

# Compensation Effect Observed in Thermally Stimulated Depolarization Currents Analysis of Polymers

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**ABSTRACT:** Thermally stimulated depolarization currents (TSDC) and differential scanning calorimetry (DSC) are performed on thermoplastic polyesters and dimethacrylate resins over temperature ranges covering the  $\alpha$  and  $\beta$  relaxation regions. The noncooperative  $\beta$  relaxation is characterized by a continuous variation of activation energies as a function of temperature and follows the activated states equation with a zero activation entropy. The cooperative  $\alpha$  relaxation shows a prominent maximum of the activation energies at the glass transition temperature. Compensation behavior is often observed by TSDC for many polymers in the glass transition temperature range. We show that this behavior is not systematic and that it appears for the  $\alpha$  relaxation if the increase of the apparent activation enthalpy is strong and if the width of the glass transition is weak. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2716–2723, 1999

**Key words:** compensation; thermally stimulated depolarization currents; glass transition; polyester; dimethacrylate

## INTRODUCTION

Analysis of thermally stimulated depolarization currents (TSDC) has been frequently employed since Van Turnhout's pioneer works<sup>1</sup> to investigate the molecular motions in polymeric materials.<sup>2–4</sup> The high interest of TSDC results is due in part to the low equivalent frequency of about  $10^{-3}$  Hz<sup>2</sup> and to its capability to resolve complex dielectric transitions into narrow distributions of relaxations.<sup>4</sup> Moreover, the high sensitivity makes TSDC quite useful for the study of main and secondary relaxations in amorphous or semicrystalline polymers. The  $\alpha$  and  $\beta$  relaxation transitions are known to be typical of all polymers<sup>5</sup>; the  $\alpha$  relaxation characterizes the liquid to the glassy

state transition upon cooling (glass transition) while the  $\beta$  relaxation is also an universal phenomenon and constitutes a local or a short scale process. In the Arrhenius diagram  $\ln \tau$  vs  $1/T$ , the compensation behavior is observed quasisystematically in the glass transition of polymeric materials by the convergence of the straight lines to a single point called compensation point of coordinates  $(1/T_c, \ln \tau_c)$ .<sup>6</sup> During the last three decades, the physical significance of the compensation point has not been well elucidated.<sup>7</sup> Some authors believe a compensation point is indicative of cooperative molecular movements and that  $T_c$  is the temperature at which all the relaxations involved in the process occur with the same relaxation time  $\tau_c$ .<sup>4,8</sup> On the contrary, Read<sup>9</sup> has refuted the idea of this unique relaxation at  $T_c$ . Indeed, the conformational entropy theories of relaxations in the equilibrium state above  $T_g$ <sup>10</sup> suggest that the cooperatively moving unit is largest at  $T_g$  and

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smaller at higher temperatures because more configurations are available. In a recent work,<sup>7</sup> Sauer and Moura Ramos have shown that compensation of liquid crystalline polymers is a natural result of the sharp increase of the activation energy as one approaches  $T_g$  from the low-temperature side, and not its cause. In this work, we propose TSDC analysis on various polymers: (1) amorphous thermoplastic polyesters as poly(ethylene terephthalate) (PET), poly(cyclohexane 1,4-dimethylene terephthalate) (PCT), poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETG), and poly(ethylene naphthalene 2,6-dicarboxylate) (PEN); (2) semicrystalline polyesters as poly(cyclohexane 1,4-dimethylene terephthalate) (PBT), and semicrystalline PET and PEN; and finally (c) photo-initiated polymerized dimethacrylate resins with two degrees of conversion. These results contribute to the interpretation of the physical significance of compensation behavior.

## EXPERIMENTAL

### Materials

Samples are about 0.5 mm thick with areas of 150 mm<sup>2</sup> for TSDC. Before experiments, samples are stored under vacuum in the presence of P<sub>2</sub>O<sub>5</sub> for two weeks at 20°C in order to avoid moisture sorption.

