Local motions in side-chain liquid crystalline polymers.
A thermally stimulated currents study

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Abstract

The technique of thermally stimulated discharge currents (TSDC) has been used in order to study the sub-glass relaxation mechanisms in a series of side-chain liquid crystalline polymers. The results obtained suggest that these relaxations arise from local molecular motions in the mesogenic moiety. On the other hand, it was observed that there is no evidence for compensation phenomena associated with these relaxations. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The so-called α-relaxation is a feature of glass-forming systems and is presently the subject of very extensive theoretical and experimental studies. The temperature dependence of the relaxation time follows a Vogel–Fulcher–Tammann behavior and, in polymeric systems, it is attributed to large-scale cooperative motions of the polymer backbone. Below the glass-transition temperature, other relaxation processes are observed. The β-relaxation is one of these low-temperature relaxation processes which merges with the α-process at temperatures near T_g and gradually separates from it with decreasing temperature, as a consequence of its lower activation energy. The relaxation strength of the β-relaxation is lower than that of the α-relaxation and the temperature depen-

dence of the relaxation time seems to follow an Arrhenius behaviour. In polymeric systems, the β-relaxation has been attributed to rotational or vibrational modes of motion in the side groups [1–5] or to motions of small segments of the polymer backbone [6,7]. This secondary relaxation has been extensively studied in polymers by different relaxation techniques [8]. The nature of the molecular motions associated with this relaxation was keenly investigated by Starkweather [9–11]. From viscoelastic measurements on a large number of polymers, this author concluded that the molecular motions should have a non-cooperative character with negligible activation entropy.

The technique of *thermally stimulated depolarisation currents* (TSDC) is a dielectric-related technique, where the thermally stimulated release of the polarisation frozen-in during a previous application of an electric field is monitored as a function of temperature on heating [12,13]. The TSDC technique is suitable for studying the dipolar relaxation mechanisms in polymers, and it can complement information obtained by other techniques, namely *dielectric*

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relaxation spectroscopy (DRS). In fact, the low characteristic frequency of TSDC ($\approx 5 \times 10^{-3}$ Hz) leads to a high-temperature resolution which allows the separation of processes appearing as overlapped in other experimental techniques. Another advantage of the TSDC technique is the possibility of using the thermal-cleaning (or windowing) experimental procedure in order to decompose a complex relaxation into discrete contributions which can nearly be considered as arising from a single relaxation-time process.

The fact that the molecular motions responsible for the β-relaxation occur in a large variety of local environments leads to a distribution of relaxation time which is responsible for the broad loss peaks observed in DRS experiments or broad depolarisation peaks in TSDC experiments. Vanderschueren [1] studied this relaxation in several polymers by the TSDC technique and concluded that the corresponding distribution of relaxation times should be ascribed to a continuous activation energy distribution. On the other hand, this distribution of relaxation times has been ascribed, in part, to a distribution of free volume [2]. From molecular-dynamics simulation of dense systems, Rigby and Roe [14] observed that, at temperatures well bellow T_g, the volume fraction distribution of cavities is extremely broad and often exhibits a bimodal or trimodal character.

Side-chain liquid-crystalline polymers (LCPs) constitute a family of chemical substances which combine the mechanical and rheological properties of polymeric materials with the anisotropic properties of low-molar-mass liquid crystals. The combination of these properties confers upon these materials a versatility which can be used in different applications, namely in optical information storage, non-linear optics and chromatography [15].

These materials usually bear a considerable dipole moment in the side groups, which constitutes a good probe for dielectric studies. In fact, the molecular motions on side-chain LCPs have been extensively studied over the last fifteen years using DRS [16], and more recently by TSDC [17]. However, TSDC results concerning the low-temperature relaxation have been scarcely discussed. In this work, we will present the results obtained on the β-relaxation of different side-chain LCPs.

