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Fragility in side-chain liquid crystalline polymers: the TSDC contribution

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Abstract

In the present work a procedure is proposed to obtain the fragility of a glass from Thermally Stimulated Depolarisation Currents (TSDC) data. From previous TSDC studies on wide series side-chain liquid crystalline polymers, and particularly from a careful thermal sampling analysis of their glass transition relaxation, the fragility parameter was obtained. The proposed fragility scale is based on the concept of deviation from the zero entropy prediction, and is such that zero is the limit of fragility for infinitely strong glasses. The fragility of 10 side-chain liquid crystalline polymers is discussed in terms of their molecular structure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Glass formers; Glass transition; Fragility

1. Introduction

After the pioneering work by Simon [1], the technique of Thermally Stimulated Depolarisation Currents (TSDC) was used in our laboratory to study the molecular dynamics in a wide series side-chain liquid crystalline polymers [2]. It was shown that the TSDC technique appears as a suitable tool for detecting and characterising the dipolar relaxations present in this family of materials. A particular attention was focused on the analysis of the deviation from the zero entropy prediction (often referred to as the compensation behaviour), which appears as an important feature of the glass transition relaxation as studied by TSDC [2,3]. It is reasonable to consider that the deviation from the zero entropy prediction is an indication of the height of the activation barriers of the material under study, and that it gives information about the topology of its potential energy surface [4]. On the other hand, the fragility of a glass, which is an important concept in glassy state physics [5,6], is considered to be connected with the features of the landscape of activation barriers [5,7]. In a simplified picture, fragility is associated with the ruggedness of the potential energy surface, and it increases with the mean amplitude and variance of the activation barriers, as well as with the number, or density, of minima in the energy landscape (number of accessible molecular configurations). Recently [4,8] we suggested a procedure to calculate the fragility of a glass from the TSDC data. This was carried out by establishing a link between fragility and the amplitude of the departure from the zero entropy prediction. In this context we defined two different scales of fragility based on TSDC data. One which is equivalent to the classical Angell's scale [9], were the value ~16 is the limit of the fragility for infinitely strong glasses. The other, based on the concept of deviation from the zero entropy prediction, which appears as an absolute scale were zero is the limit of the fragility for infinitely strong glasses. In the present work we use this procedure to calculate the fragility of 10 side-chain liquid crystalline polymers from the previously obtained TSDC data. The results were discussed in detail in terms of the molecular structure of these materials.

2. Experimental

The chemical structures of the side-chain liquid crystalline polymers whose TSDC study is the basis of the present work are presented in Table 1. Their glass transition temperatures, T_g, as well as the references of the literature were the TSDC results were originally published are also reported in Table 1.

Thermally Stimulated Depolarisation Current experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, USA) covering a range of −170 to +400°C. The parallel electrode assembly has an effective area of $\approx 38\ \text{mm}^2$. A Faraday cage shields the sample, and prior to the experiments the sample, located between the parallel plate electrodes, is evacuated to

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Table 1
Chemical structures and glass transition temperatures of the side-chain liquid crystalline polymers discussed in the text. The references of the literature where the TSDC results were originally published are also indicated

