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Comments on compensation analysis as applied to thermally stimulated current thermal sampling

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Compensation of Arrhenius relaxation curves coming to an extrapolated focus point is observed for many materials, especially in thermally stimulated current or related relaxation studies of polymers. Here we compare typical thermally stimulated current thermal sampling (t.s.c.-t.s.) data which exhibit compensation phenomena, with simulated data. The simulations were constructed on the basis of different curves of apparent activation energies, E_a, vs temperature, in an effort to represent a variety of possible experimental systems near a cooperative or high activation energy transition such as a glass transition (T_g). We show that compensation is universally observed for all simulated results, essentially independently of the nature of the cooperative transition, and proof is given that it is simply a result of mathematical manipulation of the Arrhenius equation in an under-determined system. The compensation temperature T_c must be related to T_g because of the steep Arrhenius curves. The difference, $T_c - T_g$, is indirectly related to the shape of the onset of glass transition as one approaches T_g from the low temperature side, but is not related to the 'breadth' of the main glass transition which is usually the region of interest, nor is it sensitive to the high temperature side of the transition. Correlating compensation with any physically observable quantity is ill-advised, for a variety of reasons discussed here. © 1997 Elsevier Science Ltd.

(Keywords: thermally stimulated curent (t.s.c.); glass transition; compensation; relaxation)

INTRODUCTION

The study of thermally stimulated electrical processes in materials is of considerable interest. Dielectrical breakdown of polymeric insulators is studied by thermally stimulated methods. Current technological advances include polymer electrets used for microphones and other sensing devices[1], and polymeric battery materials and other electrical storage devices. The development of materials for these applications continues at a rapid pace, as does the understanding and characterization derived from thermally stimulated current (t.s.c.). One important factor in the enhanced interest in the field is the recent availability of a commercial automated t.s.c. instrument made by Solomat, Thermold, Stamford, CT.

The t.s.c. thermal sampling technique (t.s.c.-t.s.) (also known as thermal windowing or fractional polarizations) has been applied to polymers, showing the capability of resolving complex dielectric transitions into narrow distributions of relaxations[2–10]. T.s.c.-t.s. results and the relationship of the activated parameters to glass transition phenomena are somewhat controversial[9–13]. One relatively undisputed feature is that the t.s.c.-t.s. method can resolve 'cooperative relaxations', e.g. those corresponding to high values of the apparent activation energy E_a[6–13], even in the case of weak or overlapping relaxations. It should be noted that 'high' E_a relaxations almost always correspond to those transitions exhibiting curved Arrhenius plots, e.g. those following an empirical WLF or related dependence of log (f) with reciprocal temperature for data obtained using conventional relaxation methods such as a.c. dielectric. The high sensitivity of the t.s.c.-t.s. method is due in part to the low equivalent frequency of about 10^{-3} Hz[14] and its capability of applying controlled polarization depolarization sequences. In this report we compare simulated results with those for one representative and widely studied polymer glass, PMMA. Several studies of the glass transition region in PMMA have been reported or reviewed[3,8–10,14–16], including t.s.c.-t.s. studies of PMMA[3,8–10,15].

In the discussion of t.s.c.-t.s. data, one must address the issue of compensation because of its prevalence in the literature. This is still a controversial area, regarding interpretation of the t.s.c.-t.s. results, and compensation has been reported in the majority of t.s.c.-t.s. and thermally stimulated creep relaxation studies. Compensation, also called the 'isokinetic' effect[17], has been

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controversial for more than thirty years in its application to chemical kinetics[17-19]. Compensation is the linear relationship or 'correlation' between the apparent activation energy, E_a, and the prefactor, $\log\tau_0$ (or equivalently a correlation between $\Delta H\ddagger$ and $\Delta S\ddagger$ from the Eyring analysis)[10,17]. As we see it, the controversy in chemical kinetics is similar to that in polymer relaxations. We strongly support statements such as those made by Exner[17] who discussed the danger of attempting to correlate E_a and $\log\tau_0$ because they are not independent of each other: 'Some authors were aware of a certain danger in such correlations, but the proper essence of the problem, that is, the mutual dependence of the quantities correlated, was not grasped'[17]. Garn[18] also discusses the same problems in detail. Although significant effort over thirty years has been devoted to dismissing the validity of compensation[17-19], it is still prevalent in the materials relaxation literature. We present specific and graphical examples to prove that compensation of relaxation data has almost no physical meaning.

