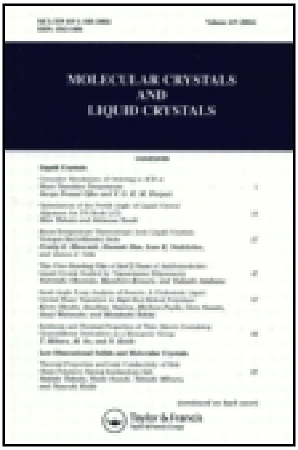


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Thermally Stimulated Currents Spectrum of Side-Chain Liquid Crystalline Polymers. A Further Contribution for the Attribution of the Different Discharges at the Molecular Level

J. J. Moura-ramos [a] , J. F. Mano [a] & D. Coates [b]

[a] Centra de Química-Flsica Molecular, Complexo 1, IST, Av. Rovisco Pais, 1096, Lisboa Codex, Portugal

[b] Merck Ltd, West Quay Road, Poole, BH15 1HX, United Kingdom

Version of record first published: 04 Oct 2006.

To cite this article: J. J. Moura-ramos , J. F. Mano & D. Coates (1996): The Thermally Stimulated Currents Spectrum of Side-Chain Liquid Crystalline Polymers. A Further Contribution for the Attribution of the Different Discharges at the Molecular Level, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 267-278

To link to this article: http://dx.doi.org/10.1080/10587259608042250

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 267–278
Reprints available directly from the publisher
Photocopying permitted by license only

The Thermally Stimulated Currents Spectrum of Side-Chain Liquid Crystalline Polymers. A Further Contribution for the Attribution of the Different Discharges at the Molecular Level

J. J. MOURA-RAMOS* and J. F. MANO

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

D. COATES

Merck Ltd, West Quay Road, Poole, BH15 1HX, United Kingdom

(Received April 07, 1995; in final form August 03, 1995)

The dipolar relaxation mechanisms in two side-chain liquid crystalline polyacrylates with very similar chemical structures have been studied by Thermally Stimulated Discharge Currents (t.s.d.c.). The only structural difference between the two polymers is in the terminal group of the mesogenic moiety: a cyano group for one polymer and a methoxy group for the other. This structural difference gives rise to differences in the t.s.d.c. thermogram of the two polymers which have been interpreted in terms of the attribution of the observed discharges to molecular motions in the liquid crystalline phase. It was also shown that the distribution of the energies of activation and of the relaxation times of the glass transition relaxation is influenced by the motions in the liquid crystalline phase. Finally, it was observed that the shorteness of the spacer which links the main-chain to the mesogenic moiety has an influence on the t.s.d.c. signature of the studied polymers.

Keywords: Thermally stimulated depolarisation, dielectric relaxation, TSC TSDC, liquid crystal polymer, phase transition, compensation.

INTRODUCTION

It is well known that the relaxation processes taking place in polymeric materials and in liquid crystals strongly affect the macroscopic properties. This is one of the reasons for the interest in the study of molecular relaxations in those materials.

Different experimental techniques have been used in this context, namely nuclear magnetic resonance and dielectric relaxation spectroscopy. The technique of Thermally Stimulated Depolarisation Currents (t.s.d.c.) is another suitable technique for the study of dielectric relaxation mechanisms in polymeric materials[1, 2] and it was recently used to study the molecular dynamics in side-chain liquid crystalline polymers

---

* Author to whom correspondence should be addressed.

(LCPs)[3-8]. It can be concluded from those studies that the t.s.d.c. spectrum of these materials shows different types of discharges. A glass transition peak, whose maximum intensity appears near the glass transition temperature (T_g) obtained by differential scanning calorimetry, is always observed. This relaxation is characterised by the so-called compensation behaviour whose manifestation is a strong increase of the activation enthalpy of the relaxation process in the glass transition region. In the glassy state (below T_g), a broad discharge peak is observed which is characterised by low values of the activation enthalpy and negligible values of the activation entropy. This low temperature relaxation is often ascribed to local and non-cooperative motions in the side groups,[9] but we must point out that some authors suggest that this relaxations below T_g involve cooperative intra- and intermolecular motions.[10] Finally, the t.s.d.c. spectrum of side-chain LCPs shows invariably relaxations in the liquid crystalline phase. One feature of these relaxations is the fact that the Arrhenius plots (log τ *versus* $1/T$) of the components show a curvature such that they are well fitted by a WLF or Vogel type equation. This behaviour is often considered as an indication of the co-operative nature of the corresponding molecular motions. The attribution, at the molecular level, of the relaxations above T_g is nevertheless a very controversial subject. Many authors consider that they arise from space-charge effects.[1,2,11,12] The peak above T_g is thus called ρ since it implies resistivity and is related to the transport of charge. Other authors believe, oppositely, that the upper T_g relaxations correspond to genuine dipolar motions.[13,14] In previous work[4,6-8] we suggested that the relaxations observed above T_g in the t.s.d.c. spectrum of side-chain LCPs seem to be related to the molecular structure of the mesogenic moieties and that they probably correspond to motions involving the transversal and longitudinal components of its dipole moment ($\mu_\perp$ and $\mu_\parallel$).

