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On the use of the compensation law to describe cooperative relaxation kinetics in thermally stimulated processes: a new view [α]

J.P. Ibar

Solomat Instrumentation, Stamford, CT 06906 (USA)

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Abstract

The use of "thermal-windowing" methods to decouple molecular motions in polymeric materials has recently become very popular by the introduction on the thermal analysis market of the automated TSC/RMA spectrometer. The data obtained are collected into a relaxation map which shows the several relaxation modes for the internal motions occurring at T_g, below T_g and above T_g. A relaxation map is a set of log τ (relaxation time) versus $1/T$ curves obtained at different polarization temperatures. The decoupling between the relaxation modes responsible for internal motion leads to a better understanding of their coupling characteristics. At T_g, the Arrhenius lines gather into packs of lines which converge to a single point, the compensation point. The coordinates of the compensation point are dependent on the actual state of the glass. The thermally stimulated current characteristics of PMMA are studied here to demonstrate the power of the analysis provided by the TSC/RMA spectrometer when thermal-windowing is used. In particular, the experimental results are replotted as the variation of the free energy of activation versus temperature for each polarization temperature, T_p, and the values of the free energy, enthalpy and entropy of activation are calculated at T_p. Plots of the thermo-kinetic variables against T_p, when T_p varies, leads to characteristic results of the relaxation map: T_g is characterized by a maximum in the entropy of activation (and also of the enthalpy), and by the intercept of two compensation lines, one positive and one negative, as T_g is crossed resulting in a "Z structure" for the relaxation lines. It is shown how the Z structure and the Z line, which it defines, relate to the corresponding positive and negative compensation lines. Finally, a new characterization method to define T_g from the Z structure is introduced.

INTRODUCTION

Several authors have expressed their concern that compensation phenomena might be the result of a poor characterization of the data, perhaps even an artifact [1,2]. Others argue that Bucci and Fieschi's relaxation times [3] should be corrected to reflect a true relaxational behavior [4]. In

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the following, one assumes that these problems of the definition of the true Debye behavior and of the accuracy of the analysis have been addressed and solved. The present author believes that the method of analysis of the depolarization curve proposed by Lacabanne and collaborators [5–10], which is used in the software of the TSC/RMA spectrometer, ignores all concerns which might invalidate the generality of the results disclosed in this article.

The views expressed here are novel, even to those familiar with the technology, although the contribution of many authors [1,3,5,11–13] in the development of this treatment is discussed below and duly acknowledged.

All experimental data presented in this article were obtained on a PMMA sample of unknown molecular weight, and the characteristics were analyzed on a TSC/RMA spectrometer model 41000.

ARRHENIUS TRANSFORM, RELAXATION MAP AND RELAXATION MAP ANALYSIS

Each elementary relaxation curve (depolarization current vs. temperature) obtained from thermal-windowing can be transformed mathematically into its Arrhenius representation, log τ versus $1/T$, which expresses the variation of relaxation time with temperature for that particular isolated relaxation mode (Fig. 1). The elementary relaxation time, τ_i, for a simple

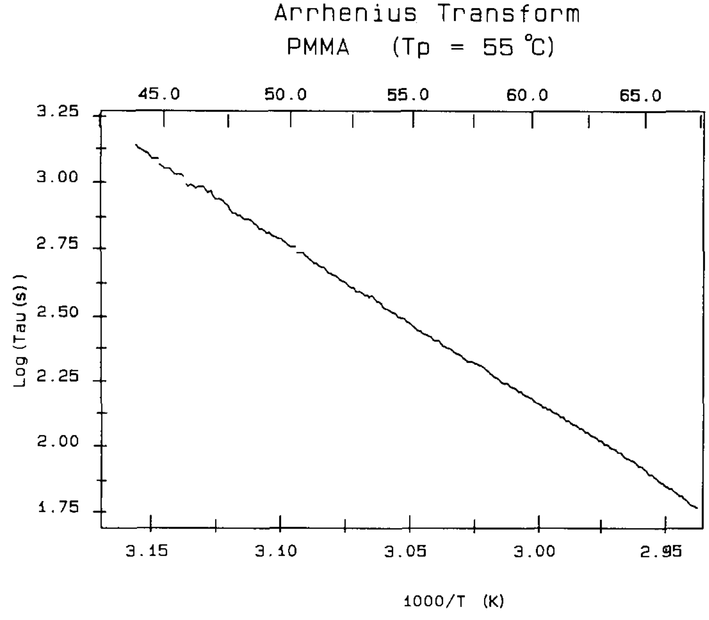

Fig. 1. The Arrhenius transform of the elementary relaxation curve.

