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Dipolar relaxations in a side-chain polyacrylate liquid crystal. A study by thermally stimulated currents

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Abstract

The dipolar relaxation mechanisms present in a side-chain liquid crystalline polyacrylate were studied in a wide temperature range covering the glassy state, the glass transition region and the liquid crystalline phase. The complex relaxation processes observed in these different temperature regions were analysed in detail using the technique of thermal cleaning. The significance of the so-called compensation behaviour, which is frequently considered as a feature of the glass transition relaxation in polymeric materials, is discussed.

Keywords: Compensation; Glass transition; Dielectric relaxation; TSC; TSDC

1. Introduction

Thermally stimulated processes include a diversity of phenomena in which a given property of a substance is measured by heating the sample in a controllable manner. Thermoluminescence, thermally stimulated depolarisation, differential thermal analysis, differential scanning calorimetry and thermogravimetry are techniques which are based on thermally stimulated processes and are widely used as methods of research and analysis in various fields in science and technology [1].

The technique of thermally stimulated depolarisation currents (TSDC) belongs to this family of experimental techniques and has been used to study a variety of materials, crystalline as well as amorphous insulators and semiconductors. The TSDC analysis of polymer solids is now recognised as a very rich source of information about dielectric properties, dipolar relaxation mechanisms and the internal structure of these materials

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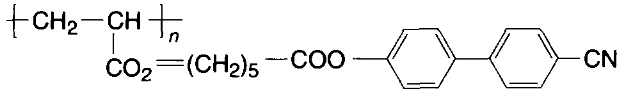
[2, 3]. As explained in detail elsewhere [4], a TSDC experiment measures the thermally stimulated release of the polarisation frozen in during a previous application of an electric field. One advantage of the TSDC technique is its low equivalent frequency [2]. In fact, it is possible to reach lower frequencies while working at low temperature, enabling better resolution of the different relaxation mechanisms. Besides, using the thermal cleaning (TC) technique (also called thermal sampling, thermal windowing or fractional polarisation) it is possible to decompose a complex relaxation mechanism into its individual or elementary components enabling analysis of the fine structure of the TSDC. spectrum. The analysis of each TC peak enables us to obtain some characteristic parameters, namely, the temperature of maximum intensity, T_m (location of the thermally cleaned peak in the TSDC spectrum), and the thermodynamic parameters associated with the corresponding relaxation process (enthalpy, $\Delta H^{\neq}$, entropy, $\Delta S^{\neq}$ and Gibbs energy, $\Delta G^{\neq}$). The TSDC technique was recently used in our laboratory to analyse molecular motion in side-chain liquid crystalline polymers (LCPs) [5–14]. These studies were carried out in wide temperature range covering the vitreous state, the glass transition region and the liquid crystalline phase and it was observed that the materials exhibit a complex pattern of relaxation mechanisms.

The purpose of the present study is to report the results obtained from the TSDC analysis of a side-chain liquid crystalline polymer not previously studied and our aim is to gain more insight into the dielectric relaxation mechanisms present in this type of material.

2. Experimental

The side-chain LCP studied in this work is from Merck (catalogue number LCP 105) and shows a glass–nematic transition at 38°C and a nematic–isotropic liquid transition at 127°C; it also has $M_n = 6470$, $M_w = 11680$ and $n = 18$ (see structure below).



Thermally stimulated depolarisation currents (TSDC) experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, USA) covering the range − 170 to + 400°C. Two kinds of experiment were performed in order to analyse the relaxation spectra of the material, namely TSDC global and thermal cleaning (TC) experiments [4]. 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_0 and the depolarisation current was measured, as a function of temperature, as the polarised sample was heated up to T_f at a constant rate. The difference between these experiments 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. The technique of thermal cleaning thus enables one to polarise specific segments of a complex global relaxation.

3. Results and discussion

In the discussion of the results we will consider three temperature regions: the sub-T_g or glassy region, the glass transition region and the region above T_g, which corresponds to the liquid crystalline phase.