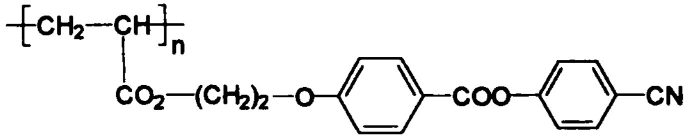
In the present work we present the results of the t.s.d.c. study of two different side-chain LCPs not studied before. The different relaxations observed in the t.s.d.c. spectrum were studied in detail and we hope, with the obtained results, to be able to give a further contribution to the discussion of the attribution, at the molecular level, of the relaxations observed above T_g.

EXPERIMENTAL

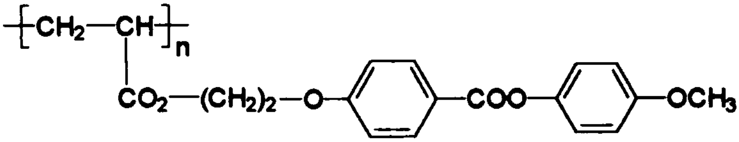
The side-chain LCPs studied in the present work are from Merck (catalogue number LCP100, {1}, and LCP92, {2}).

The glass transition temperatures, T_g, obtained by differential scanning calorimetry are 75°C for polymer {1} and 61.5°C for polymer {2}. Both polymers are nematic in the liquid crystalline phase and have clearing temperatures, T_c, of 111°C (polymer {1}) and of 113.4°C (polymer {2}). For polymer {1} $M_n = 25000$, $M_w/M_n = 2$ and $n \approx 75$ units. For polymer {2} $M_n = 13100$, $M_w/M_n = 2.83$ and $n \approx 39$ units. It is to be noted that polymers {1} and {2} have very similar chemical structures, the only difference being at the terminal group in the mesogenic moiety (a cyano group in the case of polymer {1} and a methoxy group in the case of polymer {2}).

Thermally Stimulated Depolarisation Current experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, USA) covering the



{1}



{2}

range – 170 to + 400°C. The parallel electrode assembly has an effective area of ~ 38 mm^2 and a distance between electrodes of 0.2–0.5 mm. A Faraday cage shields the sample and prior to the experiments the sample, located between parallel plate electrodes, is evaluated to 10^{-4} mbar and flushed several times with 1.1 bar of high-purity helium. In order to analyse specific regions of the t.s.d.c. spectrum, different methods of polarising the sample were used, namely the so-called t.s.d.c. global experiment and the thermal sampling (or cleaning, or windowing) experiment. In both types of experiment the sample was polarised in a given temperature range (with the field applied between T_p and $T_p' < T_p$), the polarisation was frozen in by cooling down to T_o and the depolarisation current was measured as the polarised sample was heated up from T_o to $T_f > T_p$ at a constant rate. The difference between both types of experiments is that in a TSDC global experiment $T_p' = T_o$ whereas in a thermal sampling experiment $T_p - T_p' = \Delta T$ has a small and constant value (typically 3°C) and $T_o \ll T_p$ and T_p'.

RESULTS AND DISCUSSION

T.s.d.c. global experiments

The t.s.d.c. spectrum of polymer {1} shows four different discharges. In the lower temperature region, from –150°C to –80°C, a broad relaxation is observed (Fig. 1) which will be analysed latter by the technique of thermal cleaning (for polymer {2} we were not able to analyse this low temperature relaxation owing to problems of electrical contact between the sample and the electrodes at low temperatures).

The glass transition peak (Fig. 2) shows its maximum intensity at ~ 81°C (the reported T_g is 75°C) and two discharge peaks are observed in the liquid crystalline phase. In fact, from Figure 2 (where are presented the results of different t.s.d.c. global experiments with different polarisation temperatures, T_p) we can observe a small intensity dicharge whose maximum intensity is at ~ 94°C (curve 1) and an higher intensity discharge located at ~ 104°C (curves 4 and 5) which completely disguises the relaxation at ~ 94°C.

