

# Physical Aging in Polymers: Comparison of Two Ways of Determining Narayanaswamy's Parameter

MARIE-ELODIE GODARD *and* JEAN-MARC SAITER

*Laboratoire d'Etude et de Caractérisation des Amorphes et des Polymères (LECAP)*

*UFR de Sciences et Techniques, Université de Rouen  
76821 Mont-Saint-Aignan Cedex, France*

FABRICE BUREL *and* CLAUDE BUNEL

*Laboratoire de Matériaux Macromoléculaires (L2M)  
Institut National des Sciences Appliquées de Rouen  
B.P. 08 76131 Mont-Saint-Aignan Cedex, France*

PILAR CORTES *and* SALVADOR MONTSERRAT

*Laboratori de Termodinàmica  
E.T.S. Enginyers Industrials de Terrassa  
Universitat Politècnica de Catalunya  
08222 Terrassa, Spain*

JOHN M. HUTCHINSON

*Department of Engineering  
Aberdeen University  
Aberdeen AB9 2UE, Scotland, U.K.*

In this work, we have investigated by differential scanning calorimetry the enthalpy relaxation of two poly[methyl( $\alpha$ -n-alkyl)acrylates] in which it is possible to change the length of the two alkyl chains. In particular, we have evaluated the Narayanaswamy parameter, which controls relative contribution of temperature and of structure to the relaxation times, by two methods: Grenet's method (GM) and the peak-shift method (PSM). The data obtained show that both methods lead to equivalent results. Nevertheless, PSM requires fewer experiments than GM, and PSM appears to be more practical. The results obtained on the two acrylates show that the parameter  $x$  increases with the lateral chain length, that is to say, that the temperature effects increase as the length of the alkyl chain is increased.

## INTRODUCTION

Polymers are being used to an increasing extent in engineering applications, for a variety of reasons: ease of fabrication, strength-to-weight ratio, environmental stability and many others. Because of the time-dependence of most of their properties, it is well established that an analysis of their viscoelastic response must be included in any rigorous design procedures using polymers. In addition to their viscoelasticity, however, there is a further time-dependence of their properties, whereby their physical behavior changes as a function of a so called "aging time" while the polymer is subjected to no external influences; this process has come to be known as physical aging

(1). For engineering applications, it is of prime importance to foresee the changes in physical behavior of polymers that may occur as a result of physical aging.

The aging of polymers can be understood in terms of their wholly or partially amorphous structure by reference to a typical schematic enthalpy-temperature diagram, presented in *Fig. 1*. On cooling from an equilibrium liquid, the enthalpy departs from equilibrium (for simplicity indicated here as a linear temperature dependence of the enthalpy) and forms a glass at a critical temperature called the glass transition temperature,  $T_g$ , which depends on cooling rate. The glassy state is characterized by an excess of enthalpy and consequently there will be a thermodynamic driv-

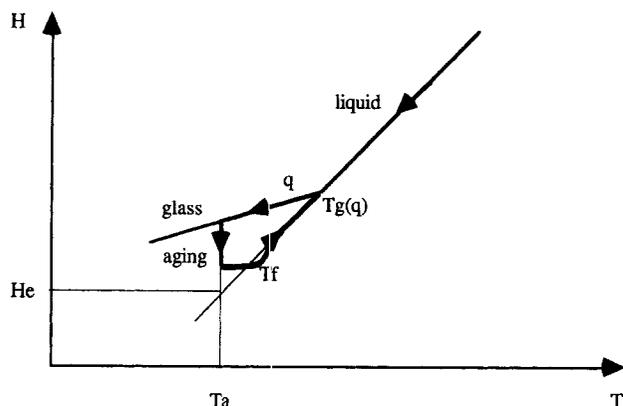


Fig. 1. Schematic enthalpy-temperature diagram showing the change in enthalpy that occurs on cooling at rate  $q$  from the equilibrium liquid, and the definition of the rate-dependent glass transition temperature  $T_g(q)$ . Aging at temperature  $T_a$  reduces the enthalpy towards an equilibrium value  $H_e$ . At any aging time, the structural state may be defined by the fictive temperature  $T_f$ , as shown.

ing force to reduce the enthalpy towards equilibrium if the aging temperature  $T_a$  is held constant after cooling through  $T_g$ . This reduction in enthalpy is sometimes called structural relaxation, and is associated more generally with the changes in properties referred to as physical aging. During this approach towards equilibrium, the structure can conveniently be characterized by the fictive temperature  $T_f$  (2), defined in Fig. 1.

A number of approaches have been adopted in an attempt to obtain a theoretical description of this phenomenon; these have been summarized in a review of physical aging (3), and in an excellent review of enthalpy relaxation (4). In particular, a number of parameters (to be discussed in detail below) are often used to describe the structural relaxation kinetics and different procedures have been adopted for experimental evaluation of the parameters. The most widely used procedure to date has been the curve-fitting method, whereby differential scanning calorimetry (DSC) provides constant heating rate scans of glasses with various structural states ( $T_f$  values) and attempts are then made to obtain a best fit of the theoretical model to these experimental data.