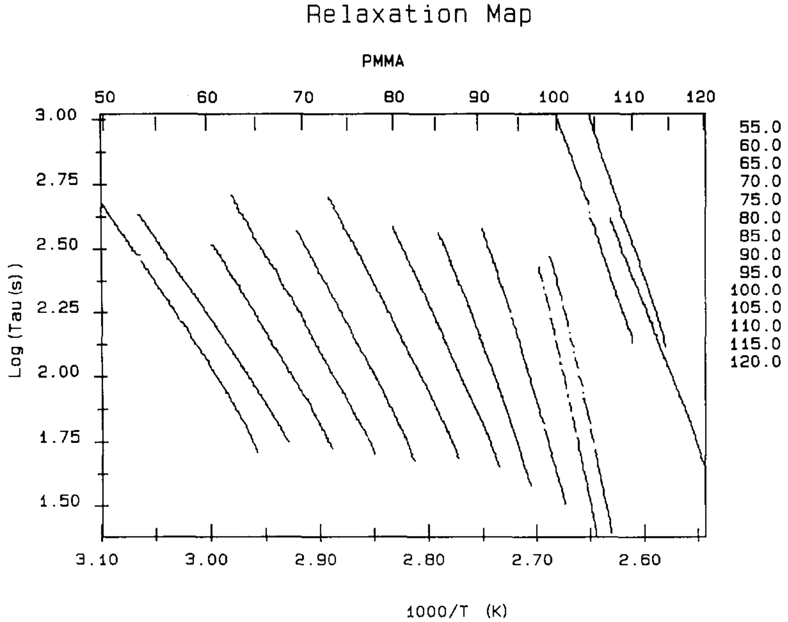

Fig. 2. Relaxation map obtained by transforming all the thermally-windowed depolarization recovery curves.

behavior described by Bucci and Fieschi's model [3], and calculated according to Lacabanne's method [10], can be written as

$$\begin{aligned} \tau_i(T) &= P(T)/J(T) \\ J(T) &= \mathrm{d}P(T)/\mathrm{d}T \end{aligned} \tag{1}$$

which can be fitted to an Arrhenius equation

$$\tau_i(T) = \tau_{0i} \exp(\Delta H/kT)$$

where τ_{0i} is the pre-exponential factor, ΔH is the activation enthalpy, and k is the Boltzmann's constant.

"Arrhenius transform" describes the use of eqn. (1) to represent the depolarization recovery data, plotted in an Arrhenius system of coordinates (Fig. 1). For each polarization temperature T_p, there is an Arrhenius transform. A relaxation map is obtained (Fig. 2) by transforming all the thermally-windowed depolarization recovery curves, obtained by varying T_p, into their Arrhenius representation.

Relaxation map analysis (RMA) tries to correlate the single relaxation modes (relaxation time versus temperature) to thermo-kinetic and/or other physical variables.

According to Eyring, the pre-exponential factor in the Arrhenius equation is directly related to the entropy of activation of the activated states involved [14].

For a given relaxation mode isolated by polarizing at T_p, the relaxation time takes the form

$$\log \tau_{i,p} = \log(\tau_i)_{0,p} + \Delta G_p/kT \tag{2}$$

with

$$\Delta G_p = \Delta H_p - T\Delta S_p \tag{3}$$

where the subindex "p" implies that these variables are functions of the temperature of polarization. According to Eyring, see ref. 14

$$\log(\tau_i)_{0,p} = -\log(kT/h) \tag{4}$$

Therefore,

$$\tau_{i,p} = (h/kT)\exp(-\Delta S_p/k)\exp(\Delta H_p/kT) \tag{5}$$

where k and h are, respectively, the Boltzmann and Planck's constants.

A plot of $(\log \tau_i + \log T + \log(k/h))$ versus $1/T$ (an Eyring plot) is a useful way to plot the variables because from the slope $(\Delta H_p/R)$ and

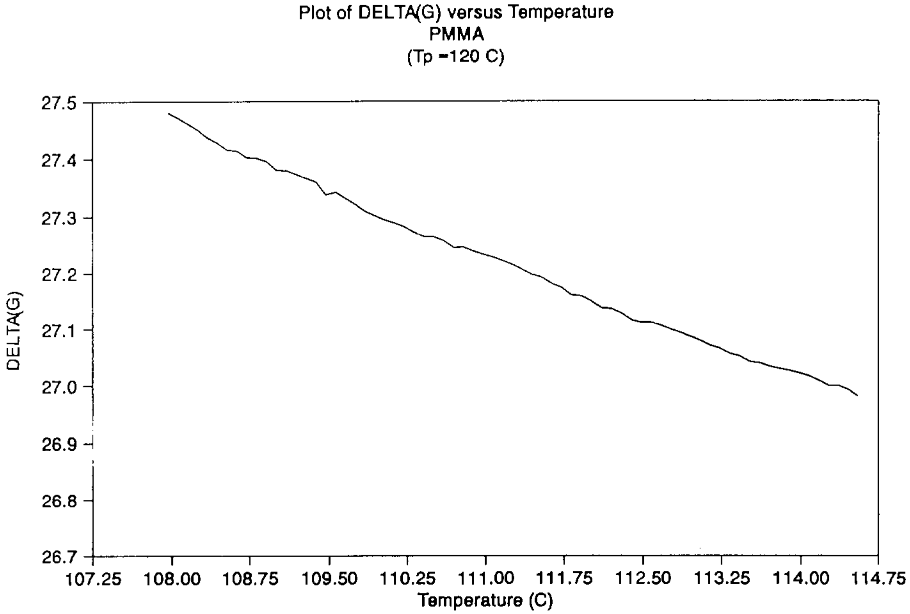

Fig. 3. Relaxation results plotted in the ΔG vs. T plane.

