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Some comments on the significance of the compensation effect observed in thermally stimulated current experiments

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In the present paper are discussed some thermodynamic aspects related with the analysis of the fine structure of the thermally stimulated depolarization currents spectrum. The physical significance of the so-called compensation law is analysed and it is suggested that the lag between the compensation temperature and the glass transition temperature is related to the breadth of the glass transition. It is also shown that the plot of $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ for the different elementary components of the global spectrum shows 'groupings' of relaxations which allow one to distinguish the different relaxation processes. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

One of the techniques widely used to study relaxation phenomena in polymeric materials is that of thermally stimulated depolarization currents (t.s.d.c.)[1–3]. The t.s.d.c. spectrum shows different discharge peaks which are often broad since they correspond to complex relaxation mechanisms, i.e. to mechanisms which are distributed in relaxation time and/or activation energy. The models used for studying relaxation processes often describe the temperature dependence of the relaxation time in terms of an activation energy and a pre-exponential factor. For processes with a single relaxation time, the position of the t.s.d.c. peak in the temperature axis is determined by a pair of values, the pre-exponential factor and the activation energy, and the same peak's position can be obtained with different pairs of such quantities. For a relaxation process distributed in relaxation time, the position of the peak will also depend on the parameters which characterize the distribution, so that the number of combinations giving rise to a given peak's position increases. It is thus very important to be able to analyse the fine structure of the t.s.d.c. global spectrum which can be done using the technique of thermal sampling (TS) (or cleaning, or windowing). In a TS experiment the polarizing field is applied in a narrow temperature range in order to allow the isolation of a group of relaxing species having a narrow distribution of activation energies and pre-exponential factors (in the limit, a TS peak can be considered to arise from a single relaxation time and a single activation energy). The TS technique allows one to decompose the broad t.s.d.c. spectrum of a relaxation into its elementary 'non-distributed' components. A TS peak is characterized by its location in the t.s.d.c. spectrum (temperature of maximum intensity, T_m) and a series of TS experiments with different polarization temperatures, T_p, gives a scanning of the distributed relaxations of the whole spectrum. From the analysis of each TS peak, the activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) of the corresponding elementary relaxation mechanisms can be calculated. There are different methods to perform such a calculation, namely Bucci's method[4], McCrum's method[5,6], Frölich's method[7], the initial rise method[2,3] and the method of temperature displacement of the TS peak as a function of the heating rate[3]. It was shown[8,9] that the Bucci and initial rise methods give the same values for the activation parameters, whereas the method of temperature displacement and that of McCrum give activation energies which are *ca* 10% higher when compared with the values obtained by the other methods. It was also shown[10] that the values of the activation energy obtained by Frölich's method agree to within a few percent with those obtained by Bucci's method. McCrum's method is probably the most accurate, but it is a very time consuming procedure since it requires an additional isothermal depolarization measurement which is difficult to measure at the beginning of the depolarization process. On the other hand, Frölich's method requires complicated fittings since the whole current peaks are fitted directly. Bucci's method is the most widely used to obtain the activation parameters of a TS peak, because of its simplicity, although variable results are sometimes found in the literature.

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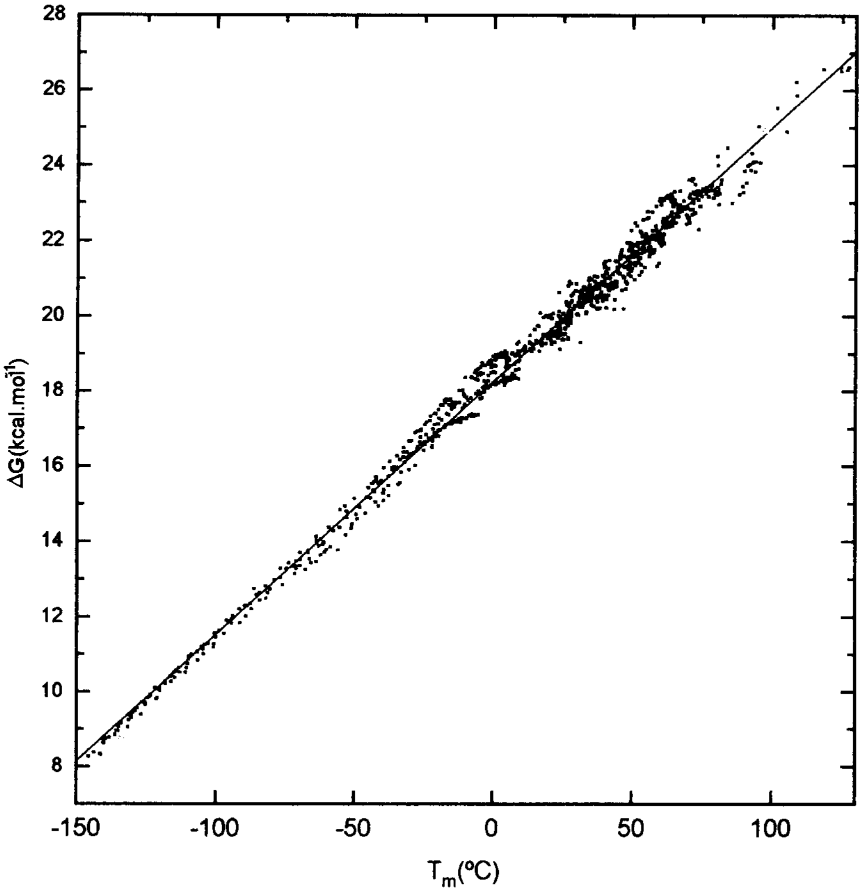