The different discharges observed in these three regions were analysed using the thermal cleaning (TC) technique in order to obtain information about the elementary components of the complex relaxations observed in the TSDC spectrum. In fact, each TC peak can be considered, to a first approximation, as corresponding to a Debye process, characterised by a single value of the activation parameters [15]. The analysis of each TC peak is usually performed using the Bucci method [16] which enables the calculation of the relaxation time, τ, as a function of the temperature:

$$\tau(T) = \frac{P(T)}{J(T)} = \frac{r^{-1}\int_{T}^{\infty} J(T')\mathrm{d}T'}{J(T)} \tag{1}$$

where r is the heating rate, P the remaining polarisation and J the current density. Fitting the $\log \tau$ vs $1/T$ points to an Arrhenius- or Eyring-type equation enables the determination of the activation parameters of the process corresponding to the TC peak.

3.1. The glassy region

A low intensity and broad relaxation mechanism was detected in this temperature region of the TSDC, spectrum (see Fig. 1).

The peak associated with this relaxation mechanism extends from $-50°\mathrm{C}$ down to $-160°\mathrm{C}$ (the lower temperature limit of temperature range accessible to our experimental apparatus). It should be noted that the peak with the maximum intensity at ca. 10°C observed on the right hand side of Fig. 1 corresponds, as will be seen later, to the lower temperature components of the glass transition relaxation.

The TC peaks obtained in the temperature range between $-160°\mathrm{C}$ and 50°C are shown in Fig. 2.

From the analysis of these peaks it can be concluded that the peaks corresponding to experiments with polarisation temperatures between $T_p = -140°\mathrm{C}$ and $T_p = -60°\mathrm{C}$ (left hand side of Fig. 2) show small activation enthalpies increasing slowly from ca. 9 kcal mol^{-1} (38 kJ mol^{-1}, for $T_p = -140°\mathrm{C}$) to ca. 12 kcal mol^{-1} (50 kJ mol^{-1}, for $T_p = -60°\mathrm{C}$) (see Table 1) and very small activation entropies of the order of -5 cal K^{-1} mol^{-1} (-21 J K^{-1} mol^{-1}). The low-temperature relaxation of this polymer is thus characterised by a narrow distribution of activation energies as has also been found for other side-chain LCPs [9, 12].

For the TC peaks with $T_p > -50°\mathrm{C}$ (right hand side of Fig. 2) the intensity increases with temperature and the same is observed for the activation enthalpy and entropy (Table 1). This observation indicates, as will be shown later, that we are approaching the glass transition relaxation. Discussion about the relaxation mechanisms at cryos-