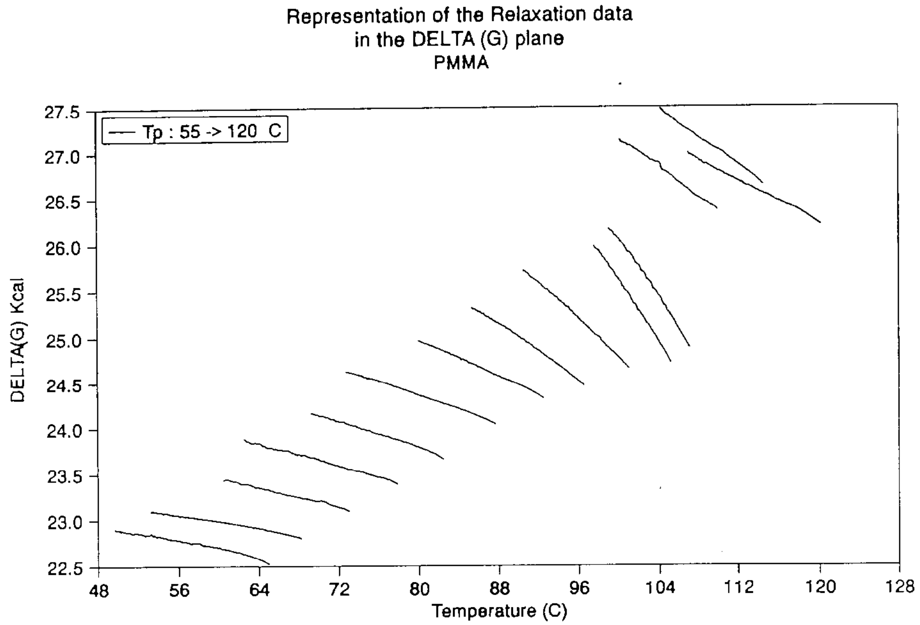

Fig. 4. Relaxation map for the data of Fig. 2 plotted in the ΔG vs. T plane.

intercept ($-\Delta S_p/R$) of the best linear fit through the data points, one can determine the mean enthalpy and entropy of activation, ΔH_p and ΔS_p.

In Fig. 3, the relaxation results are represented in a different plane, the ΔG vs. T plane, by calculating the value of ΔG at each temperature according to eqns. (2) and (4) (the temperature is given in °C in Fig. 3, add 273 to shift to the Kelvin temperature scale). Figure 4 is a relaxation map for the data of Fig. 2 in the ΔG vs. T plane. One sees that the influence of the temperature of polarization is to raise the value of ΔG, while the influence of temperature during the recovery process is to reduce its value. The slope of the spectral lines in Fig. 4 is equal to the entropy of activation, and the intercept is the enthalpy. The lines appear to be satisfactorily linear.

COMPENSATION PHENOMENA AND DEGREE OF DISORDER

When several Arrhenius lines converge to a single point, this point is called a "compensation point". In general, for amorphous polymers or for the amorphous region in semi-crystalline polymers, the behavior at T_g is characterized by at least one compensation phenomenon. The Arrhenius or the Eyring lines all converge into a single point at T_c, near T_g. The coordinates (T_c, log τ_c) of the compensation point are important because they transcribe the coupling characteristics between the different modes of relaxation observed as individual activated processes in the set of converging Arrhenius lines. The coordinates of the compensation point are related to fundamental properties of the state of the polymer, as influenced by its surroundings. If a structure is "loose", the contrary of "ordered" or "compact", i.e. when molecular mobility is less hindered by the interactive intra–intermolecular surroundings, the entropy of activation is "larger". Conversely, any parameter which acts to "organize" the structure and create a tighter environment for the bonds causes a decrease in the entropy of activation. So, the activated entropy calculated from the Eyring equation, eqn. (5), gives an indication of "the degree of disorder" (DOD) of the structure. But the entropy of activation varies with the polarization temperature, such as shown by the variation of the slope in Fig. 4. One would like to be able to define the DOD by a single number, representative of the state of the dielectric environment of the bonds. A characteristic feature of the compensation phenomenon gives us such an opportunity.

COMPENSATION SEARCH, Z STRUCTURE AND Z LINE

One can prove mathematically that a very simple and practical way to see whether a set of lines obtained at various T_p's converge, is to plot the intercept against the slope for these lines and to try to draw a straight line through the points. This type of analysis is called a "compensation search".

The coordinates of the compensation point (Y_c, X_c) are calculated from the slope and intercept of the compensation line, the intercept versus slope plot of the Arrhenius transforms. Figure 5 is the compensation line for the set of converging Eyring curves corresponding to Fig. 2. In this case, let $X_c = 1/T_c$ and $Y_c = \log \tau_c$.

