

Multiple compensation phenomena in the amorphous phase of polymers^a

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Abstract

Compensation phenomena are studied for amorphous polymers; it is shown that the number and sign of the multi-compensations observed depend on the thermal history of the cooling. An improved picture emerges of the fundamental mechanism of the overall relaxation process. The complementary roles played by the enthalpy and entropy of activation is implied.

INTRODUCTION

When several Arrhenius lines from a relaxation map converge into 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 coordinates, (T_c and $\log \tau_c$), 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. In this article, several examples of multi-compensations for PEBAX, polystyrene, and polycarbonate are presented. It was pointed out by Lacabanne and Bernes [1] that the several compensation points observed for polystyrene and polycarbonate might be caused by the presence of several amorphous phases, perhaps the indication of "local ordering", a subject of great controversy. It is true that in the case of a multi-phase system, such as a segregated blend, the relaxation map displays multi-compensations, each associated with the T_g of the corresponding phase. However, one observes that in the case of a true monophasic amorphous polymer, e.g. polystyrene, the number of compensation points found on the relaxation map depends on the thermal mechanical history: the processing variables, the cooling rate, the amount of pressure, orientation,

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etc. The origin of multi-compensations in monophasic amorphous systems is debated here, and an alternative explanation for the existence of multiple compensation laws based on the EKNET (Energetic Kinetic Network) structure of the inter-intra molecular potential energy barrier of the polymers is proposed.

MULTI-COMPENSATIONS IN A MULTI-PHASE SYSTEM

Lacabanne and collaborators have published extensively on this subject [2-5]. Figures 1 and 2 summarize the issues, with PEBA as an example (a block copolymer of PTMG, polytetramethylglycol, and PA, polyamid). In the case of the homopolymer in Fig. 1 (PTMG), only one T_g is observed. The compensation search leads to a single compensation line, and one observes one compensation phenomenon in Fig. 1. The presence of two phases in the morphology is clearly revealed in Fig. 2 by two compensations, one associated with the PTMG phase, at the lower temperature, and one associated with the polyamid phase at the higher temperature. Comparison of the respective positions of the compensation lines for the homopolymer

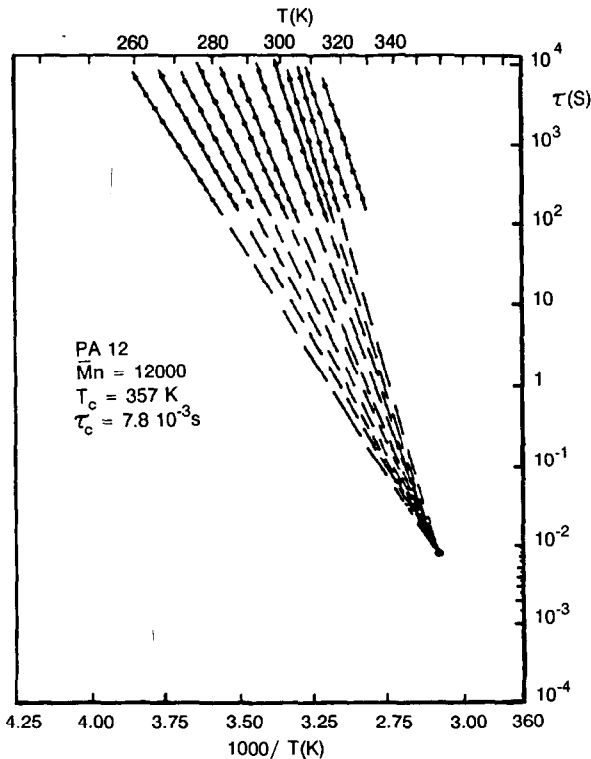


Fig. 1. The compensation phenomenon observed for PTMG homopolymer.

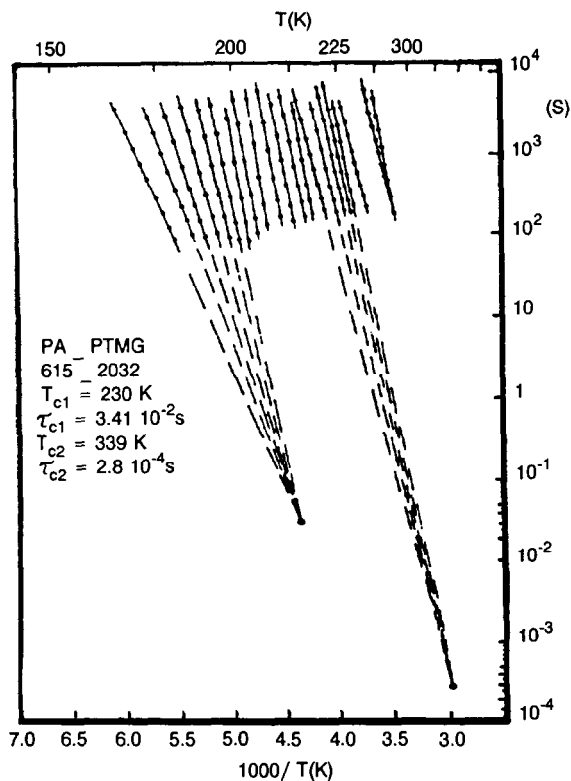


Fig. 2. The two compensation phenomena observed for PEBA copolymer.

and the block copolymer leads to a greater understanding of the segregation characteristics between the phases and, in particular, to the degree of interpenetration and local compatibility [6]. It is clear that in this case, there is a direct relationship between the number of compensations and the number of phases in the morphology.

MULTIPLE COMPENSATION PHENOMENON IN AMORPHOUS POLYSTYRENE AND POLYCARBONATE

Fifteen years ago, the existence of local order in the structure of amorphous polymers, such as polystyrene and polycarbonate [7–10] was considered controversial, but the debate rapidly settled after small-angle neutron scattering results (SANS) were presented by Benoit [11], and after it was found possible to fabricate the nodular pictures observed by Yeh [7] and Neki and Geil [8] by defocusing the ESM beam [12]. Atactic polystyrene is now considered to be a totally amorphous monophasic system [13]. Polycarbonate is susceptible to crystallization under certain circumstances, and therefore only quenched specimens are considered totally amorphous with no local ordering.

Eyring Analysis

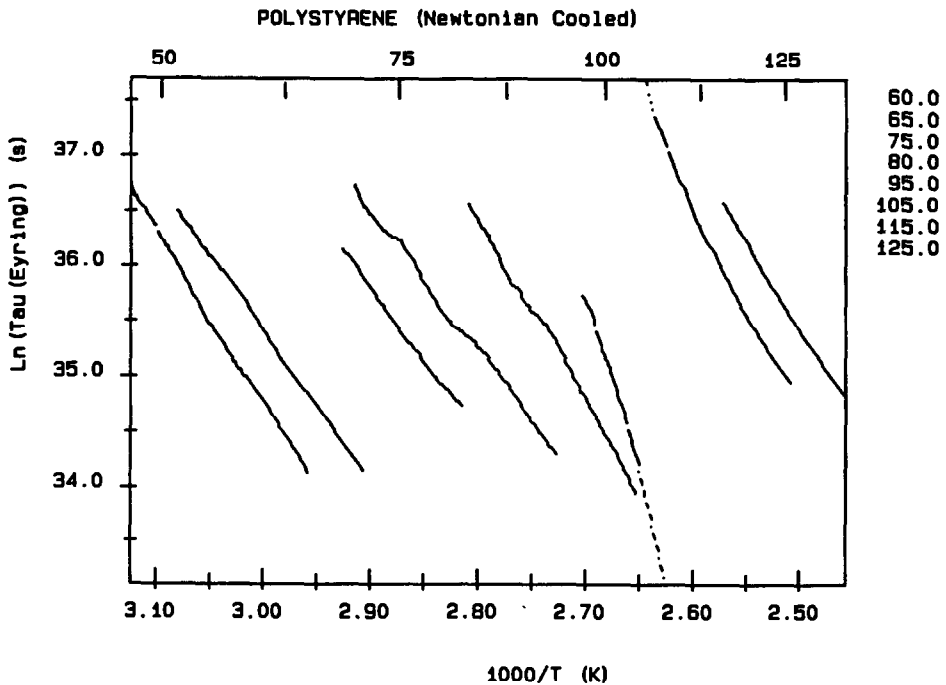


Fig. 3. Relaxation map (Eyring plane) of a slowly cooled polystyrene.