Besides this procedure, however, two other methods, which seem different, have also been used. Both methods use DSC heating scans, and analyze the changes in a particular feature, especially the peak endotherm temperature, as a function of controlled aging conditions. These two methods are referred to as that of Grenet *et al.* (5), GM, and the peak-shift methods (6), PSM.

In the present work, we compare these two methods through an investigation of the enthalpy relaxation of two poly[methyl( $\alpha$ -*n*-alkyl)acrylates] in which it is possible to change the length of the two alkyl chains. In particular, we evaluate the Narayanaswamy parameter  $x$  (7, 8), which controls the relative contributions of temperature and structure ( $T_f$ ) to the relaxation times, by two methods.

## MODEL AND METHODS

### a) Model

The isothermal relaxation of enthalpy  $H$  may be described, for a model involving only a single relaxation time  $\tau$ , by a kinetic equation of the form (9):

$$\frac{\partial H}{\partial t} = \frac{-(H - H_e)}{\tau} \quad (1)$$

where  $H_e$  is the equilibrium enthalpy at the aging temperature  $T_a$  (cf. Fig. 1) and  $t$  is the aging time.

It is well established (10) that  $\tau$  depends on both temperature  $T$  and structure, which can be characterized by the fictive temperature  $T_f$ , and the most widely employed analytical expression used to define this dependence can be attributed to Tool (2, 10), Narayanaswamy (7), and Moynihan (8) and is written in the form:

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right) \exp\left(\frac{(1-x)\Delta h^*}{RT_f}\right) \quad (2)$$

where  $\tau_0$  is a constant,  $x$  is the Narayanaswamy parameter ( $0 \leq x \leq 1$ ), and  $\Delta h^*$  is the apparent activation energy.

Equations 1 and 2 fully define the isothermal response of the glass. Constant heating or cooling rates, as used in DSC, can be included in the analysis by considering continuous changes of temperature to be approximated by a series of instantaneous small temperature jumps  $\Delta T$  followed by an isothermal hold of duration  $\Delta t = \Delta T/q$ , where  $q$  is the heating or cooling rate. The structure will relax to its equilibrium state if the relaxation time is smaller than  $\Delta t$ . Thus the  $T_g$  is defined, on cooling, as the temperature at which the relaxation time  $\tau$  becomes comparable with the isothermal hold  $\Delta t$  (11-13).

### b) The method of Grenet *et al.* (5).

The main idea of the GM is to analyze the relaxation kinetics from the measurement of the displacement of a characteristic temperature identified from the DSC heating scan, without making particular reference to the enthalpy lost during aging. This is, in fact, a similar approach to the PSM, which also makes use of the displacement, or shift, of a characteristic temperature, namely the peak endotherm temperature, as will be shown below. The GM uses an alternative form to Eq 2 for the relaxation time, a form that has also been proposed by Moynihan *et al.* (8, 9) and used in the KAHR model (14):

$$\tau = a \exp(-bT) \exp(-c(H - H_e)) \quad (3)$$

where  $a$ ,  $b$ , and  $c$  are three material constants. Assuming that:

$$H - H_e = \Delta C_p(T_f - T) \quad (4)$$

where  $\Delta C_p$  is the difference between the specific heat capacities of the liquid ( $C_{pl}$ ) and of the glass ( $C_{pg}$ ), Eq 3 can be rewritten to express  $\tau$  as a function of  $T$  and  $T_f$ :

$$\tau = a \exp(-b'T) \exp(-c\Delta C_p T_f) \quad (5)$$

where  $b' = b - c\Delta C_p$ .

The GM now makes use of the assumption, proposed years ago by Bartenev (15) and Ritland (16), that on heating at rate  $q+$  the response of the glass will show an approach to equilibrium at a characteristic temperature  $T_i$ , often referred to as an onset temperature, which depends on the heating rate according to:

$$q^+ \tau(\tau_i) = C_0 \quad (6)$$

where  $C_0$  is a constant for a glass with fixed initial state, or fictive temperature. Sometimes, the temperature  $T_i$  is referred to as a  $T_g$ , but this can be confusing.  $T_i$  and  $T_g$  are approximately equal only when the initial state of the glass is that obtained immediately after cooling, and when the cooling and heating rates are of equal magnitude.

Combining Eqs 5 and 6 leads to the relationship describing the variations of the onset temperature  $T_i$  with the heating rate, for constant values of the aging time and aging temperature, or more generally for constant values of the fictive temperature  $T_f$ :

$$\frac{d \ln q^+}{dT_i} = b' = b - c\Delta C_p \quad (7)$$

This allows the determination of  $b'$ .