The coordinates of the compensation point are obtained by linear regression completed by a simplex to integrate all the points of the Eyring lines into the calculation of the best fit for the compensation lines. $T_c = 129.65\,^\circ\mathrm{C}$ and $\ln \tau_c(\mathrm{Eyring}) = 28.58$. Therefore, $\log \tau_c = -0.5$ according to eqns. (3). A regressional fit of the 14 individual Arrhenius lines gives the entropy, enthalpy and Gibbs free energy of activation, according to eqns. (5) and (2) (Figs. 6–8). Table 1 gives the data for the PMMA studied. The Gibbs free energy is calculated at $T = T_p$. Plots of entropy, enthalpy, and ΔG_p versus T_p are presented in Figs. 6–8, respectively. The compensation search for this sample is shown in Figs. 9 and 10. Figure 9 is the classical plot, mentioned previously, of intercept versus slope obtained from the linear regression of the Arrhenius lines. Figure 10 is an "EE plot", entropy versus enthalpy. It is actually identical to a compensation search, as the entropy and enthalpy are calculated from the Eyring formulation, as expressed earlier (eqn. (5))

$$\text{slope} = \Delta H_p/k \text{ and intercept} = -\Delta S_p/k \qquad (6)$$

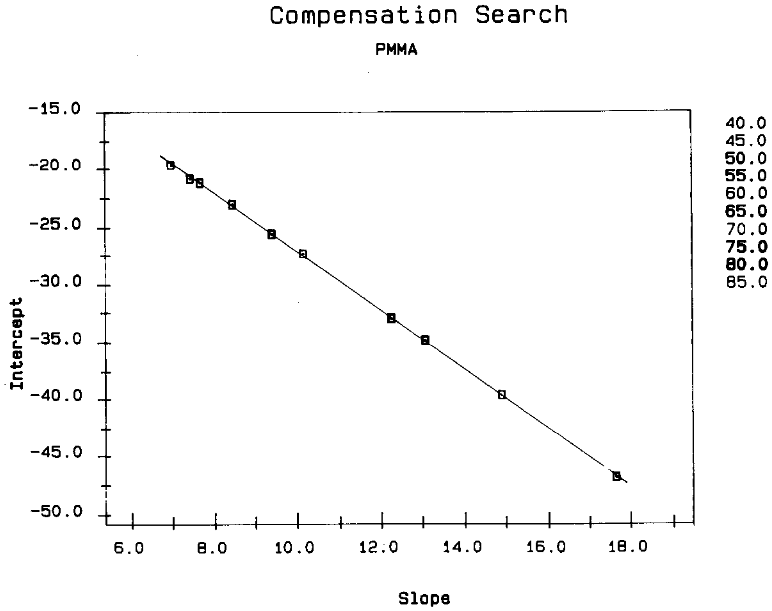

Fig. 5. The compensation line for the set of converging Eyring curves corresponding to Fig. 2. The numbers at the right indicate the polarization temperatures.

Two important observations can be made: the compensation search reveals *two* compensation lines; and as T_p increases, the points in Fig. 10 first go upward, then, as ΔH and ΔS reach their maximum, fold backward.

TABLE 1

Thermokinetics of PMMA

	T_p (°C)	T_m (°C)	Enthalpy (kcal)	Entropy (cal °C^{-1})	Gibbs (kcal)
1	55.0	65.0	30.0154	21.9978	22.8002
2	60.0	68.3	29.1053	18.3919	22.9808
3	65.0	73.1	32.3068	26.5580	23.3302
4	70.0	77.9	34.0809	30.4044	23.6522
5	75.0	82.5	36.6546	36.4496	23.9701
6	80.0	87.6	38.0073	38.6547	24.3622
7	85.0	92.6	42.7078	50.2408	24.7216
8	90.0	96.6	52.4668	75.6816	24.9944
9	95.0	101.0	62.6732	101.5688	25.2959
10	100.0	105.3	87.9523	167.1228	25.6155
11	105.0	107.1	86.2465	161.3318	25.2631
12	110.0	110.1	57.4247	81.1127	26.3585
13	115.0	120.2	48.7469	57.2885	26.5189
14	120.0	144.6	56.3012	76.4458	26.2580

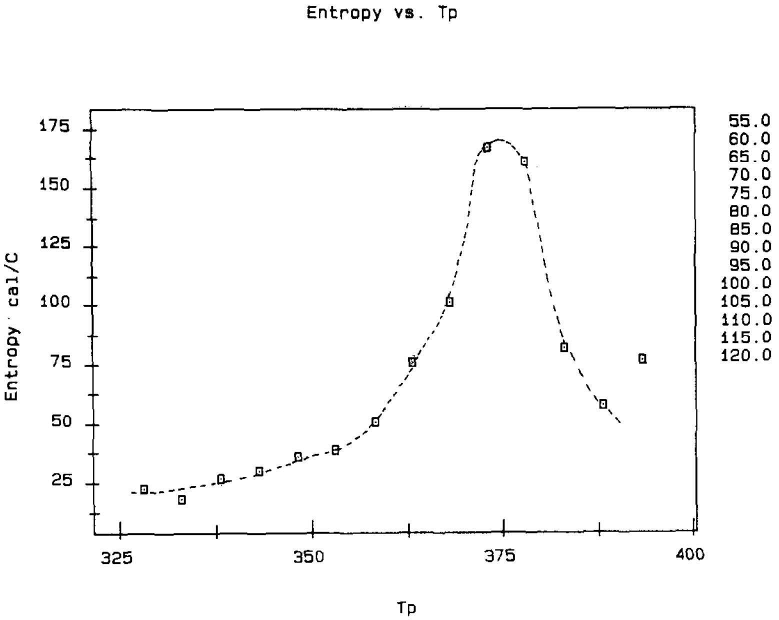

Fig. 6. Entropy plotted against T_p.

