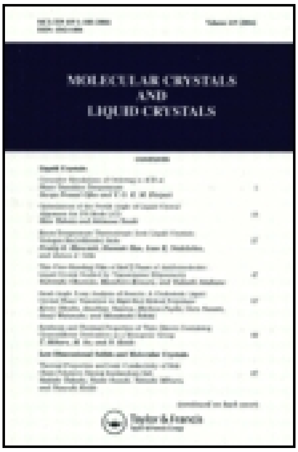

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Dipolar Motions in Two Side-Chain Liquid-Crystalline Polysiloxanes Studied by the TSDC Technique

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DIPOLAR MOTIONS IN TWO SIDE-CHAIN LIQUID-CRYSTALLINE POLYSILOXANES STUDIED BY THE TSDC TECHNIQUE

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Abstract In the present work, the technique of Thermally Stimulated Depolarisation Currents (TSDC) was used to study the dipolar relaxation mechanisms in two side-chain liquid crystalline polysiloxanes. The studied polymers differ significantly in the structure of the mesogenic side groups and this is at the origin of different features of the corresponding TSDC spectra. It is shown that the TSDC technique is able to separate the motions of the longitudinal ($\mu_{\|}$) and of the transverse ($\mu_{\perp}$) dipole moment components of the mesogenic side groups in the liquid crystalline phase.

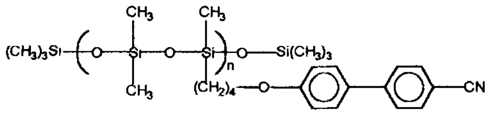
INTRODUCTION

The Thermally Stimulated Discharge Currents (TSDC) spectrum of side-chain liquid crystalline polymers (LCPs) shows different relaxation mechanisms.[1,2,3] At the glass transition temperature, T_g, the observed discharge has a characteristic feature, which is generally observed for polymeric materials,[4] and is called compensation behaviour. This corresponds to the observation that the individual components of this complex relaxation show a concomitant increase of the activation enthalpy and entropy as the temperature increases approaching T_g. This discharge observed at T_g is attributed to the cooperative brownian motions of the main-chain. In all studied LCPs a lower T_g relaxation is also observed.[5] The main features of this relaxation are that it is broad in the temperature axis and that its components show low values for the activation enthalpy and entropy. This low temperature relaxation is attributed to local and non-cooperative motions of molecular segments and arises from slightly hindered internal rotations and conformational changes[6]. In the case of side-chain LCPs the features of this relaxation seem to be strongly influenced by the length of the spacer which links the mesogenic side group to the main-chain. Above the glass transition temperature, on the other hand, the TSDC spectrum of LCPs also shows invariably a discharge[1,2,5]. The existence of this relaxation seems to be an universal feature of the TSDC spectra of polymeric materials since it is observed for amorphous polymers like poly(vinyl acetate)[4], for liquid crystalline polymers, as well as for many other polymers of diversified molecular structure[7]. Nevertheless, the molecular nature of this relaxation is a controversial subject. In fact, some authors consider that it arises from electrode polarisation effects or from charge trapping at crystal/amorphous interfaces[1,8]. Other authors, on the other hand, believe that it corresponds to a genuine dipolar relaxation process which would be associated to a liquid-liquid transition (T_{ll} process) in the case of amorphous polymers[7], or to the motions of the mesogenic moieties in the liquid crystalline phase in the case of LCPs[2].

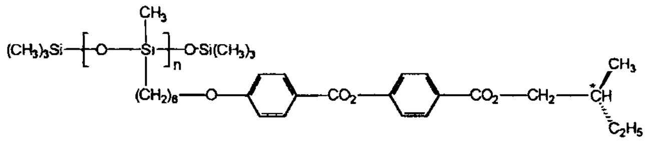
In the present work some features of the TSDC spectra of two side-chain liquid crystalline polysiloxanes are reported, namely concerning the T_g and the upper T_g relaxations.