The data of Figs. 3–22 are taken from the theses of Bernes (polystyrene) [14] and Bettacchioli (polycarbonate) [13], who both worked on samples provided by Solomat, and characterized them by TSC/RMA spectroscopy. Bernes and Bettacchioli's data are plotted differently and analyzed with a different focus here to stress the multi-compensations and to determine their characteristics and meaning. The view point and analysis presented here do not necessarily represent the opinion of these respective authors. In particular, Lacabanne and Bernes have recently [1] concluded that local ordering of the amorphous phase of polycarbonate exists, based on the results which we re-analyze here.

POLYSTYRENE

Figure 3 is a relaxation map (in the Eyring plane) of a polystyrene cooled very slowly from 180°C in a platen pressure mold. There is virtually no pressure applied on the specimen during the cooling stage. The mold is cooled by shutting off the power to the heater cartridges (Newtonian cooling). It took approximately 7 hours to cool the mold down to 50°C. Table 1 gives the thermokinetic functions as a function of the temperature of

TABLE 1

Thermokinetic functions as a function of the temperature of polarization (T_p)

	T_p ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	Enthalpy (kcal)	Entropy (cal C^{-1})	ΔG (kcal)
1	60.0	70.8	30.8906	23.6368	23.0196
2	65.0	76.6	27.1823	11.1923	23.3993
3	75.0	94.3	25.9793	4.2110	24.5138
4	80.0	99.5	25.0293	0.0593	25.0084
5	95.0	107.3	32.4905	18.5915	25.6488
6	105.0	108.8	67.5262	111.1845	25.4985
7	115.0	138.7	38.8583	28.3365	27.8637
8	125.0	144.9	30.5001	5.8074	28.1887

polarization T_p . Figure 4 is the compensation search in the EE plane. The polarization temperature is varied between 60 and 125 $^{\circ}\text{C}$ (the window temperature is 10 $^{\circ}\text{C}$). The numbers on the figure apply to increasing polarization temperatures. Two negative compensation lines are clearly observed. The first compensation line is made up of points 1, 2, 3 and 4; point 5 ($T_p = 95^{\circ}\text{C}$) seems to be lost between the two lines; points 6, 7 and 8 are aligned on another negative compensation line.

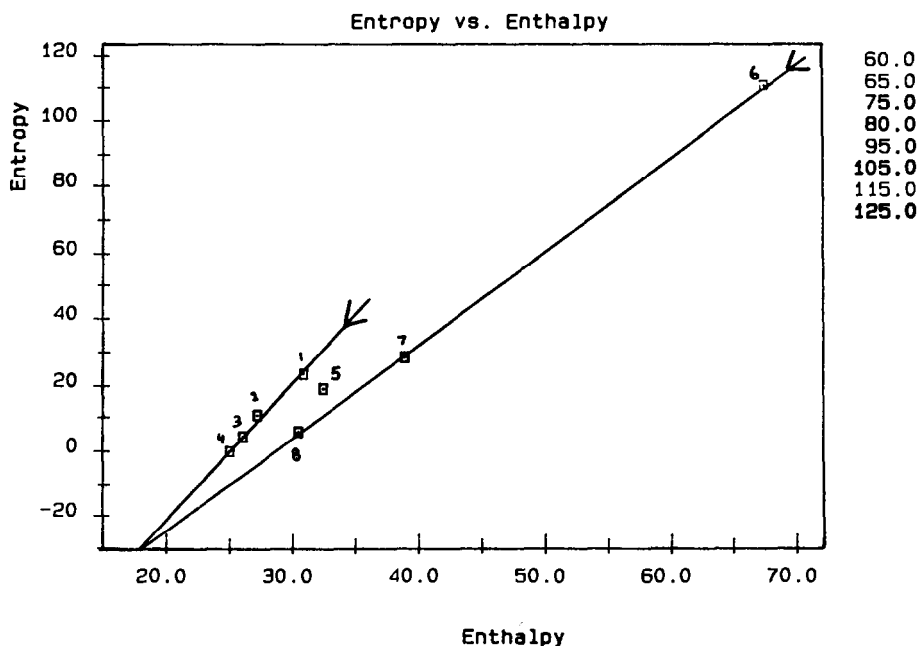


Fig. 4. Compensation search (EE plot) for the polystyrene sample in Fig. 3.

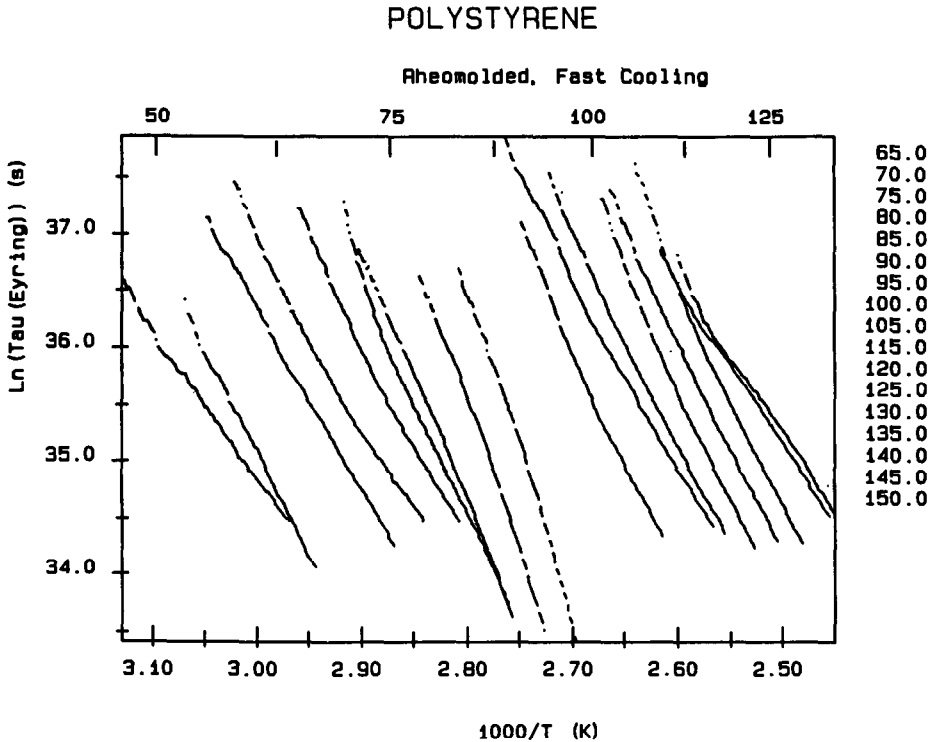


Fig. 5. Relaxation map (Eyring plane) of a polystyrene that was mechanically pressurized during a fast cooling treatment.

A more detailed analysis of this polystyrene specimen will be provided later, but at this stage, one might want to question the reasoning which consists in equating the number of glassy phases or “transitions” with the number of compensation points, and ask whether negative compensation points are valid.

Figures 5–10 relate to the same polystyrene, but mechanically pressurized during a fast cooling treatment. The mechanical treatment includes the application of vibration to induce specific thermal history patterns, a process known as “rheomolding” [15]. The mold is cooled in approximately 30 seconds. The rate of cooling when the glass transition temperature is crossed is around 7°C s^{-1} .

Using the notations and definitions presented in a companion paper of this issue [16], the following remarks can be made.