PET films with a number average molecular weight  $\overline{M}_n$  of 31,000 g/mole are isotropic and amorphous judging from birefringence, density, and x-ray diffraction measurements. The crystallinity rate of PET is low and an amorphous material can be obtained by rapid quenching from the melt while an annealing above the glass transition temperature induced cold thermal crystallization. So, a semicrystalline film (scPET) is obtained by an annealing at 133°C for 1 h and consists of semicrystalline spherulites. Its degree of crystallinity  $X_c = 26\%$  is determined by differential scanning calorimetry (DSC) from the melting enthalpy and using the calculated melting enthalpy of a wholly crystalline PET ( $\Delta H^{\circ}f = 140$  J/g; ref. 11). PEN (from Amoco Co.) is used, as PET, under an amorphous form (PEN) and under a semicrystalline form (scPEN) obtained by annealing the films at 183°C for 1 h. The degree of crystallinity  $X_c = 35\%$  is calculated, as scPET, from the melting enthalpy ( $\Delta H^{\circ}f = 103$  J/g; ref. 12). PCT (Thermx 11440 from Tennessee East-

man Co.,  $\overline{M}_n = 25,000$  g/mole) is used in the amorphous form. PETG (6763 from Tennessee Eastman Co.) is an amorphous copolymer with  $\overline{M}_n \cong 26000$  g/mole. It consists in cyclohexane dimethanol, ethylene glycol, and terephthalic acid with a molar ratio of approximately 1 : 2 : 3. So, PETG is a statistical copolymer composed of 67% PET and 33% PCT. PBT (Celanex 2500 from Hoechst Co.) is a semicrystalline polyester with a degree of crystallinity obtained by DSC  $X_c = 32\%$  ( $\Delta H^{\circ}f = 142$  J/g).<sup>13</sup> The dimethacrylate mixture was prepared few days before thermal analysis. The photoinitiator 2,2-dimethyl 2-hydroxyacetophenone (Darocure 1173) is dissolved at the concentration 0.5% (w/w) in the dimethacrylate oligomer (Akzo) under stirring at room temperature for 3 h. Just before thermal analysis, the mixture is laid down over the bottom of an aluminium photocalorimeter pan. The samples are obtained by photoinitiated polymerization inside a photocalorimeter to manage the polymerization reaction. The photocalorimeter used is a DSC 7 Perkin Elmer topped by an irradiation unit with two quartz windows. The optical part of the calorimeter includes the following elements: a light source (Hg vapor lamp 100 W), a filter remaining IR radiations, neutral filters to modulate the light intensity, and an electric shutter to control the irradiation period. The samples are irradiated at 50°C for 3 min always under inert atmosphere and with different light intensity of the UV radiation to obtain samples of different conversion value.<sup>14</sup> By this method, two samples (called DM52 and DM75) are obtained with values of conversion equal to 52 and 75%.

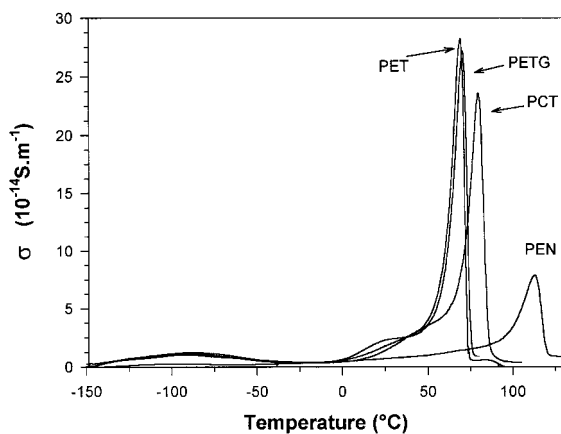
### Methods

TSDC measurements are performed with an apparatus developed in our laboratory.<sup>15,16</sup> The sample is submitted to an electric field ( $E = 10^6$  V · m<sup>-1</sup>) for a period  $t_p$  (2 min) at a polarization temperature  $T_p$  just above its glass transition  $T_g$ . This period is sufficient to orientate all dipoles in the materials. Then, this new material configuration is frozen in by decreasing the temperature down to -150°C at a constant cooling rate (10°C · min<sup>-1</sup>). At this temperature, the electric field is cut off and a short circuit is set up. The increase of temperature (at a constant rate  $r = 10^\circ\text{C} \cdot \text{min}^{-1}$ ) allows gradual relaxation of the different polarized units which results in a depolarization current  $I$  (complex spectrum). The conductivity  $\sigma$  (in Siemens per meter) is used as a normalized

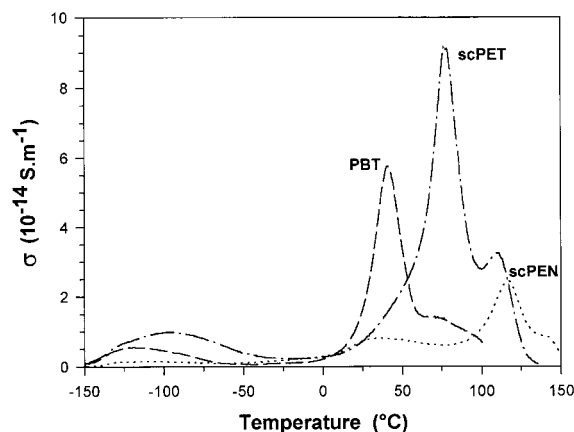
quantity instead of  $I$  ( $\sigma = I/E \cdot S$ , where  $S$  is the surface of the sample). Using this method, the complex spectra  $\sigma = f(T)$  are obtained and consist in several peaks.