Typically, when compensation is reported in the polymer literature it is because of the increase in E_a near a glass transition or some other 'cooperative' transition. This is analogous to chemical kinetics, where the rate constants characterized by a rapid change in E_a with temperature are the ones that compensate[18]. Compensation is seen most dramatically when Arrhenius (or Eyring) relaxation curves can be extrapolated to a focus point in temperature–frequency space (e.g. *Figure 1*)[8-13]. The focus point or compensation point is defined by two adjustable parameters, τ_c and T_c in the Arrhenius representation (equation (1)). Empirically, the compensation 'fit' is quite good for some polymer relaxations[8,10,13]. This is unlike the case of the analysis of chemical rate constants, where the temperature range is sometimes very narrow[17,18] and compensation may be solely due to 'the propagation of experimental errors'[19]. For polymer relaxations the temperature range can be quite broad and the increase in E_a quite strong, as is shown in *Figure 1*, leading to statistically 'significant' compensation[13]. We emphasize that compensation cannot be related to any material property for the simple reason that it is purely a result of

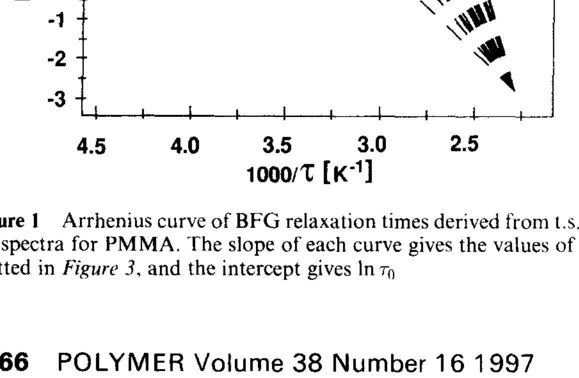

Figure 1 Arrhenius curve of BFG relaxation times derived from t.s.c.-t.s. spectra for PMMA. The slope of each curve gives the values of E_a plotted in *Figure 3*, and the intercept gives $\ln\tau_0$

mathematical manipulation of the Arrhenius or related equations, and the system is far too under-determined to meaningfully extract additional parameters such as T_c and τ_c. Because compensation analysis is firmly entrenched in the t.s.c. (and thermally stimulated creep) literature, we will provide mathematical and graphical arguments below to illustrate why compensation is not meaningful.

The compensation point is defined in frequency–temperature space by two phenomenological parameters: the compensation temperature T_c and the compensation frequency or relaxation time, $[f_c = 1/(2\pi\tau_c)]$[13].

$$\tau_0 = \tau_c \exp(-E_a/RT_c) \qquad (1)$$

This compensation equation suggests that, at the compensation point T_c, all relaxations occur at a single relaxation time τ_c, although in a substance as heterogeneous as a polymer glass this is an unlikely scenario. Studies by Read[20], experimentally examining the compensation 'point' in polypropylene[21] with low frequency mechanical measurements have refuted the idea of this unique relaxation at T_c and τ_c.

Substituting equation (1) into the Arrhenius equation:

$$\tau = \tau_0 \exp(E_a/RT) \qquad (2)$$

gives

$$\tau(T) = \tau_c \exp[E_a(1/T - 1/T_c)/R] \qquad (3)$$

According to equation (1), the slope of a plot of $\ln(\tau_0)$ vs E_a/R gives the reciprocal compensation temperature $(-1/T_c)$, and the intercept is related to the compensation frequency, $\ln(\tau_c)$. An analogous expression can be derived starting with the Eyring equation instead of the Arrhenius equation.

