

Glass transition relaxation and fragility in a side-chain liquid crystalline polymer: a study by TSDC and DSC

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Abstract

The technique of thermally stimulated depolarisation currents (TSDC) was used to study the molecular dynamics in two samples of different molecular weight of a side-chain liquid crystalline polymer. The glass transition relaxation was carefully studied in these materials using the thermal sampling procedure. It is suggested that the amplitude of the deviation from the zero entropy prediction is related to the fragility of the glass, and a definition of fragility based on the TSDC results is proposed. Results previously obtained on other side-chain liquid crystalline polymers, on the low molecular weight organic glass former glycerol and on the orientationally disordered glass cyano-adamantane have also been discussed. Moreover, the physical ageing behaviour of the metastable glass below T_g was studied by the techniques of TSDC and differential scanning calorimetry. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Glass formers; Glass transition; Fragility

1. Introduction

The first study of the molecular dynamics in a side-chain liquid crystalline polymer using the technique of thermally stimulated depolarisation currents (TSDC) was published 10 years ago [1]. Since then, we carried out extensive research work in this area [2–5] and showed that the TSDC technique appears as a very suitable tool to detect and characterise the dipolar relaxations and the corresponding distributions of relaxation time.

An important feature of the glass transition relaxation as studied by TSDC is a strong departure from the zero entropy prediction [6,7]. This behaviour is often referred as the compensation behaviour as the strong increase of the activation enthalpy with increasing temperature is concomitant with a strong increase of the activation entropy with increasing temperature. Some authors [8,9] claim that this concomitant increase of the activation enthalpy and entropy implies the existence of a compensation point of coordinates τ_c , T_c (the compensation time and the compensation temperature). However, as emphasised in previous publications [4,10], the existence of a compensation point cannot really be considered as a fundamental or basic feature of the glass transition relaxation, and the co-ordinates of this point

are pseudo-quantities which lack any real physical meaning. Nevertheless, the departure from the zero entropy prediction is a fundamental feature of the glass transition relaxation, and it is observed in polymeric glasses as well as in low molecular weight organic glasses [11].

In a recent study on molecular glasses [11], we observed that the amplitude of the departure from the zero entropy prediction varies significantly from glass to glass, and we suggested that this amplitude is closely connected with the topology of the landscape of activation barriers of the material under study. As the concept of fragility of a glass is connected with its landscape of activation barriers, it is interesting to look for a link between the departure from the zero entropy prediction, obtained from the TSDC data, and the fragility. This is important because fragility is a central concept in glassy state physics [12] that describes the non-exponentiality and the non-linearity of the relaxations below the glass transition temperature.

In the present study we report the results of a detailed TSDC study carried out on two samples of a side-chain liquid crystalline polyacrylate with different molecular weights. From the TSDC results in the glass transition region we were able to obtain the departure from the zero entropy prediction and calculate the fragility parameter for both samples. These results were then compared with those corresponding to other glasses with different fragilities. Moreover, the results of a study by TSDC and by

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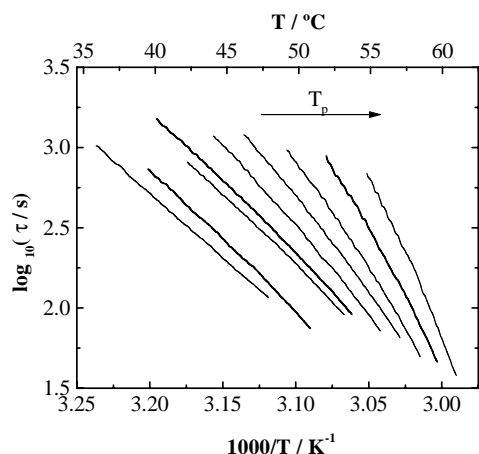
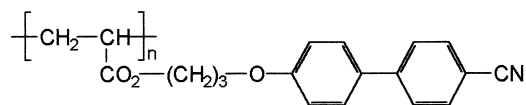


Fig. 1. Bucci lines, $\log \tau(T)$ vs. $1/T$, for the thermally sampled components of the glass transition relaxation of sample 1.

differential scanning calorimetry (DSC) on the physical ageing of this liquid crystalline polyacrylate at temperatures near and below the glass transition temperature will be reported.

2. Experimental

The side-chain liquid crystalline polymer studied in the present work is poly({3-[4-(4-cyanophenyl)phenoxy]propyloxy carbonyl}ethylene), it was supplied by Merck (catalogue number LCP95) and has the following structure:



Two different samples of this polymer were studied: sample 1 with a molecular weight $M_n = 4620$ and a polydispersity index $M_w/M_n = 1.78$ (15 repeat units) and sample 2 with $M_n = 16300$ and polydispersity index $M_w/M_n = 2.10$ (53 repeat units).