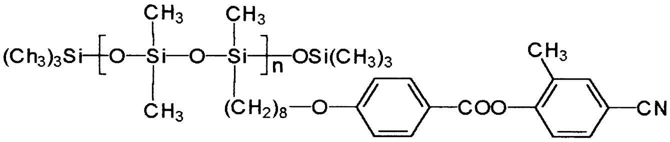
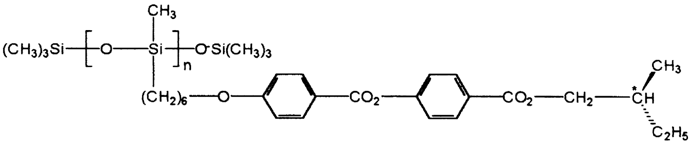
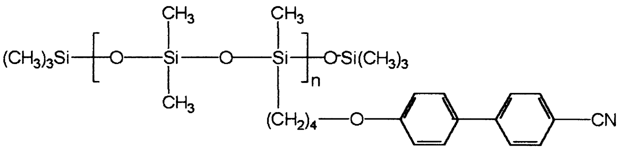
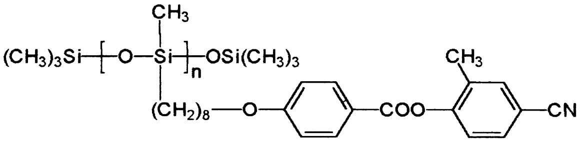
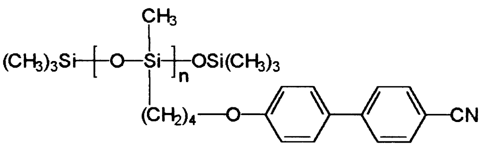
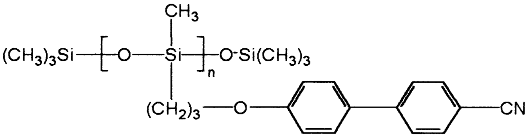
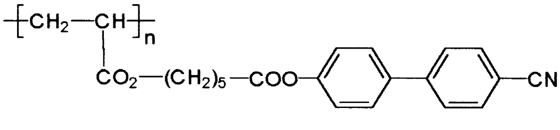
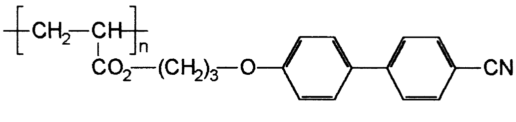
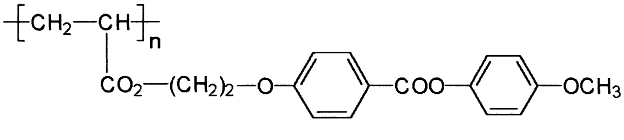
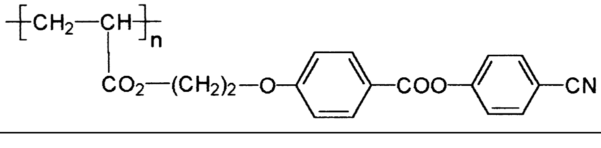
LCP	Structure	T_g/°C	Reference
1		−15	[17]
2		−7	[18]
3		−4	[19]
4		5	[17,20]
5		14	[21]
6		37	[22]
7		38	[23]
8		60	[8,24]
9		62	[25]
10		75	[25]

Table 2
Temperature of the maximum of the TS peak with higher intensity in the glass transition region, T_M, activation enthalpy at T_M, $\Delta H^{\neq}(T_M)$, for the TS peak with higher intensity in the glass transition region, departure to the zero entropy prediction, Δ, and fragilities m_1 and m_2, defined in the text

LCP	T_M (°C)	$\Delta H^{\neq}(T_M)$ (kJ mol^{-1})	Δ (kJ mol^{-1})	m_1	m_2
1	−16.4	302	230	47	61
2	−7.9	316	241	47	62
3	−5.6	326	251	49	64
4	6.7	434	354	66	81
5	20.6	524	440	78	93
6	40.1	530	440	73	88
7	43.1	465	375	62	77
8	65.9	480	382	59	74
9	62.1	439	344	53	68
10	79.9	586	485	72	87

10^{-4} mbar and flushed several times with 1.1 bar of high-purity helium. In order to analyse the 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 (or cleaning, or windowing) experiment (experimental details are given in Ref. [10]).

The technique of thermal sampling, TS, allows the polarisation of specific segments of a complex global relaxation or, otherwise stated, it allows to resolve a global peak into its individual relaxation modes. Performing different TS experiments along the global-peak's temperature region allows the selective activation of the different fractions or segments of the global peak, i.e. the separation of a broad distribution of relaxations into its narrowly distributed components. 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 to detect and localise the different relaxations in the TSDC spectrum; whereas the TS experiments are performed to study the detail of each complex relaxation (distribution of enthalpy and/or of entropy). From the current intensity versus temperature experimental data, $i(T)$, it is possible to obtain the temperature dependent relaxation time, $\tau(T)$, associated with each $i(T)$ TS peak. The procedure used to do so is explained elsewhere [4].

Readers who are not familiar with the TSDC technique and data treatment can find useful information about this subject in several general texts [11,12].