Some DRS works on side-chain LCPs, with –$(CH_2)_n$–R_1–Ø–COO–Ø–R_3 side groups (where R_1

and R_3 are polar groups and Ø a *p*-substituted phenyl group), reported one [18–22] or two [23] β-relaxations (named β_1 and β_2). In all cases, these relaxations were attributed to rotations in the side group, due mainly to the dipoles in R_1 and in the group –COO–. Despite the different chemical structure of the lateral groups in these materials, the authors in Refs. [18–22] found activation energies for all the processes between 50 and 57 kJ mol^{-1}. Moreover, other DRS studies on the relaxations of main-chain LCPs reported very similar activation energies [24–26]. The authors of Refs. [18–21] attributed the unique observed β process to the rotation of the phenyl benzoate group. On the other hand, Colomer et al. [23] associate the β_1 process (with an activation energy of 58 kJ mol^{-1}) to the same rotation and the β_2 process to the rotation of the R_1= –COO– group, with an activation energy of 40 kJ mol^{-1}. Note that the β_1 and β_2 processes appeared in this work strongly overlapped in the 10^2–10^5 Hz frequency range; that could be the reason why other authors [18–22] were not able to resolve these two relaxations.

In the present work, we tried to take advantage from the low frequency of the TSDC technique in order to resolve the β_1 and β_2 components of the low-temperature spectra. Moreover, the thermally cleaned experiments over these relaxations were performed in order to identify the corresponding thermokinetic parameters and conclude about the kind and extension of the relaxation-time distribution. Finally, the results obtained by the two dielectric-related techniques (DRS and TSDC) were compared. The experiments were undertaken on six side-chain LCPs with mesogenic side-groups having different chemical structures, allowing a most clear attribution of the different relaxations at the molecular level.

2. Experimental

Thermally stimulated depolarisation current (TSDC) experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT) covering the −170 to +400°C range. Two kinds of experiments were performed in order to analyse the relaxation spectra of the materials, namely TSDC global and thermal-cleaning experiments [27]. In both types of experiments, the sample was polarised in a
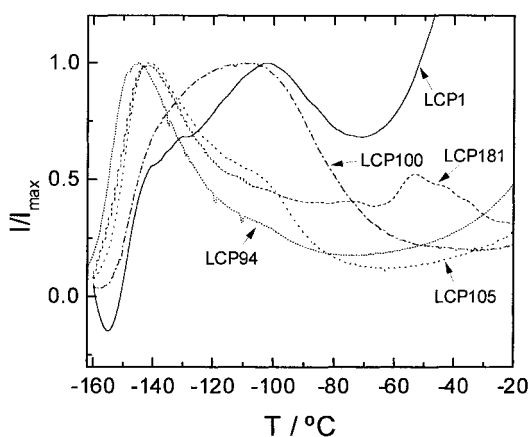
Fig. 1. TSDC global experiments in the low-temperature region (as explained in the text, the intensities of the depolarisation currents are normalised relatively to the maximum). The heating rate of the experiments was $8°C$ min^{-1}.

given temperature range (with the field applied between T_p and T'_p), the polarisation was frozen-in by cooling down to T_0 and the depolarisation current measured, as a function of temperature, as the polarised sample was heated up to T_f at a constant rate, r. The difference between both type of experiment is that, in a TSDC global experiment $T'_p = T_0$, whereas in a thermal-cleaning experiment $T_p - T'_p \sim 3°C$ and $T_0 \ll T_p$ and T'_p. In the TSDC global experiments (shown in Fig. 1), the heating rate was $r = 8°C$ min^{-1}, while it was $4°C$ min^{-1} in all thermal-cleaning experiments. More details on the TSDC technique and data treatment can be found in Ref. [28].

The side-chain LCPs studied in this work are from Merck and their catalogue number, structure and transition temperatures are presented in Table 1.

Prior to use, the samples were degassed by heating to a few degrees above the clearing temperature in a vacuum oven for several hours. This procedure prevents air-bubble formation in the sample, and warrants good electrical contact between the sample and the electrodes.