On the other hand, when measurements are made with constant heating rate and for a given aging temperature  $T_a$ , it can be shown that the onset temperature depends on the aging time  $t_a$  according to (5):

$$\frac{d\Delta T_i}{dt_a} = -\frac{\Delta T_i \exp(b'T_i)}{\tau_e} \quad (8)$$

where  $\Delta T_i = T_{ie} - T_i$  ( $T_i$  and  $T_{ie}$  are the onset temperatures after an aging time  $t_a$  and after aging to equilibrium, respectively) and  $\tau_e = a \exp(-bT_a)$  is the relaxation time in equilibrium at  $T_a$ . Thus the fit of the variations of  $T_i$  with time at a given aging temperature leads to a determination of the isothermal relaxation time in equilibrium  $\tau_e$ , while experiments carried out at different aging temperatures allows the determination of  $b$  from the change of  $\ln \tau_e$  with  $T_a$ . Thus the values of  $b$  and  $a$  are obtained, and finally the value of  $c$  can also be found if  $\Delta C_p$  is known.

One further step is needed before the value of  $x$  can be determined. Expressing the two relationships for the relaxation time, Eqs 2 and 5, in the same form by a first order development around a mean value  $T_m$  leads to (8, 17):

$$\tau = \tau_0 A \exp\left(-\frac{x\Delta h^*}{RT_m^2} T\right) \exp\left(-\frac{(1-x)\Delta h^*}{RT_m^2} T_f\right) \quad (9)$$

where  $A$  is a constant and  $\Delta h^*/RT_m^2$  can be identified as the constant  $\Theta$  of the KAHR model (14). By comparing Eqs 5 and 9, one obtains:

$$a = \tau_0 A \quad (10)$$

$$b' = x\Theta \quad (11)$$

$$c\Delta C_p = (1-x)\Theta \quad (12)$$

Finally, dividing Eq 11 by Eq 12 results in the relationship from which the value of  $x$  may be obtained:

$$x = \frac{b'}{b} \quad (13)$$

c) *The peak-shift method* (6).

The PSM makes use of the variation of the peak endotherm temperature  $T_p$ , obtained at constant heating rate in the DSC, on the experimental variables defining any three-step (cooling, annealing, heating) thermal cycle, namely the cooling rate  $q-$ , the annealing temperature  $T_a$ , the enthalpy lost during aging  $\delta_H$  and the heating rate  $q+$ . These dependences lead to a set of shifts that may be written in terms of the reduced parameters  $\tilde{D}$  ( $= \Theta\delta_H/\Delta C_p$ ),  $\tilde{Q}_1$  ( $=\Theta q-$ ) and  $\tilde{Q}_2$  ( $=\Theta q+$ ) as:

$$\hat{\xi}(\tilde{D}) = \Delta C_p \left( \frac{\partial T_p}{\partial \delta_H} \right)_{q-, q+, T_a}, \quad (14)$$

$$\hat{\xi}(\tilde{Q}_1) = \Theta \left( \frac{\partial T_p}{\partial \ln|q-|} \right)_{q+, T_a, \delta_H}, \quad (15)$$

$$\hat{\xi}(\tilde{Q}_2) = \Theta \left( \frac{\partial T_p}{\partial \ln|q+|} \right)_{q-, T_a, \delta_H}, \quad (16)$$

A theoretical analysis has shown (6, 18, 19) that these shifts are interrelated and are determined by the parameter  $x$ :

$$-\hat{\xi}(\tilde{Q}_1) = \hat{\xi}(\tilde{Q}_2) - 1 = \hat{\xi}(\tilde{D}) = F(x) \quad (17)$$

where  $F(x)$  is a function called the master curve, shown in Fig. 2. The experimental evaluation of, for instance,  $\hat{\xi}(\tilde{D})$  from Eq 14 allows the value of  $x$  to be determined directly from the master curve. In theory, any one of the shifts in Eqs 14 to 16 may be used for this evaluation, but for practical reasons the easiest to employ is Eq 14, in which the peak endotherm temperature is evaluated as a function of the enthalpy loss  $\delta_H$  during aging at a unique temperature  $T_a$  for various lengths of time, always employing the same heating rate  $q+$ . This is the method employed here.

## EXPERIMENTAL DETAILS

a) *Materials.*

The poly[methyl( $\alpha$ -n-alkyl)acrylates] used here were poly[methyl( $\alpha$ -n-pentyl)acrylate] and poly[methyl( $\alpha$ -n-octyl)acrylate], and were denoted C5 and C8 respectively (see Fig. 3). Poly[( $\alpha$ -n-alkyl)acrylic acid] was pre-

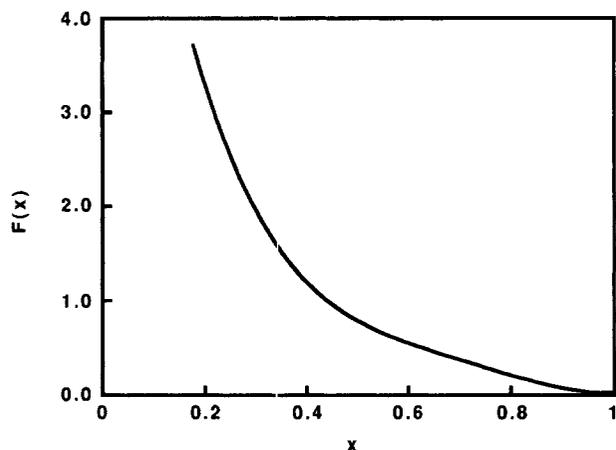
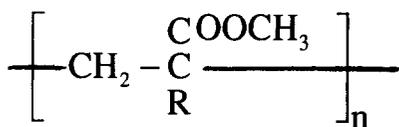


Fig. 2. Theoretically calculated dependence (master curve) of  $F(x)$  on  $x$ .