3. Results and discussion

3.1. The departure from the zero entropy prediction

An important 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 [13–15]. 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:

$$\Delta = \Delta H^{\neq}(T_M) - \Delta H_0^{\neq}(T_M) \tag{1}$$

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 [4] 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. Angell defined the fragility index of a glass-former, m, as the slope d $\log_{10} \tau(T)/\mathrm{d}T_g/T$ at T_g, where τ is the structural relaxation time which slows down to 100 s at T_g. In this context, and since the concept of fragility is connected to that of topology of the potential energy surface [5,7], we tried to set up a link between the parameter Δ and fragility.

3.2. Activation enthalpy at T_g and fragility

The glass transition temperature, T_g, provided by the TSDC technique can be defined in different ways. One can consider that T_g is the temperature of maximum intensity of the TSDC global peak in the glass transition region. This temperature, which obviously depends on the heating rate of the experiment, is usually consistent with the calorimetric glass transition temperature. On the other hand, we can consider that the T_g provided by the TSDC technique is the temperature of the maximum of the TS peak, in the glass transition region, which shows a higher activation enthalpy. This temperature is also, in general, consistent with the calorimetric glass transition temperature, but experimental difficulties may arise since the TS peaks in the high temperature side of T_g are often affected by conductivity tails or space charge peaks. Finally, we can consider that the T_g provided by the TSDC technique is the temperature of the maximum of the TS peak, in the glass transition region, which shows higher intensity (which will be designated by T_M). This temperature T_M, which depends on the heating rate of the experiment, is also consistent with the calorimetric T_g (the values of the calorimetric glass transition temperature, T_g, presented in Table 1 can be compared with the values of T_M presented in Table 2). Moreover, this definition of the glass transition temperature provided by the TSDC technique has the advantage that the TS peak, in the glass transition region, which shows higher intensity is easy to identify and is not usually affected by conductivity tails or higher temperature relaxations. We will thus define the t.s.d.c. fragility as the slope of the $\log_{10} \tau(T)$ versus T_M/T line at T_M, for the TS peak with higher intensity in the glass

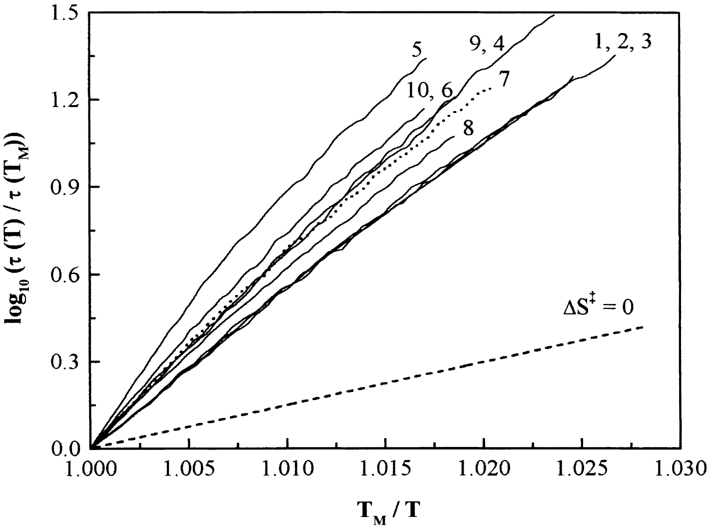


Fig. 1. Plot of $\log_{10}[\tau(T)/\tau(T_M)]$ versus T_M/T for the TS peak of maximum intensity in the glass transition region of the different materials presented on Table 1. The dashed line is the $\log_{10}[\tau'(T)/\tau'(T_M)]$ versus T_M/T line for the zero entropy prediction. The correspondence between the curves and the substances is that given in Table 1.

transition region, and we will write

$$m_1 = \left(\frac{\mathrm{d} \log_{10} \tau(T)}{\mathrm{d}T_M/T} \right)_{T=T_M} \tag{2}$$

where the derivative is taken on the $\tau(T)$ curve of the $i(T)$ TS peak with higher intensity in the glass transition region.[1] Fig. 1 shows the normalised $\tau(T)$ lines of the $i(T)$ TS peaks with higher intensity in the glass transition region, for all the side-chain liquid crystalline polymers presented in Table 1.