3. Results and discussion

3.1. TSDC Global experiments

The β-relaxations of the studied side-chain LCPs appeared in the TSDC global spectra as broad peaks,

located at low temperatures. The low intensity of the depolarisation currents ($\sim 10^{-13}$ A) is a consequence of the low amplitude of the dipolar motions at these temperatures. In order to be able to compare the β-relaxation of the different LCPs, their global TSDC spectra are shown in Fig. 1 in a normalised form: normalised current intensity, I/I_{max}, where I_{max} is the maximum intensity of the peak, as a function of temperature. This normalised representation is useful since it allows to discard the influence of the thickness of the sample and of the dipole density of the materials on the intensity of the TSDC spectra.
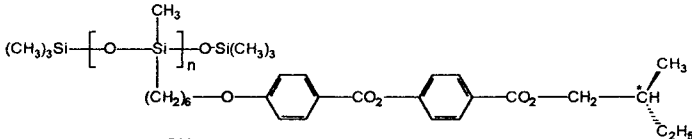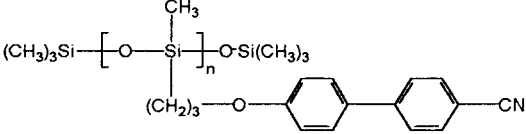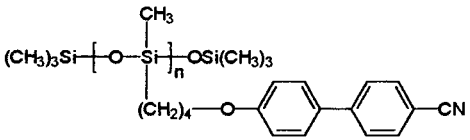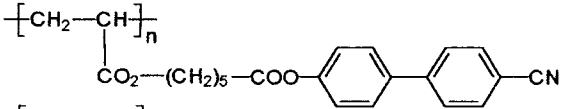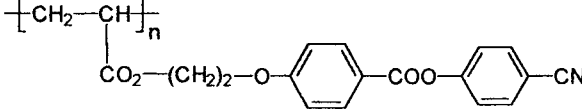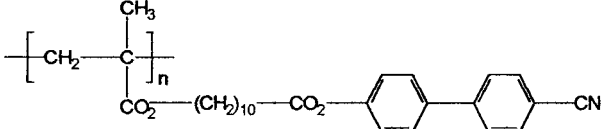
It is to be noted that the global spectrum of LCP83 is not shown in this figure since we were not able to record it on account of experimental difficulties arising from the low intensity of the signal. From Fig. 1 it comes out that the global TSDC spectra of the different LCPs show maximum intensity in two different temperature regions: a lower temperature region at ca. $-140°C$ and an upper one at ca. $-100°C$. It is to be noted that the upper temperature tail observed for LCP1, LCP105 and LCP94 corresponds to the low temperature side of the glass-transition relaxation and is not relevant for the present discussion.

Before beginning a discussion of the results, it is to be emphasised that all the LCPs studied in the present work have mesogenic groups of the type $-R_1-\emptyset-R_2-\emptyset-R_3$, with $R_3 = -CN$ for all of them, except for LCP1, where $R_3 = -COO-CH_2CH(CH_3)(C_2H_5)$. Furthermore, it may be recalled that DRS studies on similar systems suggested that the β-relaxations are associated with motions of the non-terminal dipolar groups of the mesogenic moiety, namely those of the R_1 and R_2 groups.

Taking into account the chemical structures shown in Table 1 and the results presented in Fig. 1, we can draw the following conclusions:

1. The TSDC spectrum of LCP181, in which $R_1 = -O-$ and R_2 is missing, exhibits mainly the relaxation at ca. $-140°C$.
2. The TSDC spectra of LCP94 and LCP105, whose structures are such that $R_1 = -COO-$ and R_2 is missing, also show the relaxation at ca. $-140°C$ and a small contribution of the relaxation at ca. $-100°C$.
3. Finally, for LCP100 and LCP1, where $R_1 = -O-$ and $R_2 = -COO-$, TSDC spectra exhibit a small

Table 1
Structure and transition temperatures of the studied side-chain LCPs

Name	Structure	Transition temperatures [a] (°C)
LCP1		g −7.2 S_c 76.81
LCP83		g 37.2 S_a 148.6 I
LCP181		g 14 S_a 99 N 102 I
LCP105		g 38 N 127 I
LCP100		g 75 N 111 I
LCP94		g 39.0 S_a 127.5 I

[a] g, glass; S, smectic; N, nematic; and I, isotropic liquid.

contribution of the relaxation at ca. −140°C and a large contribution of the relaxation at ca. −100°C.