Figure 1 Gibbs activation energy, $\Delta G^{\neq}$, for thermal sampling experiments as a function of temperature. The experiments were performed in polymers with very different chemical structures and properties, including poly(vinyl acetate), poly(n-hexyl isocyanate) and a series of liquid crystalline side chain polymers

In the present work we wish to discuss some thermodynamic aspects related with the analysis of the fine structure of the t.s.d.c. spectrum. We will focus our attention on the so-called compensation law which is observed systematically in the glass transition of polymeric materials and, in this context, our aim is to contribute to the interpretation and the physical significance of the compensation behaviour.

THERMODYNAMIC ASPECTS OF THE T.S.D.C. SPECTRUM

The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ obtained by Bucci's method for each elementary component (TS peak) of the t.s.d.c. spectrum enable one to calculate the activation Gibbs energy, $\Delta G^{\neq}$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_{\rm m}\Delta S^{\neq} \qquad (1)$$

where $T_{\rm m}$ is the temperature of maximum intensity of the TS peak. On the other hand, from Eyring's rate theory the relaxation time associated with the crossing of a barrier of height $\Delta G^{\neq}$ is given by

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta G^{\neq}}{RT}\right) \qquad (2)$$

which can be arranged as

$$\Delta G^{\neq} = RT[\ln(k/h) + \ln(\tau T)] \qquad (3)$$

where h, k and R are respectively the Planck, Boltzmann and ideal gas constants. Taking into account the values of the constants, and considering that $\tau = 1/(2\pi f)$, equation (3) can be written as

$$\Delta G^{\neq}_{\rm m} = RT_{\rm m}[21.922 + \ln(T_{\rm m}/f_{\rm m})] \qquad (4)$$

for the $T_{\rm m}$, of the TS peak ($f_{\rm m}$ in equation (4) is the frequency corresponding to $T_{\rm m}$)*. It should be pointed out that for non-cooperative processes (for which $\Delta S^{\neq} \approx 0$) equation (4) gives the activation enthalpy, $\Delta H^{\neq}$, so that we can compare the plot of $\Delta H^{\neq}$ according to the $\Delta S^{\neq} = 0$ prediction with the experimental data[10,11]. This is a very helpful procedure since it gives experimenters a way to check if the values of $\Delta H^{\neq}$ (or $E_{\rm a}$) obtained for non-cooperative processes are accurate. This is the case for most relaxations observed below the glass transition temperature $T_{\rm g}$, but there are some exceptions, namely materials as polyethylene, PTFE and other related high-crystallinity fluoropolymers with localized 'cooperative' gamma relaxations[12].

If we consider now a series of TS experiments on the whole t.s.d.c. spectrum, and if we calculate the quantity $\ln(T_{\rm m}/f_{\rm m})$ for the different experiments, where $T_{\rm m}$ is the

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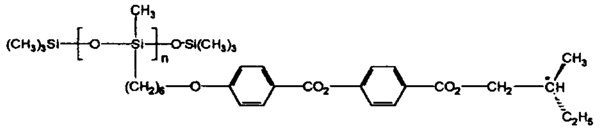
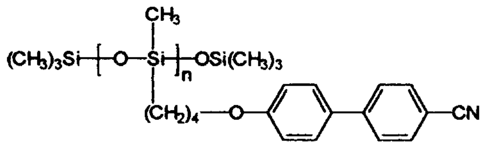
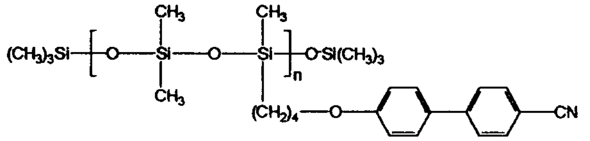
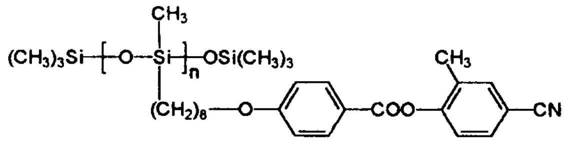
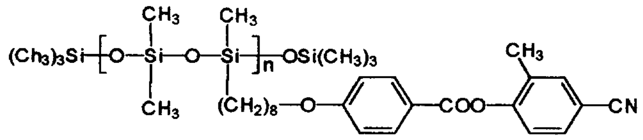
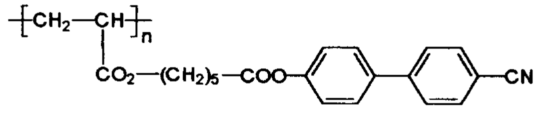
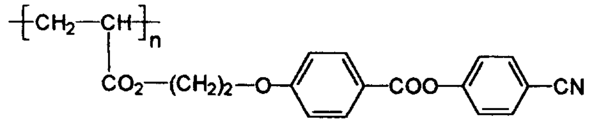
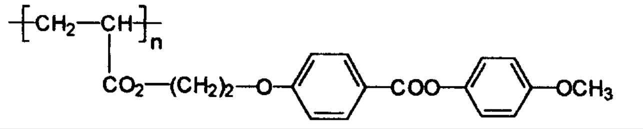
* The equivalent frequency, $f_{\rm m}$, was calculated as

$$f_{\rm m} = \frac{E_{\rm a}r}{2\pi RT_{\rm m}^2}$$

where $E_{\rm a}$ is the apparent activation energy, r the heating rate, R the ideal gas constant and $T_{\rm m}$ the temperature at which the TS peak has its maximum. Alternatively, $f_{\rm m}$ can be calculated using the Eyring equations and the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ obtained by the Bucci method for each TS experiment