The dashed line in this figure corresponds to the behaviour of infinitely strong glasses (see below). The fragility m_1 (see Eq. (2)) of each polymer thus corresponds to the slope at $T = T_M$ of the corresponding $\log_{10}[\tau(T)/\tau(T_M)]$ versus T_M/T line. It is clear from Fig. 1 that the 10 side-chain liquid crystalline polymers considered in the present work display a wide variety of fragility behaviour.

From Eq. (2), and using Arrhenius and/or Eyring equations, we obtain

$$m_1 = \frac{E_a(T_M)}{2.303 \times \mathrm{R}T_M} = \frac{\Delta H^{\neq}(T_M) + \mathrm{R}T_M}{2.303 \times \mathrm{R}T_M} \tag{3}$$

where $E_a(T_M)$ is the activation energy at T_M and $\Delta H^{\neq}(T_M)$ the activation enthalpy at the same temperature. Table 2 presents the values of T_M and $\Delta H^{\neq}(T_M)$ for the side-chain liquid crystalline polymers shown in Table 1, along with the values of fragility calculated from Eq. (3).

The values of the fragility according with Angell's definition, m, are not reported in the literature for the side-chain liquid crystalline polymers considered in the present work. Nevertheless it was recently shown [4] that, for a series of low molecular weight glass formers, there is good agreement between the values of m and those of m_1 calculated from Eq. (3). Moreover, for poly(vinyl acetate) Angell's fragility is $m = 95$ [9], while the value obtained from our TSDC data [16] using Eq. (3) is $m_1 = 85$. The difference between m_1 and m probably arises from the fact that our TSDC data [16] does not allow a very precise choice of the thermally cleaned peak with higher intensity in the glass transition region (the thermally cleaned peaks were only obtained in temperature intervals of 5°C).

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

As emphasized before, it is the departure from the zero entropy, Δ, which is the true feature of the glass transition relaxation as studied by TSDC, and not the activation energy at T_M itself. It seems thus important to try to set up a link between the parameter Δ and fragility. In this context we introduce a new definition of fragility, m_2, according to

$$m_2 = \left[\left(\frac{\mathrm{d} \log_{10} \tau(T)}{\mathrm{d}T_M/T} \right) - \left(\frac{\mathrm{d} \log_{10} \tau'(T)}{\mathrm{d}T_M/T} \right)_{\Delta S=0} \right]_{T=T_M} \tag{4}$$

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[1] The activation energy at T_M of the thermally sampled peak of higher intensity in the glass transition region was choose in the present work in order to calculate the fragility of a glass former from TSDC data. Some reasons for this choice were presented before but this problem deserves a brief comment. The TS peak with higher intensity in the glass transition region (with maximum intensity at T_M) corresponds to a situation where an higher extent of polarisation was allowed to be "freezed-in". Otherwise stated, at the polarisation temperature, T_P, of the TS peak with higher intensity in the glass transition region, the electric field was allowed (in the polarisation time t_P) to explore all the available energy barriers (including the higher ones). On the other hand, the higher temperature TS peaks in the glass transition region (with maximum intensity at temperatures higher than T_M) have intensities which decrease as T_P increases because the "freezing-in" of the polarisation is increasingly difficult, indicating the transformation to the equilibrium (ergodic) state. The temperature, T_M, of the TS peak with higher intensity in the glass transition region thus probably represents the lower temperature limit of the transformation range, defining a time scale of the system when nearly all the activation barriers were activated (a time scale of the system very near the equilibrium).

where the second factor on the right-hand side is the slope at T_M of the line of $\log_{10} \tau'(T)$ versus $1/T$ for the zero entropy prediction (which is naturally related to the activation energy (and enthalpy) at T_M for the zero entropy prediction). The fragility m_2 is thus the difference between the slope at $T = T_M$ of the $\log_{10} [\tau(T)/\tau(T_M)]$ versus 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 $\log_{10} [\tau'(T)/\tau'(T_M)]$ versus T_M/T line for the zero entropy prediction (see Fig. 1).