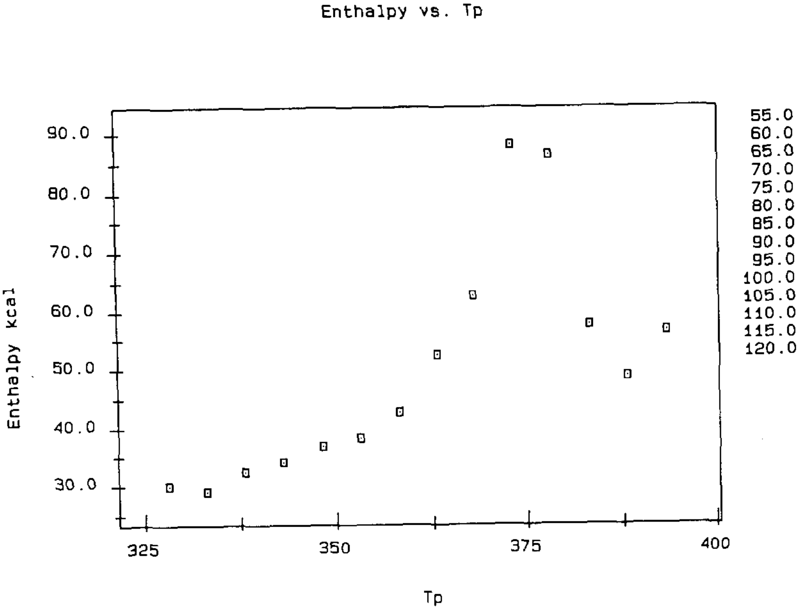

Fig. 7. Enthalpy plotted against T_p.

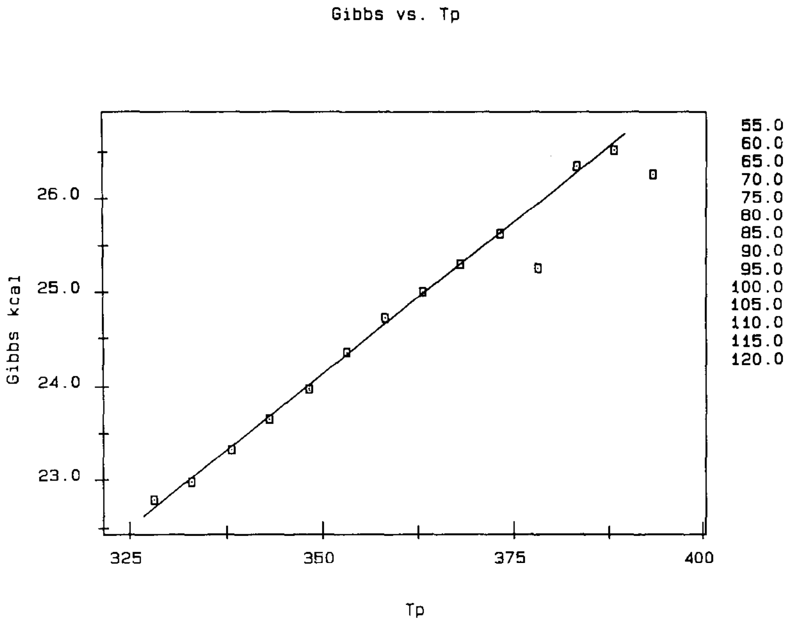

Fig. 8. ΔG_p plotted against T_p.

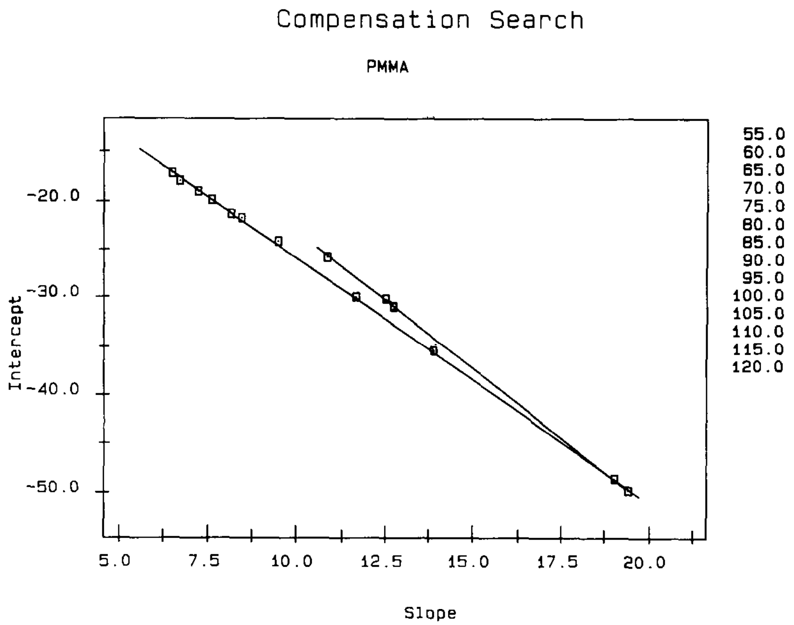

Fig. 9. The compensation search plot of intercept against slope.