For polymer relaxations studied by t.s.c.-t.s. various attempts have been made to relate compensation to material parameters. The relationship of T_c with the coefficient of thermal expansion (α_l) for the polymer liquid above the glass transition temperature (T_g) has been explored[10,22]. Although qualitative agreement was seen in describing T_c by α_l, the attempted comparison actually failed for a variety of reasons. Given the relationship that $T_c \simeq T_g$[10,23], van Krevelen's[24] observation that T_g (in Kelvin) is equal to $0.2/\alpha_l$ explains why T_c is approximately inversely proportional to α_l. Other attempts to find a relationship between T_c and the change in coefficient of thermal expansion from the glassy to the liquid state ($\Delta\alpha$) also failed for a variety of reasons[3,10,13], including a more fundamental one described below.

EXPERIMENTAL

The t.s.c. instrument was supplied by Solomat. Spectra in the t.s.c.-t.s. mode were obtained using the standard procedure indicated in *Figure 2*[2,3,10,25]. The important aspect of the t.s.c.-t.s. experiment is the very narrow temperature window over which the sample is polarized relative to the standard global t.s.c. obtained by polarizing over the 'entire' temperature region[14]. For t.s.c.-t.s., first the polarizing field is applied for 4 min at the polarization temperature T_p. With the field left on, the sample is cooled at 5°C min^{-1} to $T_p - 5$°C. At this point the field is removed and the sample allowed to depolarize for 2 min at $T_p - 5$°C. The sample is then quenched at 30°C min^{-1} with the field off to about 40°C

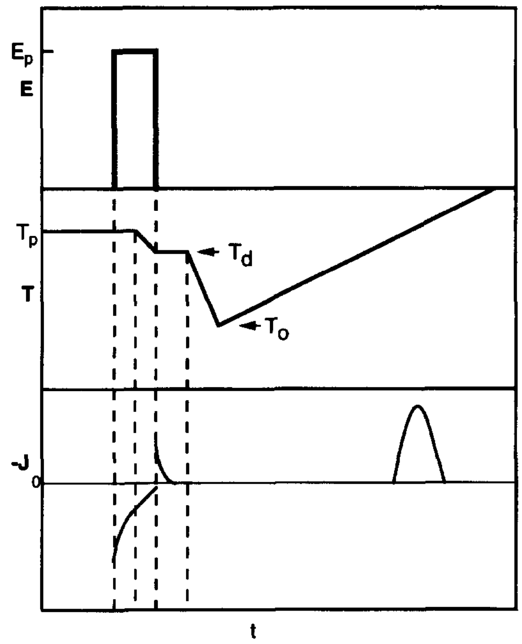

Figure 2 Schematic[25] of the t.s.c.-t.s. polarization sequence vs time, using narrow polarization temperature windows. The ordinate axis consists of polarization field strength (E), temperature, and depolarization current (J) from top to bottom, respectively. See Experimental section for details of polarization times, polarization temperatures (T_p), depolarization temperatures (T_d) and quench temperatures (T_0)

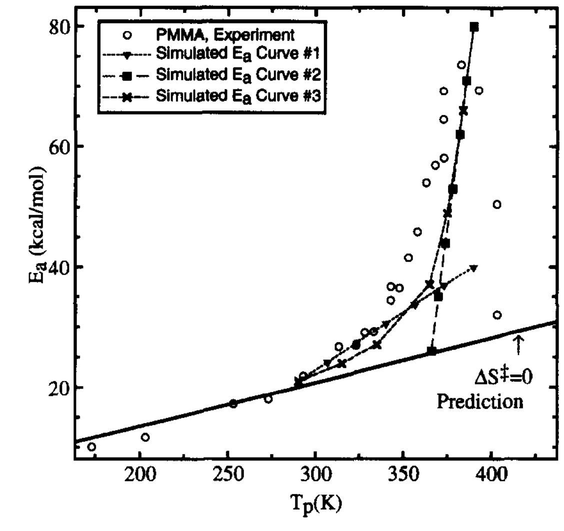

Figure 3 Apparent activation energies vs polarization temperature obtained from the t.s.c.-t.s. method showing experimental data for PMMA and three arbitrarily chosen curves for simulation purposes. The glass transition region, as examined in terms of high E_a cooperative relaxations, is broad and the values of E_a maximize at about 378 K, which is the peak glass transition for PMMA