From the foregoing observations, and from the results obtained by DRS, it seems reasonable to conclude that:

1. The relaxation at −100°C arises from rotational motions in R_2 and its intensity is higher for LCP100 and LCP1, where R_2=–COO–. This relaxation apparently corresponds to the β_1-relaxation in the notation of Colomer et al. [23].
2. The relaxation at −140°C is associated to rotational motions in R_1, near the spacer group, and it is most apparent in LCP94 and LCP105, where R_1= –COO–. In LCP1 and LCP100, where R_1=–O–, this relaxation is also observed but its intensity is

lower on account of the small value of the dipole moment of the ether group (compared to the ester group). The relaxation at −140°C probably corresponds to the β_2-relaxation in the notation of Colomer et al. [23]. In LCP181 (R_1=–O–) this relaxation at −140°C is also observed.

3. In LCP94, LCP181 and LCP105 the R_2 group is missing and, nevertheless, a small contribution from the relaxation at −100°C can be observed. This probably arises from some kind of interference or coupling between the motions of the phenyl groups and those in the R_1 group. NMR studies on side-chain LCPs [29] showed that the motions of the phenyl rings in the mesogenic moiety occur at a temperature and a frequency which are similar to those of the motions in the R_2 group as studied by

Zentel et al. [18] by dielectric relaxation spectroscopy. This suggests that the motions of the phenyl rings, whose features are similar to those observed in R_2, could induce in R_1 some kind of motions which would appear at $-100°C$, despite the absence of the R_2 group.

It is also to be noted that the R_1 group is connected to the flexible spacer group which links the mesogenic side-group to the main chain. As a consequence, the motions in the R_1 group are probably less hindered than those of the R_2 group (squeezed between two rigid phenyl groups) and that is why the corresponding motions appear at lower temperature (lower activation energy).

3.2. Thermal-cleaning experiments

In order to obtain further information about the distribution of relaxation times, characterising the β-relaxations we are dealing with in the present study, we carried out a very large number of thermal-cleaning experiments in the temperature region where these relaxations appear in the TSDC spectrum. The thermally cleaned peaks thus obtained, for the different relaxations of the different polymers, showed a linear relationship between the temperature of maximum intensity (T_m) and the polarisation temperature (T_p) of the same experiment (see Fig. 2). The trend is the
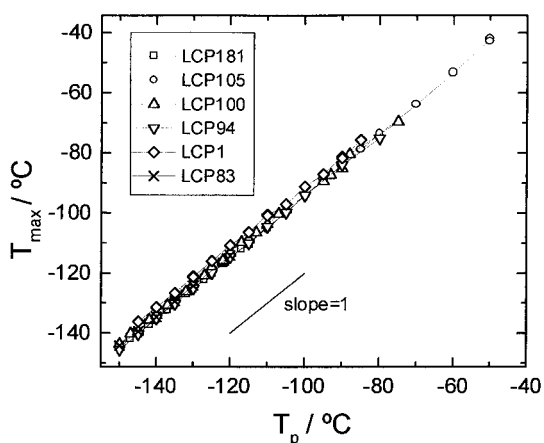

Fig. 2. Location of the thermally cleaned peaks (temperature of maximum intensity, T_m) as a function of the polarisation temperature (T_p), in the temperature region of the β-relation for the six studied LCPs.
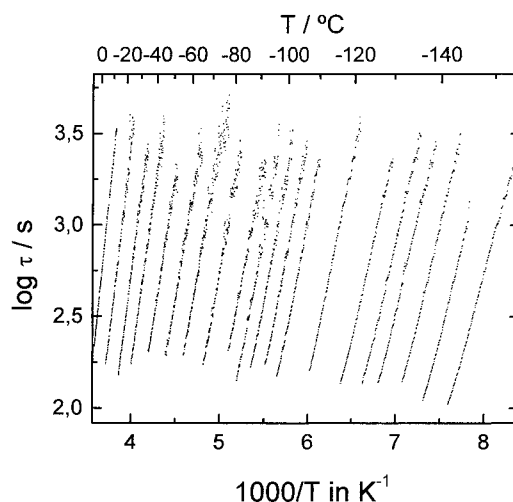

Fig. 3. Arrhenium plots for the thermally cleaned components of the β-relaxation of LCP105. The experimental conditions were: electric field strength, $E=400$ V/mm, $T_p-T_p' = 3°C$ and heating rate, $r=4°C$ min^{-1}.

same for all the studied LCPs and is such that $T_m-T_p \approx 6°C$.