DSC measurements were performed with a Setaram DSC-121 calorimeter, in the temperature range of 20–85°C, using a heating rate of 4 K min⁻¹ and argon as a purge gas. The glass transition temperatures of the sample 1 (lower molecular weight) and sample 2 (higher molecular weight), defined here as the onset temperatures, were found to be 52 and 60°C, respectively. The change in the heat capacity associated to the glass transition, ΔC_p , was determined for both polymers: ΔC_p (sample 1) = 0.39 J g⁻¹ K⁻¹ and ΔC_p (sample 2) = 0.46 J g⁻¹ K⁻¹.

TSDC experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, USA) covering the range of -170 to +400°C. In order to analyse specific regions of the TSDC spectrum, different methods of polarising the sample were used, namely, the so-called TSDC global experiment and the thermal sampling (TS)

experiment. The technique of TS allows the polarisation of specific segments of a complex global relaxation or, otherwise stated, it allows the resolution of a global peak into its individual relaxation modes (for more experimental details see for example Ref. [5]). This is indeed one of the advantages of the technique, and the experimental strategy to be implemented in a TSDC study is such that the global experiments are used in order to detect and localise the different relaxations in the TSDC spectrum, whereas the TS experiments are performed in to study the detail of each complex relaxation (distribution of enthalpy and/or of entropy). Readers who are not familiar with the TSDC technique and data treatment can find useful information about this subject elsewhere [13,14].

3. Results and discussion

3.1. The glass transition relaxation

The temperature of maximum intensity, T_m , of the TSDC global peak of the glass transition relaxation was found to be 62°C for sample 1 (lower molecular weight) and 67°C for sample 2. This is the expected behaviour since a larger length of the polymer backbone hinders the motions of the chain segments giving rise to a higher glass transition temperature, T_g . The difference of 5°C in the position of the peaks of the two samples can be compared with the DSC results: onset temperatures of 52 and 60°C; endset temperatures of 60 and 68°C.

The glass transition region of both samples was analysed using the technique of TS. The $\log \tau(T)$ vs. $1/T$ lines of the TS peaks of the T_g relaxation of the two samples were obtained by the Bucci method [15–17]. These Bucci lines are shown in Fig. 1 for sample 1 (those corresponding to sample 2 show a similar behaviour).

We can see from Fig. 1 that the low temperature components of the T_g relaxation, those with lower intensity and lower activation energy, have nearly straight Bucci lines but that those of the higher temperature components show a significant curvature. Moreover, this curvature is independent of the width of the polarisation window, ΔT . In fact, performing different TS experiments with the same polarisation temperature, T_p , but with polarisation windows, ΔT , varying from 0 to 4°C, leads to curved Bucci lines showing similar curvatures. This means that the collection of modes of motion polarised by the electric field is not narrowly distributed, even if the polarisation window is very narrow. The fact that the electric field polarises a wide diversity of modes of motion in the glass transition region, associated to the non-isothermal nature of the TSDC scan, gives rise to the observed curvature of the Bucci lines. A similar behaviour is observed for other glass-formers [11], and it can be considered as a general feature of fragile systems, connected with the topology of the surface of energy barriers. This problem will be discussed below.

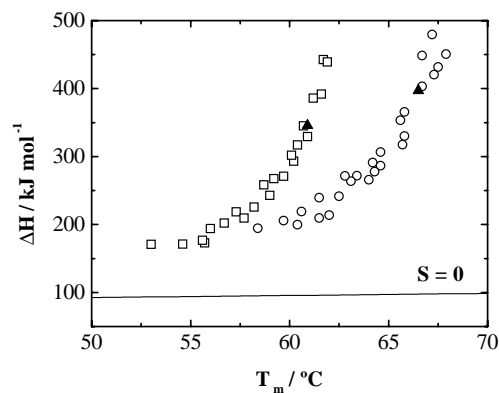


Fig. 2. Representation of ΔH^\ddagger vs. T_m (the temperature of maximum intensity of the peaks) for the thermally sampled components of the glass transition relaxation of samples 1 (squares) and 2 (circles). The continuous line corresponds to the zero entropy prediction.

The activation parameters associated with each TS peak can be obtained by fitting the corresponding $\log \tau(T)$ vs. $1/T$ line with an appropriate equation (Arrhenius or Eyring or a non-linear equation). Fig. 2 shows the activation enthalpy, ΔH^\ddagger , of the TS peaks of both samples as a function of their location, T_m (temperature of maximum intensity), in the temperature axis. The curved $\log \tau(T)$ vs. $1/T$ data was fitted to a non-linear equation and the activation enthalpy was obtained from the slope at T_m .

