Molecular motions of side-chain liquid crystalline polymers in the liquid crystalline phase studied by the thermally stimulated currents technique

João F. Mano, Natália T. Correia and Joaquim J. Moura Ramos*
Centro de Química-Física Molecular, Complexo I, IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

(Received 14 March 1994)

In the present work the thermally stimulated currents technique was used to study the upper glass transition relaxations in two side-chain liquid crystalline polysiloxanes. The nature of those relaxations at the molecular level is a controversial subject, but our results lead us to suggest thay they correspond to the reorientational motions in the liquid crystalline phase of the longitudinal and transverse components of the dipole moment of the mesogenic side group. This assignment is compatible with the conclusions from extensive studies of the dipolar relaxation behaviour of side-chain liquid crystalline polymers by dielectric relaxation spectroscopy.

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

Introduction

Thermotropic liquid crystalline polymers (LCPs) are high molecular weight materials which show a mesophase in a given temperature range. A major class of thermotropic LCPs have side-chain mesogenic groups covalently attached to the main chain, and those materials have been the subject of intense research activity in the last two decades[1]. The molecular dynamics behaviour of side-chain LCPs with acrylate, methacrylate and siloxane backbones has been studied extensively by dielectric relaxation spectroscopy (d.r.s.)[2–5], and it was demonstrated from those studies that there are essentially two relaxations in the liquid crystalline phase (upper glass transition relaxations) of these polymers. The low frequency relaxation, the so-called δ-relaxation, shows a narrow loss peak which is similar to the absorptions associated with the rotations about the short molecular axis in low molecular mass liquid crystals; however, as expected, its activation energy is larger and the characteristic relaxation times are longer compared with the low molecular mass analogues. This δ-relaxation observed by d.r.s. was found to be non-linear in the Arrhenius plot and it is believed to be caused by rotations of the longitudinal component of the dipole moment of the mesogenic side groups. The higher frequency relaxation, on the other hand, often called the α-relaxation (to be distinguished from the α-relaxation of amorphous polymers which is the glass transition relaxation), shows a very broad absorption curve and it is believed to depend on the transverse dipole component of the mesogenic side group.

The major difficulty encountered in the analysis and interpretation of the dielectric relaxation spectra of LCPs is that the loss spectra observed experimentally are often broad, highly asymmetric, with coalescence of the different bands and without clearly resolvable features. In this context it is difficult to extract the essential information regarding the molecular processes which give rise to such broad loss features. In order to assign the relaxations observed in dielectric experiments and to deduce their mechanisms, it is necessary to resolve the broad loss peaks into their various components, making assumptions regarding the reorientational modes of motion in the liquid crystalline state.

The thermally stimulated discharge currents (t.s.d.c.) technique is a dielectric related technique which is also a very suitable tool for the study of dielectric relaxation mechanisms in polymeric materials[6]. As explained in detail elsewhere[7], a t.s.d.c. experiment measures the thermally stimulated release of the polarization which was frozen in during a previous electric field poling. One advantage of the t.s.d.c. technique is its low equivalent frequency[8]. This leads to the enhanced resolution of the different relaxation processes or, in other words, the separation of the t.s.d.c. peaks along the temperature axis is increased when compared with higher frequency techniques such as d.r.s. These characteristics of the t.s.d.c. technique suggest that it would be particularly well suited for the study of dipolar relaxations of LCPs in the liquid crystalline phase and would allow resolution of the mechanisms which appear overlapped in d.r.s. Nevertheless, t.s.d.c. studies on side-chain LCPs are scarce. The first was published by Simon[9] in 1989; since then very few works have been reported on the subject[10–13]. An upper glass transition relaxation (in the liquid crystalline temperature range) was reported in all those studies but, despite the d.r.s. results previously published, it was attributed by all the authors, except Faubert *et al.*[10], to a space charge discharge and not to a dipolar relaxation of the mesogenic side group in the mesophase. This is all the more inexplicable since the existence of relaxation mechanisms of the mesogenic moieties in the liquid crystalline phase is a feature of liquid crystalline materials, as was clearly demonstrated by d.r.s. and other techniques.

---

* To whom correspondence should be addressed

0032-3861/94/16/3561–04
© 1994 Butterworth-Heinemann Ltd

In the present communication we report some t.s.d.c. results on two side-chain liquid crystalline polysiloxanes, and we will show that the different features of the upper glass transition relaxations observed in both LCPs are a consequence of the different molecular structure of the mesogenic side groups of the two polymers. Consequently, we will strengthen the opinion stated in ref. 10, according to which those relaxations observed in the t.s.d.c. spectra are intrinsic features of the liquid crystalline behaviour of LCPs.