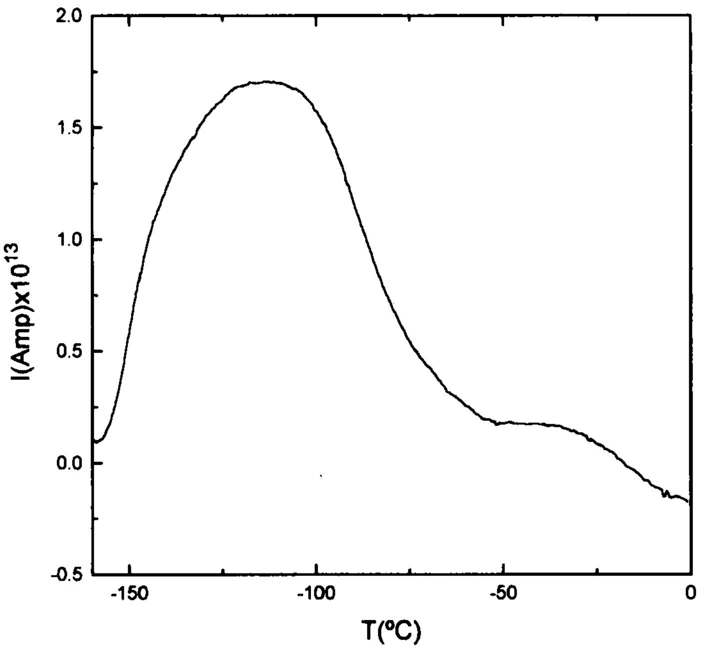


FIGURE 1 T.s.d.c. global experiments performed on polymer {1} in the low temperature region. The experimental conditions were: $T_p = -30^\circ\mathrm{C}$; $T_0 = -160^\circ\mathrm{C}$; $T_f = 10^\circ\mathrm{C}$; heating rate, $r = 8^\circ\mathrm{C/min}$; polarising field $E = 400$ V/mm.

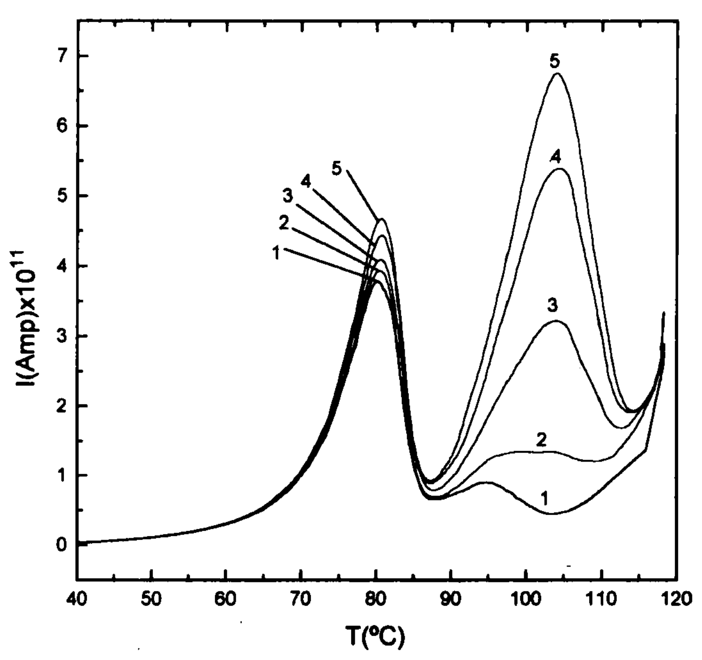


FIGURE 2 T.s.d.c. global experiments performed on polymer {1} in the glass transition region and in the liquid crystalline phase. The polarisation temperatures, T_p, were 1–100°C; 2–104°C; 3–106°C; 4–108°C; 5–110°C. The other experimental conditions were $T_0 = 30^\circ\mathrm{C}$; $T_f = 120^\circ\mathrm{C}$; heating rate, $r = 8^\circ\mathrm{C/min}$; polarising field $E = 400$ V/mm.

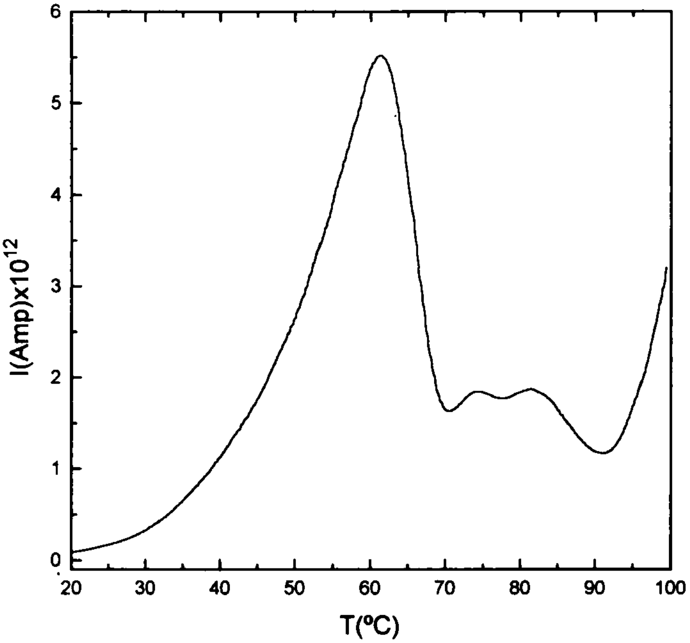


FIGURE 3 T.s.d.c. global experiment performed on polymer {2} in the glass transition region and in the liquid crystalline phase. The experimental conditions were: $T_p = 90°C$; $T_0 = 20°C$; $T_f = 120°C$; heating rate, $r = 8°C/min$; polarising field $E = 400$ V/mm.