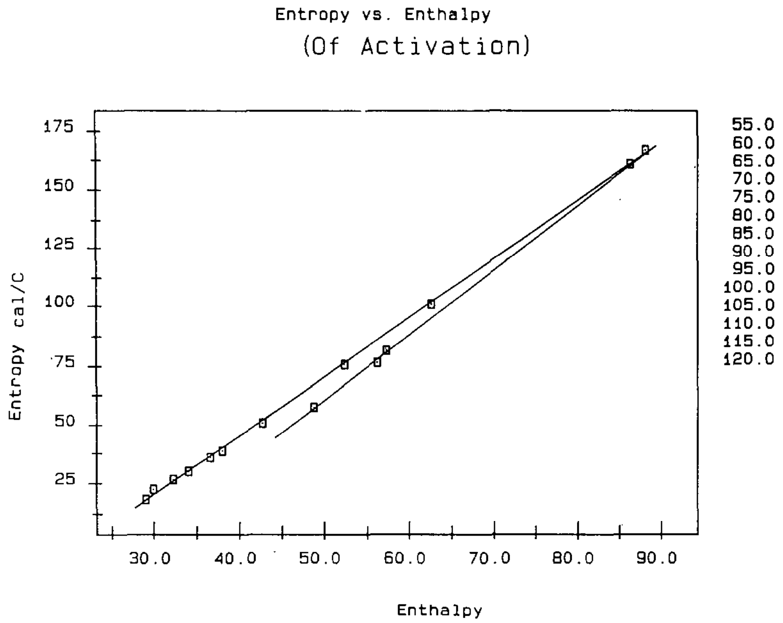

Fig. 10. The compensation search EE plot of enthalpy versus entropy of activation.

This phenomenon can be symbolized by saying that the two compensation lines observed (Fig. 9 or 10) do not have the same "sign", meaning that as T_p increases, consecutive points on the compensation lines either follow a pattern towards increasing or decreasing entropy, depending on the positive or negative sign of the compensation line. This behavior is clearly classical across the glass transition temperature. The intercept between the positive and negative compensation lines is used to determine with accuracy the value of the glass transition temperature, and the value of the entropy and enthalpy of activation at T_g.

The best linear fits for the lines of Figs. 9 and 10 have been calculated and from them, the coordinates of the compensation points. For the positive compensation

$$\begin{aligned} T_c^+ &= 127.96\,^\circ\mathrm{C} \\ \log \tau_c^+ &= -0.95 \end{aligned} \tag{7}$$

$$\Delta S_p^+ = 2.5176 \Delta H_p^+ - 55.5718 \tag{8}$$

and for the negative compensation

$$\begin{aligned} T_c^- &= 82.38\,^\circ\mathrm{C} \\ \log \tau_c^- &= 4.77 \end{aligned} \tag{9}$$

$$\Delta S_p^- = 2.8073 \Delta H_p^- - 80.3676 \tag{10}$$

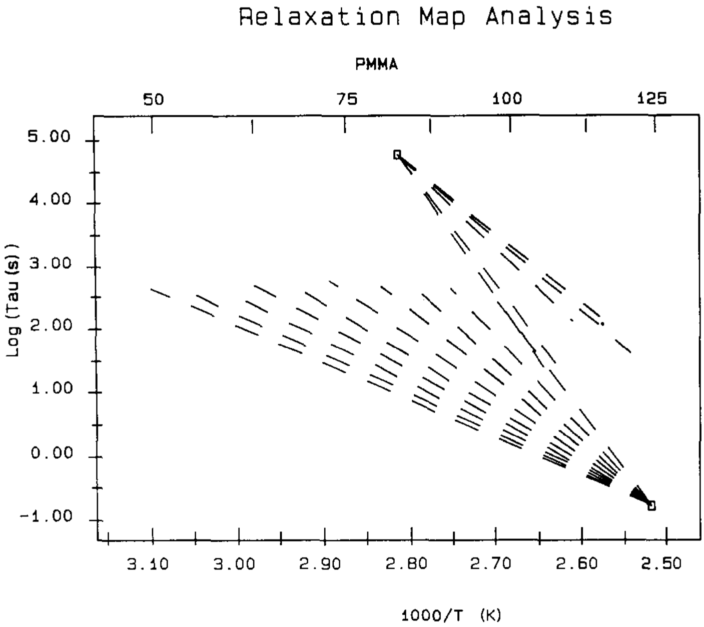

Fig. 11. The relaxation map drawn on an Arrhenius system of coordinates shows a Z structure.

The value of ΔG_c^+ and ΔG_c^- at the corresponding compensation temperatures T_c^+ and T_c^-, and the value of entropy and enthalpy at T_g, i.e. at the intercept of the positive and negative compensation lines, can now be calculated using the equation

$$\Delta G_c = \left[\log \tau_c + \log T_c + \log(k/h)\right] RT_c$$

where R is the gas constant (1.987 cal mol^{-1}). Therefore:

$$\begin{aligned} \Delta G_c^+ &= 22.11 \text{ kcal mol}^{-1} \\ \Delta G_c^- &= 28.88 \text{ kcal mol}^{-1} \end{aligned} \tag{11}$$

The intercept of the 2 compensation lines occurs for

$$\begin{aligned} \Delta H_g &= 85.59 \text{ kcal mol}^{-1} \\ \Delta S_g &= 159.91 \text{ cal } {}^\circ\text{C}^{-1} \text{ mol}^{-1} \end{aligned} \tag{12}$$

which correspond to the enthalpy and entropy of activation at T_g.