It can be observed from Fig. 2 that the components of the glass transition relaxation, including the lower temperature components, show a clear departure from the zero entropy prediction. Moreover, the amplitude of the departure from the zero entropy prediction is higher for the sample with higher molecular weight (note that the points in Fig. 2 corresponding to the TS peaks with higher intensity in the glass transition region are indicated by a triangle), which probably reflects the fact the potential energy surface of the sample with higher molecular weight shows higher maxima

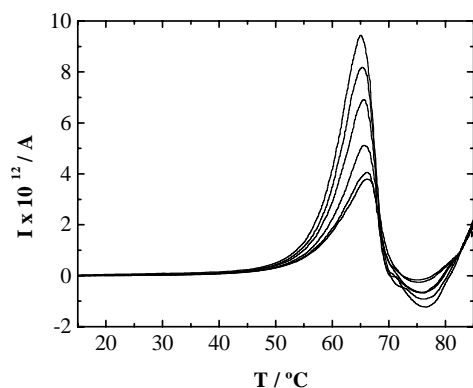


Fig. 3. Effect of the ageing time on a TS component of the glass transition peak of sample 2. The ageing times, t_a , in the order of decreasing intensity, were: 0, 15, 30, 45, 60, 120 and 180 min (the peaks obtained with $t_a = 120$ and 180 min are coincident). The other experimental conditions were: polarisation temperature $T_p = 57^\circ\text{C}$; width of the polarisation window $\Delta T = 0^\circ\text{C}$; heating rate $r = 4^\circ\text{C min}^{-1}$.

as a consequence of the hindering of the motions. On the contrary, the rate of increase of ΔH^\ddagger with T_m seems to be lower for the sample with higher molecular weight. This behaviour is probably related to the breadth of the glass transition, which depends on the length of the main chain. In fact, it is reasonable to consider that the number and diversity of modes of motion increases with increasing molecular weight, giving rise to an increase of the breadth of the glass transition relaxation.

3.2. Ageing studies

The phenomenon of ageing of the liquid crystalline polymer in the glassy state (below T_g) was analysed for sample 2 using both TSDC and DSC techniques. For TSDC experiments the glass was prepared by cooling the sample from the melt down to the polarisation temperature, below the glass transition temperature. The sample in the glassy state was then allowed to anneal at this temperature for a given period of time, t_a , and, at the end of this period of time, the aged sample was submitted to the thermal sampling experiment. Fig. 3 shows the results obtained in a series of experiments where the only parameter, which was allowed to change, was the ageing time, t_a .

It can be observed from the figure that the intensity (and the area) of the TS peaks decreases when the ageing time increases. This indicates that, as the glass approaches the equilibrium state, the total polarisation created by the electric field decreases. It can also be observed from Fig. 3 that the temperature of maximum intensity of the peaks, T_m , increases slightly as the ageing time increases. It was also found from these TSDC results that the activation energy of the TS peaks in the glass transition region decreases slightly as the ageing time increases. This decrease is indeed very weak for the liquid crystalline polymer studied in the present work, but it was found to be stronger in the molecular glass former *m*-toluidine [18]. The glass transition relaxation is characterised by a complex landscape of activation barriers, composed of an interconnected series of minima. Moreover, the essential phenomenon in glass formation is the falling out of equilibrium on cooling [19,20]. As the glass approaches the equilibrium state, i.e. as the ageing time increases, the system evolves from a stable minimum to deeper ones, the deeper minima being associated with higher densities. As the glass equilibrates, its configuration evolves in the landscape of activation energies so that the number of low activation barriers decrease and the number of high activation barriers increase. For that reason, as the glass approaches the equilibrium state, the number of modes of motion that the polarising field is allowed to activate decreases and that is why the intensity (and the area) of the TS peaks decreases with increasing annealing time. Moreover, as the molecular motions become slower as the glass approaches the equilibrium state, the total polarisation created by the electric field during a similar polarisation time, t_p , decreases. That is

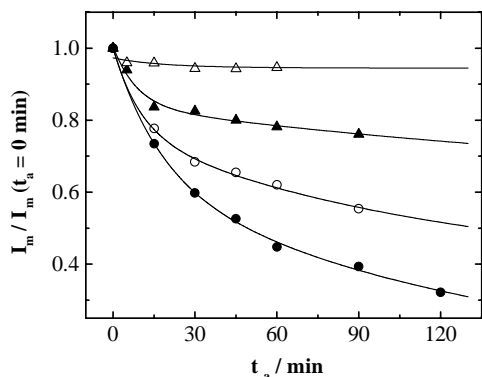


Fig. 4. Variation of the intensity of the glass transition peak as a function of the ageing time, t_a , for different ageing temperatures, T_a : ●—51°C; ○—57°C; ▲—60°C; △—62°C. The intensities are normalised relatively to the maximum intensity of the peak obtained with $t_a = 0$ min. The lines are just guides to the eye.

why the modes of motion the electric field is allowed to activate in the aged glass are such that their activation energies are lower than in the unaged glass. It is the slowing down of the molecular motions, which occurs as ageing proceeds, that makes the depolarisation process slower and produces the observed shift of the location of the peaks to higher temperatures. Moreover, the amplitude of motions is expected to decrease as a consequence of the increasing of density associated with ageing.