Experimental

The LCPs studied in this work are from Merck (catalogue numbers LCP83, structure **1**, and LCP1, structure **2**). Polymer **1** has a glass transition temperature, T_g, of 37.2°C and a smectic A–isotropic transition at 148.6°C. Polymer **2** has a T_g of -7°C and a smectic C–isotropic transition at 77°C.

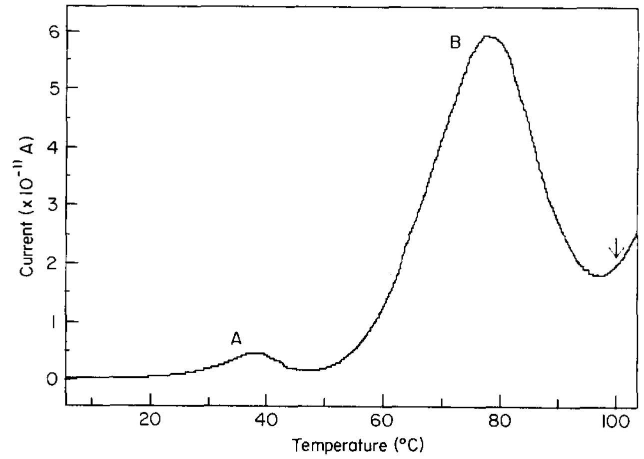
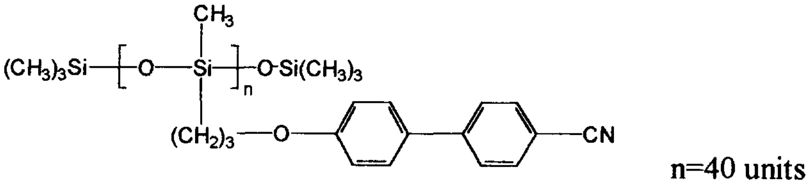
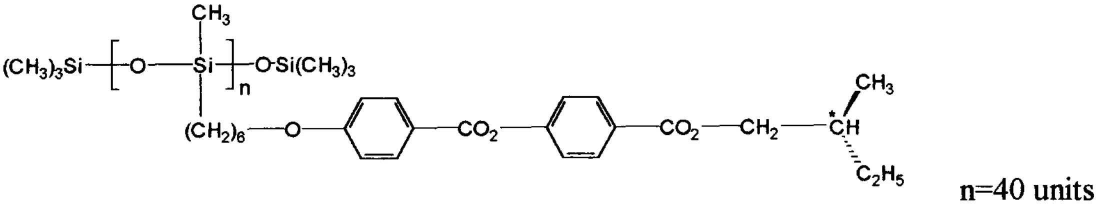


Figure 1 T.s.d.c. global thermogram of LCP **1**. The experimental conditions were: polarization temperature, $T_p = 100$°C; electric field strength 450 V mm^{-1}; $T_0 = -20$°C; $T_f = 150$°C; heating rate 4°C min^{-1}



1



2

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^{-4} mbar and flushed several times with 1.1 bar of high-purity helium. In each experiment, the sample was polarized for several minutes by a polarization voltage V_p at a temperature T_p and the polarization was frozen-in by cooling down to a temperature $T_0 \ll T_p$ in the presence of the electric field. With the field off the depolarization current was then measured as the sample was heated up at a constant rate (typically 4°C min^{-1}) to $T_f > T_p$.

Results and discussion

The t.s.d.c. global experiment thermogram obtained for polymer **1** is shown in *Figure 1*. Peak A, whose maximum occurs at 37°C, corresponds to the glass transition relaxation (the reported T_g is 37.2°C). An upper glass transition peak whose maximum occurs at 70°C (peak B) is also observed, as was the case for other LCPs[9–15].

The t.s.d.c. global thermogram for polymer **2** is shown in *Figure 2*. Peak A, whose maximum occurs at -9°C, corresponds to the glass transition relaxation (the T_g reported for this polymer is -7°C), but now two well-resolved upper T_g relaxations are observed with maxima at 8 and 31°C.

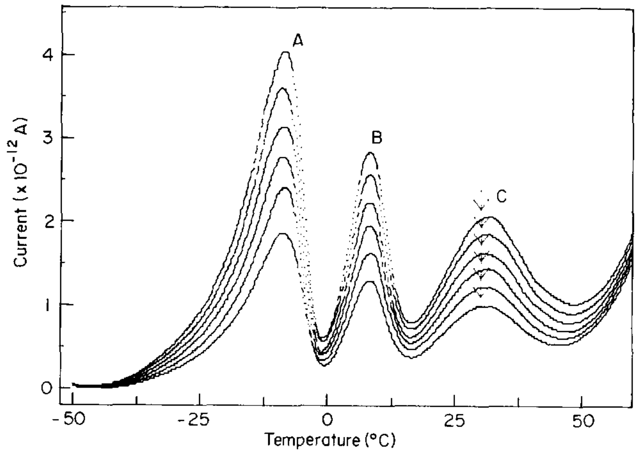


Figure 2 T.s.d.c. global thermogram of LCP **2**. The experimental conditions were: polarization temperature, $T_p = 30$°C; $T_0 = -50$°C; $T_f = 78$°C; heating rate 8°C min^{-1}. The curves correspond to different electric field strengths: 400, 500, 600, 700, 800 and 900 V mm^{-1}, in order of increasing peak intensities