Figure 5 is the relaxation map in the Eyring plane. Figure 6 is the unanalyzed EE plot. Figure 7 is an attempt to find the compensation lines, both positive and negative, in the intercept versus slope system of coordinates. A series of positive followed by negative compensation lines are observed. The following figure, Fig. 8, reveals that the positive compensation

Entropy vs. Enthalpy (Of Activation)

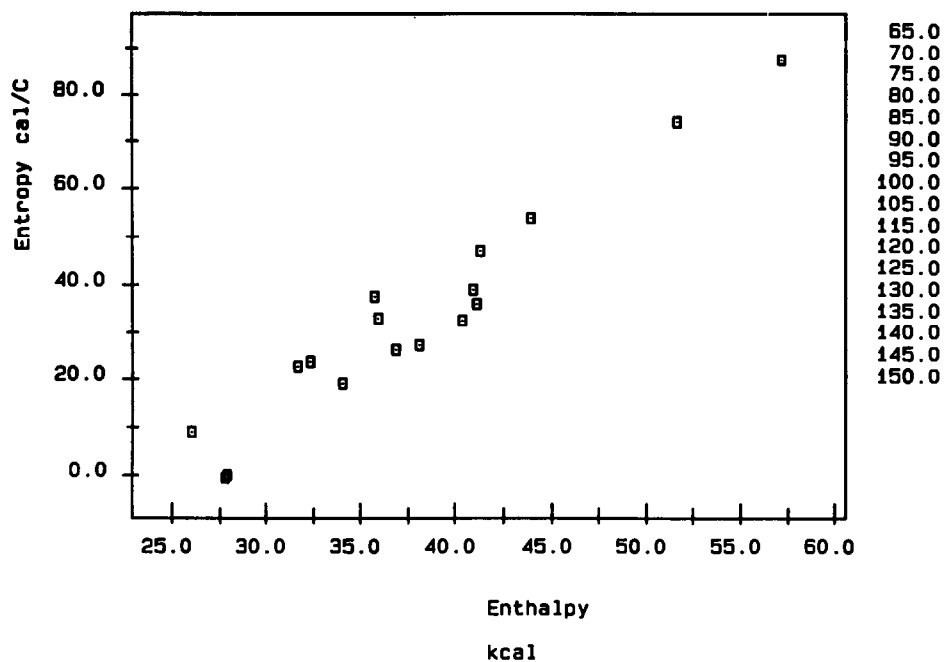


Fig. 6. Unanalyzed EE plot for the polystyrene sample in Fig. 5.

Compensation Search

Rheomolded, Fast Cooling

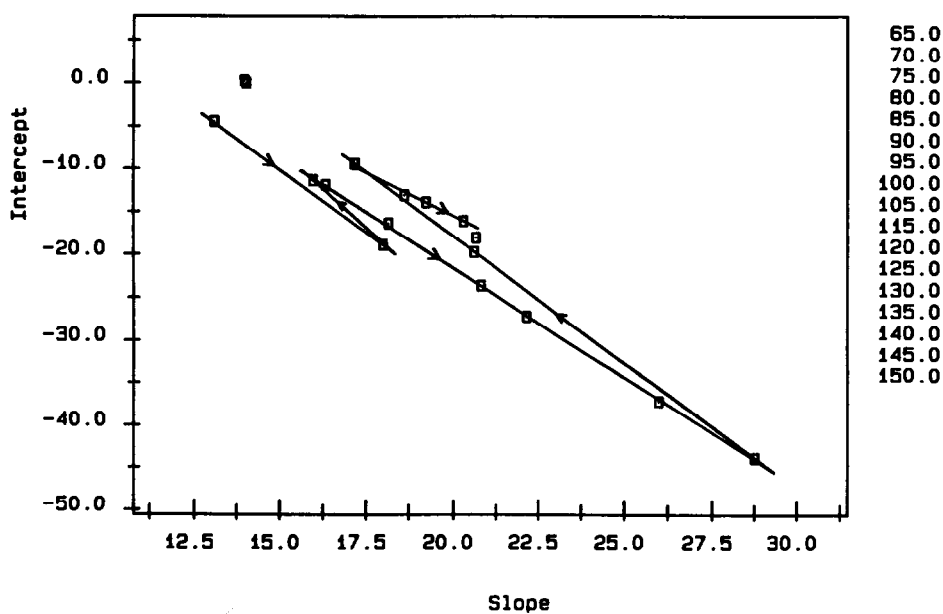


Fig. 7. Compensation search for the polystyrene sample in Fig. 5.

lines converge on the $\Delta S = 0$ axis. The corresponding value of ΔH at the intercept point is 23 kcal.

Figure 9 concentrates on the negative compensation lines. This is a more difficult analysis because of the lack of points to define the lines accurately. Nevertheless, it is possible to draw three negative compensation lines, two with confidence. Interestingly, it seems possible to force the negative compensation lines in the EE plane to intercept on either the $\Delta S = 0$ axis or the $\Delta H = 0$ axis (an attempt to draw such a feature is shown in Fig. 9). At this stage, a lack of accuracy in the determination of the negative compensation lines prevents the conclusion that such procedures are valid.

Figure 10 represents a summary of the compensation search, displaying a triple Z structure with several Z lines and 6 compensation points (3 positive, 3 negative). Note that a single line has been drawn through the positive compensation points: this feature expresses, in the Eyring plane, the convergence of the positive compensation lines in the EE plane (Fig. 8).

The following results (with ΔS_p in $\text{cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$ and ΔH_p in kcal mol^{-1}) were obtained.

$$\Delta S_p = 2.9514 \Delta H_p - 67.951 \quad 65 \leq T_p \leq 70^\circ\text{C}$$

$$\Delta S_p = 3.6268 \Delta H_p - 92.065 \quad 70 \leq T_p \leq 75^\circ\text{C}$$

$$\Delta S_p = 2.5720 \Delta H_p - 59.191 \quad 75 \leq T_p \leq 105^\circ\text{C}$$

$$\Delta S_p = 2.9603 \Delta H_p - 81.855 \quad 105 \leq T_p \leq 120^\circ\text{C}$$

$$\Delta S_p = 2.3862 \Delta H_p - 62.047 \quad 120 \leq T_p \leq 135^\circ\text{C}$$

$$\Delta S_p = 2.6381 \Delta H_p - 73.740 \quad 140 \leq T_p \leq 150^\circ\text{C}$$

The Gibbs free activation energy and the temperature of compensation at the compensation points ΔG_c and T_c can be derived from regression analysis

ΔG_c (kcal mol^{-1})	T_c ($^\circ\text{C}$)
$\Delta G_c(1)^+ = 23.02$	65.7
$\Delta G_c(1)^- = 25.38$	2.57
$\Delta G_c(2)^+ = 23.01$	115.6
$\Delta G_c(2)^- = 27.65$	64.6
$\Delta G_c(3)^+ = 26.00$	145.9
$\Delta G_c(3)^- = 27.95$	105.9

At first sight, the relaxation behavior looks chaotic and quite complex. However, it appears that the Gibbs free energy at the compensation points alternates between two values, approximately 23 and 27.75 kcal mol^{-1} . It also seems that whatever goes on at T_g itself is not inherent to that temperature, and that one can define several Z lines, one above and one below T_g . One designates the "transitions" as T_g^- and T_g^+ , defined by the corresponding Z lines, which are observed in the sub- T_g and the $T > T_g$

Entropy vs. Enthalpy
(Of Activation)