Figure 11 summarizes the situation for an Arrhenius system of coordinates, and illustrates "a Z structure". The Arrhenius lines span the relaxation map drawing a kind of "Z" when the temperature of polarization, T_p, varies. If one considers that I have mirrored the $1/T$ temperature axis so that T increases to the right (although $1/T$ is plotted), the relaxation map across T_g does actually look like a Z. The Z line is the line

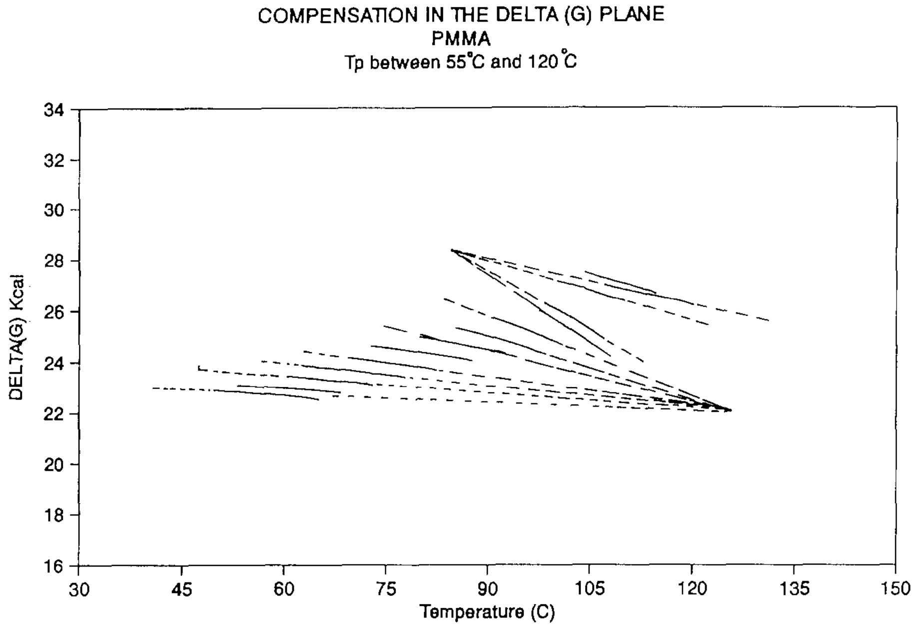

Fig. 12. The Z structure displayed in the ΔG plane.

passing through the two compensation points. Its image in the EE plane (Fig. 10) is the intercept of the two positive and negative compensation lines. Its coordinates are given by eqn. (12), and one can calculate the slope and intercept of the Z line in Fig. 11 from eqn. (6). Figure 12 displays the Z structure in the ΔG plane.

DETERMINATION OF T_g AND THE ACTIVATION ENTROPY AND ENTHALPY AT T_g

One observes that the value of the compensation temperatures are located on both sides of T_g (102 ° C), as determined for instance by DSC, or by the value of T_p at the maximum of entropy (Fig. 6). One can stipulate, for instance, that the temperature of T_g corresponds to the medium value between the ΔG_c of the positive and negative compensation points; therefore T_g can be calculated from the characteristics of the compensation points:

$$\begin{aligned} \Delta G_g &= (\Delta G_c^+ + \Delta G_c^-)/2 \\ \Delta G_g &= \Delta H_g - T_g \Delta S_g \end{aligned} \qquad (13)$$

With ΔH_g and ΔS_g as given by eqn. (12), one obtains $T_g = 102.64\,^\circ\mathrm{C}$.

Another possible, preferable, definition of T_g comes from the calculation of ΔG_p (ΔG at $T = T_b$). Figure 8 shows that ΔG_p is linearly related to T_p, and that to a first approximation

$$\Delta G_p(T_p) = a + bT_p$$

where a and b are curve-fitting constants determined by regression; for many polymeric systems, it is often found that $a = 0$ and $b = 0.0705$ kcal K^{-1} mol^{-1}. T_g can be determined as the intercept of the Z line in the ΔG plane, and the $\Delta G_p(T_p)$ vs. T_p line

$$T_g = (\Delta H_g - a)/(\Delta S_g + b)$$

The result of 101.3 °C for PMMA corresponds well with the temperature of maximum entropy, and with the DSC results for this polymer.

From the expression of the compensation lines formulated in the EE plane, eqns. (8) and (10), one can easily calculate the value of the extrapolated enthalpy $\Delta H_{o,s}$ when the entropy is zero, and compare that value with ΔH_g. According to views expressed in the theory of Gibbs and DiMarzio [15], or perhaps in the treatment by Hoffmann et al. [16] of compensation phenomena, the ratio $\Delta H_g/\Delta H_{o,s}$ would be representative of the number of elementary units moving at T_g.

From eqn. (8), $\Delta H^+_{o,s} = 22.07$ kcal mol^{-1}, and from eqn. (10), $\Delta H^-_{o,s} = 28.63$ kcal mol^{-1}. These values are obviously equal to those calculated for ΔG^+_c and ΔG^-_c (eqn. (11)) as $\Delta S_p = 0$ in eqn. (3). On the basis of eqn. (12), the number of units moving at T_g would be between 3 and 4.