Elementary TSDC spectra are obtained by means of the fractional polarization method, which allows the selection of a small range of relaxing elements for each spectrum. The sample is submitted to the same field for 2 min at a temperature  $T_p'$ . The temperature is then lowered to  $T_d = T_p' - \Delta T$  (generally  $\Delta T = 5^\circ\text{C}$ ) and a short circuit is performed during 2 min. Under these conditions, mobile dipolar units with relaxation times greater than 2 min at  $T_p'$  are not orientated by the electric field while those with relaxation times shorter than 2 min at  $T_d$  are randomized by the short circuit. The sample is finally cooled (in short circuit) to  $T_o = T_p' - 40^\circ\text{C}$ , and then the depolarization current is measured while reheating ( $r = 10^\circ\text{C} \cdot \text{min}^{-1}$ ) up to  $T_p'$ . The same procedure, performed with increasing polarization temperature  $T_p'$  allows exploration of all the transitions.

Enthalpic analysis are performed with the help of a Perkin Elmer DSC7 apparatus. Calibration is achieved from the indium and zinc temperature and melting enthalpy determination. Calorimetric measurements are made under nitrogen ambiance with a heating rate of  $10^\circ\text{C} \cdot \text{min}^{-1}$  and the DSC curves are normalized to 1 g of matter. Finally, to compare complex TSDC and DSC data in the best conditions, the same annealing treatment at  $T = T_p'$  are performed on the samples. The reported DSC curves show the variations, vs temperature  $T$ , of the heat flow proportional to



**Figure 1** Complex TSDC spectra ( $E = 10^6$  V/m,  $T_p$  just above  $T_g$ ,  $T_d = -150^\circ\text{C}$ ,  $r = 10^\circ\text{C}/\text{min}$ ) for the amorphous polyesters.



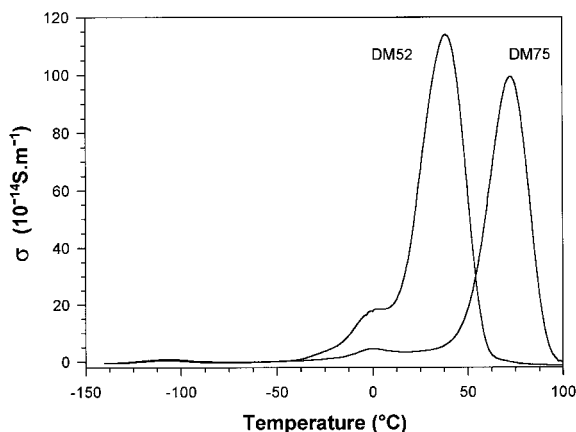
**Figure 2** Complex TSDC spectra ( $E = 10^6$  V/m,  $T_p$  just above  $T_g$ ,  $T_d = -150^\circ\text{C}$ ,  $r = 10^\circ\text{C}/\text{min}$ ) for the semicrystalline polyesters.

$C_{p_s}(T) - C_{p_r}(T)$  where  $C_{p_s}(T)$  is the heat capacity of the sample and  $C_{p_r}(T)$  is the heat capacity of the reference.

## RESULTS

The complex TSDC spectra of amorphous polyesters (Fig.1), semicrystalline polyesters (Fig. 2), and dimethacrylate resins (Fig. 3) show between  $-150$  and  $+150^\circ\text{C}$  several currents maxima. For the different thermoplastic materials, the respective DSC curves are displayed in Figure 4 for the glass transition temperature range, and the different thermal data are reported in Table I. Below the glass transition temperature, no thermal phenomena is observable. For sake of clarity, the different curves are shifted vertically. DSC analysis of photopolymerized resins does not gives significant deviation of the baseline. Only an ageing allows the location of the glass transition.