C5 : R=C<sub>5</sub>H<sub>11</sub> and C8 : R=C<sub>8</sub>H<sub>17</sub>

Fig. 3. Structural formula for poly[methyl( $\alpha$ -*n*-alkyl)acrylates].

pared by radical polymerization in bulk at 50°C under N<sub>2</sub> with 2,2'-azobis(2-methyl-propionitrile) (AIBN) at 0.5% mol as initiator for 24 h. Purification was completed by two further reprecipitations into 50 ml of methanol from 5 ml diethylformamide (DMF) solution. The precipitate was dried *in vacuo* at 40°C for 48 h. Quantitative methylation with CH<sub>2</sub>N<sub>2</sub> led to poly[methyl( $\alpha$ -*n*-alkyl)acrylate]. A 15 ml yellow dimethyl-ether solution of diazomethane, ready for use and prepared by adding alcoholic solution of KOH to 300 mg of Diazald, was poured into 0.5 g of polymer while stirring. Solubilization occurred progressively with methylation and discoloration was observed. The procedure was repeated until the solution remained yellow. After evaporation of diethylether, polymer was twice precipitated in methanol from chloroform solution and dried *in vacuo* at 40°C for 48 h. The molecular weight,  $M_n = 55,000$  for C5 and  $M_n = 24,400$  for C8, was measured by size exclusion chromatography (SEC) in toluene with polystyrene standards for calibration (20).

#### b) Experimental.

The differential scanning calorimeter that was used for the various experiments to evaluate  $x$  was a Perkin-Elmer DSC-4. Calibration of the temperature and the heat flow were made using the fusion of *n*-dodecane. The same sample of each polymer, sealed in an aluminum pan, was used and kept in the DSC throughout the aging times required for these experiments. The sample was first kept 5 min at a rejuvena-

tion temperature  $T_r$ , sufficiently far above  $T_g$  to erase the effects of the previous thermal history, prior to beginning the aging experiments. The sample at  $T_r$  is cooled at  $q^- = 320^\circ\text{C}/\text{min}$  to an aging temperature  $T_a$  ( $T_a = T_g - 10^\circ\text{C}$  for the PSM), kept at this temperature for an aging time  $t_a$ , cooled again at  $320^\circ\text{C}/\text{min}$  to the scan starting temperature  $T_0$ , and then reheated to  $T_r$  at  $q^+ = 20^\circ\text{C}/\text{min}$  for the PSM and at various different rates for the GM. A second scan is made on the same sample for the PSM by cooling at  $q^- = 320^\circ\text{C}/\text{min}$  to  $T_0$  and immediately reheating at  $q^+ = 20^\circ\text{C}/\text{min}$ , to obtain the zero aging time reference curve. For the GM, the onset temperature  $T_i$  is obtained from the intersection of the extrapolated glassy line and the inflectional tangent to the rise of the endotherm.

## RESULTS

According to the methods outlined above, we need to analyze the variations of the onset temperature and of the peak temperature with the heating rate and the aging time, and for different aging temperatures for the GM. Typical heating endotherms obtained for C5 are shown in Fig. 4 for various heating rates. It can be seen that the faster the heating rate, the higher is the onset temperature, which is clearly consistent with a positive value of  $b'$  in Eq 7.

Figure 5 shows the endotherm obtained for the same C5 sample when it was annealed at  $T_a = 10^\circ\text{C}$  for various aging times, and for a heating rate of  $20^\circ\text{C}/\text{min}$ . A shift of the onset and peak temperatures toward higher values is observed when the aging time increases. The enthalpy loss  $\bar{\delta}_H$  required for the PSM analysis is calculated by integrating, between two defined temperatures in the glassy and equilibrium liquid regions, the difference between the  $C_p(T)$  curve for aging time  $t_a$  and the reference  $C_p(T)$  curve for  $t_a = 0$ . The dependence of  $\bar{\delta}_H$  on aging time is shown in Fig. 6; as expected,  $\bar{\delta}_H$  increases with increasing aging time. Similar results were obtained when other annealing temperatures were used. The particular sets of data