Table 1 Chemical structures, glass transition temperature, T_g, and clearing temperature, T_{cl}, and compensation temperature, T_c, for the studied side-chain liquid crystalline polymers

		T_g, T_{cl} (°C)[a]	T_c (°C)
1		g − 7.2 Sc 76.8 l	−1.7
2		g 20 Sa 129 l	26.4
3		g − 3.9 Sa 79.1 l	5.2
4		g 5 Sa 95 l	10.2
5		g − 15 Sa 57 l	−8.7
6		g 38 N 127 l	48.8
7		g 75 N 111 l	83.5
8		g 61.5 N 113.4 l	70.2

[a] g: glass; S: smectic; N: nematic; l: liquid

temperature of maximum intensity of each peak and f_m its equivalent frequency*, we conclude that the calculated quantities do not present any appreciable variation from experiment to experiment and show values which are comprised in the interval 11.5 ± 0.7. This implies that the quantity between square brackets in equation (4) shows variations with T_m which are less than 2% and that the activation Gibbs energy of the different TS experiments shows a linear dependence on the temperature

$$\Delta G^{\neq} = \alpha T_m \tag{5}$$

In *Figure 1* $\Delta G^{\neq}$ values are plotted for 960 TS experiments performed on different polymers including poly(vinyl acetate)[13,14], poly(n-hexyl isocyanate)[15] and a series of side-chain liquid crystalline polysiloxanes[16–19], polycrylates[20,21] and polymethacrylates[22]. Despite the very different chemical nature of the polymers, and the very different nature of the studied relaxation mechanisms, it can be seen from *Figure 1* that there is a good linear relationship between $\Delta G^{\neq}$ and T_m, which confirms the previous discussion. This behaviour was previously observed and explained by one of us[11].

Moreover, the linear fitting of the 960 points in *Figure 1* leads to a negligible intercept ($\sim -0.15\,\mathrm{kcal\,mol^{-1}}$) and to a slope of $\alpha = 67\,\mathrm{cal\,K^{-1}\,mol^{-1}}$ which is very similar to the value of 33.4 $R = 66\,\mathrm{cal\,K^{-1}\,mol^{-1}}$ (33.4 is the value of the quantity in square brackets in equation (4)). Equation (5) is thus confirmed experimentally. We can conclude that $\Delta G^{\neq}$ is a 'universal' property which depends only on the temperature and not on the sample properties or chemical structure, nor on the relaxation process under study[11]. It is to be emphasized that this conclusion rules out the legitimacy of using a $\Delta G^{\neq}$ vs T_m plot in order to distinguish and characterize the different relaxation mechanisms in a given material. In fact, this was done by Crine[23] who suggested that such a plot for different TS peaks of a given relaxation would give access respectively to the activation entropy and to the activation enthalpy of the studied process. Our previous considerations show without any ambiguity that this pretension is not founded.

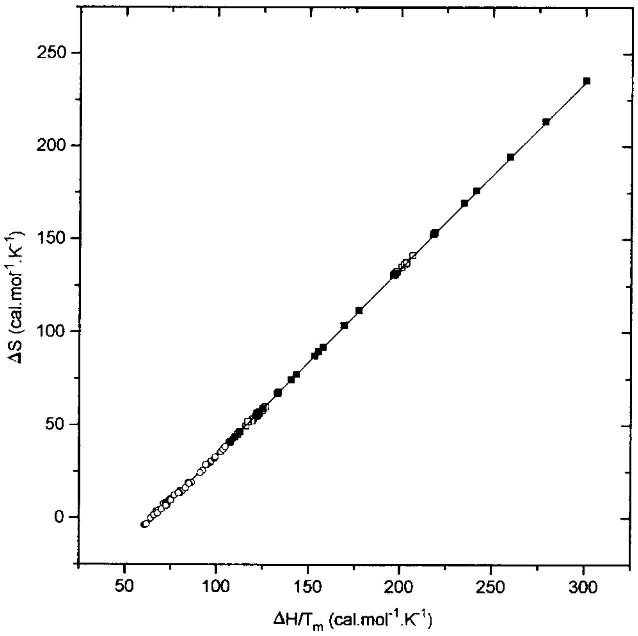


Figure 2 Plot of $\Delta S^{\neq}$ vs $\Delta H^{\neq}/T_m$ for the thermal sampling experiments performed on the different relaxation mechanisms of polymer 1 of *Table 1*. The empty circles correspond to the relaxation below T_g, the full squares correspond to the glass transition relaxation and the empty squares correspond to the relaxation observed above T_g

From equations (1) and (5) we have

$$\Delta S^{\neq} = \frac{\Delta H^{\neq}}{T_m} - \alpha \qquad (6)$$

which indicates that it must exist a linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}/T_m$ (with slope equal to unity and intercept equal to $-\alpha = -67\,\mathrm{cal\,K^{-1}\,mol^{-1}}$) valid for all relaxations in all materials. This relationship is shown in *Figure 2* for a particular side-chain liquid crystalline polysiloxane studied before[16,24] (polymer 1 in *Table 1*). The points in *Figure 2* correspond to all the relaxations observed in the t.s.d.c. spectrum of this polymer, including the glass transition relaxation (full squares), the relaxations below T_g (open circles), as well as the relaxations observed above T_g (open squares).