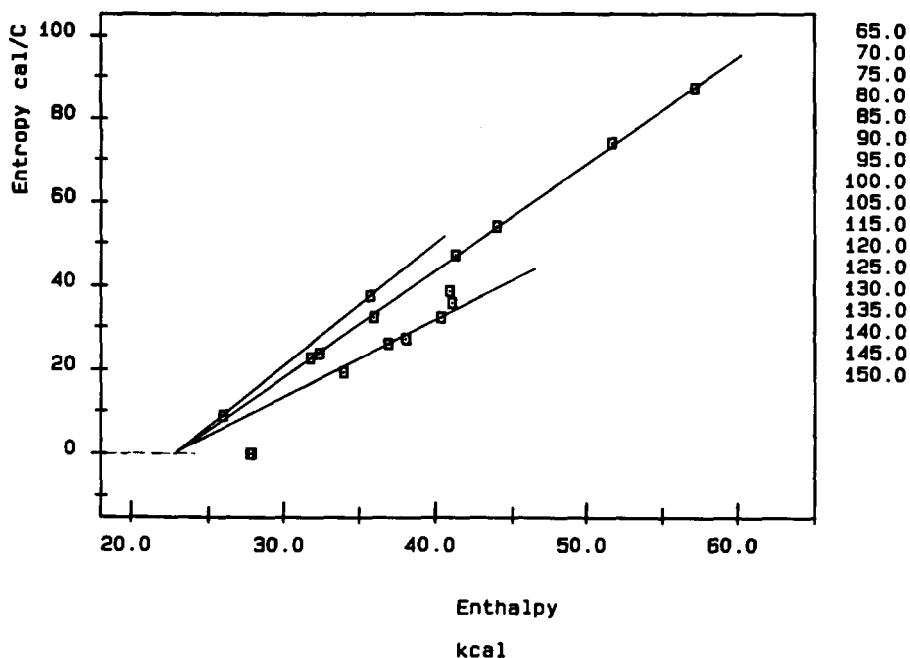


Fig. 8. The positive compensation lines of Fig. 6 compensate on the $\Delta S = 0$ axis.

regions: their values can be determined from the crossing of the positive and negative compensation lines

$$\begin{cases} \Delta S_g^- = 37.42 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1} & T_g^- = 66.2^\circ\text{C} \\ \Delta H_g^- = 35.70 \text{ kcal mol}^{-1} \end{cases}$$

$$\begin{cases} \Delta S_g = 90.93 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1} \\ \Delta H_g = 58.37 \text{ kcal mol}^{-1} & T_g = 102.6^\circ\text{C} \end{cases}$$

$$\begin{cases} \Delta S_g^+ = 48.72 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1} & T_g^+ = 140.0^\circ\text{C} \\ \Delta H_g^+ = 46.42 \text{ kcal mol}^{-1} \end{cases}$$

Figure 11 is a plot in the ΔG plane of the three Z lines corresponding to T_g^- , T_g and T_g^+ . It becomes clear that the "transitions" which are revealed by this type of analysis match closely what other authors describe as the T_β , T_α and $T_{1,1}$ transitions. Figure 11 could be compared with a "frequency map" [17], obtained with a dynamical a.c. device (dielectric or mechanical). The data collected for the relaxation map analysis (RMA) are much richer in detail than those transcribed from other thermal analysis techniques: this is

Entropy vs. Enthalpy
(Of Activation)

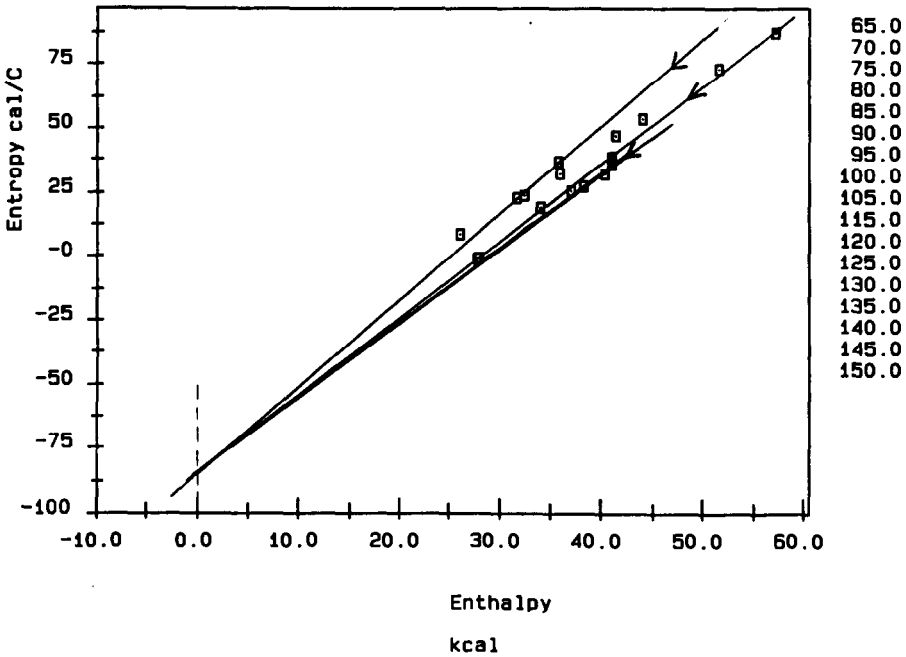


Fig. 9. The negative compensation lines of Fig. 6 compensate on the $\Delta H = 0$ axis.

demonstrated in Figs. 12 and 13 which plot the variation of entropy and free energy of activation versus T_p . RMA seems to indicate that the transitions perceived below and above T_g have the same relaxation origin as T_g itself. This is the same overall mechanism of relaxation which seems to unfold with T_p , perhaps as a result of structuring of the free energy into a network, as suggested by the EKNET theory [18]. Furthermore, the detailed structure of the kinetics of relaxation is suggested by the way the compensation lines of the EE plot gather into 2 sets, one possibly emerging from the $\Delta S = 0$ axis, and the other from the $\Delta H = 0$ axis. Figure 14 is an attempt to schematize this speculative situation. Another interesting question concerns the number of discrete compensation lines in the EE plane, and also their absolute value. Can one obtain a continuous series of discrete compensation lines by changing the thermo-mechanical history of the polymer, or is this effect quantified?

Returning to the analysis of the slowly cooled sample PS-VA, it was said that two negative compensations are clearly visible (Fig. 4). One can now re-examine the situation: point 5 ($T_p = 95^\circ\text{C}$) seems to line up with points 4 and 6 to form a positive compensation line. The positive compensation line

Relaxation Map Analysis

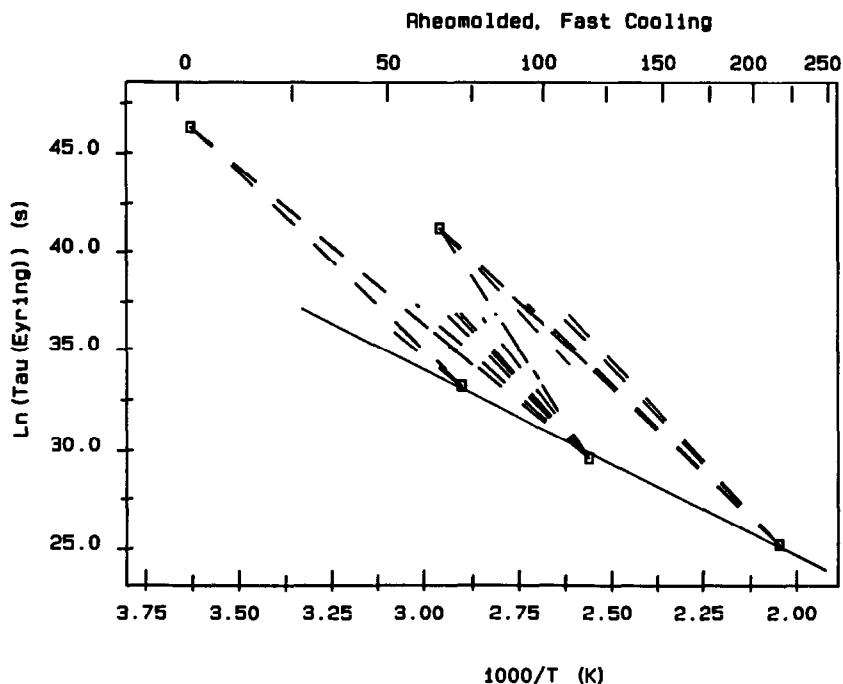


Fig. 10. A summary of the compensation search in the Eyring plane.

is not defined with certainty in this case, as there is only *one* intermediate point between 4 and 6 to determine its slope and intercept.