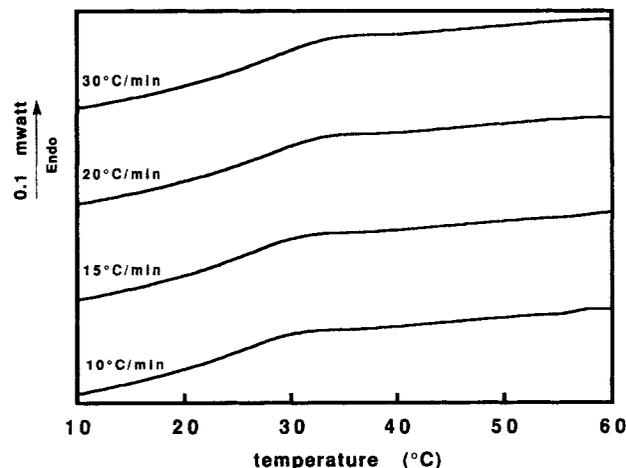


Fig. 4. DSC curve obtained for C5 at zero aging time for various heating rates indicated against each curve.

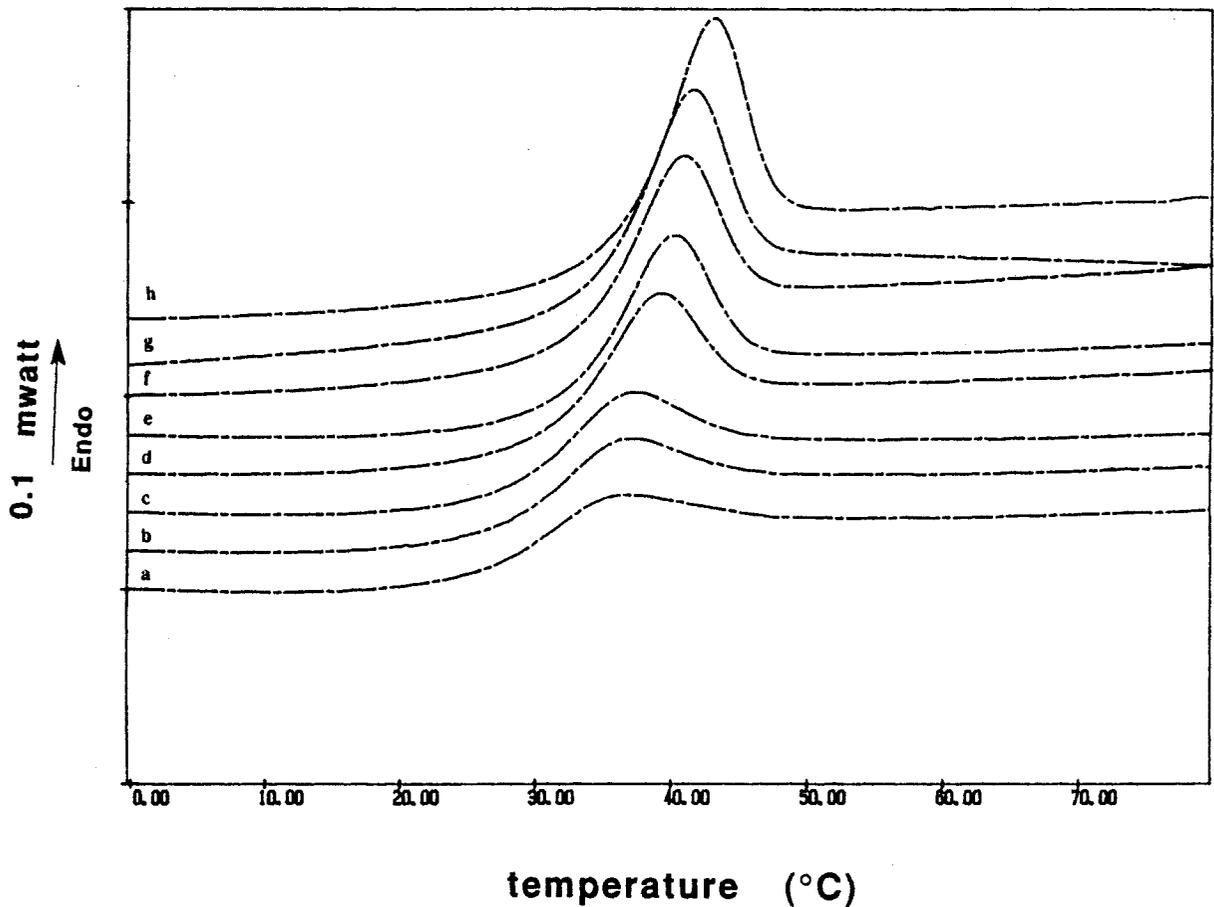


Fig. 5. DSC curves obtained for C5 at  $T_a = 10^\circ\text{C}$  for various aging times  $t_a$  and for a heating rate of  $20^\circ\text{C}/\text{min}$ . (a:  $t_a = 1\text{h}$ , b:  $t_a = 1.5\text{h}$ , c:  $t_a = 2\text{h}$ , d:  $t_a = 8\text{h}$ , e:  $t_a = 15\text{h}$ , f:  $t_a = 24\text{h}$ , g:  $t_a = 46\text{h}$ , h:  $t_a = 111\text{h}$ ).