It is clear from *Figure 2* that the points corresponding to different relaxation processes fall in the same straight line (which has a slope equal to unity and an intercept equal to $-\alpha = -33.4R$, in agreement with equation (6)). From equation (6) and from *Figure 2* it follows that the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ associated with the TS peaks are not independent variables but that, on the contrary, the variations of these two parameters are mutually connected.

COMPENSATION BEHAVIOUR

Many thermally stimulated processes obey the so-called compensation law which is a linear relationship between the logarithm of the pre-exponential factor of the Arrhenius equation and the apparent activation energy[25,26]. In terms of the Eyring equation of the rate theory the compensation law can be described as a linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$[23,27,28]. Such an experimental compensation behaviour, which has been evidenced in many different fields of biology, biochemistry and physics, has been the object of debate during many years. In fact, this behaviour can be purely artefactual, the linear dependence of entropy vs enthalpy being a consequence of a statistic compensation pattern that arises solely from experimental errors[29–32]. On the other hand, the compensation behaviour may in many cases reveal a real physical behaviour and this seems to be the case for some relaxation mechanisms in polymeric materials studied by thermally stimulated techniques (dielectric and mechanical). In fact, McCrum *et al.*[33] validated the compensation rule showing that it was in good agreement with theoretical predictions. The compensation behaviour was observed for the glass transition relaxation of many polymeric materials but it was also claimed that this behaviour was characteristic of some sub-glass transition relaxations.

For a process with a single relaxation time the temperature dependence of τ can be described by the Arrhenius equation

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right) \qquad (7)$$

where τ_0 is the pre-exponential factor and E_a the apparent activation energy. If the compensation behaviour is observed, there is a concomitant increase of τ_0 and E_a so that the Arrhenius lines converge to a single point of coordinates τ_c and T_c such that

$$\tau_0 = \tau_c \exp\left(-\frac{E_a}{kT_c}\right) \qquad (8)$$

Substitution of equation (8) into equation (7) gives

$$\tau_0 = \tau_c \exp\left[\frac{E_a}{k}\left(\frac{1}{T} - \frac{1}{T_c}\right)\right] \qquad (9)$$

which is the well-known compensation equation, which can also be written as

$$\tau = \tau_0 \exp\left[\frac{T_c}{T}\ln\left(\frac{\tau_c}{\tau_0}\right)\right] \qquad (10)$$

On the other hand, according to the Eyring equation

$$\tau = \frac{h}{kT}\exp\left(-\frac{\Delta S^{\neq}}{k}\right)\exp\left(\frac{\Delta H^{\neq}}{kT}\right) \qquad (11)$$

where $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are respectively the entropy and the enthalpy of activation. The pre-exponential factor in the Arrhenius equation (7) is directly related to the activation entropy. For a process with a single relaxation time, the representation of $\ln(\tau T)$ vs $1/T$ (the so-called Eyring plot) gives a straight line whose slope is related to $\Delta H^{\neq}$ and whose intercept is related to $\Delta S^{\neq}$. If the compensation behaviour is observed, the Eyring lines of the different TS experiments will converge to the compensation point. As the temperature of the TS experiments increases, the activation enthalpy and the activation entropy increase concomitantly and the temperature of the compensation point, T_c, is the slope of the plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$. The physical significance of the compensation point and of the compensation behaviour is far from being elucidated. Some authors consider that all relaxation processes obey a compensation law[28], but this seems not to be the case since many relaxation processes studied by t.s.d.c. and by thermally stimulated creep (TSC) do not present any compensation behaviour. The compensation behaviour in polymeric

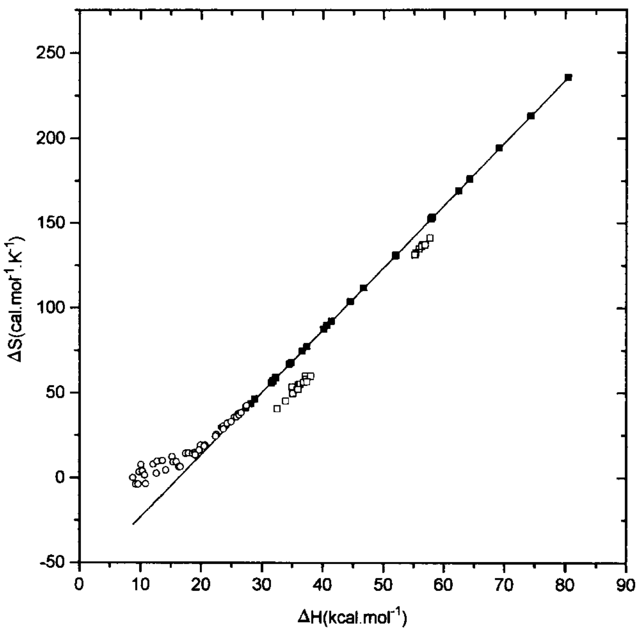


Figure 3 Plot of $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ for the thermal sampling experiments performed on the different relaxation mechanisms of polymer 1 of *Table 1*. The significance of the symbols are the same as in *Figure 2*