EXPERIMENTAL

The liquid crystalline polymers studied in this work (structures {1} and {2}) are from Merck (catalogue numbers LCP93 and LCP1 respectively). Polymer {1} has a glass transition temperature T_g=-3.9°C and a smectic A/isotropic transition at 79.1°C. Polymer {2} has T_g=-7°C and a smectic C/isotropic transition at 77°C.



{1}



{2}

Experimental details concerning the used apparatus and the different techniques for obtaining the TSDC spectra are explained in ref.(4).

RESULTS and DISCUSSION

Figure 1 shows a TSDC global spectrum of polymer {1} whereas Figure 2 shows a TSDC global spectrum of polymer {2}. Peak 1 in Figures 1 and 2 have a maximum intensity respectively at -4°C and -9°C and correspond to the glass transition relaxation of each polymer.

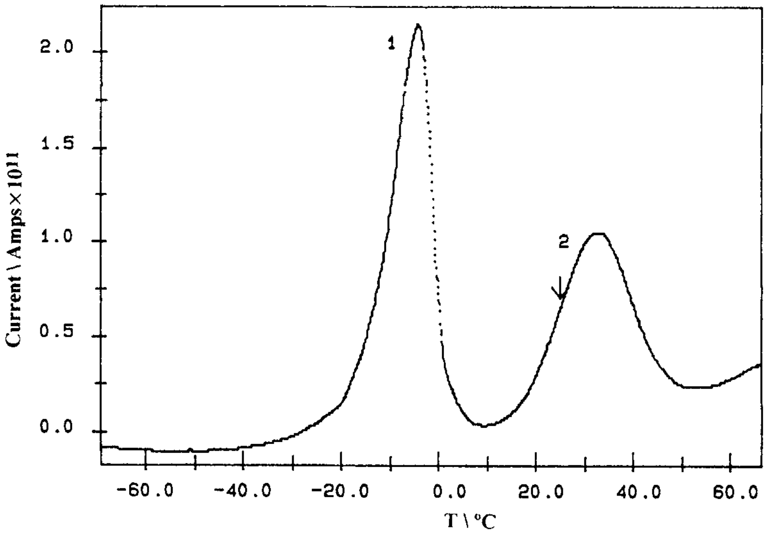


FIGURE 1 TSDC global experiment of polymer {1}. Experimental conditions: polarisation voltage 400 V/mm; T_p=25°C; T_o=-110°C; heating rate 8°C/min.

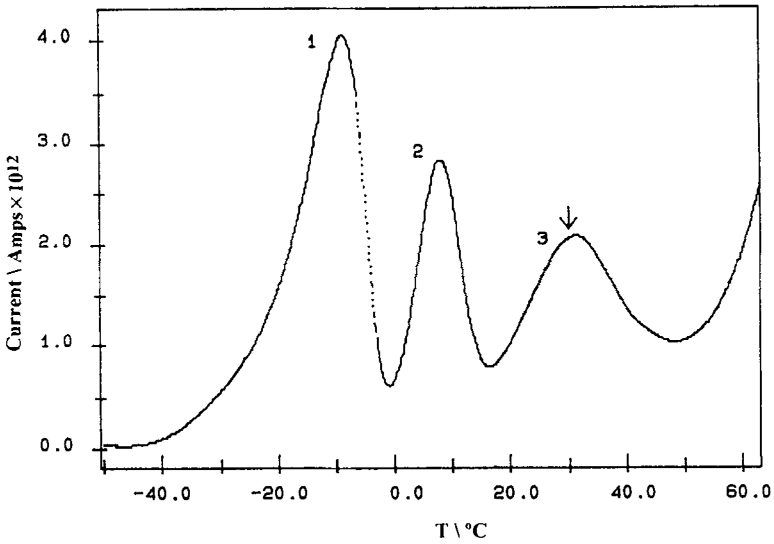


FIGURE 2 TSDC global experiment of polymer {2}. Experimental conditions: polarisation voltage 900 V/mm; T_p=30°C; T_o=-50°C; heating rate 8°C/min.