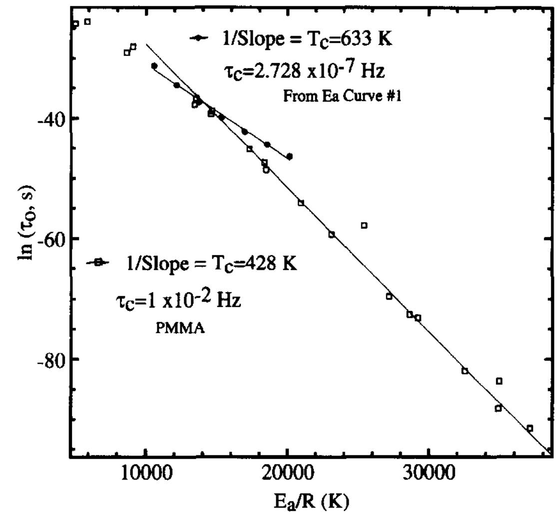

Figure 4 'Compensation plot' of $\Delta S\ddagger$ vs $\Delta H\ddagger$ for experimental (PMMA) and simulated data. The linear dependence is an indication of the quality of the fit to the compensation equation. The experimental points not on the line are for data which are not expected to compensate (low and high temperature data). The theoretical data cover a range of values governed by the values of E_a chosen for the simulation. The compensation parameters determined from the linear fit are listed on the plot

below T_p. The t.s.c.-t.s. depolarization current is then measured upon reheating at 7°C min^{-1} to values about 40°C above T_p. Essentially the same polarization sequence has been used in many previous reports[2,3,6–13], and the resulting activated parameters are remarkably insensitive to small differences in the exact details of the polarization sequence. The t.s.c.-t.s. technique effectively detects only a narrow distribution of relaxations under the conditions we have chosen.

RESULTS AND DISCUSSION

Compensation is typically observed when there is an increase in E_a (or $-\log \tau_0$, or $\Delta H\ddagger$, or $\Delta S\ddagger$ or any other activated parameter) as one approaches T_g. The value of the compensation temperature T_c is generally just above T_g for compensating relaxation curves taken near a glass transition. This is because the high values of E_a associated with the glass transition generally lead to steep Arrhenius curves which naturally come to a focus slightly above T_g (e.g. *Figure 1*).

For almost any increase in E_a as one approaches a 'cooperative' transition, we will show that compensation is universally seen for mathematical reasons, regardless of the breadth or shape of the glass transition. In the following, we arbitrarily choose E_a as the activated parameter which we will use to discuss the phenomena, but it could as well be any *one* of the other activated parameters. The so-called Bucci–Fieschi–Guidi (BFG)[26] analysis of a single t.s.c.-t.s. spectrum gives rise to one Arrhenius curve of relaxation times τ. Using many choices of T_p, several of these curves can be generated as shown in the Arrhenius plot in *Figure 1* for PMMA. The slope of each of these curves gives the values of E_a plotted in *Figure 3*. Physically, the rate of increase in E_a with T_p is believed to be somehow related to the onset of the glass transition, i.e. the breadth of the glass transition as it extends to low temperatures[6–13]. For example, it is broad for poly(ethyl methacrylate)[10] and PMMA (*Figure 3*)[8–10], leading to compensating lines over a wide range of T_p (*Figure 1*).