In order to obtain the second factor on the right-hand side of Eq. (4), we need to first define the line of $\log_{10} \tau'(T)$ versus $1/T$ for the zero entropy prediction.

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

$$\tau'(T) = \frac{h}{\mathrm{k}T} \exp\left(\frac{\Delta H_0^{\neq}}{\mathrm{R}T}\right) \tag{5}$$

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:

$$\tau'(T_m) = \frac{h}{\mathrm{k}T_m} \exp\left(\frac{\Delta H_0^{\neq}}{\mathrm{R}T_m}\right) \tag{6}$$

Eliminating $\Delta H_0^{\neq}/\mathrm{R}$ in Eqs. (5) and (6) we obtain:

$$\ln \tau'(T) = \ln\frac{h}{\mathrm{k}T} + \frac{T_m}{T} \ln\left(\frac{\mathrm{k}T_m \tau'(T_m)}{h}\right) \tag{7}$$

The dashed line in Fig. 1 is the representation of this equation, which describes the temperature dependence of the relaxation time for relaxations with zero activation entropy.

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

$$\frac{\mathrm{d} \ln \tau'(T)}{\mathrm{d}T_m/T} = \frac{T}{T_m} + \ln\left(\frac{\mathrm{k}T_m \tau'(T_m)}{h}\right) \tag{8}$$

In order to obtain the second factor on the right-hand side of Eq. (4) we must use decimal logarithms and calculate Eq. (8) at $T = T_m = T_M$, the temperature of the maximum of the TS peak of higher intensity in the glass transition region. Thus we have:

$$\left(\frac{\mathrm{d} \log_{10} \tau'(T)}{\mathrm{d}T_M/T}\right)_{T=T_M} = \frac{1}{2.303}\left[1 + \ln\left(\frac{\mathrm{k}T_M \tau'(T_M)}{h}\right)\right] \tag{9}$$

or, using Eq. (6),

$$\left(\frac{\mathrm{d} \log_{10} \tau'(T)}{\mathrm{d}T_M/T}\right)_{T=T_M} = \frac{1}{2.303}\left[1 + \frac{\Delta H_0^{\neq}(T_M)}{\mathrm{R}T_M}\right] = \frac{1}{2.303}\left[\frac{\Delta H_0^{\neq}(T_M) + \mathrm{R}T_M}{\mathrm{R}T_M}\right] \tag{10}$$

where $\Delta H_0^{\neq}(T_M)$ is easily obtained from the equation of the activation enthalpy for the zero entropy prediction [10]:

$$\frac{\mathrm{R}T_M^2}{r(\Delta H_0^{\neq} + \mathrm{R}T_M)} = \frac{h}{\mathrm{k}T_M} \exp\left(\frac{\Delta H_0^{\neq}}{\mathrm{R}T_M}\right) \tag{11}$$

where r is the heating rate of the TSDC experiments.

3.4. Departure from the zero entropy prediction and fragility

Taking Eqs. (2), (3) and (10) into account, and remembering that $\Delta = \Delta H^{\neq}(T_M) - \Delta H_0^{\neq}(T_M)$, we can define fragility in terms of the departure from the zero entropy behaviour (Eq. (4)) as

$$m_2 = \frac{\Delta}{2.303 \times \mathrm{R}T_M} \tag{12}$$

The values of m_2 calculated using Eq. (12) are shown in Table 2. It can be concluded from this table that the difference $m_1 - m_2$ is nearly the same, and equal to $15 - 16$, for all the liquid crystalline polymers considered in the present work. In fact, the quantity

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

calculated from Eqs. (10) and (11), which is precisely the difference $m_1 - m_2$ between the two scales of fragility, shows a very weak dependence on the temperature. For example, it is 14.8 for $T_M = -120$°C (153 K) and 15.6 for $T_M = +120$°C (393 K). It is to be noted that Angell's scale of fragility, which leads to values of m similar to our scale m_1, is such that the limit of m for infinitely strong glasses is $m = 16$ [5,8]. The limit of our scale m_2 for infinitely strong glasses will thus be $m_2 = 0$, so that this scale of fragility appears as an absolute scale. This arises from the fact that, for fragile systems, it is the departure from the zero entropy which is the true feature of the glass transition relaxation as studied by TSDC, and not the activation energy at T_M itself.