Curve 2 in this Figure is very broad since it is a superposition of the two discharge peaks. Polymer {2}, on the other hand, also shows two relaxations above the glass transition temperature (Fig. 3).

From that Figure we can observe that the glass transition peak has a maximum intensity at ~62°C (the reported T_g is 61.5°C) and that we have two partially superposed discharges in the liquid crystalline phase located at ~75°C and ~83°C.

Comparing Figures 2 and 3 we conclude that the t.s.d.c. thermogram in the liquid crystalline phase is very different for polymers {1} and {2}. Since the only structural difference between both polymers lies in the fact that polymer {1} has a side-chain with a terminal cyano group whereas polymer {2} has a methoxy group in the equivalent position, it seems reasonable to consider that the differences observed in the t.s.d.c. thermogram arise from those structural differences. In this context, it would seem sensible to consider that the higher temperature discharge, which has higher intensity in polymer {1} when compared with polymer {2}, arises from molecular motions involving the longitudinal component of the dipole moment, $\mu_{\parallel}$, of the mesogenic side group (which is higher for polymer {1} due to the presence of the rigid and highly polar cyano group). This is an interesting finding since, as emphazised before, the attribution at the molecular level of the discharges observed in the liquid crystalline phase of the t.s.d.c. thermogram is a problem under discussion. In previous works on side-chain LCPs[7, 8] we suggested that the relaxations observed above T_g in the t.s.d.c. spectrum arise from the motions of the mesogenic side groups and not from space charge effects. One argument to strength this attribution was that the features of the space charge peaks strongly depend on the polarisation conditions and previous annealing procedures, whereas the peaks we observe above T_g do not show this dependence on the electrical and.thermal conditions. Another argument was that the t.s.d.c. spectrum of side chain LCPs shows, in some cases, more than one relaxation in the liquid crystalline phase and this observation seems to be directly related with the molecular structure of the mesogonic side group.[3, 4, 7] In fact, in previous works[7, 8] we observed that two seperated relaxations were present above T_g when the mesogenic side-group had both longitudinal, $\mu_\parallel$, and transverse, $\mu_\perp$, components of the dipole moment, whereas a single relaxation above T_g was observed when the mesogenic side group had only the longitudinal component, $\mu_\parallel$. It is to be noted that polymers {1} and {2} have phenyl benzoate type side groups which present thus both $\mu_\parallel$ and $\mu_\perp$. It seems thus sensible, in this context, to consider that the two relaxations observed in the liquid crystalline phase correspond to molecular motions involving respectively $\mu_\perp$ and $\mu_\parallel$. Comparing with the results obtained by dielectric relaxation spectroscopy (d.r.s.), where the α-process (involving $\mu_\perp$) appears at higher frequencies when compared with the δ-process (involving mainly $\mu_\parallel$), we must consider that the higher temperature peak in t.s.d.c. should correspond to the lower frequency relaxation in the dielectric relaxation spectrum, and vice-versa. In this context the peak appearing at higher temperature in the t.s.d.c. spectrum (peak at ~ 104°C for polymer {1} and at ~ 83°C for polymer {2}) should correspond to the d.r.s. δ-process while the other discharge observed in the liquid crystalline phase (peak at ~ 94°C for polymer {1} and at ~ 75°C for polymer {2}) should correspond to the d.r.s. α-process. The fact that the peak at ~ 104°C in polymer {1} has higher intensity when compared with the peak at ~ 94°C, whereas for polymer {2} both peaks observed above T_g have similar intensities, is an interesting experimental result which strengthens the previous reasoning and reinforces the proposed attributions.

Another interesting behaviour of the studied polymers is shown on Figure 4 for polymer {2} (polymer {1} shows exactly the same behaviour).

From this Figure it can be observed that when the polarisation temperature, T_p, is sufficiently high in order to activate the peak at ~ 75°C (curves 1 and 2) the glass transition peak slightly decreases and broadens. This behaviour suggests that the activation, by the polarising field, of the motions corresponding to the peak at ~ 75°C ($\mu_\perp$) leads to a significant modification of the shape of the T_g peak (modification of the distribution of the energies and of the relaxation times). This observation suggests that there is some kind of coupling between the molecular motions corresponding to the first relaxation above T_g and the brownian motions of the backbone associated to the glass transition.