materials is often considered as indicative of cooperative molecular movements[25,26] and has been ascribed to the relaxations of entities with variable length[34]. The enthalpy distribution displays, in this context, motions which are hierarchically correlated with a disperse spectrum of movements. The maximum of the activation enthalpy was considered to be related to the amplitude of the molecular motions[25] which is probably not correct since the amplitude of motions is even higher above T_g, even if the activation energy decreases. On the other hand, it was suggested[9] that the compensation behaviour would be originated by a transfer of information between the two activation parameters due to some kind of thermal mechanism. This would be in agreement with the idea according to which the compensation law exists if the system contains elements moving with different energy barriers and coupled to a thermal bath with the same coupling function[35]. An effort to understand compensation behaviour was also developed[36–38] on the basis of Ngai *et al.*'s coupling model[39].

In order to analyse the compensation behaviour in polymer 1 of *Table 1*, whose results were presented in *Figure 2*, we transformed this figure in a $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ plot, which is shown in *Figure 3*. We must point out that from the study of this side-chain liquid crystalline polysiloxane[16,24] we observed four different relaxations in the t.s.d.c. spectrum: the glass transition relaxation, a relaxation in the vitreous state (below T_g) and two well separated relaxations above the T_g. It can be observed from *Figure 3* that not all the points fall in the same straight line, as was the case for *Figure 2*. In fact, there is a set of points (which correspond to TS experiments with polarization temperatures between $T_p = 254\,K$ and $T_p = 268\,K$, i.e. in the glass transition region) which define a straight line in the $\Delta S^{\neq}/\Delta H^{\neq}$ plane (full squares). For these experiments a larger increase of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is observed with increasing T_p, which means that they obey a compensation law. From the slope of this straight line we obtain $T_c = 272\,K$ which is slightly higher when compared with the T_g obtained by differential scanning calorimetry (d.s.c.), $T_g = 266\,K$, and with the temperature of maximum intensity of the glass transition t.s.d.c. global peak, 265 K. From *Figure 3* we can also observe that there are three sets of points which do not fall in the compensation line of the glass transition relaxation. It is to be noted that the observation of 'groupings' of relaxations in the $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ plot has been previously reported[11]. The points on the left hand side of the figure (represented by open circles) correspond to the TS experiments in the vitreous state (below T_g) and do not show any compensation behaviour; the two sets of points situated in the right hand

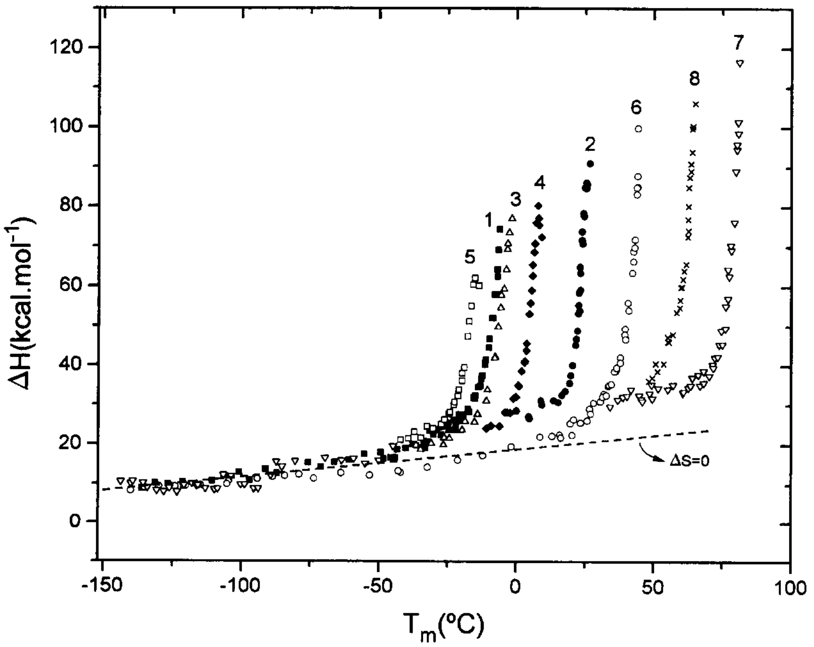


Figure 4 Representation of $\Delta H^{\neq}$ vs T_m for the thermal sampling experiments performed on the side chain liquid crystalline polymers shown in *Table 1*. The experiments were performed in the glass and sub-glass regions. The dashed straight line corresponds to the $\Delta S^{\neq} = 0$ prediction