It was also observed that the rate of ageing decreases as the ageing temperature decreases, as expected. Some relevant results are shown in Fig. 4 where the relative intensity of the TS peaks are shown as a function of the ageing time, t_a , for four series of experiments, similar to that shown in Fig. 3, with different ageing temperatures, T_a .

The fact that ageing is slower for lower ageing temperatures suggests that the search for deeper minima in the landscape of activation barriers becomes statistically more difficult as the temperature decreases.

Ageing processes were also studied using DSC, which allows to monitor the decrease of the enthalpy of the glass

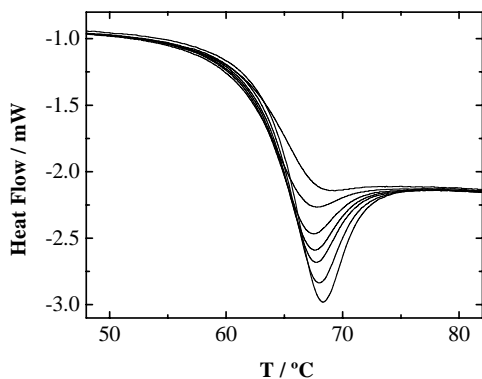


Fig. 5. DSC curves for sample 2 obtained after different ageing times, t_a , at the ageing temperature $T_a = 57^\circ\text{C}$. The ageing times, in the order of increasing intensity of the endothermic peak, were $t_a = 0, 2, 10, 20, 30, 60$ and 120 min.

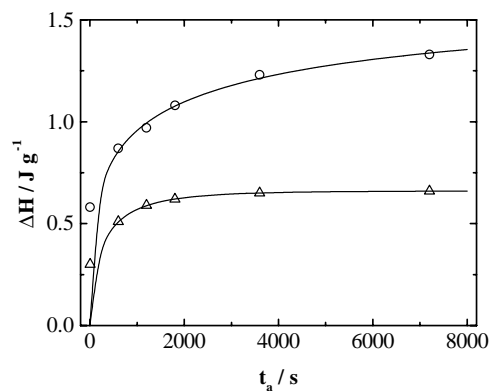


Fig. 6. Variation of the relaxation enthalpy, $\Delta H(t_a, T_a)$, with the ageing time, t_a , for two ageing temperatures, $T_a = 57^\circ\text{C}$ (circles) and $T_a = 60^\circ\text{C}$ (triangles).

as it approaches the equilibrium state. Using this technique, an endothermic peak near T_g appears when the sample is aged at a temperature below the glass transition temperature. The equivalence between the energy absorbed during heating through the glass transition and the enthalpy loss associated with the isothermal ageing process is well established [21,22]. The sample (sample 2) was subjected to a thermal history similar to the one used in the TSDC experiments. The polymer was quenched from the melt, at a cooling rate of approximately $20^\circ\text{C min}^{-1}$, to a temperature below the glass transition temperature. The sample was then allowed to anneal for a given period of time, t_a . At the end of this period, the aged sample was quenched to the starting temperature, 20°C , and submitted to a heating experiment up to 85°C , at 4°C min^{-1} . The heating curves of the aged polymer show an endothermic peak associated to the transition from glassy to rubbery state. The magnitude of these peaks depends both on the ageing temperature and on the ageing time or, in more general terms, depends on the thermal history of the polymer. In order to obtain the enthalpy lost on ageing, the heating curve of the unaged sample, for which $t_a = 0$, has to be subtracted from the heating curve of the aged sample, according to

$$\begin{aligned} \Delta H &= \int_{T_1}^{T_2} (C_{p,\text{aged}} - C_{p,\text{unaged}}) dT \\ &= \frac{1}{m} \int_{t_1}^{t_2} (P_{\text{aged}} - P_{\text{unaged}}) dt \end{aligned}$$

where $C_{p,\text{aged}}$ and $C_{p,\text{unaged}}$ are the specific heat capacities for the aged and unaged samples and P_{aged} and P_{unaged} are the output power signals for the aged and unaged samples, respectively. Fig. 5 presents the DSC curves which have been obtained on sample 2 after different ageing times, t_a , at the ageing temperature $T_a = 57^\circ\text{C}$, and they show, as expected, an endothermic peak which is a consequence of the structural relaxation process that the material undergoes.