Another structural feature of the side-chain LCPs studied in the present work is the shortness of the spacer ($n = 2$) which links the mesogenic moiety to the polymer backbone. The consequence, at the molecular level, of this short spacer is that the motions of the mesogenic side-groups may be significantly coupled with those of the main chain. Our t.s.d.c. results show an interesting manifestation of this coupling. In fact, from Figure 2 it can be observed that the increase of the peak at ~ 104°C (induced by the increase of the polarisation temperature, T_p) is accompanied by an increase of the intensity of the glass transition peak. This behaviour, which was not observed in the t.s.d.c. studies of side-chain LCPs with longer spacers,[7, 8] suggest that when the

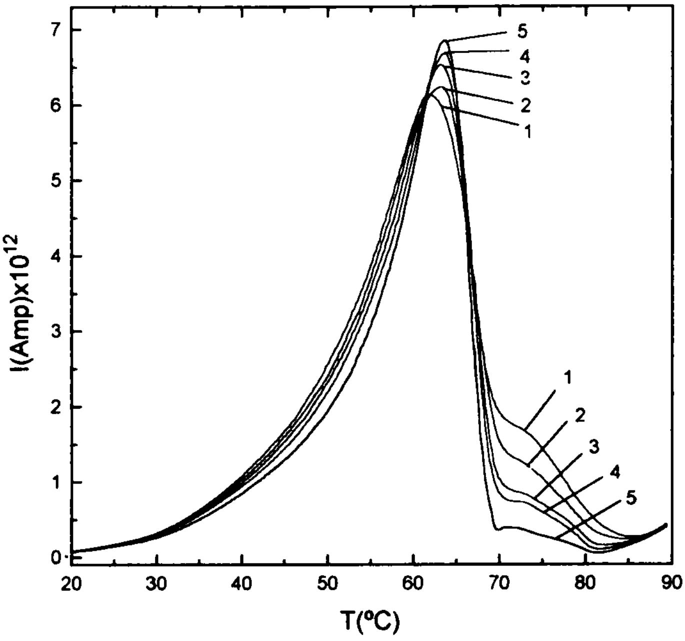


FIGURE 4 The modification of the shape of the glass transition peak. The polarisation temperature, T_p, of the different t.s.d.c. global experiments (performed on polymer {2}) were: 1–63°C; 2–62°C; 3–61°C; 4–60°C; 5–58°C. The other experimental conditions were $T_0 = 20°C$; $T_f = 120°C$; heating rate, $r = 8°C/min$; polarising field $E = 400$ V/mm.

polarising field activates the higher temperature relaxation (motions of $\mu_{\parallel}$) it also increases the amplitude of the brownian motions of the backbone. The reported phenomenon is reversible as shown in Figure 5.

The results presented on this Figure correspond to experiments which are similar to those shown in Figure 2 but now they have been performed in the order of decreasing T_p. In this case the intensity of the glass transition peak decreases as the peak at ~ 104°C decreases (as T_p decreases). The fact that the final temperature, T_f, of the experiments shown in Figures 2, 4 and 5 is situated in the isotropic phase, associated with the fact that the behaviour shown in those figures is independent of T_f and of the annealing time at T_f between two successive experiments suggests that the observed behaviour cannot be attributed to a memory of the sample about the previous thermoelectric treatments, but is probably a consequence of the coupling between the motions of the mesogenic groups and those of the main chain. We believe thus that we are able to conclude from these results that the t.s.d.c. signature of a side-chain LCP shows some features which are manifestation of the coupling between the motions of the backbone and those of the mesogenic moieties.

Thermal cleaning experiments

The different relaxations observed in the t.s.d.c. global spectrum of polymers {1} and {2} were analysed in detail by the technique of thermal cleaning (also called thermal