The statistics of compensation are best judged by the linear dependence[10,13,18] of $\log \tau_0$ with E_a (*Figure 4*) or, equivalently, the linear dependence of $\Delta H\ddagger$ or $\Delta S\ddagger$. The onset of the glass transition is abrupt for many polymers such as polycarbonate, leading to compensation over a narrow range of T_p[27]. For the narrow transition materials T_c occurs only a few degrees above T_g[10,23,27], while for materials like PMMA T_c is sometimes more than 50°C above T_g[8–11,23] (*Figure 1*). The 'zero entropy prediction' shown in *Figure 3* is determined from the rearranged Eyring's activated states equation[28].

$$E_a = \Delta H\ddagger + RT = RT[1 + \ln(k/h) + \ln(T\tau)] + T\Delta S\ddagger$$
$$= RT[24.76 + \ln(T\tau)] + T\Delta S\ddagger \quad (4)$$

Knowing that the equivalent frequency of t.s.c. is fixed at about $f = 5 \times 10^{-3}$ Hz one can generate the line in *Figure 3*, which shows that E_a calculated assuming $\Delta S\ddagger = 0$ is essentially linearly dependent on temperature (in Kelvin). It has been shown in numerous cases that the values of E_a for low temperature non-cooperative relaxations follow the semi-empirical zero activation curve[6,10,11,28] while those for cooperative transitions, including the glass transition, show large departures[6-13].

Now we use simulated data to prove that compensation will occur whenever there is an increase in E_a, essentially independently of the nature of the increase in E_a as one approaches a given transition. The linearity of typical $\log \tau_0$ and E_a experimental data is shown in *Figure 4* for PMMA. To simulate compensation data, we arbitrarily choose three sets of E_a vs T_p curves (*Figure 3*), labelled simulated E_a curves #1, #2 and #3. *Figure 5* shows the seven simulated Arrhenius curves corresponding to 'E_a curve #1' in *Figure 3*. These were calculated from the values of E_a and T_p by first determining an intercept using the equivalent frequency of t.s.c. ($\tau = 1/(2\pi f) = 200$ s):

$$\tau_0 = (200\,\text{s}) \times \exp(-E_a/RT_p) \quad (5)$$

Once τ_0 is calculated, then the Arrhenius equation can be used to generate the solid curves in *Figure 5* using the seven indicated values of E_a. Extrapolated lines are forced through the compensation point in the figure. The linearity or goodness of fit of the 'compensation plot' is seen to be roughly comparable to that for actual experimental data (*Figure 4*). It should be noted that the values of E_a used to generate the extrapolated curves in *Figure 5* correspond to those with the 'flattest' dependence of E_a on T_p (curve #1 in *Figure 3*), so even with relatively weak simulated 'cooperative' relaxations compensation is observed, as is known from experiment.

The compensation plots corresponding to simulated E_a curves #2 and #3 from *Figure 3* are shown in *Figure 6*. The linearity is almost perfect over the compensating region, showing that compensation is almost perfect. The compensation fit is indeed quite universal for essentially any experimental cooperative or slightly cooperative relaxations that one could imagine, but this is an artefact of the strong mathematical interdependence of slope and intercept, and this interdependence becomes dominant for any significant increase of E_a with temperature, as is the case with chemical rate constant analysis[18]. The analysis lacks physical meaning for this reason. For a gentler dependence of E_a with temperature, compensation will not fit the data as well. For example, consider a situation where E_a vs T values fall on the $\Delta S\ddagger = 0$ curve for 'non-cooperative' relaxations in *Figure 3*. In this case one can show that compensation is not well defined, although in some cases small experimental errors will lead to approximate compensation in the analysis of non-cooperative relaxation data, especially over narrow temperature ranges. This again illustrates the pitfalls of using empirical analysis.