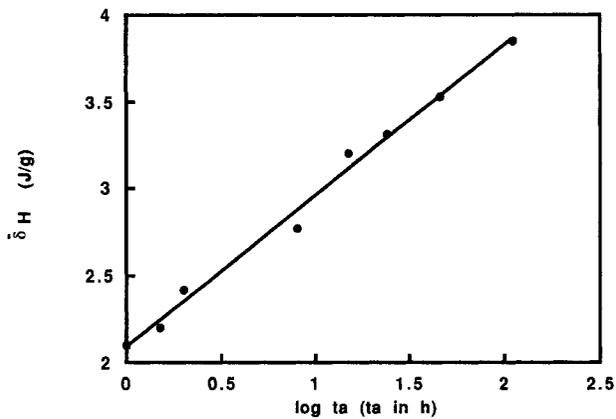


Fig. 6. Variations of the enthalpy loss  $\bar{\delta}_H$  with  $\log t_a$  for C5.

obtained for the GM and PSM methods are outlined separately below.

a) Data obtained for the GM.

In Fig. 7, the variation of the onset temperature with the heating rate for sample C5 is reported, from which the value of  $b'$  is obtained from the slope of the straight line (Eq 7). Similar behavior is obtained for C8, and the data are summarized in Table 1.

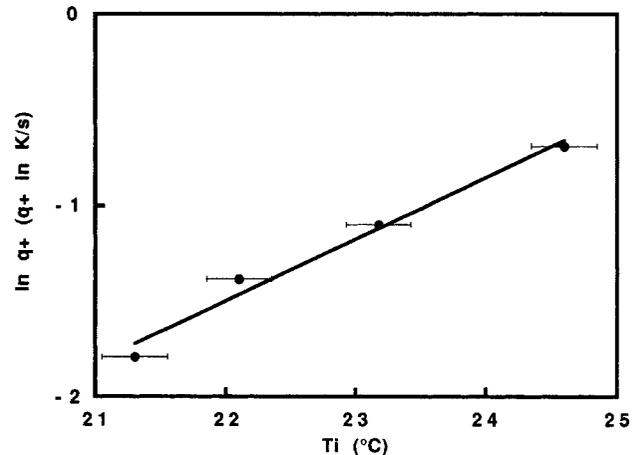
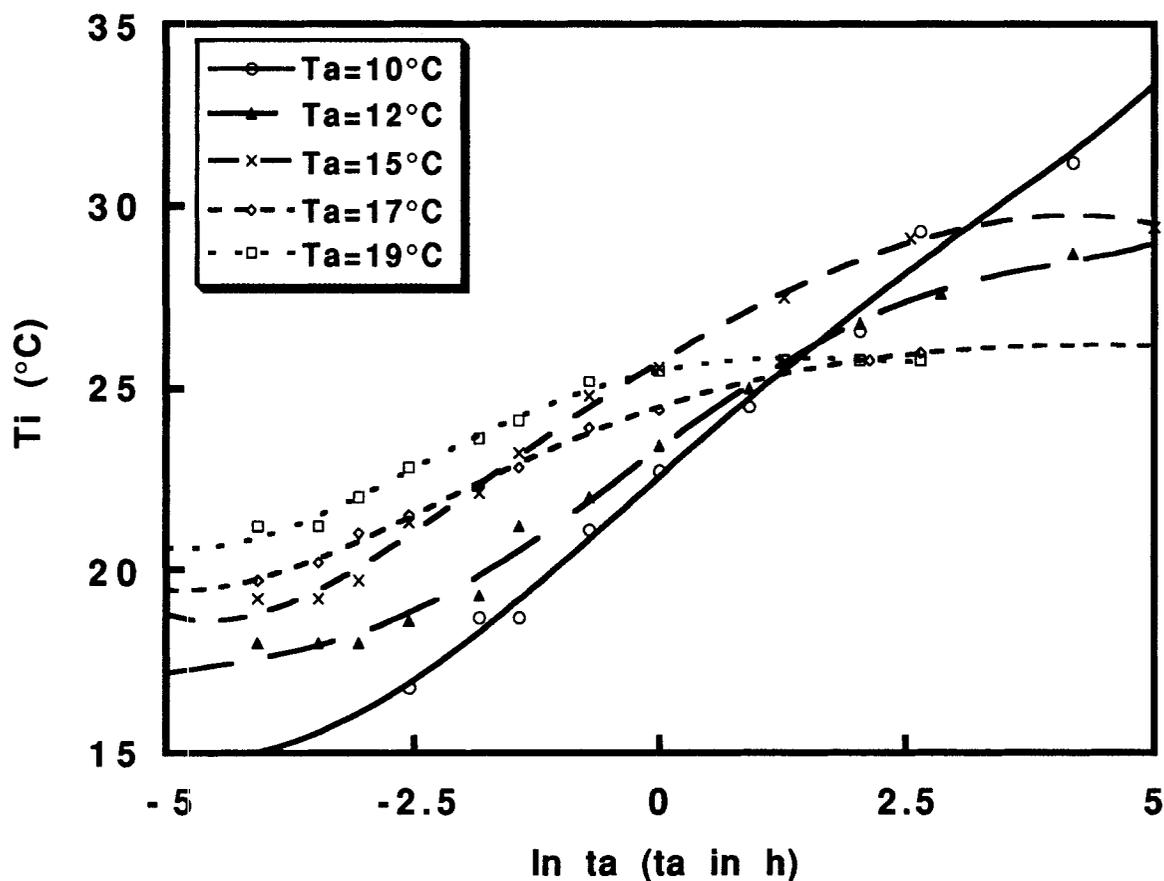