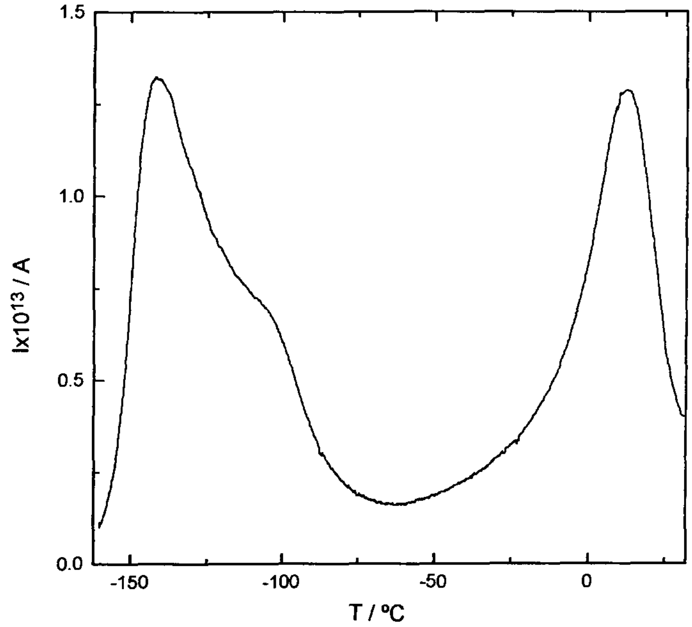


Fig. 1. TSDC global experiment in the lower temperature region. The experimental conditions were: polarisation temperature $T_p = 0°C$; $T_o = -160°C$; $T_f = 40°C$; heating rate, $r = 8°C\ min^{-1}$, electric field strength $E = 400\ V\ min^{-1}$. The peak observed in the right hand side of the figure corresponds to the low temperature side of the glass transition peak shown in Fig. 3.

tatic temperatures is very scarce. Previous TSDC studies [17] revealed that motion in polymeric materials can occur even at very low temperatures (for polarisation temperatures below 50 K). Since the backbone is completely frozen at those temperatures, it is reasonable to believe that the observed motions occur in the side-groups. On the other hand, for temperatures below T_g, the free volume remains essentially constant but the occupied volume will increase with temperature as a consequence of the amplitude of the thermal vibrations. The low temperature relaxations must thus arise from local and low-amplitude motions which occur within the available free volume [18, 19]. This is the reason why those relaxations are characterised by low-intensity discharges, by small activation enthalpies and by negligible activation entropies (or non-cooperative character [18]).

It should be noted that the features of the low temperature relaxation observed in this polymer are very similar to those of the same relaxation observed in a side-chain liquid crystalline polymethacrylate we have previously studied [9]. The polymer studied in the present work and that studied in Ref. [9] have the same mesogenic moiety but have different spacers (five methylene groups for the polymer studied here (see structure); ten methylene groups for the polymer studied in Ref. [9]). It seems thus that the spacer length has little influence in the general features of the lower temperature relaxation.

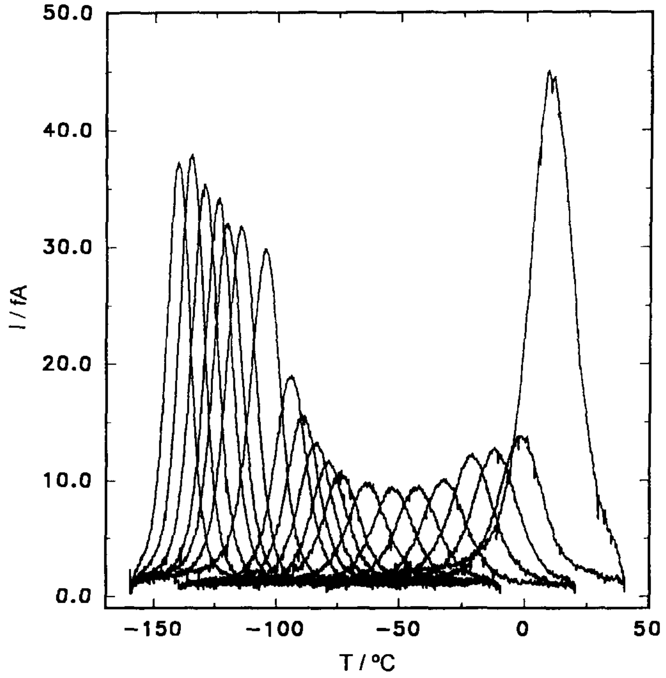


Fig. 2. Thermally cleaned peaks obtained in the lower temperature region (with T_p between − 145 and 0°C). The window width of the experiments, $\Delta T = T_p - T_p'$, was 3°C, the electric field strength $E = 400$ V mm^{-1} and the heating rate, $r = 4$°C min^{-1}.

3.2. *The glass transition region*

The glass transition global peak shows a maximum intensity at ca. 40°C (see Fig. 3. peak 1).

It is to be noted that the glass transition temperature obtained by differential scanning calorimetry is $T_g \approx 38$°C, which is very similar to the temperature of maximum intensity as observed by TSDC.

The TC peaks obtained by partial polarisation of the glass transition peak are shown in Fig. 4.