In addition to the danger of attempting to make sense of compensation parameters in an under-determined system, one also must avoid falling into the related trap of trying to obtain more than one activated parameter from the analysis of the data. The problem is illustrated in *Figure 7*, where one can see that the values of $\Delta S\ddagger$ mimic those of $\Delta H\ddagger$ as is known in the literature[8,10,29]. The same trend would be seen with E_a and $-\log \tau_0$. The reason for this is simple but not always well recognized. $\Delta G\ddagger$ is always constrained to moderate values defined by equation (7) (also plotted in *Figure 7*, for example). Thus, if $\Delta H\ddagger$ increases, then equation (6) shows that the value of $\Delta S\ddagger$ must increase to counterbalance this. Thus, $\Delta H\ddagger$ and $\Delta S\ddagger$ are highly dependent on each other, and only one of them need be chosen for analysis. The same argument applies to the Arrhenius analysis, where only E_a or $\log \tau_0$ could possibly have any physical

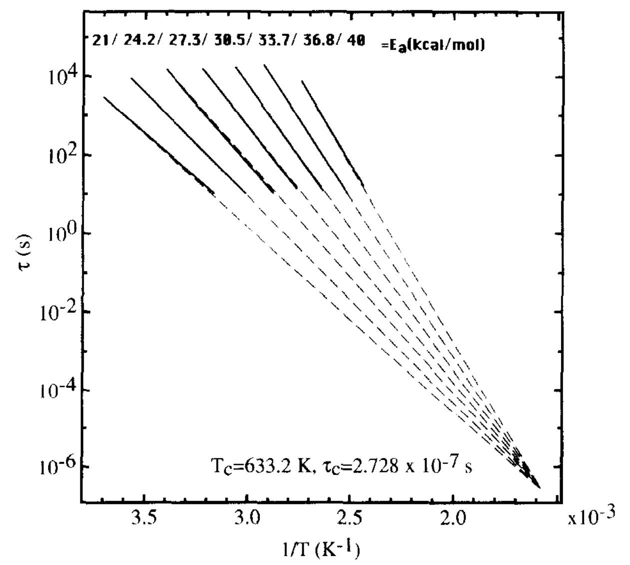

Figure 5 Simulated relaxation times (solid curves) generated starting with the values of E_a and T_p indicated by curve #1 from *Figure 3* (see text). The values of E_a used to generate the curves are indicated on the plot. The extrapolated Arrhenius lines (dashed) were generated using the compensation parameters indicated

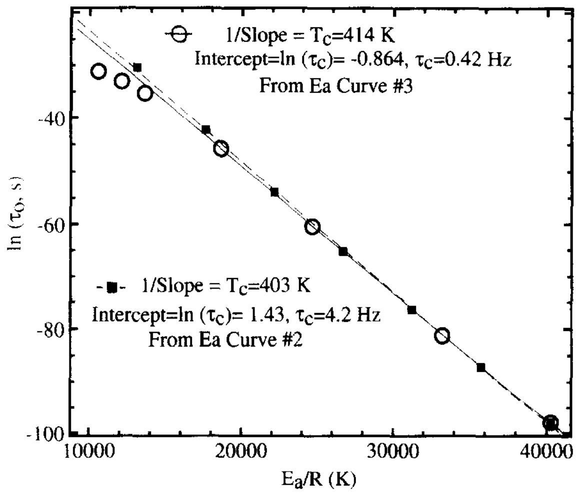

Figure 6 'Compensation plot' of $\Delta S\ddagger$ vs $\Delta H\ddagger$ for two sets of simulated data. The linear dependence is an indication of the quality of the fit to the compensation equation. The points which are not on the compensating line corresponding to E_a curve #3 are for the lower temperature data, and are not expected to compensate because of the moderate rate of change of E_a with T (see text). The theoretical data cover a range of values governed by the values of E_a chosen for the simulation. The compensation parameters are listed on the plot