3.5. The fragility of side-chain liquid crystalline polymers

It can be seen from Table 2 that the fragility of this set of side-chain liquid crystalline polymers varies in a relatively wide range of values: m_1 from 47 to 78 and m_2 from 61 to 93. It is to be noted that low molecular weight organic glass formers as glycerol, maltitol and *m*-toluidine show values of fragility in this range [4]. It is also to be noted that the polysiloxanes in Table 2 have values of T_M (or T_g) which are lower than those of the polyacrylates.

In order to allow an easier discussion of the data in Table 2 we plotted in Fig. 2 the fragility, m_2, as a function of Δ, and in Fig. 3 the fragility, m_2, as a function of T_M, for the different side-chain liquid crystalline polymers.

From Figs. 2 and 3 we can outline the following comments:

1. Homopolymers 4 and 5 are very fragile compared with

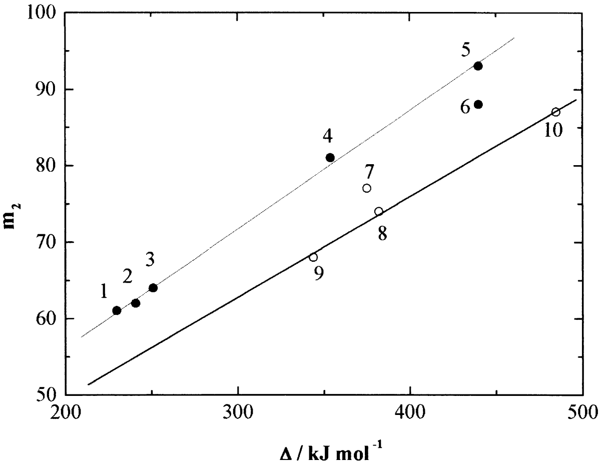

Fig. 2. Fragility, m_2, of the different side-chain liquid crystalline polymers as a function of the deviation from the zero entropy prediction, Δ. The solid lines are just guides to the eye. The family of polysiloxanes on the one hand (filled circles), and that of polyacrylates on the other hand (open circles), show different behaviours. At $m_2 = \text{const.}$, Δ is higher for polyacrylates than for polysiloxanes. At $\Delta = \text{const.}$, the fragility increases from polyacrylates to polysiloxanes.

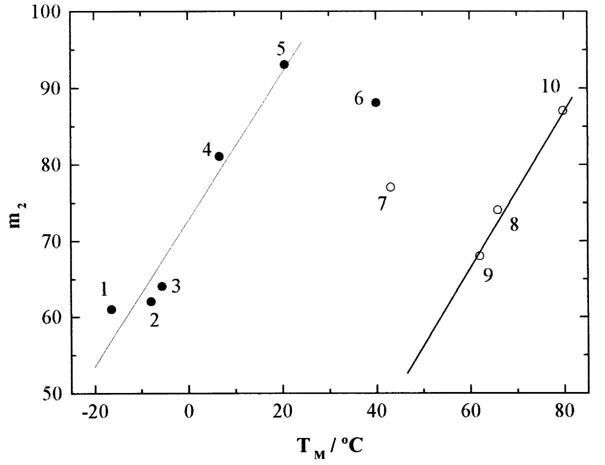

Fig. 3. Fragility, m_2, of the different side-chain liquid crystalline polymers as a function of the temperature of the maximum of the TS peak with higher intensity in the glass transition region, T_M. The solid lines are just guides to the eye. The glass transition temperature, T_g ($\approx T_M$), of the polysiloxanes (filled circles) is lower than that of polyacrylates (open circles). For a given T_M (or T_g) the fragility is higher for polysiloxanes than for polyacrylates.

the corresponding copolymers 1 and 3. Considering Eqs. (3) and (12) we can conclude that this behaviour arises from the fact that the deviation from the zero entropy prediction is stronger in homopolymers when compared with the corresponding copolymers (despite the fact that the higher T_g, or T_M, of the homopolymers would tend to decrease their fragility). The lower T_g of the copolymers is often ascribed to the higher flexibility of their backbones (compared with those of the homopolymers), which may be associated to a higher number of accessible molecular configurations, i.e. to a higher density of minima in the potential energy surface. On the other hand, as previously noted, the amplitude of the departure from the zero entropy prediction, Δ, seems to describe the height of the barriers in the potential energy landscape. In this context, a given system would show a large amplitude of the departure from the zero entropy prediction if the landscape of activation barriers is mountainous, with high peaks and deep minima, and would show a small amplitude of the departure from the zero entropy prediction if this landscape is relatively flat. We would thus say that the difference in fragility between homopolymers and copolymers is dominated by Δ rather than by T_g.