It is observed that the activation enthalpy and the activation entropy of these elementary processes increase with increasing polarisation temperature, T_p, and that this increase is such that there is a linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (see Table 1). This behaviour is the so-called compensation behaviour which is believed to be a feature of the glass transition of polymeric materials as studied by the TSDC technique. The Arrhenius lines converge thus to a single point, the compensation point, whose coordinates enable one to define two phenomenological compensation parameters: the compensation time, τ_c, and the compensation temperature, T_c. In the present case we obtain $\tau_c = 5.2$ s and $T_c = 48.8$°C (see Fig. 5).

Table 1
Temperature of maximum intensity, T_m, activation enthalpy, $\Delta H^{\neq}$, and activation entropy, $\Delta S^{\neq}$, for different thermally cleaned peaks obtained at different polarisation temperatures, T_p, in the glassy state and in the glass transition region. The experimental conditions for the thermal cleaning experiments were: window width, $\Delta T = T_p - T_{p'} = 3$°C, electric field strength $E = 400$ V min^{-1} and heating rate, $r = 4$°C min^{-1}

T_p/°C	T_m/°C	$\Delta H^{\neq}$/(kcal mol^{-1})	$\Delta S^{\neq}$/(cal. mol^{-1} K^{-1})
−145	−140.2	8.1	−4
−140	−134.9	8.9	−1
−135	−129.8	9.3	−1
−130	−124	9.2	−4
−125	−120.1	9.5	−4
−120	−114.8	9.6	−6
−110	−105.2	9.8	−8
−100	−94.1	11.3	−4
−95	−88.7	11.7	−3
−90	−84.2	12.0	−3
−85	−78.9	12.3	−3
−80	−73.6	11.3	−10
−70	−63.8	12.7	−7
−60	−53.3	12.1	−13
−50	−42.9	13.3	−10
−40	−32.3	14.2	−9
−30	−21.2	16.0	−4
−20	−12.2	17.2	−2
−10	−1.8	19.5	4
0	8.6	21.9	9
5	13.1	22.1	9
7	15.8	22.5	10
10	19.7	25.3	18
12	23.4	25.4	18
15	27.1	27.7	25
17	27.6	25.4	17
20	31.4	32.1	38
22	33.9	35.1	47
25	36.4	39.0	59
27	37.8	42.1	69
30	39.6	49.4	91
32	40.7	56.0	112
35	42.6	68.8	152
37	43.2	71.8	161
40	43.9	84.9	202
45	46.4	102.2	254

In Fig. 5 it can be observed that the Arrhenius lines in the right hand side of the figure (which correspond to TC peaks with higher polarisation temperatures) show a curvature which indicates that the corresponding TC peaks are not strictly Debye-like.

The physical significance of the compensation behaviour is the subject of some controversy. In fact, in many cases, the narrow experimental temperature range and the propagation of experimental errors can lead to a linear $\Delta H^{\neq}/\Delta S^{\neq}$ relationship [20].