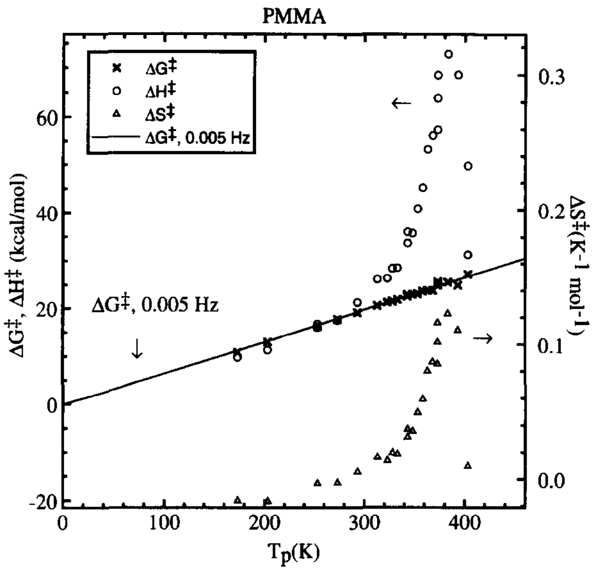

Figure 7 Eyring activation free energy ($\Delta G\ddagger$), enthalpy ($\Delta H\ddagger$) and entropy ($\Delta S\ddagger$) vs temperature. The values of $\Delta H\ddagger$ differ from the values of E_a in *Figure 3* only by a factor of RT, and show the same trend with a prominent maximum near $T_g (= 378\,K)$. Values of $\Delta S\ddagger$ are calculated from the intercepts of Eyring plots of $\ln(\tau T)$ vs $1/T$ and also show the same trend as $\Delta H\ddagger$ (see text). The solid line is calculated using equation (7) and the individual points (x) are calculated using equation (6), with some small amount of imprecision

significance.

$$\Delta G\ddagger = \Delta H\ddagger - T\Delta S\ddagger \qquad (6)$$

or, equivalently,

$$\Delta G\ddagger = RT\ln[\tau kT/h] = RT[23.76 + \ln(\tau T)] \qquad (7)$$

Note that τ is constrained to about 200 s because this is the equivalent frequency of the t.s.c. measurement. With the narrow range of τ and T, the log term is almost constant, and $\Delta G\ddagger$ can be approximated as being nearly linearly dependent on T as was discussed above (see also *Figure 7*).

The basic fault of compensation analysis for relaxations is that, whenever E_a increases, $\log \tau_0$ must decrease because they are intimately related to each other by the Arrhenius equation due to the fixed time scale of the measurement ($\tau \simeq 200\,s$ or $f \simeq 0.001\,Hz$). Thus, approximately independently of the nature of the rise in E_a with T_p (*Figure 3*), compensation is universally seen for this mathematical reason in the vicinity of 'cooperative' relaxations. Because compensation analysis is purely mathematical, its occurrence is a natural result of the increase in E_a, and not its cause, on the low temperature side of the cooperative transition.

The compensation temperature T_c must be related to T_g because of the steep Arrhenius curves. The difference $T_c - T_g$, is indirectly related to the sharpness of the onset of the glass transition as one approaches T_g from the low temperature side, but $T_c - T_g$ is not related to the 'breadth' of the main glass transition extending past this onset region. The onset region is in many cases only a small part of the overall phenomena of interest, and is in many cases independent of crystallinity and phase morphology, which explains why Lacabanne and coworkers found that $T_c - T_g$ was independent of crystallinity in PET[12,23] and PEEK[23,30], while other techniques clearly showed that the breadth of the main glass transition was increased. An alternative approach was applied to the t.s.c.-t.s. data for PEEK and related systems[31], like that applied to PMMA in *Figure 3*, where the entire broadened glass transition regions are quantified in terms of their 'cooperative' relaxations. These t.s.c.-t.s. results were shown to be quantitatively consistent with those from other thermal analysis techniques[31], whereas compensation analysis makes little contact with other relaxation techniques for the reasons discussed above. We take the view that those analyses which are simpler, less empirical, and make better contact with standard analysis of thermal and relaxation data are the preferred ones. We also feel that the experimental results and conclusions thus derived could be judged more easily for their consistency and relevance throughout the literature if an essentially mathematical treatment such as compensation analysis were abandoned.

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