In the  $-150-0^\circ\text{C}$  region, one can observe in TSDC spectra the secondary  $\beta$  relaxation peaks of the polymers, which have low values of the current, while in the  $+20$  to  $+150^\circ\text{C}$  range, the main  $\alpha$  peaks and other currents maxima appear. For dimethacrylate resins, a secondary current maximum called  $\alpha'$  peak appears close to  $-10^\circ\text{C}$ . The shape of the  $\beta$  relaxation peaks are very close for PET, PETG, and PCT. The  $\beta$  relaxation peaks appear with a temperature  $T_\beta$  at the maxima close to  $-92^\circ\text{C}$  for these polyesters, close to  $-105^\circ\text{C}$  for resins and at  $-120^\circ\text{C}$  for PBT. The main transition, characterized by the  $\alpha$  peak, is clearly observed on the different TSDC complex



**Figure 3** Complex TSDC spectra ( $E = 10^6$  V/m,  $T_p$  just above  $T_g$ ,  $T_d = -150^\circ\text{C}$ ,  $r = 10^\circ\text{C}/\text{min}$ ) for dimethacrylates.

spectra. For semicrystalline polyesters, an extra peak is observed at a temperature higher than  $T_p$ . This transition attributed to space charges<sup>1</sup> is not discussed here. By DSC, a change of the heat capacity called  $\Delta C_p$  indicates the glass transition. It appears that the temperature  $T_\alpha$  at the maximum of the TSDC relaxation peaks is close to that observed by DSC measurements for the onset of the glass transition temperature. It is possible to compare the width at half maximum  $\Delta T_{1/2}$  of the TSDC  $\alpha$  peaks with the width of the DSC glass transition zone, which is characterized by  $\Delta T_g = T_{g\text{ high}} - T_{g\text{ low}}$ , where  $T_{g\text{ low}}$  is the temperature that corresponds to the beginning of the glass transition phenomena and  $T_{g\text{ high}}$  is the temperature at which the glass transition phenomena is finished (these values are determined graphically). It appears that  $\Delta T_{1/2}$  and  $\Delta T_g$ , which characterize the heterogeneity of the amorphous phase, are very close to  $10^\circ\text{C}$  for amorphous polyester except for PEN ( $\Delta T_g = 15^\circ\text{C}$ ), and vary in the same way. The value of  $\Delta T_g$  increases for semicrystalline samples (from  $17^\circ\text{C}$  for PBT to  $22^\circ\text{C}$  for scPEN) due to the increase of  $T_{g\text{ high}}$  of approximately  $7^\circ\text{C}$ . For resins,  $\Delta T_{1/2}$  is close to  $27^\circ\text{C}$ , which is indicative of an important heterogeneity of the amorphous phase. From DSC investigations performed in the glass transition range, it is very interesting to determine the value of the fictive temperature  $T_f$  as defined by Tool.<sup>17</sup> When the samples are analyzed immediately after cooling (without aging), the temperature  $T_f$  is very close to the fictive equilibrium temperature  $T_f$ , which can be regarded as the "ideal" glass transition temperature. This is the temperature that separates the

glassy and the liquid states.<sup>6</sup> According to the method proposed by Moynihan<sup>18</sup> and largely described elsewhere,<sup>6,16</sup> the values of  $T_f$  are reported in Table I.

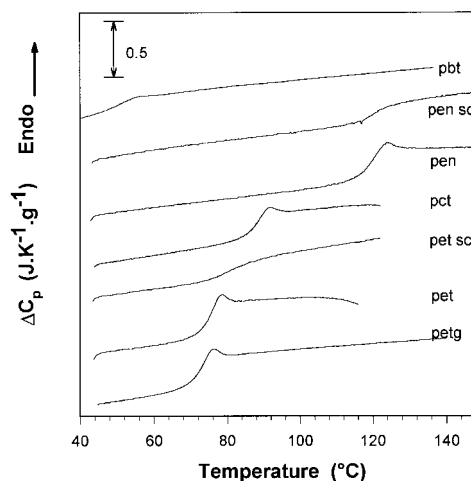
## DISCUSSION

Figure 5 shows, as example, elementary spectra obtained on the PETG sample. Because of the narrowness of the  $T_p - T_d$  polarization window, each elementary spectrum is considered as characteristic of sequences relaxing with the same relaxation time. Then, the Debye analysis of the current-temperature curves gives the relaxation time  $\tau(T)$  using the standard Bucci method.<sup>1</sup> In this case, it is established that the relaxation time shows an Arrhenius temperature dependence of the relaxation time  $\tau(T)$ :

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

where  $E_a$  is the apparent activation energy,  $R$  is the ideal gas constant, and  $\tau_0$  is the preexponential factor. So, each elementary process could be described by an Arrhenian diagram (see, as example, Fig. 6 for PETG). For each sample and for each elementary spectrum,  $E_a$  can be derived from the slope of the straight lines.

For the  $\beta$  region, the straight lines are quasi-parallel while for the  $\alpha$  region, the eight straight



**Figure 4** DSC curves obtained for polyesters. The curves are normalized to 1 g of matter and shifted on the  $\Delta C_p$  axis for legibility. The heating rate is  $10^\circ\text{C} \cdot \text{min}^{-1}$ .