Figure 2 also shows the effect of the polarization voltage on the intensity of these relaxation peaks. These results are presented in a different manner in *Figure 3*, where the maximum intensity, I_m, is plotted as a function of the electric field strength, E, for the peaks A, B and C. It can be observed from the figure that there is a linear dependence of I_m *versus* E for the three relaxation peaks,

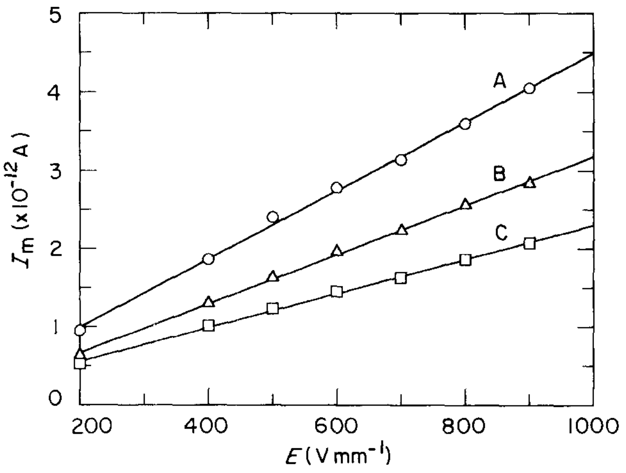


Figure 3 Intensity of the maximum, I_m, of peaks A, B and C of polymer 2 as a function of the strength of the polarizing electric field, E

a fact that is considered to indicate the dipolar nature of the corresponding relaxation processes.

On the other hand, the relaxations due to space charge motions are reported to be weakly dependent on the electric field[11] and very susceptible to electret forming conditions (low reproductivity)[9]. Those features were not observed for the upper T_g peaks in polymers **1** and **2**. We thus believe that peaks B and C of *Figures 1* and *2* arise from the dipolar mechanisms which are present in the LC phase and correspond to the δ and α processes which were detected and extensively studied by dielectric relaxation spectroscopy[2].

The analysis of peak B for polymer **1** by the Bucci method[16] gave values of $\sim$40 kcal mol^{-1} for the activation enthalpy ($\Delta H^{\neq}$) and of $\sim$45 kcal K^{-1} mol^{-1} for the activation entropy ($\Delta S^{\neq}$). On the other hand for polymer **2** the values obtained were $\Delta H^{\neq} \approx 48$ kcal mol^{-1} and $\Delta S^{\neq} \approx 100$ cal K^{-1} mol^{-1} for peak B and $\Delta H^{\neq} \approx 25$ kcal mol^{-1} and $\Delta S^{\neq} \approx 20$ cal K^{-1} mol^{-1} for peak C. The fact that the intensity of peak B when compared with the T_g peak is higher in polymer **1** than in polymer **2** indicates that this peak is very sensitive to the presence of the strong dipole of the cyano group and suggests that it corresponds to the motions of the mesogenic group around the main chain (δ-process, corresponding to the motions of the longitudinal component of the dipole moment). On the other hand, the high activation entropy of peak B of polymer **2** probably arises from the longer spacer, which allows a higher mobility of the side chain, and also from its higher molecular volume. This $\Delta S^{\neq}$ value also explains the fact that the corresponding peak appears at lower temperatures than peak C (lower Gibbs activation energy).