The analysis of the fine structure of these T_g relaxations was performed by the partial polarisation (or thermal cleaning) technique and is illustrated on Figure 3 for polymer {2}.

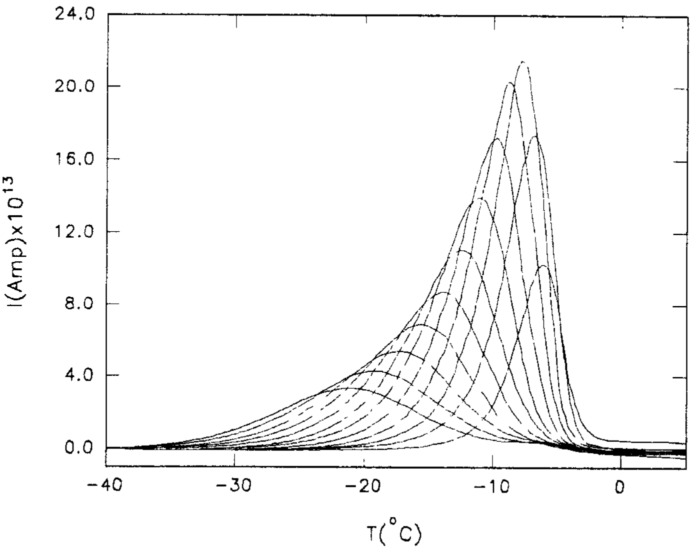


FIGURE 3 Thermally cleaned components of the glass transition of polymer {2}. The polarisation voltage was 600 V/mm, the window width 2°C and the heating rate 4°C/min. The polarisation temperatures were -32, -30, -28, -26, -24, -22, -20, -18, -16, -14, -12 and -10°C.

It can be seen from that Figure that there is an appreciable change in the shape of the thermally cleaned peaks which sharp significantly as the polarisation temperature, T_p, increases. This behaviour, which is also observed for polymer {1}, is a manifestation of the so-called compensation behaviour. The analysis of the thermally cleaned components of Figure 3 allows to obtain the relaxation time as a function of temperature, $\tau(T)^9$. The obtained results are presented on Figure 4 for polymer {2} in the form of Arrhenius plots of $\log(\tau)$ *versus* 1/T.

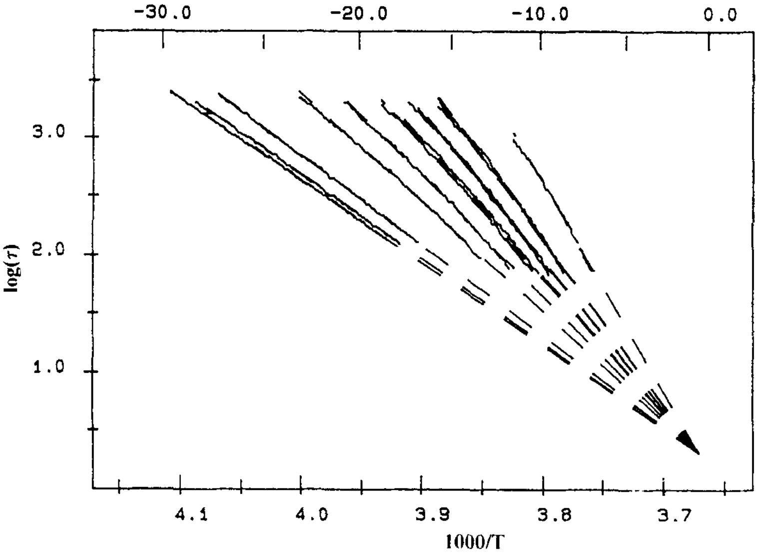


FIGURE 4 Arrhenius lines (log(τ(T)) *versus* 1/T) for polymer {2} for different thermally cleaned components of the glass transition relaxation.