**Table I** TSDC and DSC Parameters<sup>a</sup>

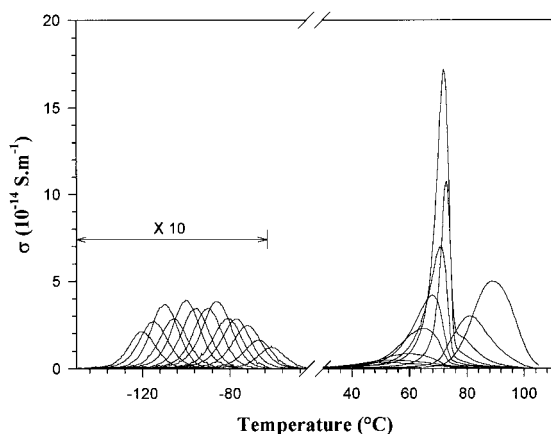
	TSDC Parameters						DSC Parameters			
	$T_\beta$ (°C)	$T_\alpha$ (°C)	$\Delta T_{1/2}$ (°C)	$\Delta H_{\max}^*$ (kJ · mol <sup>-1</sup> )	$T_c$ (°C)	$\tau_c$ (s)	$T_g$ Onset (°C)	$\Delta C_p$ (J · g <sup>-1</sup> · K <sup>-1</sup> )	$\Delta T_g$ (°C)	$T_f$ (°C)
PET	-91	69	8	457	76	10	73	0.31	10	76
PET <sub>sc</sub>	-96	77	23	378	78	24	76	0.11	18	82
PEN	-99	113	15	365	122	6	117	0.29	15	121
PEN <sub>sc</sub>	-96	116	26	412	125	5	117	0.16	22	120
PBT	-120	41	21	246	52	0.6	47	0.08	17	50
PCT	-91.6	80	10	277	85	24	86	0.22	10	88
PETG	-92.5	70	9	369	77	6	77	0.28	11	77
DM75	-105	73	25	168	no	no	no	no	no	no
DM52	-105	40	27	188	no	no	no	no	no	no

<sup>a</sup> TSDC parameters: temperatures  $T_\beta$  and  $T_\alpha$  of the maximum of the TSDC peaks, width at half maximum of the peaks  $\Delta T_{1/2}$ , apparent activation enthalpies  $\Delta H^*$ , compensation temperatures  $T_c$ , compensation times  $\tau_c$ . DSC parameters: onset temperature of the glass transition  $T_g$ , variation of the heat capacity at the glass transition  $\Delta C_p$ , width of the glass transition  $\Delta T_g$ , and fictive thermodynamic equilibrium temperature  $T_f$ . The no means no observable.

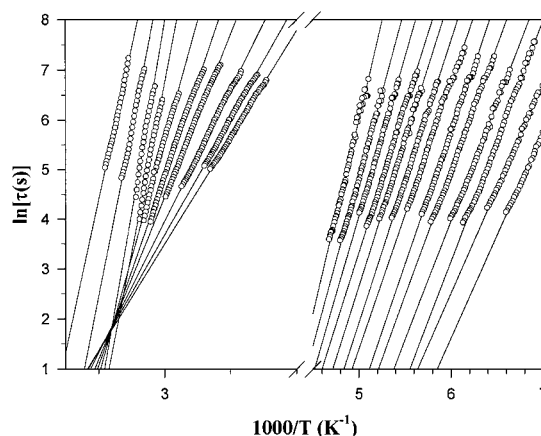
lines corresponding to the eight elementary spectra converge to a single point called compensation point of coordinates  $(1/T_c, \ln \tau_c)$ . The last two straight lines of the  $\rho$  region did not converge and are eliminated on the other figures. The other amorphous polyesters PET (Fig. 7), PEN, PETG, and PCT have a similar behavior,<sup>19</sup> all the straight lines of the  $\alpha$  region converge to the compensation point (Table I). For sc polyesters, the compensation behavior in the  $\alpha$  transition temperature range is less accurate because only the half of the straight lines converge, as shown in Figure 8 for PBT and Figure 9 for scPET. Indeed,

the  $\alpha$  region is larger than for the amorphous polyesters ( $\Delta T_g$  and  $\Delta T_{1/2}$  are around 20°C) and only four straight lines converge to the compensation point.