This linear relationship between T_m and T_p, i.e. the constancy of the difference T_m-T_p, can be an indication of a smooth and continuous distribution of relaxation times, and it is observed in thermally cleaned peaks obtained by computer simulation postulating a uniform distribution of activation energies. It is noteworthy that this behaviour is not observed for the thermally cleaned peaks of the glass-transition relaxation. In this case, the difference T_m-T_p is not constant as a consequence of the strong modification of the shape of the peaks which arises from a wide distribution of activation energies and of pre-exponential factors [30,31].

The peak obtained in each thermal-cleaning experiment was treated according to the so-called Bucci method [32], in order to determine the relaxation time as a function of temperature, $\tau(T)$. Fig. 3 shows the relaxation map obtained for LCP105 in the region of the β-relaxation. The relaxation maps of the other LCPs studied in the present work were qualitatively similar.

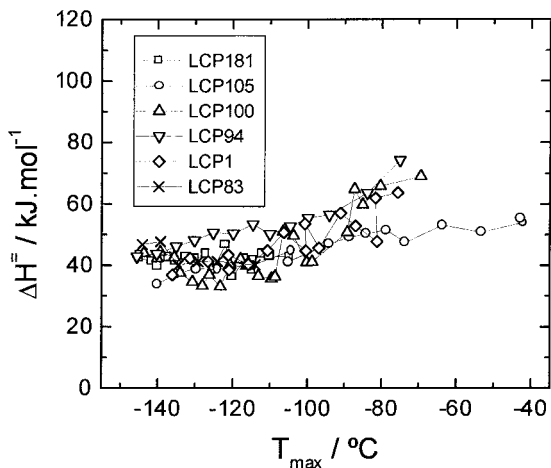The lines of the relaxation map can be fitted with the Arrhenius equation:

Fig. 4. Activation enthalpy, $\Delta H^{\neq}$, for different thermally cleaned peaks in the temperature region of β-relaxation, for the six studied LCPs.

Fig. 5. Activation entropy, $\Delta S^{\neq}$, for different thermally cleaned peaks in the temperature region of β-relaxation, for the six studied LCPs.

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \qquad (1)$$

where τ_0 is the pre-exponential factor and E_a the apparent activation energy, or with the Eyring equation, derived from the theory of absolute reaction rates:

$$\tau(T) = \frac{h}{kT} \exp\left(-\frac{\Delta S^{\neq}}{R}\right) \exp\left(\frac{\Delta H^{\neq}}{RT}\right) \qquad (2)$$

where $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are, respectively, the entropy and the enthalpy of activation. This fitting allows the determination of the thermokinetic parameters which characterise each thermally cleaned peak. It can be seen from Fig. 3 that the cleaned peaks of the β-relaxation reasonably follow the Arrhenius behaviour, as expected.

Fig. 4 shows the activation enthalpies of the thermally cleaned peaks of the β-relaxation as a function of their location in the temperature axis, T_m, and this for the six LCPs studied in the present work.