Peak C is absent from the t.s.d.c. thermogram of polymer **1**. The lower values of the activation parameters of this relaxation correspond to a more localized motion when compared to those associated with peak B. In order to suggest an assignment to this relaxation process we must analyse the molecular differences in the two side-chain groups. In polymer **1** the mesogenic moiety is a rigid cyano biphenyl group which has mainly a longitudinal dipole moment associated with the cyano group. In polymer **2**, on the other hand, there is a phenyl benzoate group, where the ester between the two phenyl rings destroys the mutual conjugation of the π-electron system and allows internal rotation of one of those rings relative to the other. In the mesogenic side group of polymer **2** we have thus a significant transverse component of the dipole moment (associated with the ester groups) and the possibility of changing the direction of this component by internal rotation around ester–carbon/phenyl–carbon bonds. It is thus reasonable to believe that peak C, observed in the t.s.d.c. thermogram of polymer **2**, arises from the reorientational motions of the transverse dipole moment of the mesogenic group and corresponds to the higher frequency α-process observed by d.r.s. From *Figure 2* it can also be observed that peak C is broader than peak B, as was the case for the α and δ peaks in dielectric relaxation spectroscopy. This suggests that the α-relaxation can probably not be described by a single molecular motion but is composed of different motions. In fact, the reorientation of the transverse dipole moment can be achieved by internal rotations about the two covalent bonds which link the two ester groups to the phenyl rings, and probably also by internal rotations involving the oxygen atom which links the mesogenic group to the spacer. We must finally note that the dielectric strengths of processes B and C in polymer **2** are not very far apart. This can probably be explained by the fact that the longitudinal as well as the transverse dipole moment of the side chain in polymer **2** arises mainly from the ester group. Had this mesogenic side group a terminal cyano group, for example, this would cause the longitudinal dipole to be stronger than the transverse one; in this situation we would expect peak B to have a greater dielectric strength when compared to peak C.

Conclusions

We have discussed the nature of the upper glass transition relaxations observed in side-chain LCPs on the basis of the results of some t.s.d.c. experiments on two side-chain liquid crystalline polysiloxanes. For one of these LCPs, two well-resolved upper T_g relaxations were observed (for the first time in the literature); these results lead us to contest the view of most authors, according to whom those relaxations arise from space charge or electrode effects, and to suggest that in contrast they correspond to dipolar motions of the mesogenic side groups in the liquid crystalline phase. Comparison of the t.s.d.c. and d.r.s. results seems to confirm the t.s.d.c. technique as a powerful tool to resolve relaxation mechanisms which appear overlapped in other experimental techniques. In order to interpret without any ambiguity the t.s.d.c. spectra of side-chain LCPs, we nevertheless need more research work. In this context we are studying different LCPs[14,15] in order to gain insight into the structural influences on the t.s.d.c. spectra. Side-chain LCPs are constructed from three types of structural unit: the backbone, the side group and the spacer which joins the side group to the backbone. By studying different LCPs with different backbones, different spacer lengths and different mesogenic side groups, we hope to be able to understand the relationship between these structural features and the characteristics of the t.s.d.c. spectra, and to ascribe without ambiguity the observed relaxations to well-defined molecular motions.

Acknowledgements

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 Superfícies-Programa Ciência). J.F.M. acknowledges JNICT for his research grant. The authors are indebted to Merck (UK) for the kind gift of some LCP samples.

References

1 McArdle, C. B. (Ed.) 'Side-Chain Liquid Crystal Polymers', Blackie, Glasgow, 1989

2 Haws, C. M., Clark, M. G. and Attard, G. S. in 'Side-Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie, Glasgow, 1989, p. 7

3 Attard, G. S., Araki, K., Moura Ramos, J. J. and Williams, G. *Liq. Cryst.* 1988, **3**, 861

4 Bormuth, F. J., Haase, W. and Zentel, R. *Mol. Cryst. Liq. Cryst.* 1987, **148**, 1

5 Parneix, J. P., Njeumo, R., Legrand, C., Le Barny, P. and Dubois, T. C. *Liq. Cryst.* 1987, **2**, 167

6 Carr, S. H. in 'Electric Properties of Polymers' (Ed. D. A. Seanor), Academic Press, New York, 1982

7 Dias, A. B., Correia, N. T., Moura Ramos, J. J. and Fernandes, A. C. *Polym. Int.* 1994, **33**, 293

8 van Turnhout, J. 'Thermally Stimulated Discharge of Polymer Electrets', Elsevier Scientific, Amsterdam, 1975

9 Simon, G. P. *Polymer* 1989, **30**, 2227

10 Faubert, F., Gilli, J. M., Sixou, P., Dandurand, J. and Lacabanne, C. *Mol. Cryst. Liq. Cryst.* 1990, **178**, 133

11 Kohler, W., Robello, D. R., Dao, P. T. and Willand, C. S. *J. Chem. Phys.* 1990, **93**, 9157

12 Sauer, B. B., Dipaolo, N. V., Avakian, P., Kampert, W. G. and Starkweather, H. W. Jr *J. Polym. Sci., Polym. Phys. Edn* 1993, **31**, 1851

13 Sauer, B. B., Beckerbauer, R. and Wang, L. *J. Polym. Sci., Polym. Phys. Edn* 1993, **31**, 1861

14 Mano, J. F., Moura Ramos, J. J., Fernandes, A. C. and Williams, G. *Polymer* in press

15 Mano, J. F. and Moura Ramos, J. J. *J. Thermal Anal.* submitted

16 Bucci, C. and Fieschi, R. *Phys. Rev.* 1966, **148**, 816