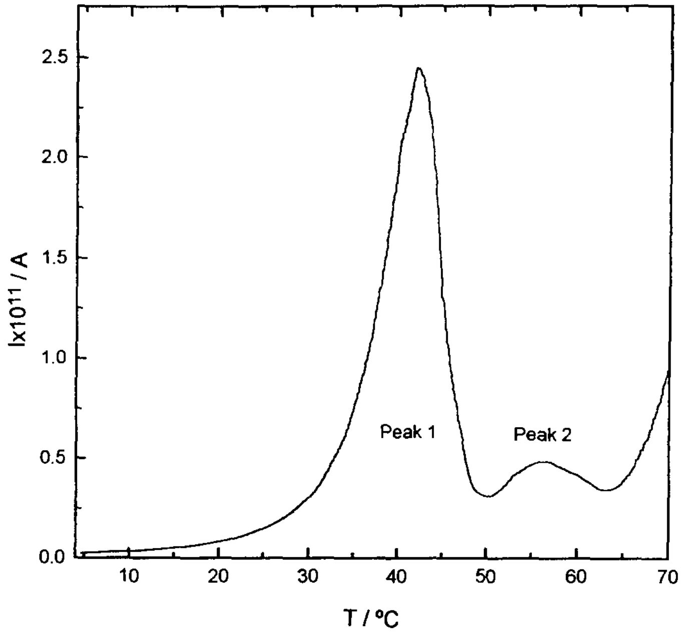


Fig. 3. TSDC global experiment in the glass transition region and in the liquid crystalline phase. The experimental conditions were: polarisation temperature $T_p = 70°C$; $T_o = -50°C$; $T_f = 110°C$; heating rate, $r = 4°C\ min^{-1}$; electric field strength $E = 400\ V\ mm^{-1}$. The higher intensity peak (peak 1) is the glass transition peak. The lower intensity and higher temperature peak (peak 2) corresponds to a relaxation observed in the liquid crystalline phase.

Nevertheless, simple statistical calculations were used [12, 21] which show that the compensation phenomena observed in the glass transition relaxation of polymeric materials is not an artefact but is caused by a true extrathermodynamic effet. The compensation behaviour in polymeric materials is often considered as indicative of cooperative molecular motions [22, 23] and has been ascribed to the relaxations of entities with variable length [24]. On the other hand, its was suggested that the physical significance of the compensation temperature, T_c is the temperature at which all relaxations involved in the process occur with the same relaxation time, τ_c. Nevertheless, this suggestion was refuted by Read [25] who observed a distribution of relaxation times at T_c from a study of polypropylene by dynamical mechanical relaxation. The compensation temperature, T_c, obtained from the experimental data is generally some degrees above T_g [47, 14, 22] and this is also observed for the present polymer for which $T_c = 48.8°C$ and $T_g = 40°C$ (temperature of maximum intensity of the T_g peak). The lag $T_c - T_g$, on the other hand, was attributed to kinetic effects and is believed to depend on the stiffness of the polymeric chain [22]. In previous work [26] we observed that there is no clear relationship between $T_c - T_g$ and the chemical structure of the polymers and we suggested that this lag was probably related to the breadth of glass transition.

In order to obtain the coordinates of the compensation point we must carefully choose the TC peaks which really belong to the compensation region. Normally this

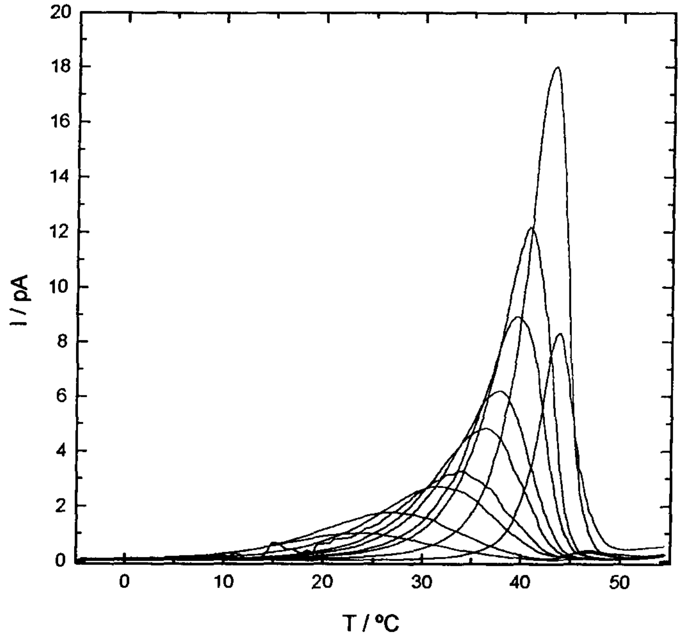


Fig. 4. Thermally cleaned peaks obtained in the glass transition region (with T_p between 12 and 42°C). The window width of the experiments, $\Delta T = T_p - T_p'$, was 3°C, the electric field strength $E = 400\ \mathrm{V\ mm^{-1}}$ and the heating rate, $r = 4°\mathrm{C\ min^{-1}}$. It is to be noted the change of the shape of the TC peaks which is characteristic of the glass transition relaxation and is a manifestation of the compensation behaviour.