The results show some scatter which is due to the narrow range of activation enthalpies we are dealing with, on the one hand, and to the small intensity of the relaxation peaks, on the other. Nevertheless, it is apparent from Fig. 4 that the values of activation enthalpy tend to increase with increasing temperature, from ∼33 to ∼67 kJ mol^{-1}. These results agree well with those reported from dielectric relaxation studies.
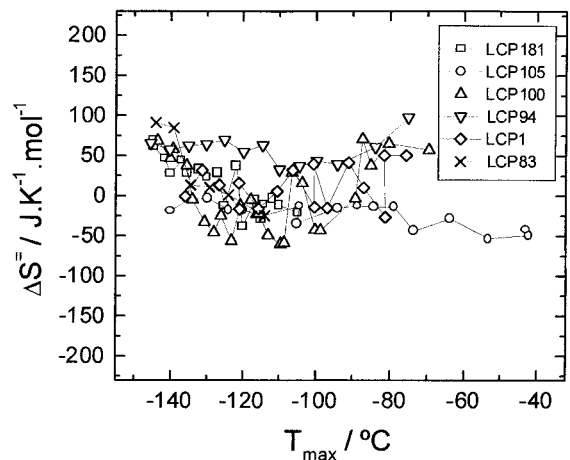
Moreover, our results strengthen the previous attribution, according to which the lower temperature mode of the β-relaxation observed by TSDC at ca. −140°C corresponds to the β_2-relaxation of Colomer et al. [23] with an activation energy of 40 kJ mol^{-1}, whereas the higher temperature mode observed at ca. −100°C corresponds to the β_1-relaxation with an activation energy of 59 kJ mol^{-1}. It is, however, to be noted that the transition from the lower to the higher relaxation mode, which is relatively clear in Fig. 1, does not correspond to any clear discontinuity in the representation of the activation enthalpy as a function of temperature (Fig. 4).

Fig. 5 shows the activation entropies of the thermally cleaned peaks of the β-relaxation for the six LCPs studied in the present work.

Despite the scatter of the results, it can be concluded that the values of the activation entropies are very small and do not show any particular tendency to change with temperature. Following the conclusions of Starkweather [9–11], zero activation entropies observed in thermally cleaned peaks have been considered to be a feature of the non-cooperative motions which are responsible for the secondary relaxations observed in polymers [4,7,33]. The foregoing observations thus suggest that the distribution of relaxation times of the β-relaxation arises mainly from a distribution of activation energies. Moreover, if we assume the zero-entropy behaviour, the basic

equations of the TSDC technique allow to obtain, without any adjustable parameter, the variation of the activation energy (or enthalpy) with the location of the thermally cleaned peaks, T_m [7,28,33]. The equation which describes this variation can be written as (see Ref. [28]):

$$\frac{RT_m^2}{r(\Delta H^{\neq} + RT_m)} = \frac{h}{kT_m}\exp\left(\frac{\Delta H^{\neq}}{RT_m}\right) \qquad (3)$$

where r is the heating rate of the TSDC experiment. This equation expresses the so-called 'zero-entropy prediction'. Eq. (3) allows to compare the plot of $\Delta H^{\neq}$ vs. T_m according to the $\Delta S^{\neq}=0$ prediction with the experimental data, which is very helpful for checking if the values of $\Delta H^{\neq}$ obtained for non-cooperative processes are accurate. It is to be noted that the equation for the $\Delta S^{\neq}=0$ prediction previously proposed in the literature [4,7,33] is somewhat different from Eq. (3), and is obtained by introducing the $\Delta S^{\neq}=0$ condition in the Eyring equation (Eq. (2)) written at T_m:

$$\Delta H^{\neq} \equiv RT_m\left[\ln\left(\frac{k}{h}\right) + \ln\left(\tau_m T_m\right)\right]$$
$$= RT_m\left[21.922 + \ln\left(\frac{T_m}{f_m}\right)\right] \qquad (4)$$

and considering the equivalent frequency, f_m, as a constant (considered equal to 0.005 Hz). It is easy to show that Eqs. (3) and (4) lead to results which are not very different from each other. Nevertheless, it is to be emphasised that Eq. (3) is a more general and more rigorous formulation of the 'zero-entropy prediction', since it does not imply the approximation of the constancy of the equivalent frequency, although the usually observed variations in f_m do not greatly affect the results obtained by Eq. (4). The results obtained from Eq. (3) agree very well with the experimental data obtained on the low-temperature relaxation of the materials studied in the present work [17,34].