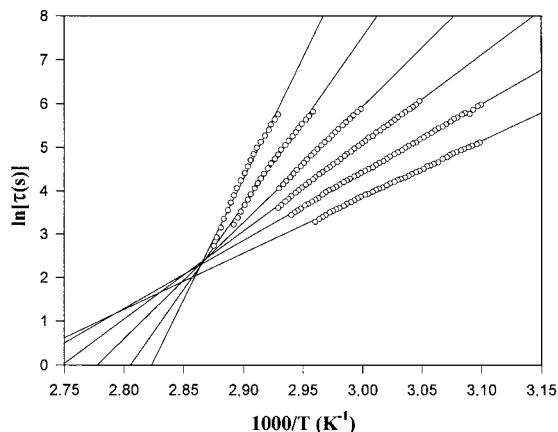
If we compare the different characteristic temperatures ( $T_g$ ,  $T_\alpha$ ,  $T_c$ , and  $T_f$ ) it appears that the value of  $T_c$  and  $T_f$  are very close, and above  $T_g$  and  $T_\alpha$ . In a previous work on various PET,<sup>6</sup> we have also shown that  $T_c$  is very close to the fictive thermodynamic equilibrium temperature. On the other hand, a recent work of our group on polymethyl( $\alpha$ -*n*-pentyl)acrylate<sup>20</sup> have shown that values of  $T_f$  and  $T_c$  could be different ( $T_f - T_c \sim 30^\circ\text{C}$ ). For Lacabanne and co-workers, the lag



**Figure 5** Elementary spectra in the  $\beta$  and  $\alpha$  temperature range for PETG ( $E = 10^6$  V/m,  $T_p$  varies from  $-130^\circ\text{C}$  to  $+80^\circ\text{C}$ ,  $r = 10^\circ\text{C}/\text{min}$ ).



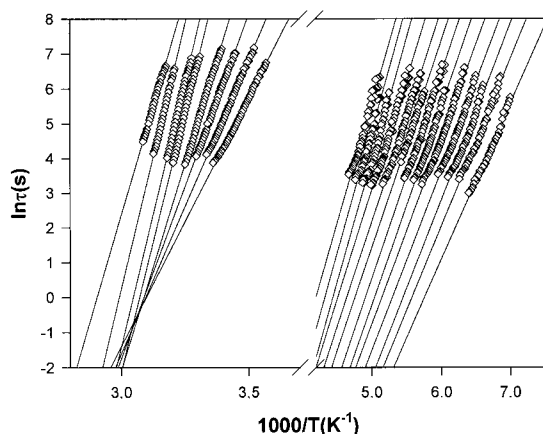
**Figure 6** Arrhenius plots for each elementary spectrum of Figure 5 (PETG).



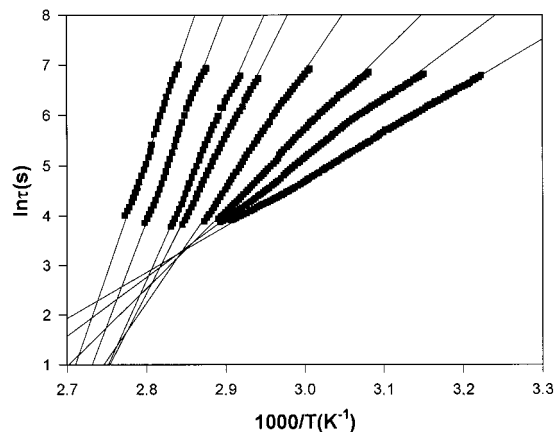
**Figure 7** Arrhenius plots for PET in the  $\alpha$  temperature range.

$T_c - T_\alpha$  is attributed to kinetic effects and is believed to depend on the stiffness of the polymeric chains.<sup>4</sup> J. J. Moura Ramos<sup>7,21</sup> had shown that  $T_c$  must be higher than the glass transition temperature and suggested that  $T_c - T_g$  is related to the width of the glass transition. These relations are not obvious for our studied polymers.

For dimethacrylate DM75 and DM52 resins, elementary spectra shown similar Arrhenius plots (Figs. 10 and 11, respectively). At the difference of the polyesters, no compensation behavior can be observed in the  $\alpha$  temperature range. Of course, one can force three lines to compensate over a narrow temperature range, due to experimental uncertainty and the length of the extrapolation. So it appears that the observation of compensation depends, in part, of the width of the glass transition. If the value of  $\Delta T_g$  is more than