It can be seen from Fig. 5 that the position and area of this endothermic peak varies with the ageing time, in such a way

Table 1
Ageing parameters of the Cowie–Ferguson equation for two different ageing temperatures, T_a

T_a (°C)	$\Delta H_\infty(T_a)$ (J g ⁻¹)	t_c (s)	β
57	1.61	1359	0.34
60	0.66	306	0.58

that the area and the temperature of the minimum increase with ageing time. Since the temperature of the endothermic peak corresponds to the process of recovery of enthalpy during the heating of the aged sample, the increase of this temperature as the ageing time increases is due to the decrease with ageing, of the molecular mobility of the chain segments (required for the recovery of the enthalpy to take place) as a consequence of the decrease in the free volume. It is to be recalled that the same behaviour was observed in our TSDC studies. Fig. 5 shows, as noted, an increase of the area of the endothermic peak (enthalpy relaxation, ΔH) as the ageing time increases. The variation of the relaxation enthalpy, $\Delta H(t_a, T_a)$, with the ageing time, t_a , is presented in Fig. 6 for the two ageing temperatures, T_a .

It can be concluded from this figure that the slope of the $\Delta H(t_a, T_a)$ vs. t_a curves, which is a measure of the relaxation rate, is high at the beginning and falls with increasing t_a . This behaviour is also a manifestation of the slow down of the relaxation kinetics that occurs as the metastable equilibrium state is approached. A similar behaviour was observed earlier from our TSDC results. Moreover, it can be concluded from Fig. 6 that the relaxation rate is higher for higher ageing temperatures. In fact, the time required for the fast increase of the relaxation enthalpy up to the saturation value is shorter for higher ageing temperatures (it is very high when the ageing temperature is 57°C, and substantially short when the ageing temperature is 60°C (which corresponds to the calorimetric glass transition temperature)).

The curves of $\Delta H(t_a, T_a)$ vs. t_a shown in Fig. 6 have been fitted using the empirical equation of Cowie and Ferguson [23,24]:

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)[1 - \Phi(t_a)] \quad (1)$$

where $\Phi(t) = \exp[-(t/t_c)^\beta]$. In Eq. (1) $\Delta H_\infty(T_a)$ is the limit of the relaxation enthalpy for very long ageing times, and the function $\Phi(t)$ is the Kohlrausch–Williams–Watts function which describes the non-exponentiality of glassy state relaxations. As pointed out by Hodge [25,26], non-linearity is also a very important feature of the relaxation phenomena near and below the glass transition temperature, which needs to be taken into account for an accurate prediction of the ageing behaviour. Eq. (1) neglects non-linearity in the analysis of enthalpy relaxation data. Despite this fact, we will use Eq. (1) just as an empirical equation for fitting our data, and we are aware that the parameters obtained from the fitting may lack any deep theoretical significance.

Table 1 shows the values of the parameters $\Delta H_\infty(T_a)$, t_c

and β obtained from the fitting of our data for two different ageing temperatures. It can be concluded from these values that: (1) $\Delta H_\infty(T_a)$ increases as the ageing temperature decreases (as the difference between the glass transition temperature and the ageing temperature increases), which is the expected behaviour since the enthalpy loss during the equilibration process is larger when the glass is far from the metastable equilibrium state; (2) t_c increases as the ageing temperature decreases indicating that the relaxation processes below T_g become increasingly slow as the temperature decreases; (3) β , which describes the width of the distribution of relaxation times, decreases with decreasing ageing temperature.

3.3. Departure from the zero entropy prediction and fragility

A feature of the glass transition relaxation as studied by the TSDC technique is the strong departure of the activation energy from the zero entropy prediction, and it was Howard Starkweather who pointed out first the importance of the zero entropy prediction as a reference behaviour to interpret the TSDC data [6,7,27]. We will quantify this amplitude, which will be designated by Δ , in the following way: Δ is the difference between the activation enthalpy calculated at T_m of the TS peak of maximum intensity in the glass transition region, T_M , and the activation enthalpy, calculated at the same T_M , on the basis of the zero entropy approximation:

$$\Delta = \Delta H^\ddagger(T_M) - \Delta H_0^\ddagger(T_M) \quad (2)$$

According to this definition we obtain $\Delta = 363 \text{ kJ mol}^{-1}$ for sample 1 and $\Delta = 382 \text{ kJ mol}^{-1}$ for sample 2. The amplitude of the departure from the zero entropy prediction is thus higher for the sample with higher molecular weight, which probably reflects the fact the potential energy surface of the sample with higher molecular weight shows higher maxima as a consequence of the hindering of the motions.