A problem calling for an interesting discussion in the present context is that of the existence, or not, of a compensation phenomena associated with the sub-glass relaxations. The manifestation of the compensation behaviour is the occurrence of a linear relationship between the activation energy and the pre-exponential factor (or between the activation enthalpy
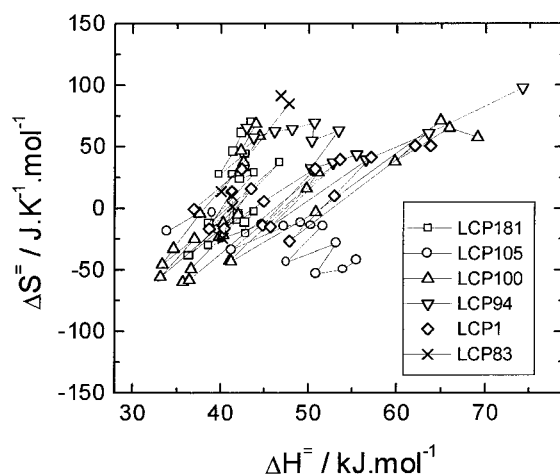

Fig. 6. Representation of the activation enthalpy, $\Delta H^{\neq}$, as function of the activation entropy, $\Delta S^{\neq}$, for the thermally cleaned peaks of β-relaxation of the six studied LCPs.

and the activation entropy) arising from the convergence of the Arrhenius lines of the thermally cleaned peaks into a single point, namely the compensation point (with coordinates τ_c, the compensation time, and T_c, the compensation temperature). The physical significance of this compensation point has been recently discussed [34,35]. Some authors believe that the compensation behaviour is observed in the β-relaxation of some amorphous and semi-crystalline polymers [6,36–38]. However, it is to be noted that the Arrhenius lines of the low-temperature relaxations are often found to be nearly parallel (see, e.g. Fig. 3). The extrapolation of the Arrhenius lines to the compensation point is thus a very long extrapolation, leading to large statistical errors in the coordinates of the compensation point. In fact, the compensation times, τ_c, reported for the β-relaxations are often exceedingly small (e.g. $\tau_c \approx 10^{-9}$ s in Ref. [37]) and difficult to interpret in a realistic physical basis. Fig. 6 shows the representation of the activation enthalpy, $\Delta H^{\neq}$, as a function of the activation entropy, $\Delta S^{\neq}$, for the thermally cleaned peaks of the β-relaxation of the six LCPs studied in the present work. No evidence of compensation behaviour emerges from Fig. 6.

As pointed out in a recent paper [34], an intrinsic feature of the TSDC technique is that the relationship

$$\Delta S^{\neq} = \frac{\Delta H^{\neq}}{T_m} - \alpha \qquad (5)$$

with $\alpha \sim 280$ J K^{-1} mol^{-1}, is observed for all the thermally cleaned peaks in the TSDC spectrum, independently of the chemical nature of the materials and of the relaxations under study. For a relaxation characterised by a sharp distribution of activation enthalpies (such that $\Delta H^{\neq}$ strongly increases with T_m in a narrow temperature range), Eq. (5) transforms in a pseudo-linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$. This is observed for the glass transition in amorphous polymers and leads to the so-called compensation behaviour. The β-relaxation is characterised by a distribution such that a relatively narrow range of activation enthalpies is spread out in a wide temperature range and, thus, does not present any compensation behaviour.

4. Conclusions

The dipolar relaxation mechanisms present in the cryogenic temperature region (β-relaxation) of six side-chain LCPs were studied by the thermally stimulated discharge currents technique. From the results reported in this work we can draw the following conclusions:

1. From the TSDC global spectra of the studied polymers, two components in the peaks were detected: the lower temperature one (at ca. -140°C) which was ascribed to the rotation of the polar group located between the spacer and the inner phenyl group of the mesogenic moiety; the higher temperature component (at ca. -100°C) which probably arises from the rotation of the polar group between the phenyl groups of the mesogenic moiety or from the motions of the phenyl groups themselves.
2. The values of activation energy obtained for the thermally cleaned peaks of the two β-relaxation modes vary between 33 and 67 kJ mol^{-1}; this finding is compatible with the results reported in recent DRS studies. The corresponding activation-entropy values are negligible. We may thus consider that the distribution of the relaxation times must be a result of a broad distribution of activation energies.
3. There is no evidence for a compensation relationship in this relaxation.

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