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DIELECTRIC BEHAVIOUR OF A SIDE-CHAIN-BEARING LIQUID-CRYSTALLINE POLYSILOXANE

A thermally stimulated depolarization current study

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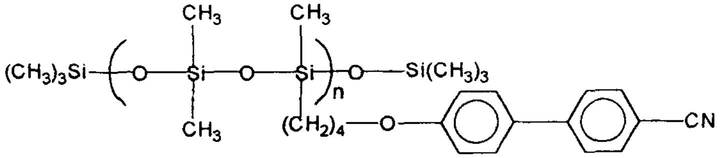
Abstract

The relaxation of electric field-induced polar orientation in a side-chain-bearing liquid-crystalline polysiloxane was measured by means of thermally stimulated depolarization currents. Different relaxation mechanisms were identified and characterized: the glass transition cooperative relaxation exhibits compensation behaviour. On the other hand, lower T_g and upper T_g discharges were observed and their molecular nature is discussed.

Keywords: compensation, dielectric relaxation, LCP, side-chain, TSDC

Introduction

The purpose of the present work was to investigate the molecular relaxation mechanisms in a liquid-crystalline siloxane polymer (structure {1}) in order to improve our understanding of the dynamics of the molecular motions in this type of material.



{1}

The thermally stimulated depolarization current (TSDC) technique was used in this context to investigate the transitions and the relaxational behaviour of this polymer.

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The first TSDC study of liquid-crystalline polymers was carried out by Simon [1]; since then, not many works have been published [2, 3]. The TSDC method is closely related to dielectric relaxation, and van Turnhout [4] has shown that a TSDC experiment is equivalent to a low-frequency dielectric loss experiment. The low equivalent frequency of the TSDC technique leads to an enhancement of the resolution of the different relaxation processes, meaning that the separation of the peaks along the temperature axis is greater in TSDC than in other higher-frequency techniques such as dielectric relaxation spectroscopy. The TSDC technique is thus a very useful tool for the study of polymers, which often present overlapping peaks which are difficult to separate by other techniques.

Experimental

The liquid-crystalline polymer studied in this work (structure {1}) is from Merck (catalogue no. LCP93) and has, according to the supplier, a glass transition temperature $T_g=-3.9$°C and a smectic A/isotrope transition at 79.1°C (obtained by DSC).

TSDC 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 order to analyse specific regions of the TSDC spectrum, different methods of polarizing the sample were used: the TSDC global experiment and the thermal windowing (or cleaning) experiment [5, 6]. In both types of experiment, the sample was polarized in a given temperature range (with the field applied between T_p and T_p', the polarization was frozen in by cooling down to T_o and the depolarization current was measured as the polarized sample was heated up to T_f at a constant rate. The difference between the two types of experiment is that in a TSDC global experiment $T_p'=T_o$, whereas in a thermal windowing experiment $T_p-T_p'\sim3$ deg and $T_o \ll T_p$ and T_p'. The technique of thermal windowing therefore allows the polarization of specific segments of a complex global relaxation.

Results and discussion

The TSDC spectra of side-chain-bearing liquid-crystalline polymers exhibit at least three relaxations [5]: one at low temperatures, characterized by low activation enthalpy and entropy and attributed to local motions arising from internal rotations around covalent bonds in the side groups; the glass transition relaxation, which displays compensation behaviour; and an upper glass transition relaxation, considered by some authors [2] to arise from charge trapping at crystal/amorphous interfaces or from electrode polarization effects, but is believed by others [7] to correspond to a genuine dipolar relaxation process referred to as a T_{ll} process (liquid –liquid transition). In the following, we analyse these three relaxations for our liquid-crystalline polysiloxane. The TSDC global experiments carried out on this polymer showed two discharges (Fig. 1): one with maximum at $T = -4$°C, and which presumably corresponds to the glass transition relaxation, and a higher-temperature discharge with maximum at $T \sim 35$°C. The usual lower-temperature discharge was not observed in those global experiments, but was revealed, as shown later, by the thermal windowing technique.

