalline polymer by the technique of thermally stimulated currents, as well as the results reported in the present paper, systematically show the existence of relaxations above the glass transition temperature. These relaxations appear as a single peak when the mesogenic side group essentially has a longitudinal component of its dipole moment (as is the case for cyanobiphenyl groups) and appears as two more-or-less well separated peaks when the dipole of the mesogenic moieties has both longitudinal and transverse components (as is the case for phenylbenzoate groups). It seems thus reasonable to believe that these relaxations observed above  $T_g$  in the t.s.d.c. spectra of side-chain LCPs arise from molecular motions of the mesogenic units in the liquid crystalline phase and not to space charge effects as was suggested by some authors. Dielectric relaxation studies in the ultra-low frequency range would probably be useful in order to clarify these attributions.

One of the polymers studied in the present work shows two relaxations in the mesophase and the results reported could be indicative of some kind of coupling between the modes of motion associated with these two processes. This behaviour has not been reported previously in the literature and, in order to be elucidated, more research work is needed. In the near future we will carry out t.s.d.c. studies on different side-chain LCPs whose mesogenic moieties present both transverse and longitudinal components of the dipole moment, and we believe that these results will lead us to the understanding of the features of the t.s.d.c. spectra of such materials.

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