**Figure 8** Arrhenius plots for PBT in the  $\beta$  and  $\alpha$  temperature ranges.



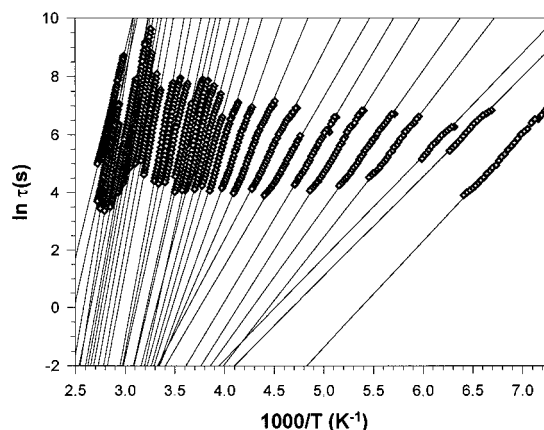
**Figure 9** Arrhenius plots for semi crystalline PET in the  $\alpha$  temperature range

25°C, compensation is sometimes not observed. Other works of our group on Polyurethane acrylate resins<sup>22</sup> have shown similar behavior. For this material, the glass transition is wide ( $\Delta T_g \sim 50^\circ\text{C}$ ) and do not show any compensation phenomenon.

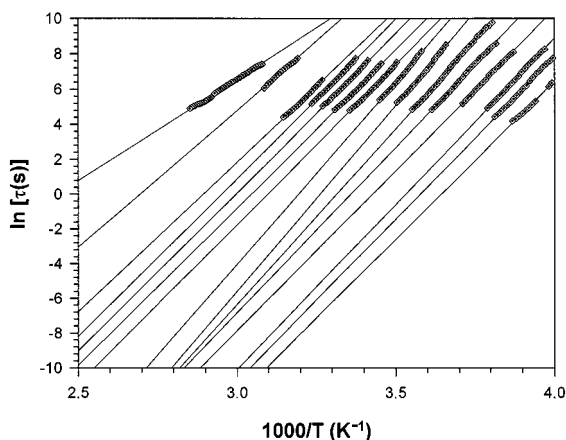
The arrhenian dependence of the relaxation time  $\tau(T)$  on temperature can be described by the Eyring's activated states equation where the relaxation time is associated with the crossing of a barrier of height  $\Delta G^*$ :

$$\begin{aligned} \tau(T) &= \left(\frac{h}{kT}\right) \exp\left(\frac{\Delta G^*}{RT}\right) \\ &= \left(\frac{h}{kT}\right) \exp\left(\frac{-\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \quad (2) \end{aligned}$$

where  $h$ ,  $k$ , and  $R$  are respectively the Planck, Boltzmann, and gas constants,  $\Delta S^*$  and  $\Delta H^*$  are



**Figure 10** Arrhenius plots for DM75 in the  $\beta$  to  $\alpha$  temperature ranges



**Figure 11** Arrhenius plots for DM52 in the  $\alpha$  temperature range.

the apparent activation entropy and the apparent activation enthalpy respectively,  $\Delta H^*$  and  $\Delta E_a$  are related by

$$E_a = \Delta H^* + RT \quad (3)$$

Maximum values of  $\Delta H^*$  (i.e., maximum values of  $E_a$ ) are given in Table I. In order to decide whether the relaxations are cooperative or noncooperative, Starkweather<sup>23</sup> has rewritten the activated states equation:

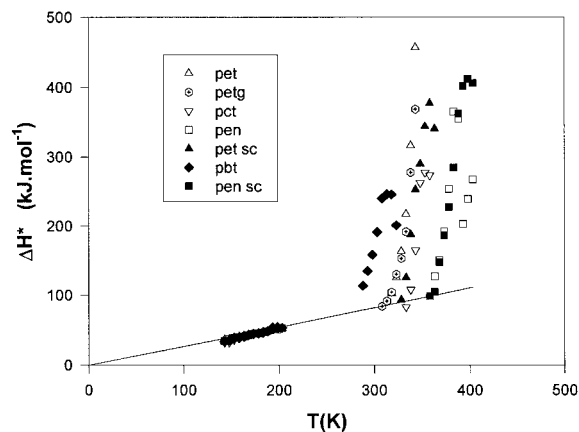
$$\Delta G^* = \Delta H^* - T\Delta S^* = RT[\ln(k/h) + \ln(\tau T)] \quad (4)$$

Taking into account the values of the constants, eq. (4) can be written as

$$\Delta H^* = RT[21.92 + \ln(T/f)] + T\Delta S^* \\ \text{or } E_a = RT[22.92 + \ln(T/f)] + T\Delta S^* \quad (5)$$