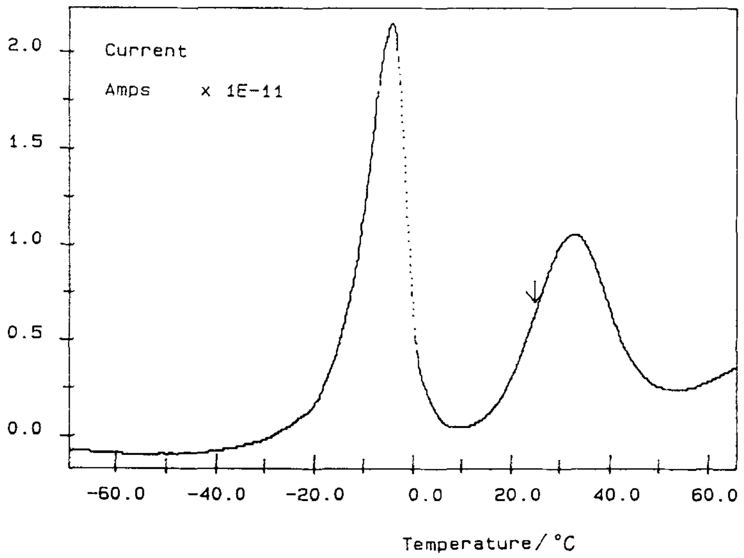

Fig. 1 TSDC global experiment showing two relaxation mechanisms whose maxima are located at −4°C and 35°C. Experimental conditions: polarisation voltage 400 V/mm, T_p=25°C, T_o=−110°C, T_f=70°C, heating rate 8 deg·min^{-1}

The lower-temperature relaxation

Figure 2 depicts three components of this lower-temperature discharge, obtained from thermal cleaning (or windowing) experiments. It can be seen that they are very low-intensity discharges.The fact that they appear in the extreme lower limit of the studied temperature range suggest that they are probably residuals of a relaxation which would be observed at temperatures lower than the available temperature range of our apparatus.

In an LCP studied earlier [5], this low-temperature discharge was much easier to observe, which is probably related with the mobility of the polymer

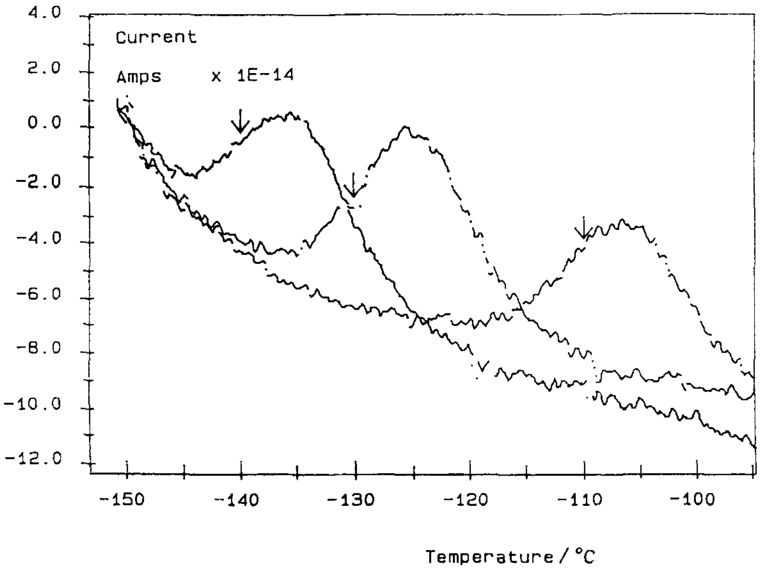

Fig. 2 Thermally cleaned components of the lower temperature relaxation mechanism. Experimental conditions: polarisation voltage 400 V/mm, window width 5°C, heating rate 4 deg·min^{-1}, polarisation temperatures (indicated by the arrows) −140, −130 and −110°C

chain. In fact, the earlier polymer was a polyacrylate, whereas the LCP studied here has a more mobile polysiloxane main chain. Moreover, the distance between the side groups in the polysiloxane is longer than that in the acrylate. These molecular characteristics of our polysiloxane polymer lead to a higher mobility (the glass transition temperature is lower (T_g=−3.9°C) than that of the methacrylate LCP (T_g=47°C)), which makes the local motions less hindered or faster. We therefore expect them to appear at lower temperatures in the TSDC spectra. Analysis of the discharges shown in Fig. 2 lead us to conclude that they are characterized by low activation enthalpies and entropies.

The glass transition relaxation

The discharge at −4°C in Fig. 1 was analysed in detail by using the thermal cleaning technique. Figure 3 shows different components of this global peak. It is obvious that there is an appreciable change in the shape of the discharge peaks as the polarization temperature, T_p, varies. It is evident that near the glass transition the thermally cleaned spectrum sharpens significantly, which is an indication of a high activation energy process.