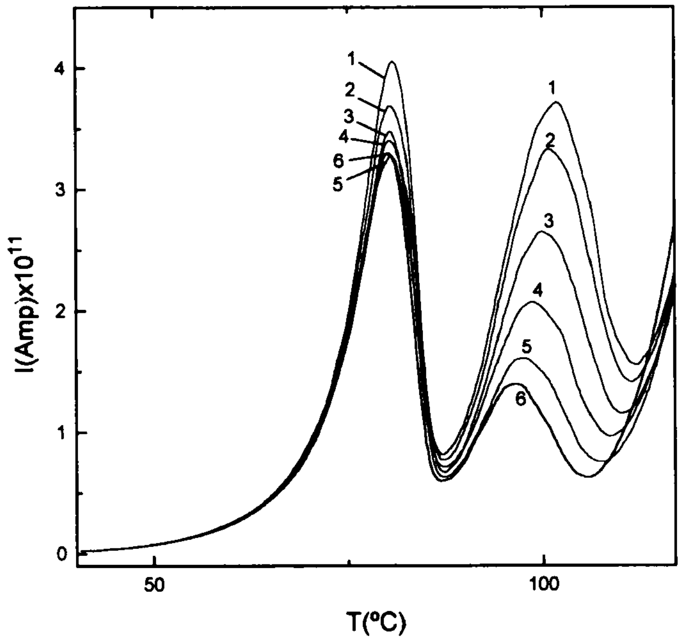


FIGURE 5 T.s.d.c. global experiments performed on polymer {1}. The polarisation temperatures, T_p, of the different experiments were 1–109°C; 2–107°C; 3–105°C; 4–103°C; 5–101°C; 6–99°C. The other experimental conditions were $T_0 = 35°C$; $T_f = 120°C$; heating rate, $r = 8°C/min$; polarising field $E = 400$ V/mm. These experiments show that the intensity of the glass transition relaxation is influenced by the motions of the mesogenic groups in the liquid crystalline phase.

sampling or thermal windowing). Figure 6 shows different thermal cleaning peaks of the relaxation below T_g of polymer {1} (as pointed out before, for polymer {2} we were not able to analyse this low temperature relaxation owing to problems of electrical contact between the sample and the electrodes at low temperatures).

The analysis by the Bucci method[15] of these thermal cleaned peaks showed that the components of this low temperature relaxation have identical activation enthalpy (~ 42 kJ mol^{-1}) and negligible activation entropy. The existence of this low temperature relaxation in the t.s.d.c. spectrum is a feature of other side chain LCPs we studied before and the values of the activation parameters suggest that it corresponds to local and non-cooperative motions involving the spacer and the mesogenic side-groups. Nevertheless, as pointed out before, the exact nature of this relaxation is not known and is a subject of some controversy.[10]

The glass transition relaxation and the relaxations above T_g have also been analysed by the thermal cleaning technique for polymer {1} as well as for polymer {2}. Each thermal cleaned peak is characterised by a given location in the t.s.d.c. spectrum (temperature of maximum intensity, T_m), and its activation parameters can be obtained using the Bucci method.[15] In Figure 7 each point corresponds to a thermal cleaned peak and this Figure shows the representation of T_m as a function of the polarisation temperature, T_p, for polymers {1} and {2}. The Figure shows the curvature characteristic of the glass transition region (from $T_p = 20°C$ to 75°C for polymer {1} and

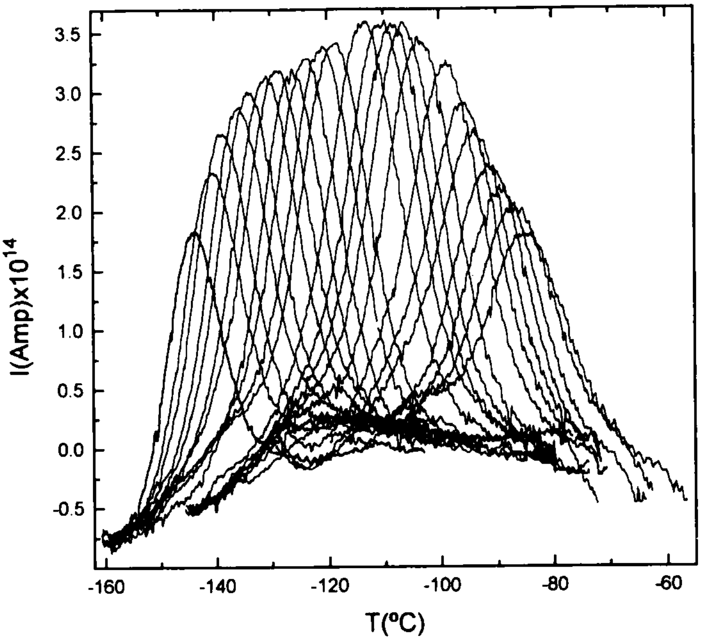


FIGURE 6 Thermally cleaned components of the lower temperature relaxation of polymer {1}. The polarisation temperatures, T_p, varied from − 150°C and − 93°C. The other experimental conditions were heating rate, $r = 4°C/min$; window width, $\Delta T = 2°C$; polarising field $E = 400$ V/mm.

from $T_p = 35°C$ up to 63°C for polymer {2}) which arises from the modification of the shape (broadness,'steepness) of the peaks in the glass transition region.

On the other hand, the points on the right hand side of Figure 7 correspond to the thermal cleaned peaks in the liquid crystalline phase ($T_p > 80°C$ for polymer {1} and $T_p > 64°C$ for polymer {2}).