choice is performed by looking at the activation parameters of the different TC peaks and taking those for which a sharp increase of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with increasing temperature is observed. (As pointed out before, the log τ vs $1/T$ points can be fitted to the Arrhenius equation or to the Eyring equation in order to obtain the thermokinetic parameters associated with each TC peak. The concomitant increase of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with increasing temperature (Eyring language) is thus equivalent to a concomitant increase of E_a and the pre-exponential factor, log τ_0, with increasing temperature (Arrhenius language).) After obtaining the coordinates of the compensation point in this way, we can check if the choice of the points in the compensation region was correct by using the following procedure. If we take the compensation equation in the Arrhenius formalism [22]

$$\tau_0 = \tau_c \exp\left(-\frac{E_a}{kT_c}\right) \tag{2}$$

where τ_0 is the pre-exponential factor in the Arrhenius equation, E_a the activation energy, τ_c the compensation time and T_c the compensation temperature, and if we introduce it in the condition of maximisation of the TC peak [2]:

$$\frac{kT_m^2}{rE_a} = \tau_0 \exp\left(\frac{E_a}{kT_m}\right) \tag{3}$$

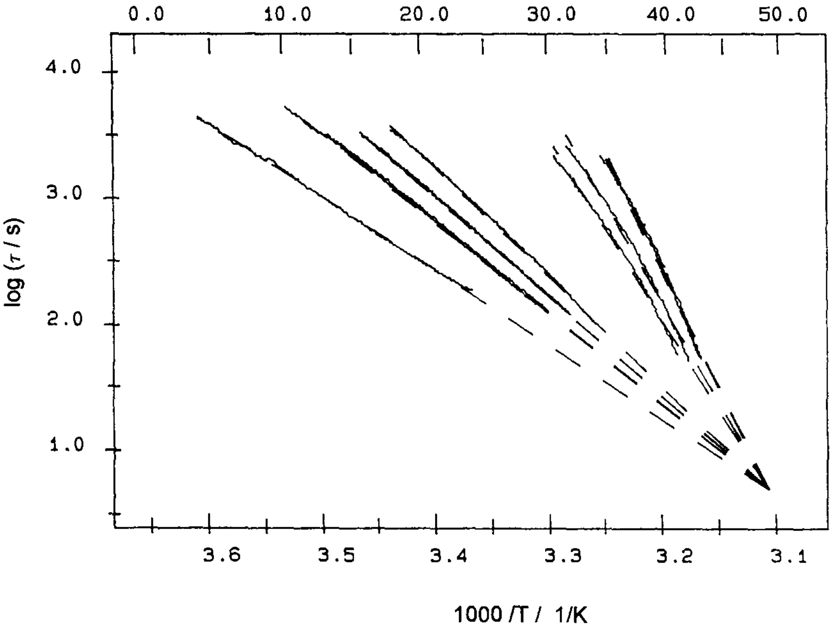


Fig. 5. Arrhenius lines (log τ versus 1/T) of some TC peaks obtained in the glass transition region. The compensation behaviour is clearly shown.

where T_m is the temperature of maximum intensity of the TC peak, k the Boltzmann constant and r the heating rate of the experiment, we obtain a relationship between E_a and T_m which depends only on the coordinates τ_c and T_c of the compensation point. Introducing the values of τ_c and T_c in Eqs. (2) and (3) we can thus obtain the function $E_a(T_m)$ and to compare it with the experimental results. Fig. 6 shows this comparison.