This is a key feature of the glass transition observed with the TSDC technique: since the slopes of the peaks are proportional to the activation energy,

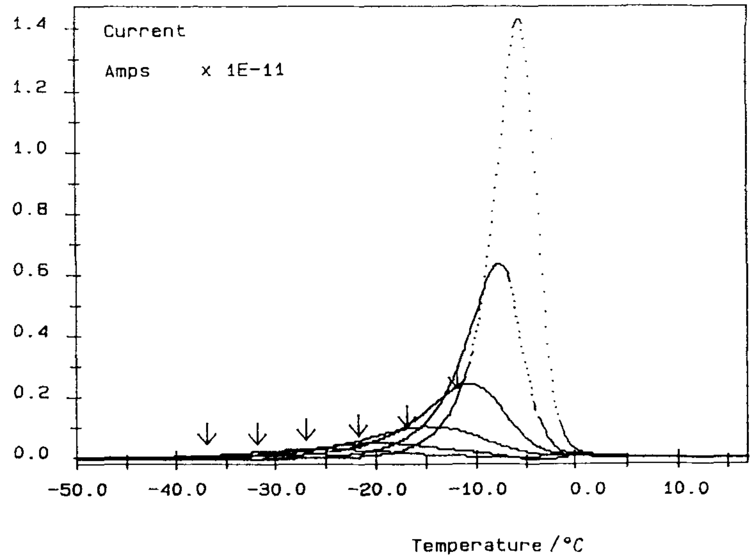

Fig. 3 Thermally cleaned components of the glass transition relaxation mechanism. Experimental conditions: polarisation voltage 400 V/mm, window width 3°C, heating rate 4 deg·min^{-1}, polarisation temperatures (indicated by the arrows) –37, –32, –27, –22, –17 and –12°C

there is a steepening of the slope near T_g, which is a manifestation of the compensation behaviour (a concomitant increase in the enthalpy and the entropy of activation as T_p increases, approaching T_g). Careful observation of the thermally cleaned components near T_g led us to consider two different types of components. These can be seen clearly from Figs 4 and 5. In Fig. 4, the difference T_m–T_p between the temperature of maximum intensity of each individual peak and the corresponding polarization temperature is plotted as a function of the polarization temperature, T_p, for thermally cleaned components of the TSDC spectrum. This difference T_m–T_p may be regarded as a measure of the sharpness of the peak: it will be small for a sharp peak and large for a broad one. The left-hand side of the Figure corresponds, as in Fig. 5, to the glass transition peak, whereas the right-hand side corresponds to the upper T_g peak. From the points corresponding to the T_g peak (negative values of T_p), we can conclude that the lower-temperature components (T_p between –50 and –20°C) give values of T_m–T_p which are nearly constant, whereas the higher-temperature components (T_p between –20 and 0°C) give T_m–T_p values which decrease markedly as T_p increases (the peaks sharpen markedly).

In Fig. 5, on the other hand, the activation enthalpy of different thermally cleaned components of the TSDC spectrum is plotted as a function of T_p. As in Fig. 4, the left-hand part of Fig. 5 corresponds to the T_g peak and it seems clear

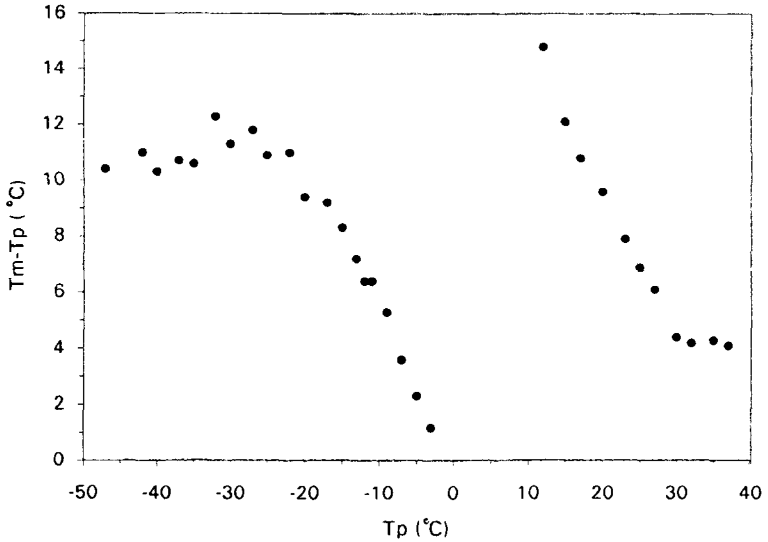

Fig. 4 T_m–T_p *vs.* T_p for different thermally cleaned components of the TSDC spectrum. The points on the left hand side (negative values of T_p) correspond to the glass transition relaxation whereas those on the right hand side correspond to the upper T_g relaxation