Figure 8 shows, on the other hand, the activation enthalpy of the different thermal cleaned peaks as a function of its location in the t.s.d.c. spectrum defined as the reduced temperature $T_r = T_m/T_g$ where T_m is the temperature of maximum intensity of the peak and T_g is the glass transition temperature (considered as the temperature of maximum intensity of the peak which shows the maximum activation enthalpy).[16]

The representation of Figure 8 corresponds to the formulation of a kind of Corresponding States Principle where the variables are expressed in its reduced form. The advantage of this kind of representation is that the points will collapse to form a single curve (a "master" curve) for polymers with relaxation mechanisms with similar characteristics, even if they have different glass transition temperatures. It is clear from Figure 8 that the points corresponding to both polymers lie in the same curve. This is an expected result since the two studied polymers have very similar chemical structures and thus the glass transition relaxation must have similar features.

The increase of the activation enthalpy for the thermal cleaned peaks in the glass transition region is a feature of the T_g relaxation in polymeric materials and is often

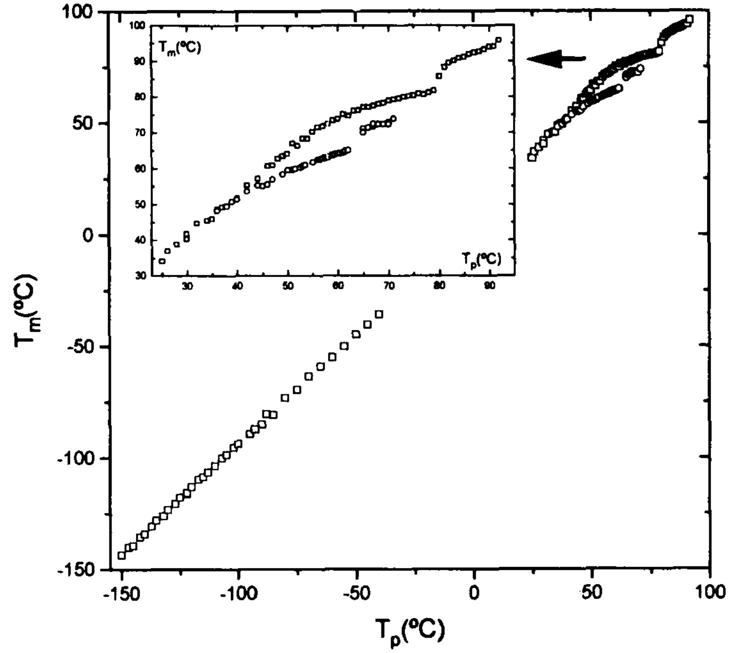


FIGURE 7 Location of the thermally cleaned peaks, T_m, as a function of the polarisation temperature, T_p, in the whole studied temperature range (the squares refer to polymer {1}, the circles refer to polymer {2}). The experimental conditions for all the experiments were: polarising field, $E = 400$ V/mm; heating rate, $r = 4$°C/min; window width, $\Delta T = 2$°C.

called compensation behaviour. The location of the peak in the glass transition region which shows the higher value of the activation enthalpy is considered to be coincident with the glass transition temperature.[16] For polymer {1} the peak with maximum activation enthalpy is located at $T_m = 81$°C whereas for polymer {2} this peak is located at $T_m = 65$°C. Remember that the glass transition temperatures obtained by differential scanning calorimetry are, as pointed out in the experimental section, $T_g = 75$°C for polymer {1} and $T_g = 61.5$ for polymer {2}. The points on the right hand side of Figures 7 and 8 correspond to the thermal cleaned peaks obtained in the liquid crystalline region. Despite the fact that Figures 7 and 8 do not allow to distinguish the two different relaxations observed in the liquid crystalline phase, we can note that the activation energy of those processes, obtained from the thermally cleaned peaks, is $\sim 330\,\text{kJ.mol}^{-1}$ ($79\,\text{kcal.mol}^{-1}$).

CONCLUSIONS

We presented a t.s.d.c. study of two side-chain liquid crystalline polymers whose only structural difference is in the terminal group of the mesogenic moiety (cyano or methoxy). Both polymers show two relaxations in the liquid crystalline phase and it was observed that for polymer {1} (cyano terminal group) the higher temperature