It is apparent from that figure that the points with $T_m > \sim 25°\mathrm{C}$ belong to the compensation region. On the other hand, the points in the left side of the figure, with $T_m < 25°\mathrm{C}$ correspond to segments of the glass transition global peak which do not fall on the curve $E_a(T_m)$ predicted from Eqs. (2) and (3) (solid line in Fig. 6). Moreover, the activation energy of these components is similar to that corresponding to the $\Delta S^{\neq} = 0$ prediction (dashed straight line in Fig. 6). This behaviour was observed in other TSDC studies of side-chain LCPs [5, 8] and shows that Eqs. (2) and (3) are not able to characterise the glass transition relaxation fully. This can be understood if we remember that an important characteristic of the TSDC technique is that there is an universal linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}/T_m$ for all the TC peaks of the TSDC spectrum, irrespective of the materials and of the relaxation process under study [26–28]. This linear relationship is such that the slope is equal to unity and the intercept is 67 cal $\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$ [28]. On the other hand, in a particular zone of the glass transition region a strong increase of $\Delta H^{\neq}$ with increasing T_m is observed, which is concomitant with a strong increase of $\Delta S^{\neq}$. This behaviour gives rise to a pseudo-linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ which arises from the fact that the change of the

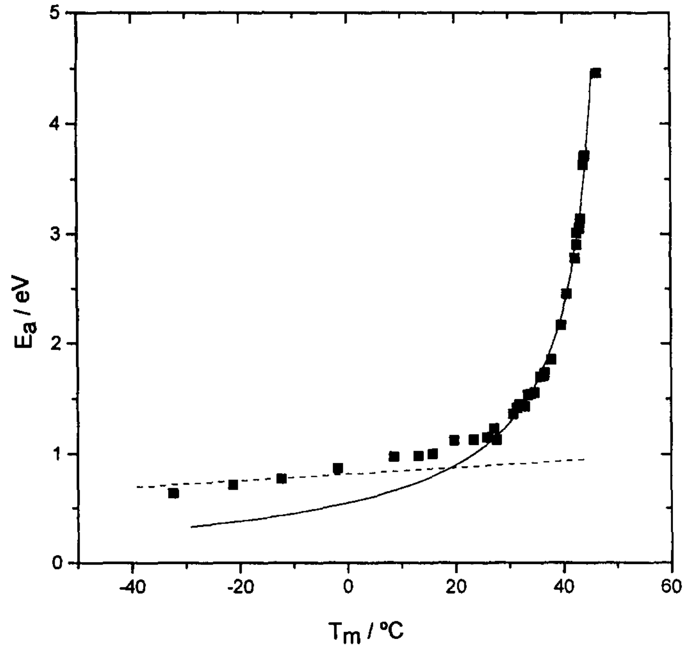


Fig. 6. Activation energy of the TC components of the glass transition relaxation as a function of T_m (temperature of maximum intensity or location in the TSDC spectrum). The solid line corresponds to the prediction based on the values of the coordinates of the compensation point (τ_c, T_c). The dashed straight line corresponds to the $\Delta S^{\neq} = 0$ prediction.

function $\Delta H^{\neq}/T_m$ is dominated by $\Delta H^{\neq}$ when this quantity changes strongly. Otherwise stated, the two linear relationships (between $\Delta S^{\neq}$ and $\Delta H^{\neq}/T_m$ and between $\Delta S^{\neq}$ and $\Delta H^{\neq}$) are compatible only in the situation where $\Delta H^{\neq}$ strongly changes with T_m. When the linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ holds, the solid line in Fig. 6 is obeyed. Our point of view is thus that the linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ (the so-called compensation behaviour) cannot be considered as a fundamental or basic feature of the glass transition relaxation but that it is just a mathematical consequence of the fundamental relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}/T_m$ in the situation where $\Delta H^{\neq}$ is a strongly increasing function of T_m.