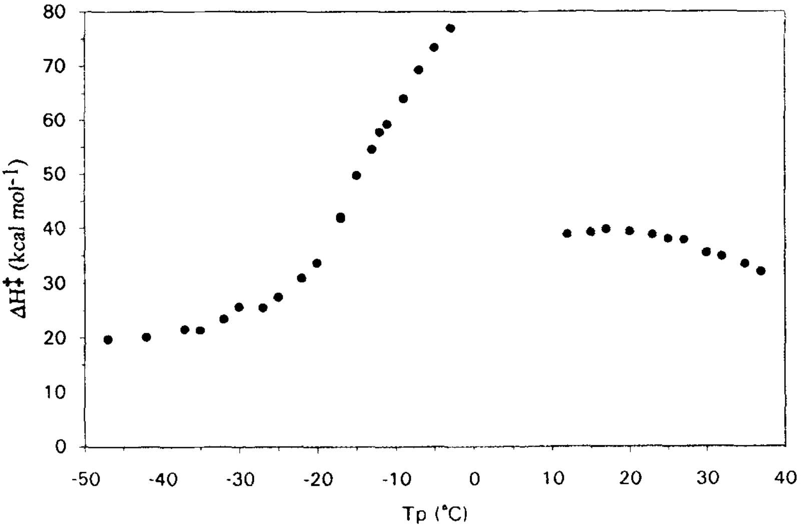

Fig. 5 Activation enthalpies, $\Delta H^{\ddagger}$, *vs.* T_p for different thermally cleaned components of the TSDC spectrum. The points in the left hand side correspond to the glass transition relaxation whereas those on the right hand side correspond to the upper T_g relaxation

that the lower-temperature components of the T_g peak exhibit activation enthalpies which do not change appreciably with T_p whereas the higher temperature components have activation enthalpies which increase markedly with T_p. The same behaviour is observed if we plot the activation entropy of the different components as a function of the polarization temperature.

We can conclude from these observations that the global glass transition discharge in the TSDC spectrum of this liquid-crystalline polymer arises from two different types of mechanisms: one with low and constant activation enthalpy and entropy ($\Delta H^{\ddagger}=20$ kcal·mol^{-1} and $\Delta S^{\ddagger}=17$ cal·K^{-1}·mol^{-1}), and another one where compensation behaviour is manifested by a concomitant variation of the enthalpy and of the entropy of activation of its components. Figure 6, which presents the Arrhenius plots (log $\tau(T)$ *vs.* $1/T$) of different thermally cleaned components of the global T_g discharge, illustrates the reported behaviour. The lines on the left-hand side are parallel to each other (do not show compensation behaviour), whereas those on the right-hand side converge to a single point, the compensation point, as a consequence of the concomitant variation of the enthalpy and the entropy of activation.

Thus, we can conclude that, as the temperature increases, approaching T_g, some local molecular motions are released, giving rise to TSDC discharges with well-defined activation parameters and which probably correspond to hindered internal rotations on the side groups made easier by the thermal motions

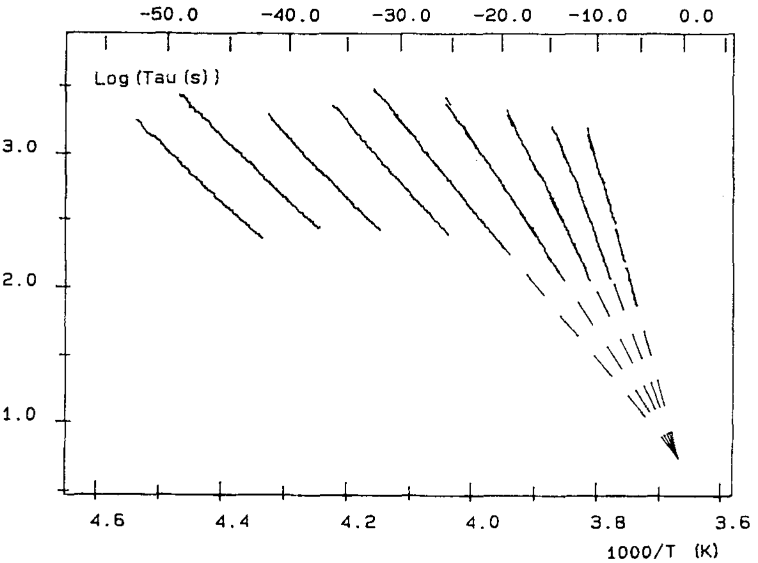

Fig. 6 Arrhenius lines (log $\tau(T)$ *vs.* $1/T$) for different thermally cleaned components of the glass transition relaxation. The coordinates of the compensation point are $T_c=-0.7$°C and $\tau_c=5.6$ sec

of the main chain. A further increase of temperature gives rise to the cooperative motions which characterize the glass transition and are expressed by the reported compensation behaviour.