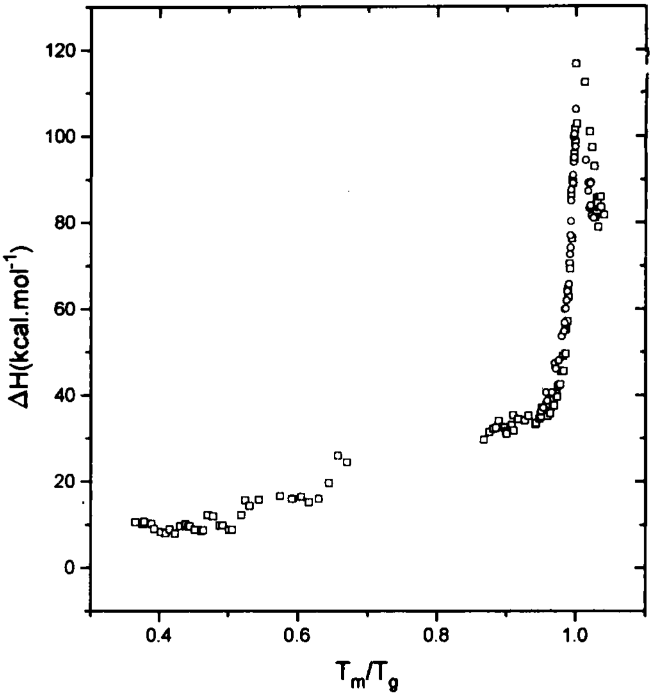


FIGURE 8 Activation ehthalpy, ΔH^{*}, of the different thermally cleaned components as a function of its location expressed as the reduce temperature T_m/T_g (the squares refer to polymer {1}, the circles refer to polymer {2}).

relaxation had a much higher intensity when compared with the lower temperature relaxation, whereas for polymer {2} (methoxy terminal group) both relaxations in the liquid crystalline phase had intensities of the same order of magnitude. This fact was interpreted considering that the higher temperature relaxation corresponds to motions involving the longitudinal component of the dipole moment of the mesogenic group, which is higher in the polymer carrying the cyano group. On the other hand, the relaxation observed above T_g at lower temperature probably arises from internal rotations involving the esther group of the phenyl benzoate side-group and are probably related with reorientational motions of the transverse component of the dipole moment of the mesogenic moiety. Moreover, the obtained results suggest that when the polarising electric field is applied at temperatures such that these motions in the liquid crystalline phase are activated, the glass transition relaxation broadens and its maximum intensity decreases (modification of its distribution of energies and relaxation times).

The presented results showed, on the other hand, that when the polarising electric field is applied at temperatures such that the higher temperature mechanism (motions of the mesogenic moiety as a whole) is activated, the intensity of the glass transition relaxation increases. This behaviour was considered to be a consequence of the shortness of the spacer group in the studied polymers, and to arise from the coupling between the motions of the side-groups as a whole and the motions of the backbone.

Acknowledgments

This work was carried out in the context of the *Divisão de Química e Física de Materiais* of the ICEMS (Instituto de Ciência e Engenharia de Materiais e Superficies-Programa Ciência). J.F.M. acknowledges JNICT for his research grant. The authors are indebted to Merck (U.K.) for the kind gift of some LCP samples.

References

1. J. van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets*, Elsevier Scientific Publishing Company, Amsterdam (1975).
2. S. H. Carr, in *Electric Properties of Polymers* (Ed. D. A. Seanor), Academic Press, New York, (1982).
3. J. F. Mano, J. J Moura Ramos, A. C. Fernandes and G. Williams, *Polymer*, **35**, 5170 (1994).
4. J. F. Mano, N. T. Correia and J. J. Moura Ramos, *Polymer*, **35**, 3561 (1994).
5. J. F Mano, N. T. Correia, J. J Moura Ramos and A. C. Fernandes, *J. Polym. Sci., Polym. Phys. Ed.*, **33**, 269 (1995).
6. J. F. Mano and J. J. Moura Ramos, *J. Thermal Anal.*, **44**, 1037 (1995).
7. J. F. Mano, N. T. Correia, J. J. Moura Ramos and D. Coates, *Macromol. Chem. Phys.*, **196**, 2289 (1995).
8. J. F. Mano, J. J. Moura Ramos and D. Lacey, *Polymer*, accepted.
9. H. W. Starkweather Jr., *Polymer*, **32**, 2443 (1991) and references therein.
10. B. Schartel and J. H. Wendorff, *Polymer*, **36**, 899 (1995).
11. W. Köhler, D. R. Robello, P. T. Dao, C. S. Willand and D. J. Williams, *J. Chem. Phys.*, **93**, 9157 (1990).
12. G. P. Simon, *Polymer*, **30**, 2227 (1989).
13. R. F. Boyer, in *Computational Modelling of Polymers*, by J. Bicerano, ed., Marcel Dekker, New York (1992).
14. F. Faubert, J. M. Gilli, P. Sixou J. Dandurand and C. Lacabanne, *Mol. Cryst. Liq. Cryst.*, **178**, 133 (1990).
15. C. Bucci, R. Fieschi and G. Guidi, *Phys. Rev.*, **148**, 816 (1966).
16. B. B. Sauer, N. V. Dipaolo, P. Avakian, W. G. Kampert and H. W. Starkweather, *Jr. J. Polym. Sci., Polym. Phys. ed.*, **31**, 1851 (1993).