Fig. 7. Variations of  $T_i$  with heating rate for C5.

In Fig. 8, the variation of the onset temperature with the aging time is shown for C5 for different annealing temperatures. Similar behavior is found also for C8. Fitting Eq 8 to these data leads to the evaluation of  $\tau_e$ , and the parameter values used to obtain the best fits are recorded in Table 1. The dependence of  $\tau_e$  on annealing temperature is shown in Fig. 9 for both C5 and

**Table 1.** Parameter Values Obtained for C5 and C8 by the Method of Grenet *et al.* (5) and by the Peak-Shift Method (PSM) (6).  $T_{i0}$  and  $T_{ie}$  Are the Zero Annealing Time and Equilibrium Values, Respectively, of the Onset Temperature  $T_i$ .

	GM					PSM					
	$b'$ ( $K^{-1}$ )	$T_{i0}$ ( $^{\circ}C$ )	$T_{ie}$ ( $^{\circ}C$ )	$\tau_e$ (h)	$b$ ( $K^{-1}$ )	$x$	$\frac{\partial T_p}{\partial \delta H}$ ( $Kg/J$ )	$\Delta C_p$ ( $J/gK$ )	$F(x)$	$x$	
C5	0.30	10	14.9	33.7	130	0.66	0.46	3.72	0.22	0.82	0.52
		12	17.0	32.0	70						
		15	18.8	29.5	6.5						
		17	19.5	26.0	1.4						
		19	20.6	20.7	0.5						
C8	0.26	-15	-9.5	8.0	165	0.41	0.63	2.75	0.21	0.58	0.59
		-10	-4.9	5.5	19						
		-8	-4.0	4.0	6						
		-6	-1.4	3.3	3						

**Fig. 8.** Variations of  $T_i$  with the aging time for C5, for different aging temperatures, as indicated, and for a heating rate of  $20^{\circ}C/min$ . The lines are the fits of Eq 8 to the data points, using the parameter values reported in Table 1.

C8, from which the value of  $b$  is obtained from the slope. Finally, from the knowledge of  $b'$  and  $b$ , the parameter  $x$  can be evaluated (Eq 13). All the results for C5 and C8 are collected in Table 1.

#### b) Data obtained for the PSM.

In accordance with Eq 14, Fig. 10 shows the evaluation of the peak endotherm temperature  $T_p$  with the enthalpy loss during aging for aging at  $10^{\circ}C$  and  $-15^{\circ}C$  for C5 and C8 respectively. A linear relationship is observed, and the slope multiplied by  $\Delta C_p$  leads to the value of  $F(x)$  from which  $x$  is obtained using the

master curve (Fig. 2). The value of  $\Delta C_p$  is obtained in the usual way, and the results for both C5 and C8 are collected in Table 1.

## DISCUSSION

As can be seen from Table 1, the values of  $x$  obtained by the two methods (GM and PSM) agree within an uncertainty of  $\pm 0.04$ , and show the same trend with increasing length of alkyl chain. Nevertheless, it is worth pointing out the possible origins of any discrepancies between the two methods, which may

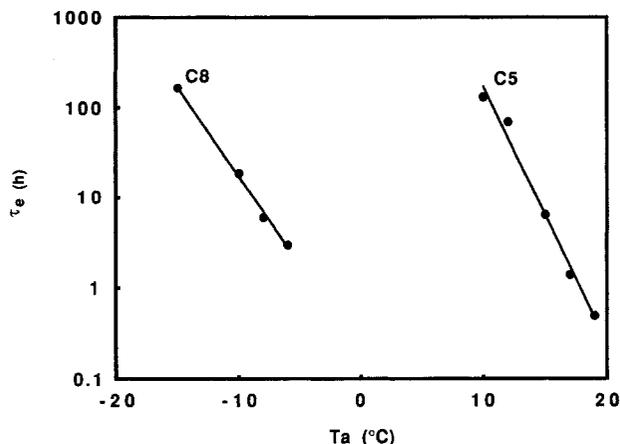


Fig. 9. Variations of  $\tau_e$ , on a logarithm scale, with annealing temperature  $T_a$  for both C5 and C8.