2. For a given T_g (or T_M) the fragility of polysiloxanes is higher than that of polyacrylates since the deviation from the zero entropy prediction, Δ, is higher for polysiloxanes.
3. For $m = \text{const.}$, the deviation from the zero entropy prediction, Δ, is higher for polyacrylates than for polysiloxanes. On the other hand, for $\Delta = \text{const.}$, fragility will be higher for polysiloxanes than for polyacrylates (see Fig. 2). In this context, if Δ essentially reflects the amplitude of the barriers, then we would say that the density of minima of the potential energy surface is higher in polysiloxanes than in polyacrylates.
4. Polyacrylates 9 and 10 have very different fragilities despite the fact that they have very similar chemical structures (see Table 1). In fact, the only difference is that 9 has a metoxy group at the end of the mesogenic group while 10 has a cyano group. On the other hand, 10 has 75 repeat units in the backbone while 9 has only 39 (see Ref. [25]) which is at the origin of the higher T_g of 10 (when compared to 9). It can be concluded from Figs. 2 and 3 that the higher fragility of 10 compared to 9 is dominated by Δ rather than by T_g.
5. Conversely, acrylate 9 and siloxane 4 have similar Δ but very different fragilities (in this case the difference in fragility is determined by $T_g \approx T_M$). This is also the case for polysiloxanes 5 and 6 which have, as only structural difference, the length of the spacer which links the mesogenic side group to the backbone. Polymer 6 shows a higher T_M as a consequence of its shorter spacer, and this fact determines its lower fragility (since Δ is the same for 5 and 6).

Finally, our data do not allow to detect any eventual influence of the nature of the mesophase in the fragility of the studied systems. In fact, all the studied liquid crystalline polymers are smectic above T_g, except polymers 7, 9 and 10 which are nematic (and all have an acrylate main chain). It would appear reasonable to assume that the glass formed by cooling down from a highly ordered smectic phase would exhibit little sign of fragile behavior when compared with the glass formed by cooling from a nematic phase. The discussion of this problem is difficult as many different parameters are involved (molecular weight, nature of the main chain, structural features of the mesogenic side group, length of the spacer). Even if we limit the discussion to the acrylates 7, 8, 9 and 10, we see that polymer 8, which is smectic, is more fragile than polymer 9 which is nematic. We thus conclude that our data do not allow any conclusion concerning the influence of the structure of the liquid crystalline phase on fragility.

4. Conclusions

In the present work we suggested a procedure in order to calculate the fragility parameter of a glass from data obtained by the technique of Thermally Stimulated Depolarisation Currents. The fragility of ten side-chain liquid crystalline polymers (four polyacrylates and six polysiloxanes) was then calculated and the results were discussed in terms of the molecular structure of these substances. In the family of polysiloxanes it was found that homopolymers are substantially more fragile than the corresponding copolymers despite the fact that T_g is higher for homopolymers. This arises from the fact that the amplitude of the deviation from the zero entropy prediction, which is connected with the height of the energy barriers in the potential energy landscape, is much higher in homopolymers when compared with the corresponding copolymers. It was also found that, for a given value of the amplitude of the deviation from the zero entropy prediction, Δ, the fragility is higher for polysiloxanes than for polyacrylates. This probably arises from the higher flexibility of the polysiloxane backbone (lower T_g) which probably reflects a higher density of minima in the potential energy surface, i.e. a higher number of accessible molecular configurations. The results which are available at the present moment lead us to believe that the technique of TSDC is a very useful technique in order to determine the fragility parameter of amorphous polymers and of other glass-formers.

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