The upper T_g relaxation

An upper T_g discharge ($T_m \approx 35$°C) was observed for this LCP polymer, as shown in Fig. 1. The existence of this relaxation seems to be a universal feature of the TSDC spectra of polymeric materials, from amorphous polymers such as poly(vinyl acetate) [6] to liquid-crystalline polymers [2, 5], including many other polymers of very diversified molecular structure [7]. As reported earlier, the molecular nature of this relaxation is controversial subject, but here we merely try to characterize the relaxation in this particular polymer. Figure 7 shows the results of several thermal cleaning experiments on the temperature range of this peak.

Analysis of these components of the upper T_g discharge reveals that there is no compensation behaviour as was the case for the T_g peak (see right-hand side of Fig. 5, which shows that the activation enthalpies of the different components are nearly constant). On the other hand, the Arrhenius plots of these components display a slight WLF curvature and the calculated mean activation enthalpy is 39 kcal·mol^{-1}, whereas the corresponding entropy is 60–

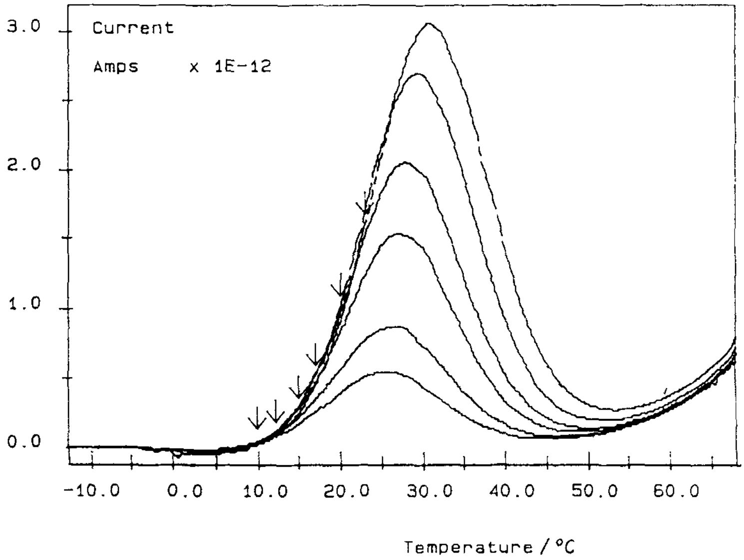

Fig. 7 Thermally cleaned components of the upper T_g relaxation mechanism. Experimental conditions: polarisation voltage 400 V/mm, window width 3°C, heating rate 4 deg·min^{-1}, polarisation temperatures (indicated by the arrows) 10, 12, 15, 17, 20 and 23°C

65 cal·K^{-1}·mol^{-1}. Despite the lower activation enthalpy, as compared with the T_g peak (Fig. 5), this peak is situated at higher temperatures because of the relatively low value of the activation entropy (high value of the pre-exponential factor).

The right-hand side of Fig. 4 shows that the sharpness of the components of this relaxation (as measured by the quantity T_m–T_p) increases as T_p increase, as was the case for the T_g peak, but this sharpening is not a consequence of a distribution of activation energies.

Conclusions

The TSDC analysis of this liquid-crystalline side-chain-bearing siloxane polymer revealed essentially three discharge mechanisms: 1) a lower-temperature relaxation, which was difficult to observe since it was located at the lower limit of the available temperature range, and which is attributed to non-cooperative local motions; 2) the glass transition relaxation, which shows the usual compensation behaviour and therefore corresponds to a distribution of activation energies and entropies; on the other hand, this T_g relaxation showed a low-temperature tail, which is probably related with hindered motions which presage the glass transition on heating; 3) an upper T_g relaxation, whose molecular nature is a controversial subject and which has been attributed to a liquid-liquid transition [7], to a space charge phenomenon [2], or to the motions of the mesogenic side groups as a whole [3]. More research work is needed to clarify the molecular nature of this discharge.

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Zusammenfassung — Mittels thermisch stimulierter Depolarisierungsströme wurde die Relaxation der durch elektrische Felder induzierten polaren Ausrichtung in flüssigkristallinen Polysiloxanen mit Seitenketten gemessen. Es konnten verschiedene Relaxationsmechanismen gefunden und beschrieben werden: die mit der Glasumwandlung verbundene Relaxation zeigt Kompensationsverhalten. Andererseits wurden untere T_g und obere T_g Entladungen beobachtet und deren molekulare Natur diskutiert.