DOD NUMBER

Another interesting parameter seems to be $\Delta S_{o,h}$, i.e. the extrapolated value of the entropy of activation for $\Delta H_p = 0$. This is the intercept of the compensation lines themselves, eqns. (8) and (10):

$$\begin{aligned} \Delta S^+_{o,h} &= -55.572 \text{ cal } {}^\circ\text{C}^{-1} \text{ mol}^{-1} \\ \Delta S^-_{o,h} &= -80.368 \text{ cal } {}^\circ\text{C}^{-1} \text{ mol}^{-1} \end{aligned} \tag{14}$$

If these values are multiplied by T_c (in K), from eqns. (7) and (9), one finds

$$\begin{aligned} T^+_c \Delta S^+_{o,h} &= -22.290 \text{ kcal mol}^{-1} \\ T^-_c \Delta S^-_{o,h} &= -28.573 \text{ kcal mol}^{-1} \end{aligned} \tag{15}$$

which again, obviously, equal the respective $-\Delta G_c$'s because ΔH_p is zero this time.

T_c can be rewritten thermodynamically

$$T_c = \Delta H_{o,s}/(-\Delta S_{o,h}) \tag{16}$$

which is the ratio of an enthalpic to an entropic term, as in the case of a first-order thermodynamic transition. One cannot attribute any specific meaning to this equation at this stage. I show in a companion paper that the two terms entering eqn. (16) play a role in determining the location of the branches of a multi-compensation plot in the EE plane. The $(-\Delta S_{o,h})$ term is as important as $\Delta H_{o,s}$ or T_c in the determination of the actual state of the polymeric system, and provided two parameters are specified, the third can be calculated from eqn. (16). One can choose any one of them, say the entropic term (the value of ΔS at $\Delta H = 0$) to define the DOD number of the material:

$$\mathrm{DOD} = 100 + \Delta S_{o,h} \tag{17}$$

The number 100 is arbitrarily added to $\Delta S_{o,h}$ in order to shift all values to the positive side. Based on results obtained in the sub-EE plane (not presented here, but introduced at another meeting [17], it is suggested that a better physical meaning is actually achieved if 72 is used instead of 100 to obtain the true atomic entropic term. However, for the moment, one can simply consider eqn. (17) as a formula to define the DOD number, nothing else. Normally, only the positive compensation line is used to characterize the structure with the DOD number. For instance, the DOD for the PMMA of Fig. 2 is 44.43.

I stipulate that the value of $(T_c^+ - T_g)$ is also significant in representing the internal state of the glass below T_g. The larger $(T_c^+ - T_g)$, the less "internally stressed" the structure.

Finally in this section on the compensation phenomena in the EE plane, the possible significance of the results will be examined. Rewriting eqn. (2) at T and T_c, and combining, the compensation phenomenon is often described in the literature [3] in the Arrhenius plane

$$\log(\tau/\tau_c) = (\Delta G_p/k)(1/T - 1/T_c)$$

which puts the emphasis on the coordinates of the compensation point. How is T_c related to T_g? And why is it empirically found that T_c^+ is often located at 23 °C above the T_g of the polymer [6], as characterized by DSC? Should one shift the origin of the axes to the point of compensation to rescale the data?

DUALITY AT T_g

I prefer to emphasize the result differently, and rewrite the compensation equation in the ΔG plane:

$$\begin{aligned} \Delta G_p &= \Delta H_p - T\Delta S_p \\ \Delta H_p &= T_c(\Delta S_p - \Delta S_{o,h}) \end{aligned} \tag{18}$$

and

$$T_c = [\Delta H_{o,s}/(-\Delta S_{o,h})] = [\Delta H_p/(\Delta S_p - \Delta S_{o,h})] \tag{19}$$

by analogy, it seems interesting to define $\Delta S_{\mathrm{og,h}}$ at T_g by

$$T_g = \left[\Delta H_g / (\Delta S_g - \Delta S_{\mathrm{og,h}})\right] \tag{20}$$

I have found empirically that $\Delta S_{\mathrm{og,h}}$ takes value between -72.0 and -68.0 cal $°\mathrm{C}^{-1}$ mol^{-1} for a large number of polymers tested with this formula (T_g is measured at the maximum of the entropy vs. T_p plot, or calculated using the Z line crossing technique explained previously, and ΔH_g and ΔS_g are given by the intercept of the two compensation lines (Fig. 10)). For instance, for the PMMA analyzed here with T_g equal to 101.3, one finds $\Delta S_{\mathrm{og,h}} = -70.5$.

The shifting value of approximately -70 cal $°\mathrm{C}^{-1}$ mol^{-1} seems to play a role when determining the intercept of branches of multi-compensation lines.

Our emphasis is therefore on the Z line itself, and the duality which exists at T_g: what is happening at $T = T_g$, which compensation "world" prevails (in choosing between the two compensations), is there a structured balance of driving forces leading to oscillation, or some sort of chaotic behavior with large fluctuation? Why is the entropy going through a maximum at T_g, and should our understanding of the T_g process be improved from it? In particular, should we not use the enthalpy, entropy and free energy of activation defined from the Z line to compare the TSC results with those obtained by other dynamic electrical thermal analysis techniques?

CONCLUSION

Based on this study on PMMA, and many similar results obtained for a variety of polymers, it seems possible to conclude that relaxation map analysis and compensation phenomena can be used to characterize the amorphous state of polymers in a manner fundamentally different from other traditional thermal analysis instruments.

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