On that Figure it can be seen another manifestation of the compensation behaviour: the Arrhenius lines converge to a single point, the compensation point. The existence of the compensation point associated with the glass transition relaxation is, as reported before, a consequence of a concomitant increasing, as T_p increases, of the enthalpy and the entropy of activation of the thermally cleaned components of the T_g relaxation. The coordinates of the compensation point are T_c=-0.7°C and τ_c=5.6 sec for the polymer {1} and T_c=-0.7°C and τ_c=2.0 sec for the polymer {2}. We can conclude from those values that the compensation temperature, T_c, is closer the glass transition temperature, T_g, for polymer {1} than for polymer {2}. As we pointed out previously[10], the difference T_c-T_g is presumably a parameter which depends on the polymer structure, on the mobility of the polymeric chains and on the width of the glass transition region. Nevertheless, the amount of available data is not enough to enable our understanding of the physical significance of such a parameter.

The most striking difference between Figures 1 and 2 is the fact that in polymer {1} we observe only one discharge above T_g (peak 2 of Figure 1) whereas in polymer {2} two separate discharges are observed in the mesogenic phase (peaks 2 and 3 of the Figure 2). Since these discharges appear in the liquid crystalline phase, it seems reasonable to consider that they arise from the motions of the mesogenic side groups. Moreover, the fact that polymer {1} presents only a discharge above T_g, whereas polymer {2} shows two well separated discharges, strengthens this attribution since the differences in the TSDC spectra of the two polymers in the liquid-crystalline phase can be ascribed to the structural characteristics of the mesogenic moieties of the two polymers. In fact, in polymer {1} the mesogenic moiety is a cyano biphenyl group which is a rigid group having a longitudinal dipole moment, $\mu_{\|}$, associated with the cyano group. In polymer {2}, on the other hand , the side-chain is a phenyl benzoate group which is not rigid since the ester group between the two phenyl rings destroys the mutual conjugation of the π-electron system allowing internal rotation of one of those rings relative to the other. Moreover, in this mesogenic side group of polymer {2} we have a transverse component of the dipole moment, $\mu_{\perp}$, (associated with the ester group). The spatial orientation of $\mu_{\perp}$ can be changed by internal rotation around the carbon-ester/carbon-phenyl bond as well as by the conformational changes involving the spacer. We thus suggest that the peak 3 in Figure 2 arises from the reorientational motions of the transverse dipole moment of the mesogenic side group. Peak 2 in Figures 1 and 2 would , on the other hand, be the consequence of the reorientational motions of $\mu_{\|}$. Finally, we would like to emphasise that the analysis, by the thermal cleaning technique, of peak 2 in Figure 1 (polymer {1}) and of peaks 2 and 3 in Figure 2 (polymer {2}) show that the components of these relaxations observed in the mesogenic phase show a WLF behaviour. On the other hand, the relaxation 3 of polymer {2} (reorientation of $\mu_\perp$) is characterised by activation enthalpies and entropies which are lower than those associated with the relaxation 2 of both polymers. This observation constitutes probably a confirmation of the attribution we suggested for the different relaxation mechanisms in the liquid-crystalline phase, since it seems reasonable to suppose that the motions of the mesogenic side group as a whole (longitudinal dipole moment) are characterised by higher enthalpies and entropies of activation when compared with the motions involving only a segment of the mesogenic group.

CONCLUSIONS

From the study of the TSDC spectra of two polysiloxanes LCPs we can draw the following conclusions:

1- The glass transition relaxation shows a compensation behaviour for both polymers, but in the case of polymer {1} the compensation temperature, T_c, is closer to the glass transition temperature, T_g, than in the case of polymer {2}.

2- The relaxations observed above T_g are not artifacts or space charge effects, but correspond to the motions of the mesogenic moieties in liquid crystalline phase.

3- The fact that polymer {1} presents only a relaxation above T_g whereas polymer {2} present two such relaxations, arises from the different structural characteristics of the side group of the two polymers, namely that in polymer {1} the side group only presents a longitudinal component of the dipole moment whereas in polymer {2} it presents also a transverse component.

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