The physical significance of the amplitude, Δ , of the departure from the zero entropy prediction in the glass transition region is not yet completely elucidated. In a recent TSDC work on low molecular weight organic glasses [11] we suggested that this amplitude is connected to the topology of the potential energy surface, i.e. to the landscape of activation barriers of the relaxation processes associated with the glass transition. In this context, and since the concept of fragility, m , defined by Angell as the slope ($d \log_{10} \tau(T)/dT_g/T$) at T_g [28], is connected to the topology of the potential energy surface [29], we tried to set up a link between the parameter Δ and fragility. We thus defined fragility as

$$m_1 = \frac{\Delta}{2.303 \times RT_M} \quad (3)$$

where T_M is the temperature of the maximum of the higher intensity TS peak of the glass transition relaxation. It is to be recalled that the Δ values were calculated at T_M (which

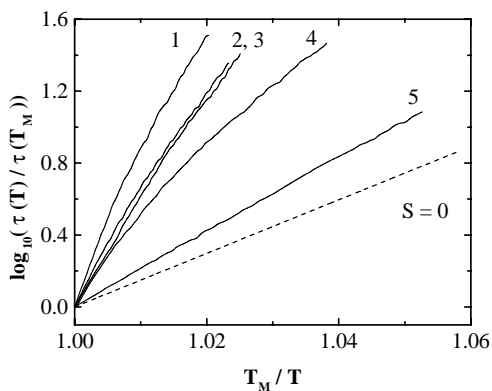


Fig. 7. Plot of $\log_{10} [\tau(T)/\tau(T_M)]$ vs. T_M/T for the TS peak of maximum intensity in the glass transition region of the different materials considered in the text. The dashed line is the $\log_{10} [\tau'(T)/\tau'(T_M)]$ vs. T_M/T line for the zero entropy prediction. The correspondence between the curves and the substances is as follows: 1—LCP181; 2—LCP95, sample 2; 3—LCP95, sample 1; 4—glycerol; 5—cyanoadamantane.

depends of course on the heating rate as is the case for the calorimetric glass transition temperature). In this context, Eq. (3) could be written as

$$m_1 = \left[\left(\frac{d \log_{10} \tau(T)}{dT_M/T} \right) - \left(\frac{d \log_{10} \tau'(T)}{dT_M/T} \right)_{\Delta S=0} \right]_{T=T_M} \quad (4)$$

where the second factor in the right-hand side is the slope at T_M of the line of $\log_{10} \tau'(T)$ vs. $1/T$ for the zero entropy prediction (which is related to the activation enthalpy at T_M for the zero entropy prediction). The calculation procedure to obtain the second factor in the right-hand side of Eq. (4) is presented in Appendix A. The difference between the fragility as defined by Angell, m , and that defined by Eqs. (3) or (4), m_1 , arises from the fact that the main concept of our definition of fragility is the amplitude, Δ , of the departure from the zero entropy approximation (defined according to Eq. (2)), while Angell's definition is just based on the activation energy at T_g . If we neglect this enthalpy of the zero entropy approximation, and define a fragility m_2 just based on the activation enthalpy of the peak of maximum intensity in the glass transition region, $\Delta H_{\neq}(T_M)$, we will thus have

$$m_2 = \frac{\Delta H_{\neq}(T_M)}{2.303 \times RT_M} \quad (5)$$

The definition of fragility according to Eq. (5) can be expressed in a different form, similar to that of Angell's definition, as

$$m_2 = \left(\frac{d \log_{10} \tau(T)}{dT_M/T} \right)_{T=T_M} \quad (6)$$

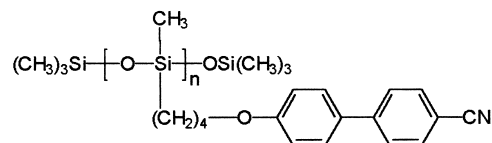
where T_M is, as noted before, the temperature of the maximum of the TS peak with higher intensity in the glass transition region.

Let us recall and comment the difference between the

definitions of fragility m_1 and m_2 . As pointed out before, the definition of m_1 is based on the concept of deviation from the zero entropy prediction at T_M , while the definition of m_2 (as well as Angell's definition) are just based on the value of the activation energy at T_M ($\cong T_g$). Angell's scale of fragility is such that the limit of m for infinitely strong glasses is $m = 16$ [28]. This is also the case for m_2 . If Eqs. (3) or (4) are used to define fragility, the limit of m_1 for infinitely strong glasses should be $m_1 = 0$, so that this scale of fragility appears as an absolute scale. This arises from the fact that, for fragile systems, the true feature of the glass transition relaxation as studied by TSDC is the departure from the zero entropy and not the activation energy at T_M itself. In fact, it can be shown, from the basic features of the TSDC technique (see Appendix A), that the second factor in the right-hand side of Eq. (4) has indeed a value of ~ 15 , similar to the limit of the fragility for infinitely strong glasses according to Angell's scale.