The following parameters have been calculated.

$$1^- \quad \Delta S_p = 3.9900 \Delta H_p - 99.034 \quad 60 \leq T_p \leq 80^\circ \text{C}$$

$$2^+ \quad \Delta S_p = 2.6236 \Delta H_p - 66.080 \quad 80 \leq T_p \leq 105^\circ \text{C}$$

$$3^- \quad \Delta S_p = 2.8573 \Delta H_p - 81.931 \quad 105 \leq T_p \leq 125^\circ \text{C}$$

The coordinates of the compensation points are found from the equation of the EE curves

$$1^- \quad T_c = -22.37^\circ \text{C}, \quad \ln(\tau_c(\text{Eyr})) = 49.83$$

$$2^+ \quad T_c = 108.08^\circ \text{C}, \quad \ln(\tau_c(\text{Eyr})) = 33.31$$

$$3^- \quad T_c = 75.47^\circ \text{C}, \quad \ln(\tau_c(\text{Eyr})) = 41.61$$

The intercept of lines 1^- and 2^+ is apparently point 4, which is located on the $\Delta S = 0$ horizontal line. Therefore, the free activation energy of the first two compensation points is the same: $\Delta G(1^-) = \Delta G(2^+) = 25.0 \text{ kcal mol}^{-1}$.

PLOT OF Z-LINES IN THE DELTA(G) PLANE
 Polystyrene (Fast cooled, Rheomolded)

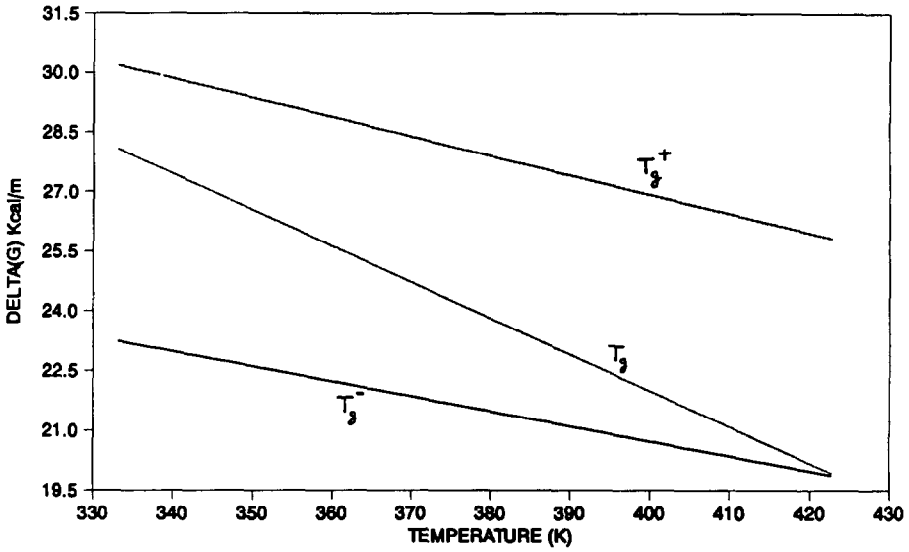


Fig. 11. A plot in the ΔG plane of the three Z lines corresponding to T_g^- , T_g and T_g^+ .

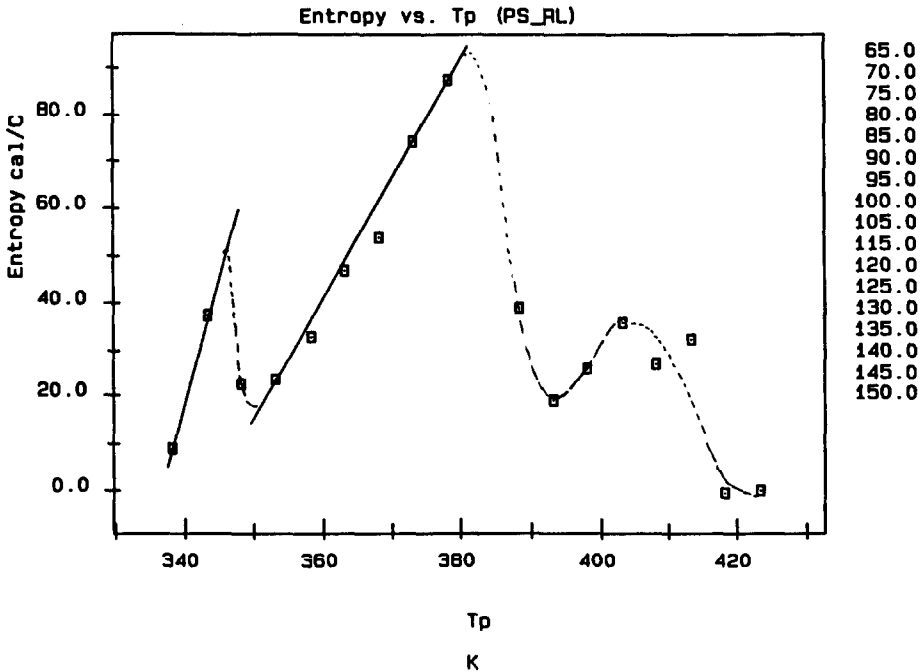


Fig. 12. Variation of entropy with T_p .

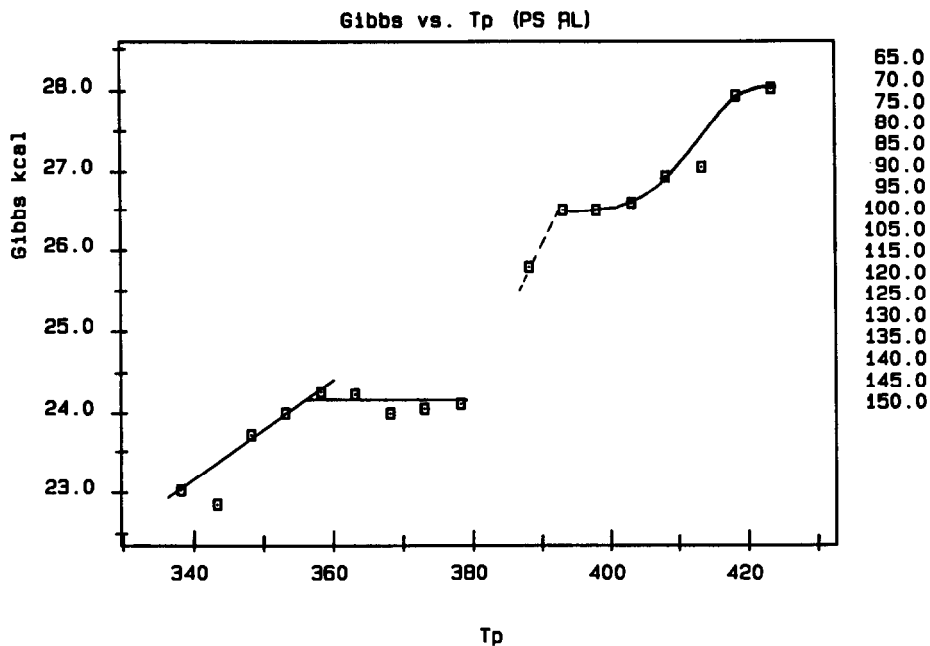


Fig. 13. Variation of free energy of activation with T_p (fast cooled rheomolded polystyrene).