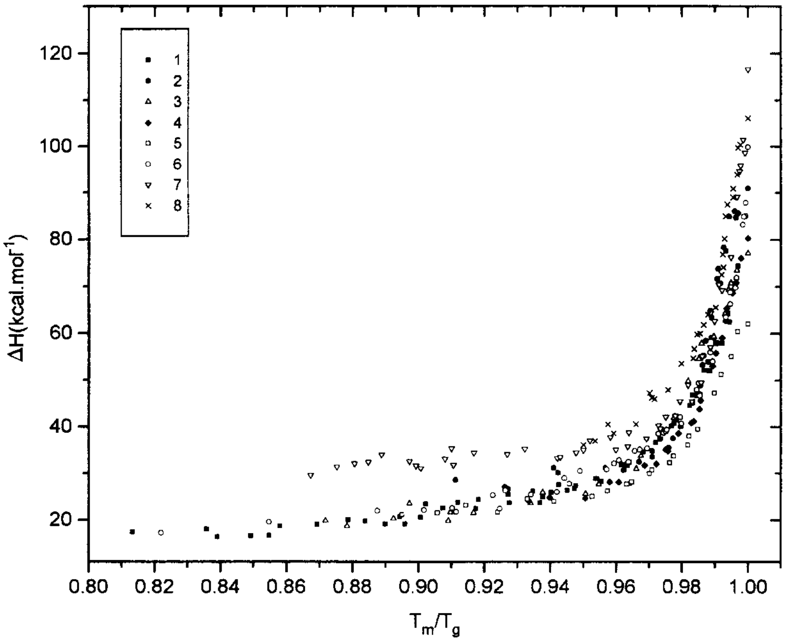


Figure 5 Representation of ΔH vs T_m/T_g for the same data shown in *Figure 4*. The plot shows that the shape of the curves in the glass transition region is similar despite the different chemical nature of the studied polymers

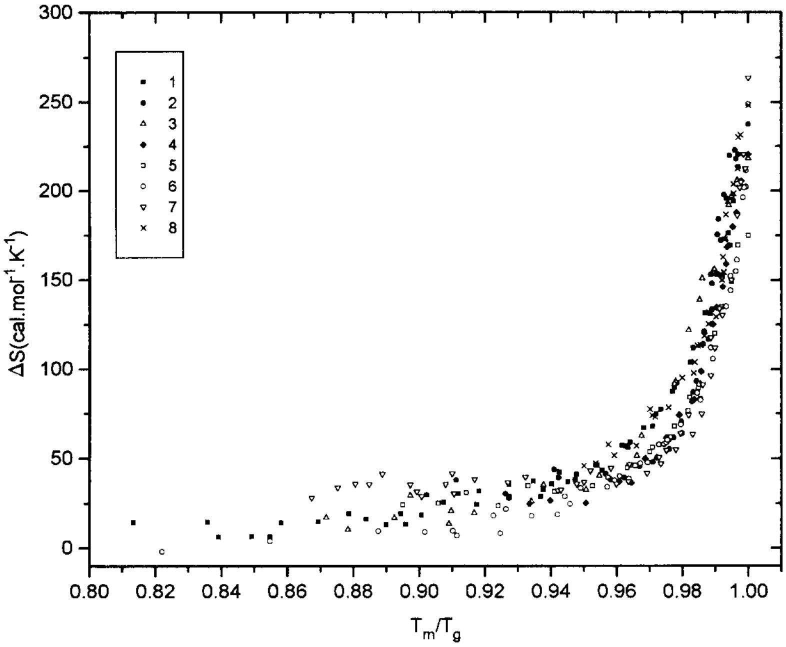


Figure 6 Representation of $\Delta S^{\neq}$ vs T_m/T_g for the polymers presented in *Table 1*. As in *Figure 5* it is apparent that the shape of the curves in the glass transition region is similar despite the different chemical nature of the studied polymers

side of the compensation line (open squares) correspond to the two relaxations observed above T_g and they also do not show any compensation behaviour. In fact, the variations of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ associated with these relaxations are very small and the increase of those parameters is not concomitant with the increase of T_p. We can conclude from those results that the glass transition relaxation of this polymer shows a clear compensation behaviour whereas the other relaxation processes do not obey any clear compensation law. This conclusion was also obtained from the t.s.d.c. study of other polymers[14–22,40]. It was previously shown that there exists a unique linear relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}/T_m$, which is observed for all materials and all relaxation processes (see *Figure 2*). From this fact it follows that, in order to characterize the compensation behaviour of a given relaxation it is sufficient to know the temperature dependence of one of the activation parameters, $\Delta H^{\neq}$ or $\Delta S^{\neq}$. *Figure 4* shows the representation of $\Delta H^{\neq}$ as a function of T_m for TS experiments performed in the region of the glass transition for different side-chain liquid crystalline polymers with very different chemical structures (siloxanes and acrylates, homopolymers and copolymers). The chemical structures of these polymers, as well as some relevant properties, are shown in *Table 1*.

The strong increase in $\Delta H^{\neq}$ observed for all these polymers is the manifestation of the compensation behaviour, and is associated with the liberation of the motions which occurs at the glass transition. In rare cases compensation was observed in pseudo 'cooperative' relaxations such as the gamma relaxation in polyethylene, PTFE and related materials. In fact these relaxations show compensation because of the increase in $\Delta H^{\neq}$ and they are believed to be cooperative since they present $\Delta H^{\neq}$ values which are high relative to the $\Delta S^{\neq} = 0$ prediction. It is to be noted that the sequence of the curves in *Figure 4*, from left to right in the temperature axis, is that of increasing T_g (see *Table 1*). It is also to be noted that the maximum activation enthalpy reached for each polymer seems to increase with increasing T_g[*]. On the other hand, the shape of the different curves seems to be very similar. This is confirmed in *Figure 5* where the results shown in *Figure 4* were plotted using the abscissa variable in a reduced form (T_m/T_g). *Figure 6* shows a similar plot for the activation entropy. In fact, from *Figures 5* and *6* it can be seen that the different curves present small shape differences, despite the facts that the studied polymers are very different from a chemical point of view and that their main chains have very different degrees of mobility. This behaviour shows how difficult it is to try to characterize the glass transition relaxation using parameters such as its 'broadness' or 'sharpness'.