For the liquid crystalline polymer studied in the present work we obtain $m_1 = 57$ and $m_2 = 72$ for sample 1 and $m_1 = 59$ and $m_2 = 74$ for sample 2, which indicates a very slight increase of the fragility with increasing molecular weight. These high values of the fragility are expected since it is known that polymeric systems often appear as very fragile glasses [28,29].

Finally, it is interesting in this context to compare the values of fragility of the polymer studied in the present work with those of other glass-formers studied previously by TSDC. Fig. 7 shows Angell's type plot of $\log_{10} [\tau(T)/\tau(T_M)]$ vs. T_M/T for the TS peak of maximum intensity in the glass transition region of different materials: a side-chain liquid crystalline polysiloxane recently studied by TSDC [5] (catalogue number LCP181, material 1) whose chemical structure is as follows:



the side-chain liquid crystalline polymer studied in the present work, samples 1 (material 2) and 2 (material 3), glycerol (material 4) [11] and cyanoadamantane (material 5) [30].

The $\log_{10} [\tau'(T)/\tau'(T_M)]$ vs. T_M/T line for the zero entropy prediction (dashed line), which represents the limit of behaviour for infinitely strong glasses, is also shown. The fragility m_2 thus corresponds to the slope at $T = T_M$ of the $\log_{10} [\tau(T)/\tau(T_M)]$ vs. T_M/T line for the TS peak of maximum intensity in the glass transition region. The fragility m_1 is the difference between the slope at $T = T_M$ of the $\log_{10} [\tau(T)/\tau(T_M)]$ vs. T_M/T line for the TS peak of maximum intensity in the glass transition region and the slope, at the same temperature, of the $\log_{10} [\tau'(T)/\tau'(T_M)]$ vs. T_M/T line for the zero entropy prediction. Table 2

Table 2

Glass transition temperature, T_g ; temperature of the maximum of the TS peak of maximum intensity in the glass transition region, T_M ; amplitude of the departure from the zero entropy prediction, Δ , and fragility parameters, defined in the text, for the glass-formers shown in Fig. 7. The values of m , which correspond to the classical definition by Angell, have been taken from the literature

Glass former	T_g (K)	T_M (K)	Δ (kJ mol ⁻¹)	m	m_1	m_2
LCP181 (material 1)	287	294	440	–	78	93
LCP95 (sample 1) (material 2)	325	334	363	–	57	72
LCP95 (sample 2) (material 3)	333	339	382	–	59	74
Glycerol (material 4)	185	193	159	53 ^a	43	58
Cyanoadamantane (material 5)	177 ^a	179	19.2	35 ^a	5.6	20.5

^a From Ref. [28].

presents the values of the calorimetric glass transition temperature, T_g , the temperature of the maximum of the TS peak of maximum intensity in the glass transition region, T_M , the amplitude of the departure to the zero entropy prediction, Δ , Angell's fragility, m (when available), and also the values of m_1 and m_2 . It can be seen from Fig. 7 that the slope at $T = T_M$ of the different curves, which increases with increasing fragility, is higher for the polysiloxane material and lower for cyanoadamantane. It is well known that the orientationally disordered glass cyanoadamantane behaves as a strong glass and the value of $m_2 = 20.5$ that we obtain from our TSDC data [30] confirms this behaviour. However, this value is significantly lower than the value of $m = 35$ reported in the literature [27]. For glycerol, a moderately fragile glass, we have $m \approx m_2$. For the polymeric systems presented in Fig. 7 and Table 2, the corresponding fragilities are not reported in the literature, but it is known that the polymeric systems often behave as very fragile systems [28,29]. The values of fragility obtained for these systems from our TSDC results, and presented on Table 2, confirm that they are indeed fragile glasses. On the contrary, the liquid crystalline polysiloxane (material 1) shows a high fragility when compared with the liquid crystalline polyacrylate studied in this work (materials 2 and 3). The mesogenic side group is similar in these materials, but they have different backbones. The higher mobility of the siloxane backbone as well as the strong departure from the zero entropy prediction observed in material 1 is at the origin of its higher fragility.