This is an intriguing result: how could the free energy of activation be the same for two adjacent compensation points? In the case of the fast-cooled rheomolded polystyrene, the free energy is the same every other compensation point, which suggests a periodic return to the same state after a cycle. Figure 15 shows the result of the compensation search in the Eyring plane. The Z line for the transition between the first (negative) and the second (positive) compensation lines is represented in the Eyring plane as the straight line joining the first two compensation points. It is almost obvious from Fig. 15 that the two compensation points do not represent the same state. Could it be that the activation enthalpy and entropy are very different at T_c^+ and T_c^- , although structuring the same value of the free energy? The value of the enthalpy and entropy at the compensation points is unknown, but one can, for instance, speculate that $\Delta H_c^+ = 0$ for positive compensations and $\Delta S_c^- = 0$ for negative compensations, hence

$$\Delta G_c^+ = -T_c^+ \Delta S_c^+ \quad \text{and} \quad \Delta S_c^+ = \Delta S_{o,h}$$

$$\Delta G_c^- = \Delta H_c^- \quad \text{and} \quad \Delta H_c^- = \Delta H_{o,s}$$

The temperature T_p corresponding to the upper limit of the first Z line is 80°C. Up to that temperature, the Gibbs free energy of activation (Fig. 16) varies linearly with T_p (K)

$$\Delta G_p = 0.1018T_p - 10.96(33).$$

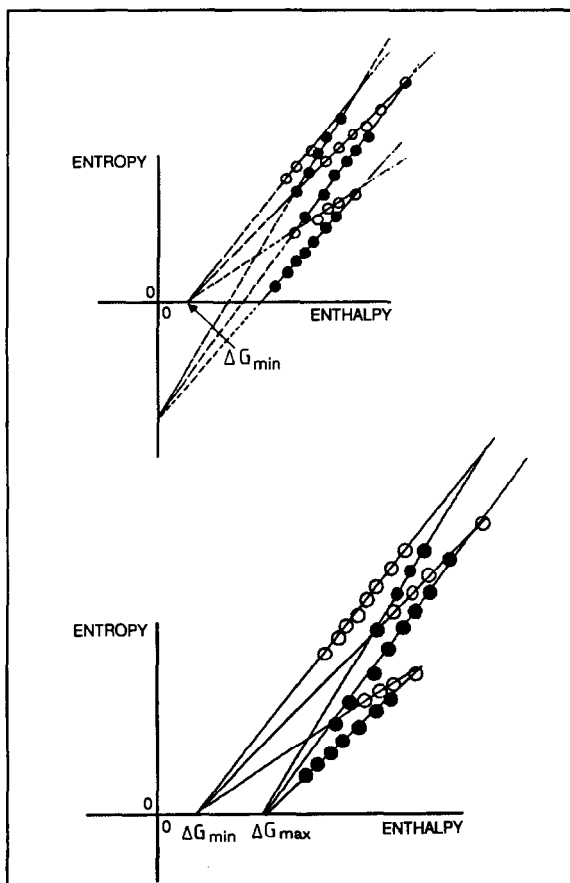


Fig. 14. Attempts to reconstruct the experimental results showing multi-compensations. Open circles are on positive compensations, filled circles on negative compensations.

Above 80°C and up to 105°C , the free energy seems to be constant at 25.52 kcal. Then the second Z line occurs at T_g , which shows up as a discontinuous change in ΔG_p and a return to a linear relationship between ΔG_p and T_p . Hence, on crossing the first Z line at 80°C , there is a radical change in the structure of the free energy.

The free energy of activation at the third compensation point is $\Delta G(3^-) = 28.675 \text{ kcal mol}^{-1}$. This time, the alternation from one compensation line to the next seems to result in a change of free energy for the compensation point.

In conclusion, the relaxation behavior for the slowly cooled specimen presents interesting characteristics which are not observed in the case of a fast quenched sample. Again, one can observe a series of positive and negative compensation lines which can be analyzed in the same systematic way. The analogy between what goes on in the EE plane and the $\log \tau$ versus $1/T$ plane is striking: one observes a Z structure in the EE plane.

Relaxation Map Analysis

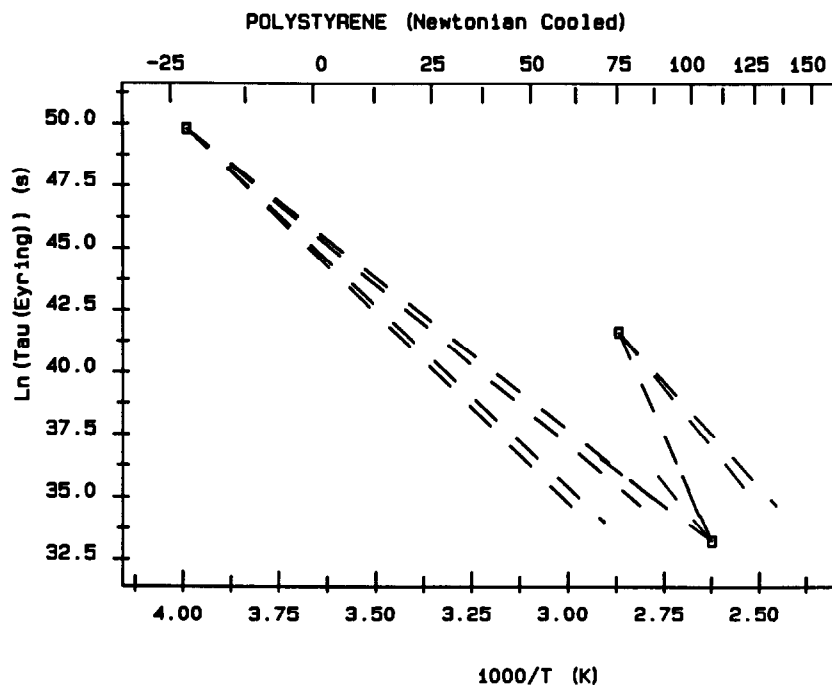


Fig. 15. Compensation search in the Eyring plane for the slowly cooled polystyrene sample.

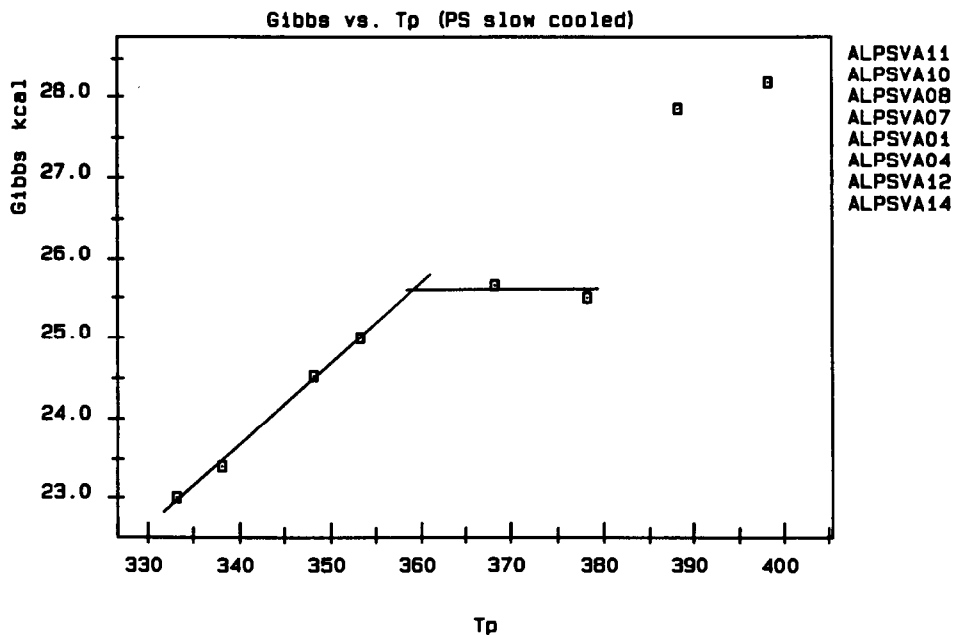


Fig. 16. Gibbs free energy of activation plotted against T_p for the slowly cooled polystyrene.