THE COMPENSATION TEMPERATURE

It seems unquestionable that the glass transition relaxation of polymeric materials displays a compensation behaviour when studied by thermally stimulated techniques and particularly by the t.s.d.c. technique. A consequence of the compensation behaviour is the existence of a compensation point of coordinates (τ_c, T_c) which is the point of convergence of the Arrhenius (or Eyring) lines of the TS experiments performed in the compensation region. As pointed out before, the physical significance of the compensation point is not yet elucidated. Some authors believe that T_c is the temperature at which all relaxations involved in the process occur with the same relaxation time, τ_c[25]. Nevertheless, this suggestion was refuted by Read[41] on the basis of experimental evidence. The T_g can be determined by the t.s.d.c. technique considering that it corresponds to the temperature of maximum intensity of the glass transition global peak or, alternatively, considering that it corresponds to the location, in the temperature axis (T_m), of the TS peak which shows a maximum activation enthalpy[42]. These two ways of defining T_g lead to similar values (it should be recalled that the location of the different peaks in the t.s.d.c. spectrum depends on the heating rate used in the experiments). The compensation temperature, T_c, obtained from the experimental data is generally a few degrees above T_g[14,17,19,21,26] and the lag $T_c - T_g$ was attributed to kinetic effects and is believed to depend on the stiffness of the polymeric chains[26]. This lag would thus be absent in transitions where no kinetic effects are present. *Figure 7* shows the plot of the difference $T_c - T_g$ as a function of T_g for the polymers presented in *Table 1*. It can be seen from the figure that the relation between the lag $T_c - T_g$ and the stiffness of the chains is not obvious, at least in this family of polymers. The fact that the $T_c - T_g$ values shown in *Figure 7* are similar means that the shape of the glass transitions of the studied polymers are the same as shown in *Figures 5* and *6*. We can thus say that the rate at which $\Delta H^{\neq}$ increases as one approaches T_g from the low temperature side governs the difference $T_c - T_g$ which is thus related to the breadth of the glass transition.

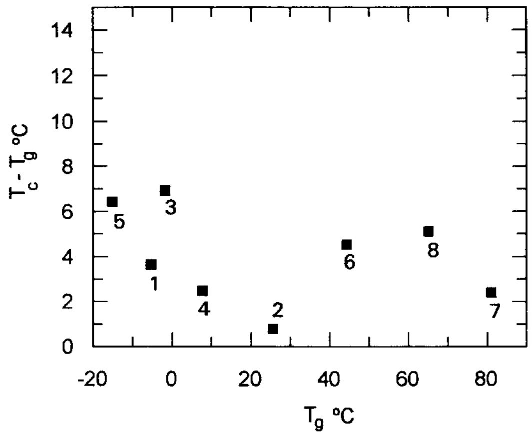


Figure 7 Difference $T_c - T_g$ between the compensation temperature and the T_g as a function of T_g. The figures correspond to those of *Table 1* and the T_g values were taken as the location of the TS peak for which the activation enthalpy is maximum

On the other hand, some authors[33,43] consider that T_c is related to the reciprocal of the jump of the isobaric thermal expansion coefficient, $\Delta\alpha$, across the glass transition. However it was pointed out[44] that this assignment may be fortuitous since $\Delta\alpha . T_g$ is roughly constant irrespective of the nature of the polymer. It has also been proposed[45,46] that the glass transition in polymeric materials was characterized by the so-called Z-structure, originating two compensation points, one with $T_c > T_g$ (positive compensation) and the other with $T_c < T_g$ (negative compensation). Since $\Delta H^{\neq}$ increases to a maximum when the temperature increases approaching T_g, a decrease of the activation energy with increasing temperature is expected just above T_g. The negative compensation point seems thus to be a consequence of this natural decrease of the activation energy, so that we do not attribute any real physical significance to this 'negative compensation point'.

The fact that T_c shows values which are higher than T_g, can be understood looking at *Figure 8* and recalling that the slope of $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ plot (the compensation line) is $1/T_c$. In fact, on the left hand side of *Figure 7* is presented a set of eleven points in a representation of $\Delta S^{\neq}$ vs $\Delta H^{\neq}/T_m$.

These points are abstractly believed to belong to a compensation line, and we will suppose that the point in the left hand side (the point with lower $\Delta H^{\neq}/T_m$ and $\Delta S^{\neq}$ in the compensation line) corresponds to a TS peak located at T_{m_1} whereas the opposite point (higher

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[*] As previously stated, the belief of some authors[25] that the maximum activation enthalpy is related to the amplitude of the motions is probably not founded, since the amplitude of the motions must be higher above T_g, and then the activation energy should be even higher for the melt above T_g, which is not observed. Another possibility is to take the view of Adam and Gibbs and to consider that the large size of the cooperatively moving units is at the origin of the large activation energy