3.3. The liquid crystalline region

The low intensity relaxation in the liquid crystalline phase shown in Fig. 3 was analysed by the TC technique (Fig. 7). The Arrhenius lines (log τ vs $1/T$) corresponding to the different TC peaks showed a slight WLF curvature which was also observed in the upper T_g relaxations of other side-chain LCPs [5, 8, 9] and have mean values of the activation enthalpy and entropy which are respectively 75 kcal mol^{-1} (314 kJ mol^{-1}) and 160 cal K^{-1} mol^{-1} (670 J K^{-1} mol^{-1}).

We want to point out that we observed relaxations in the liquid crystalline phase in all our previous TSDC studies of side-chain LCPs and those relaxations were not

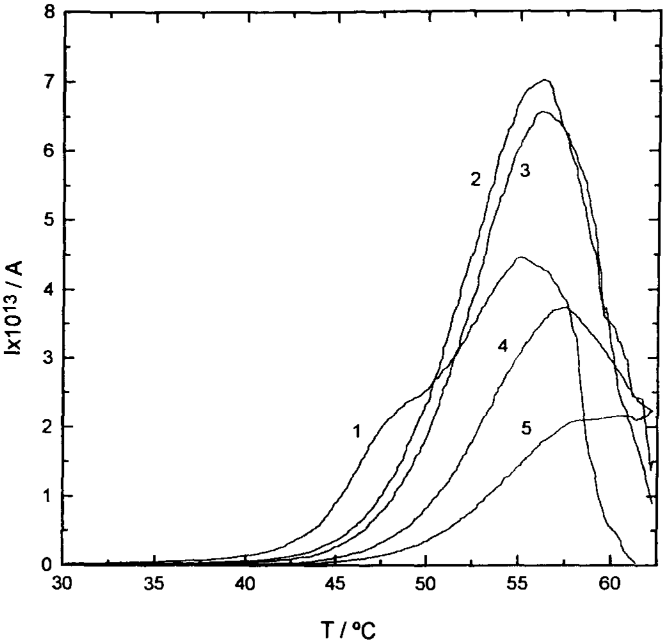


Fig. 7. Thermally cleaned components of the relaxation observed in the liquid crystalline phase. The polarisation temperatures were 1, 47°C; 2, 50°C; 3, 52°C; 4, 55°C; 5, 57°C. The window width of the experiments, $\Delta T = T_p - T_p'$, was 3°C, the electric field strength $E = 400$ V mm^{-1} and the heating rate, $r = 4$°C min^{-1}. The bimodal character of peak 1 arises from the fact that the polarisation temperature (47°C) is near the glass transition region so that the peak shows a contribution, in the lower temperature side, of the glass transition relaxation.

observed in the DSC scan we performed on some of them [5, 7]. On the other hand, there are some indications that the features of relaxations observed by TSDC in the liquid crystalline phase can be attributed to particular characteristics of the chemical structure of the mesogenic side groups. At the present stage we are not able to go into this subject more deeply. The molecular origin of the relaxations observed above T_g in the TSDC spectrum of side chain LCP_S is thus a problem under discussion [9, 13]; this problem will be considered in detail in a future paper.

4. Conclusions

The dipolar relaxation mechanisms present in a side-chain polyacrylate liquid crystal were studied by thermally stimulated discharge currents. The study was carried out in a wide temperature range covering the glassy state, the glass transition region and the liquid crystalline phase and it was shown that different relaxation processes are observed in each of these temperature regions. These complex relaxations were studied in detail using the technique of thermal cleaning and it was shown that the molecular motions in the glassy state are non-cooperative ($\Delta S^{\neq} \approx 0$) and are characterised by low values of the activation energy. On the other hand, a strong increase of the activation enthalpy with increasing temperature was observed in the glass transition region (as is usual in polymeric materials). Nevertheless, it was suggested that the so-called compensation behaviour, which is described as a concomitant increase, with increasing temperature, of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ (linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ in the glass transition region) is not a statistical artefact but it cannot be considered as a real feature of the glass transition relaxation.

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