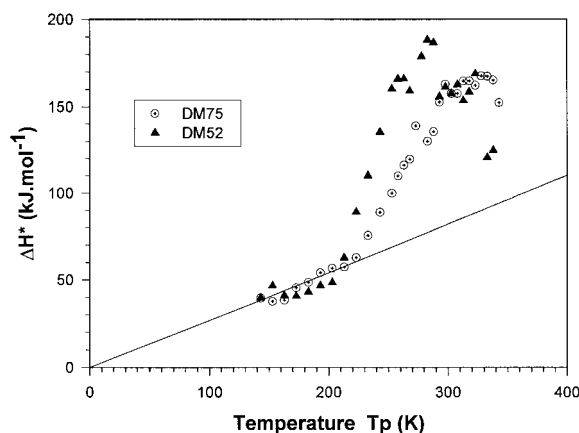
with  $f = 1/2\pi$ .  $\tau$  is the equivalent measurement frequency of TSDC. This equivalent frequency is calculated using Van Turnhout's method (it links the strength of the TSDC transitions to the ac dielectric transitions<sup>1</sup>) and is for our studies of  $5 \cdot 10^{-3}$  Hz.

The transitions are categorized as cooperative or not based on their activation entropy<sup>23</sup>: a finite activation entropy is equivalent to a "high" apparent activation energy and is known to be associated to cooperative transitions, glass transitions in most cases.<sup>24,25</sup> The solid curve drawn through the experimental data in Figures 11 and 12 is calculated using eq. (5) with the apparent activation entropy equal to zero and a frequency of 5



**Figure 12** Apparent activation energies  $\Delta H^*$  vs polarization temperature  $T_p$  for polyesters. The values of  $\Delta H^*$  are from the slopes of the Arrhenius lines and the solid curve is calculated using the activated states equation with  $\Delta S^* = 0$  and  $f = 5 \cdot 10^{-3}$  Hz.

$\cdot 10^{-3}$  Hz. It appears that the activation energies agree with the zero apparent entropy prediction for the polymers studied in the  $\beta$  region. In agreement with Sauer and Avakian,<sup>25</sup> we may conclude that the motions that occurs during the  $\beta$  relaxation are localized and noncooperative. For the  $\alpha$  relaxation, the data deviate significantly from the zero entropy prediction. The increase of the apparent activation enthalpy in the  $\alpha$  region is very important for amorphous and semicrystalline polyesters. The measured values of  $\Delta H^*$  show a narrow maximum near  $T_g$  as observed for many other polymers.<sup>26</sup> For dimethacrylate resins, the



**Figure 13** Apparent activation energies  $\Delta H^*$  vs polarization temperature  $T_p$  for dimethacrylates. The values of  $\Delta H^*$  are from the slopes of the Arrhenius lines and the solid curve is calculated using the activated states equation with  $\Delta S^* = 0$  and  $f = 5 \cdot 10^{-3}$  Hz.

data deviate at low temperature and the  $\alpha'$  relaxation can be categorized as cooperative. The increase of  $\Delta H^*$  is progressive (on more than 100°C). Furthermore, this augmentation is less than for polyesters, approximatively the half (as example,  $\Delta H_{\max}^* = 365$  and  $168 \text{ kJ} \cdot \text{mol}^{-1}$  for PEN and DM75 respectively). This evolution is less dramatical than for polyesters, and can explain the disappearance of compensation. So, as J. J. Moura Ramos,<sup>21</sup> we can explain compensation phenomena by the sharp increase of  $\Delta H^*$  as one approaches  $T_g$  from the low temperature side. The observation of a compensation point is only due to the width of the main  $\alpha$  peak and the increase of  $\Delta H^*$ . For amorphous polyesters, the width of the glass transition is close to 10°C, and the increase of the apparent activation enthalpy at  $T_\alpha$  is important ( $\Delta H_{\max}^*$  in the range 280–460  $\text{kJ} \cdot \text{mol}^{-1}$ ). For these materials, compensation is clearly observed. For semicrystalline polyesters, the increase of the apparent activation enthalpy at  $T_\alpha$  is also important ( $\Delta H_{\max}^*$  in the range 250–410  $\text{kJ} \cdot \text{mol}^{-1}$ ) but the width of the glass transition is larger and close to 20°C. So, compensation is also observed but less accurate. For dimethacrylate resins, the width of the glass transition is very large (more than 25°C), the increase of the apparent activation enthalpy at  $T_\alpha$  is weak ( $\Delta H_{\max}^*$  close to 180  $\text{kJ} \cdot \text{mol}^{-1}$ ). In consequence, compensation is not observed.

In conclusion, existence of the compensation in the  $\alpha$  transition region is not systematic, and depends on the heterogeneity of the amorphous phase and the degree of cooperativity of the motions. Observation of compensation behavior is linked to glass transition parameters. So, it appears that correlating compensation parameters with any physical or chemical parameters (as  $T_g$ ) is ill-advised due to their low physical interest.

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