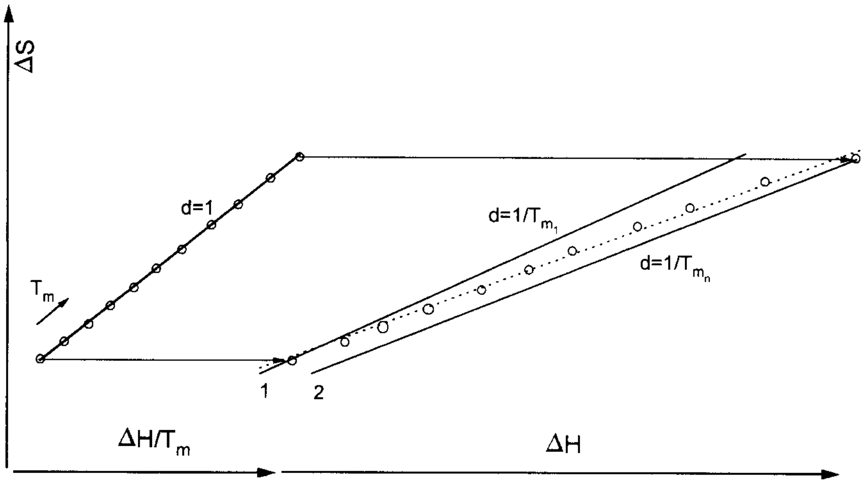

Figure 8 Representation showing that the slope of the compensation line (dotted line), $1/T_c$, should be lower than the slope of both curves 1 and 2

$\Delta H^{\neq}/T_m$ and $\Delta S^{\neq}$), which is the point in the compensation set which shows a maximum activation enthalpy, corresponds to a TS peak located at T_{m_n} (we thus have $T_{m_l} < T_{m_n} \approx T_g$). On the other hand, it must be recalled that the slope of such a representationshould be equal to unity ($d = 1$), as indicated on *Figure 8*. On the right hand side of this figure is presented the plot of $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ for the same points shown on the left. In order to go from one representation (on the left) to the other (on the right) we need to multiply by T_m the abscissa of each point. Line 1 was obtained by multiplying the abscissa of all points by the same value T_{m_l}, and its slope is thus $1/T_{m_l}$. Line 2, on the other hand, was obtained by multiplying the abscissa for all points by the same value, T_{m_n}, and its slope is thus $1/T_{m_n}$. Since the location of the TS peaks increases from T_{m_l} until T_{m_n}, the real compensation line (dotted line), whose slope is $1/T_c$, will be obtained by the linear regression of the points which lie between lines 1 and 2. Since $T_{m_n} = T_g$, it comes out from *Figure 8* that the slope of the compensation line, $1/T_c$, must be smaller than $1/T_g$ and thus that $T_c > T_g$.

On the other hand, it can be shown that

$$T_c - T_g = \frac{\Delta H^{\neq}_{m_n}}{\Delta H^{\neq}_{m_l}} \left(\frac{T_c}{T_{m_l}} - 1 \right) T_g \qquad (12)$$

where $\Delta H^{\neq}_{m_n}$ and $\Delta H^{\neq}_{m_l}$ are respectively the activation enthalpies of the TS experiments located at $T_{m_n} = T_g$ and T_{m_l}. Since T_{m_l} is the temperature location of the TS experiment with lower activation enthalpy in the compensation region, the quantity T_c/T_{m_l} in equation (12) can be considered as a measure of the width of the glass transition region (the temperature range in which the compensation occurs). The quantity $\Delta H^{\neq}_{m_n}/\Delta H^{\neq}_{m_l}$, on the other hand, it proportional to the amplitude of the glass transition region (i.e. the extent of the increase of the activation enthalpy in the compensation region). We can thus predict that the lag $T_c - T_g$ will increase with increasing width and amplitude (as previously defined) of the glass transition region. These conclusions should allow, at first sight, use of the quantity $T_c - T_g$ in order to characterize the glass transition relaxation of different polymers. Nevertheless the values of this quantity and of its variations are small and, as emphasized before, it is not easy to interpret those values in terms of the molecular characteristics of the polymeric chains.

CONCLUSIONS

Compensation behaviour is a feature of cooperative relaxations including glass transitions in polymeric materials, but it is not characteristic of many relaxations observed above and below T_g. Compensation is a result of the sharp increase of $\Delta H^{\neq}$ as one approaches T_g from the low temperature side (which is equivalent to a concomitant increase of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with increasing temperature) and it is characterized by a compensation point. It was demonstrated that the compensation temperature, T_c, also called the isokinetic temperature, must be higher than the glass transition temperature, T_g. On the other hand, it was shown that it was difficult to establish clear relations between the quantity $T_c - T_g$ or its variations and the molecular structure of the polymers or the phenomenological characteristics of the glass transition (broadness, amplitude). Nevertheless, it was suggested that the difference $T_c - T_g$ was related to the breadth of the glass transition.

As a consequence of the general proportionality between the Gibbs activation energy of the elementary components of the t.s.d.c. spectrum (the thermally sampled components) and the temperature, a linear relationship exists between $\Delta S^{\neq}$ and $\Delta H^{\neq}/T_m$. This linear relationship, which is valid for all thermally sampled components of the t.s.d.c. spectrum, is the same for all materials and relaxation processes, and has a slope equal to the unity and an intercept of $-67\,\mathrm{cal\,K^{-1}\,mol^{-1}}$. On the other hand, the plot of $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ shows 'groupings' of relaxations. From the results obtained on a particular liquid crystalline polymer it was shown that the elementary components of the t.s.d.c. spectrum lead to groups of points in the $\Delta S^{\neq}/\Delta H^{\neq}$ plot, each group corresponding to a different relaxation process.

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