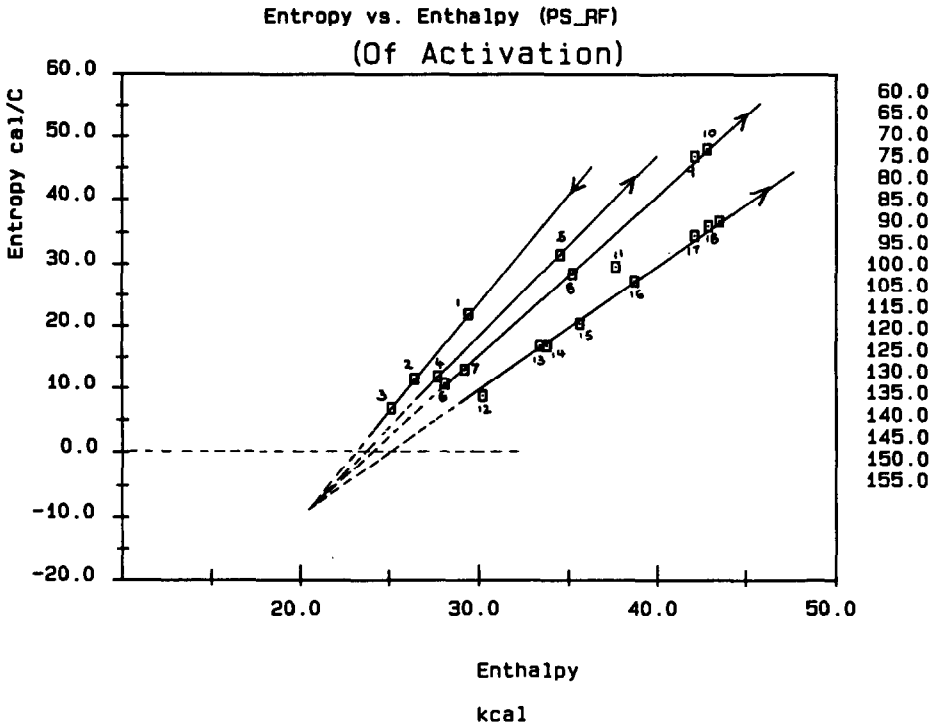


Fig. 17. Relaxation map (EE plot) of polystyrene sample PS-RF.

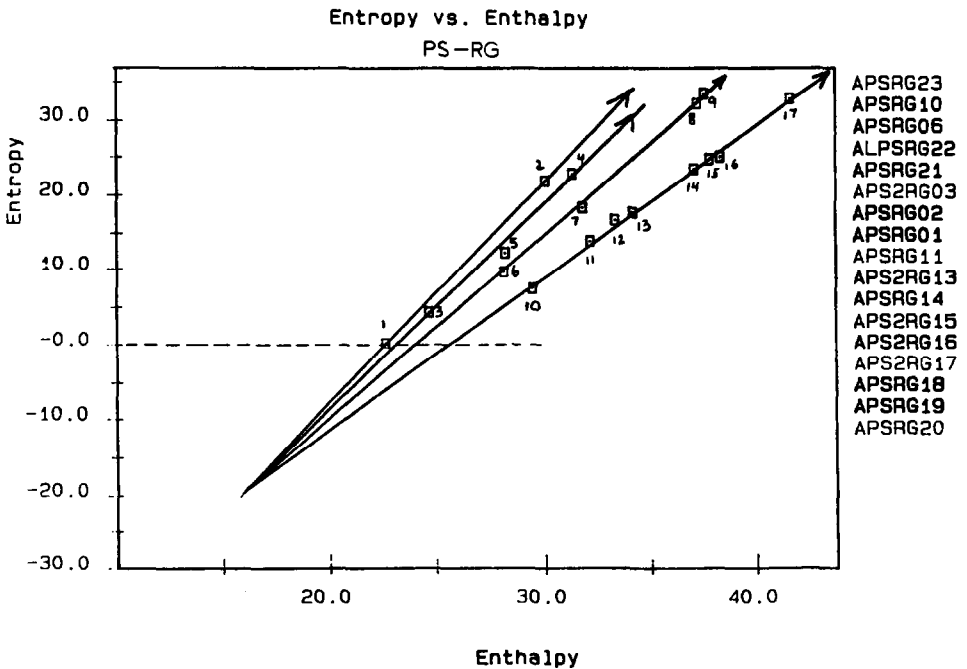


Fig. 18. Relaxation map (EE plot) of polystyrene sample PS-RG.

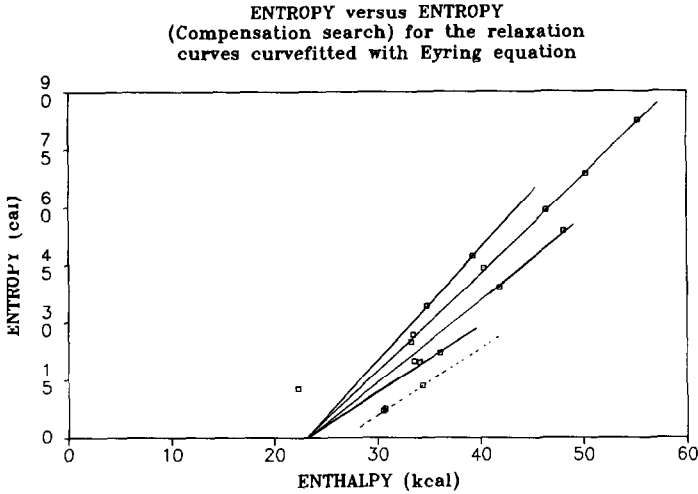


Fig. 19. Relaxation map (EE plot) of polystyrene sample PS-RO.

Figures 17–20 are EE plots obtained on the same polystyrene specimen submitted to a variety of thermo-mechanical treatments. These relaxation maps are provided to illustrate the generality of the phenomenon of multi-compensations, and to present some of their additional features.

In Fig. 17 (sample PS-RF), it is observed that points 1 and 2, 3 and 4, 6–9 and 10–17 group into 4 positive compensation lines which themselves compensate. The lack of points to determine the first two compensation lines with accuracy limits the validity of our findings. However, it seems that

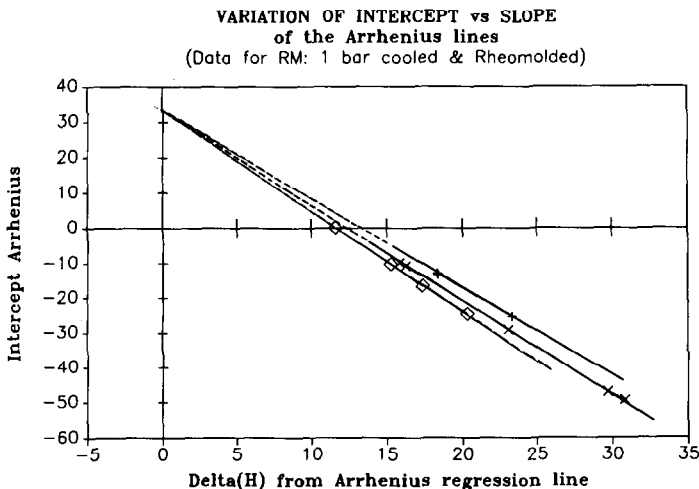


Fig. 20. Relaxation map (EE plot) of polystyrene sample PS-RM.