It was noted before that the $\log_{10} \tau(T)$ vs. $1/T$ lines for the TS peaks near the glass transition temperature show a significant curvature. Fig. 7 seems to show that the curvature of the lines tends to increase with increasing fragility. The curvature of the $\log_{10} \tau(T)$ vs. $1/T$ lines of the TS peaks near T_g is, very probably, a manifestation of the complexity of the Gibbs energy landscape of the α -relaxation in these fragile glass-formers. This complexity is such that small variations of temperature below and near T_g give rise to pronounced modifications of the structural configuration of the glass (distribution of the molecular entities among the available energy minima), which is at the origin of the so-called fragile behaviour. It is this fragility that generates the pronounced departure from the Arrhenius behaviour. It

is also because of this fragility that the electric field, in a narrow window TS experiment, polarises a variety of modes of motion with different activation energies. The non-isothermal nature of the TSDC technique thus produces the observed curvature of the $\log \tau(T)$ vs. $1/T$ lines.

4. Conclusions

A careful TSDC study has been carried out in a side-chain liquid crystalline polymer in the glass transition region and the results have been compared for two samples with different molecular weight. The ageing processes near and below the glass transition temperature were studied by both TSDC and DSC techniques, for one of the samples of this polymer. From the DSC study it was concluded that the limit of the relaxation enthalpy for very long ageing times increases, and the rate of equilibration of the glass becomes lower, as the ageing temperature decreases. The TSDC data confirmed that the process of equilibration of the glass becomes slower for lower ageing temperatures. Moreover, the TSDC study showed that the activation energy of the relaxation processes associated with the glass transition relaxation decreases slightly as the glass approaches the metastable equilibrium state.

Finally, it was shown that the TSDC data allows an easy determination of the fragility parameter. This is an important result since fragility is a central parameter in glassy state physics, which describes the non-exponentiality and the non-linearity of the relaxations below the glass transition temperature.

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Appendix A. The line of $\log_{10}\tau'(T)$ vs. $1/T$ for the zero entropy prediction

For a TS peak of a relaxation with zero activation entropy we have, according to Eyring's equation:

$$\tau'(T) = \frac{h}{kT} \exp\left(\frac{\Delta H_0^\ddagger}{kT}\right) \quad (\text{A1})$$

where the subscript zero in the enthalpy indicates that we are dealing with relaxations with zero activation entropy.

At the temperature of maximum intensity, T_m , of the same TS peak we will thus have:

$$\tau'(T_m) = \frac{h}{kT_m} \exp\left(\frac{\Delta H_0^\ddagger}{kT_m}\right) \quad (\text{A2})$$

Eliminating $\Delta H^\ddagger/k$ in Eqs. (A1) and (A2) we obtain:

$$\ln\tau'(T) = \ln\frac{h}{kT} + \frac{T_m}{T} \ln\left(\frac{kT_m\tau'(T_m)}{h}\right) \quad (\text{A3})$$

Since T_m and $\tau'(T_m)$ are characteristics of the TS peak under consideration, we can deduce:

$$\frac{d \ln \tau'(T)}{dT_m/T} = \frac{T}{T_m} + \ln\left(\frac{kT_m\tau'(T_m)}{h}\right) \quad (\text{A4})$$

In order to obtain the second factor of the right-hand side of Eq. (4) we must use decimal logarithms and calculate (A4) at $T = T_m = T_M$, the temperature of the maximum of the TS peak of higher intensity in the glass transition region. We have thus:

$$\left(\frac{d \log_{10} \tau'(T)}{dT_M/T}\right)_{T=T_M} = \frac{1}{2.303} \left[1 + \ln\left(\frac{kT_M\tau'(T_M)}{h}\right) \right] \quad (\text{A5})$$

or, using Eq. (A2),

$$\left(\frac{d \log_{10} \tau'(T)}{dT_M/T}\right)_{T=T_M} = \frac{1}{2.303} \left[1 + \frac{\Delta H_0^\ddagger(T_M)}{kT_M} \right] \quad (\text{A6})$$

where $\Delta H_0^\ddagger(T_M)$ is easily obtained from the equation of the activation enthalpy for the zero entropy prediction [5]:

$$\frac{kT_M^2}{r(\Delta H_0^\ddagger + kT_M)} = \frac{h}{kT_M} \exp\left(\frac{\Delta H_0^\ddagger}{kT_M}\right) \quad (\text{A7})$$

where r is the heating rate of the TSDC experiments.

The value of

$$\left(\frac{d \log_{10} \tau'(T)}{dT_M/T}\right)_{T=T_M}$$

calculated from Eqs. (A6) and (A7) is 14.8 for $T_M = -120^\circ\text{C}$ (153 K) and 15.6 for $T_M = +120^\circ\text{C}$ (393 K), values which are indeed similar to the value of the limit of fragility for infinitely strong glasses according to Angell's scale.

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