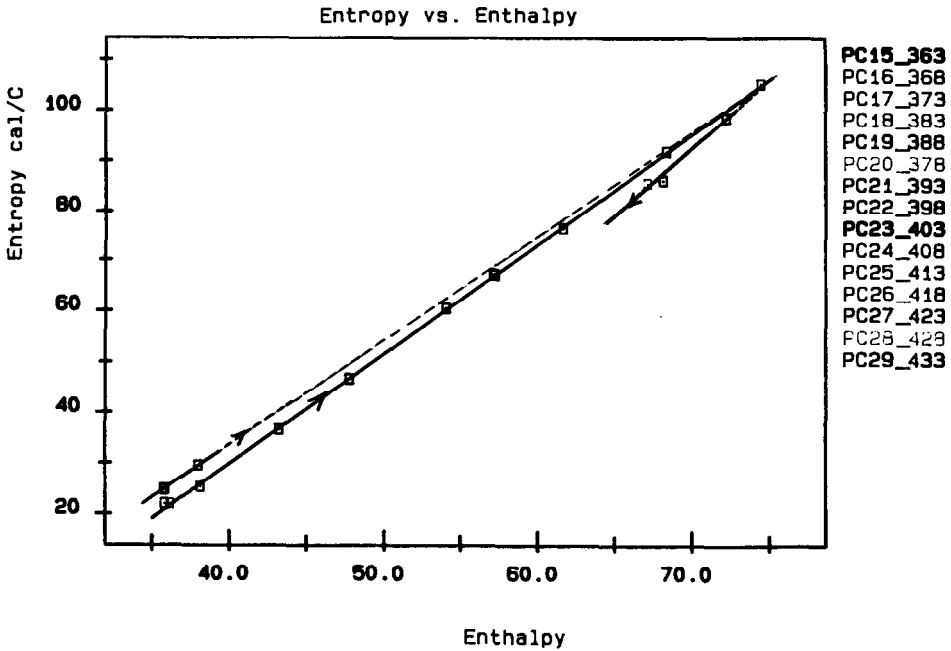


Fig. 21. EE plot for a polycarbonate sample annealed at 175 °C for 1 min.

the compensation lines converge into a point which is neither located on the $\Delta H = 0$ nor on the $\Delta S = 0$ axis (one could force the fit differently, but one does not know which way is justified). The point of convergence between the compensation lines is $-7 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$ and 20 kcal mol^{-1} . The behavior of the polystyrene sample of Fig. 18 (PS–RG) is quite similar, with approximately the same value for the converging point of the compensation lines in the EE plane, although the individual compensation lines do not have the same T_c , and they do not collect the same T_p (in other words the fragmentation of the T_p temperature span is different). Figure 19 gives the case of PS–RO for another thermal treatment: a set of compensation lines emerges from a point located on the $\Delta S = 0$ axis ($\Delta H_c = 23 \text{ kcal mol}^{-1}$). Figure 20 (PS–RM) illustrates an example of compensation lines seemingly compensating from a point of the $\Delta H = 0$ axis the compensation search is shown here as intercept Arrhenius lines versus their slope).

Polycarbonate

Figures 21 and 22 are the EE plots for two polycarbonate specimens which have been annealed at either 175 °C for 1 minute (Fig. 21) or 265 °C for 5 minutes (Fig. 22). Although Izod impact tests were not performed to check the assertion, it is believed that the first annealing treatment did not induce any change in the mechanical ductility of the polymer, whereas the

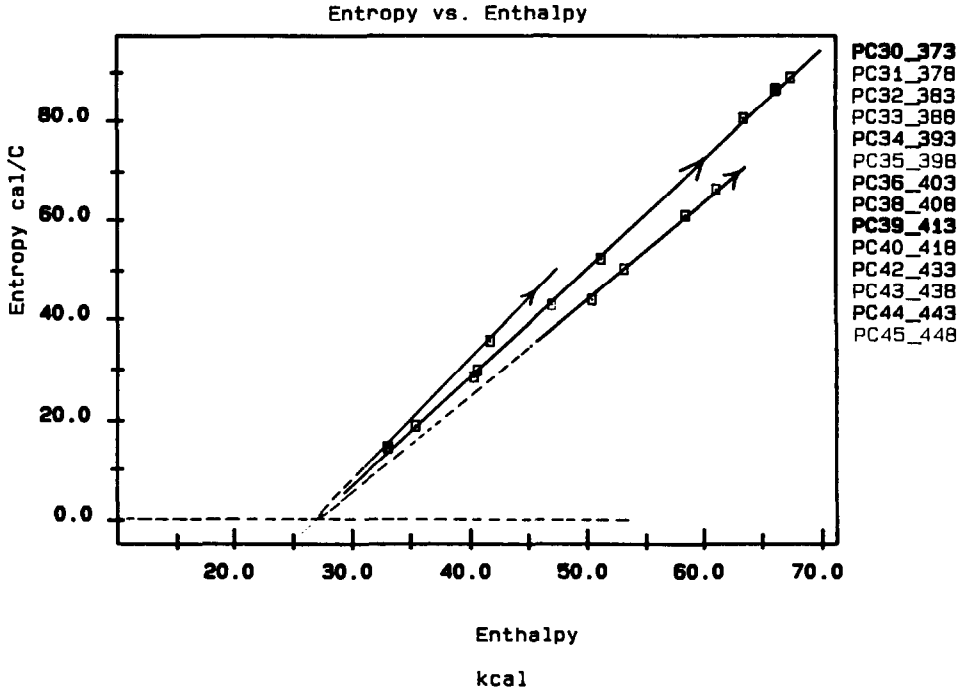


Fig. 22. EE plot for a polycarbonate sample annealed at 265°C for 5 min.

second treatment induced brittleness [19]. It is known [19] that aging polycarbonate below T_g makes it lose its impact strength entirely, the material behaving like a brittle polystyrene. The challenge here is to see whether the characterization by RMA of the annealed or unannealed specimens can throw some light on the matter.

The two EE plots are very different: the compensation lines for the extensively annealed PC converge on a point of minimum entropy, i.e. on the $\Delta S = 0$ axis. This behavior is reminiscent of polystyrene. The case of the ductile polymer reveals that the compensation lines now emerge from the point of maximum entropy or enthalpy of activation. This behavior is unique and unforeseen for brittle amorphous polystyrene. Based on this observation, could one set up a simple criterion for the ductility of amorphous polymers, and devise means to treat the material to induce ductility (for instance by a particular rheomolding treatment [15])? This interesting subject is beyond the scope of the present paper.

CONCLUSION

In conclusion, it can be seen that the thermally stimulated relaxation curves for an apparently classical amorphous polymer can be gathered into separate groups, each with a characteristic compensation point. It can be

claimed [1], on the basis of this behavior, that the structure of polystyrene or polycarbonate is made up of several "phases", each corresponding to a specific compensation diagram. It is true that in the case of segregated phases, such as in incompatible blends or block copolymers, the separate phases show up on a relaxation map as separate compensations. The result brought forward here is that the number and sign of the multi-compensations depend on the thermal history on cooling. Also, the fact that one can find simple relationships between the various compensation lines in the EE plane, strongly suggests that the relaxation processes described by the individual compensation lines, i.e. occurring below T_g , at T_g and above T_g , are all inter-related, perhaps revealing that it is the same process which repeats itself several times.

A better picture of the fundamental mechanism for the overall relaxation process starts to emerge from this study, and it looks more and more like the unfolding, by the effect of temperature, of an apparent chaotic phenomenon whose inner structure seems to be relatively simple. The distinct and complementary role played by the enthalpy and entropy of activation is implied in the unfolding mechanism.

It is stipulated in this paper that the phenomenon of multiple compensations can be the result of the energetic and kinetic nature of the interactions between the three-bond elements (the conformers) making up the grand statistical ensemble of bonds (belonging or not to the same macromolecules). The dual split kinetics theory [16,20] proposes an explanation for the existence of compensation laws based on the inter-intra molecular potential energy barrier. The concept of energetic kinetic network (EKNET) may help to understand the existence of the multiple compensations, their sign, and the apparent alternation between them [18]. The EKNET theory claims that the different compensation points observed at T_g^- (T_β), T_g and in the vicinity of the $T_{1,1}$ transition (T_g^+) are the result of a competition between two mechanisms—the tendency to create a free energy network, and the structuring of the energetic kinetic systems of this network to comply with the dual split kinetic model. In other words, it is believed that the visco-elastic and relaxation response of amorphous polymers reveals the fractalian structure of the free energy, which results in a pseudo-chaotic type of relaxation pattern, as illustrated in Figs. 3–22. This subject is beyond the scope of the present paper and is introduced elsewhere [16,18,20].

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