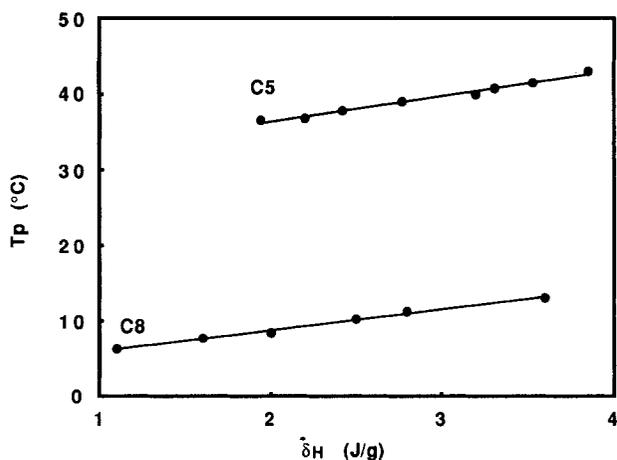


Fig. 10. Variation of  $T_p$  with  $\bar{\delta}_H$  obtained for C5 at  $T_a = 10^\circ\text{C}$  and for C8 at  $T_a = -15^\circ\text{C}$ .

come either from the experimental measurements or from the theoretical approximations used in the analysis, and to compare critically these two approaches.

First, and of some practical importance, is the consideration of the number and length of experiments required for each analysis. The GM requires considerably more experiments than does the PSM for the evaluation of  $x$ . This is because the dependence of  $T_i$  on heating rate is required to give  $b'$ , and then the dependence of  $T_i$  on annealing time at various aging temperatures is needed to find  $\tau_e$  and hence  $b$ . Furthermore, these latter experiments should ideally proceed to equilibrium so that a reliable fit of Eq 8 to the data may be obtained without the need to consider  $T_{ie}$  as an adjustable parameter; clearly this will involve very long aging times, particularly if  $T_a$  is low with respect to  $T_g$ . On the other hand, PSM requires fewer experiments, as only the dependence of  $T_p$  on  $\bar{\delta}_H$  in this case is needed, in addition to  $\Delta C_p$ . It should be noted, however, that increasingly reliable values of the slope  $\partial T_p / \partial \bar{\delta}_H$  (Fig. 10) will be obtained for longer aging time.

In this analysis, the GM assumes that the variation of  $T_i$  with heating rate is according to Eq 6. The validity of this relationship is restricted to the heating rate being approximately equal to the cooling rate, and therefore the range of heating rates available is small. This can introduce a significant uncertainty in the value of  $b'$  (Fig. 7), which will have a corresponding effect on the fit of Eq 8 to the data, and hence on the value of  $b$ , and ultimately on the value of  $x$ .

In addition, the problem of thermal lag in the sample should really be addressed when different heating rates are used, as in the GM. The advantage of using the particular variant selected here for the PSM, namely the use of Eq 14 is that this problem is avoided by virtue of a unique heating rate ( $20^\circ\text{C}/\text{min}$ ) for all experiments. The other variant of the PSM, in which the peak endotherm is evaluated as a function of heating rate for glasses of fixed fictive temperature, embodied in Eq 16, is less practicable in this respect as allowance should be made then for thermal lag in the sample, though this can be done (6).

In summary, the difference between the values of  $x$  obtained by the two methods appears to be within the usual experimental uncertainty of such measurements, and both methods lead to equivalent results. Nevertheless, the PSM requires significantly fewer experiments than does the GM, and further appears to offer reduced experimental and analytical uncertainty. Thus PSM appears generally to be more practical and reliable.

Finally, the data show that the value of  $x$  is greater for C8 than it is for C5, while the apparent activation energy,  $\Delta h^*$ , or more particularly the equivalent measure  $\Theta (=b'/x)$ , is higher for C5 ( $\Theta = 0.61 \pm 0.04 \text{ K}^{-1}$ ) than it is for C8 ( $\Theta = 0.42 \pm 0.02 \text{ K}^{-1}$ ). This correlation between  $x$  and  $\Delta h^*$  (or  $\Theta$ ) is generally observed (4). The trend of increasing  $x$  with increasing length of alkyl chain seems to indicate an increase of the temperature effects on the relaxation kinetics.

## NOMENCLATURE

### Narayanaswamy Formalism—PSM Method

- $T_g$  = Glass transition temperature ( $^\circ\text{C}$ ).
- $\tau, \tau_o, \tau_e$  = Relaxation times (h).
- $x$  = Narayanaswamy parameter.
- $\Delta h^*$  = Apparent activation energy (J/g).
- $T_f$  = Fictive temperature ( $^\circ\text{C}$ ).
- $T_p$  = Temperature of the maximum of the endotherm peak associated to the glass transition ( $^\circ\text{C}$ ).
- $\bar{\delta}_H$  = Enthalpy lost during aging (J/g).

### Moynihan Formalism—GM Method

- $\tau, \tau_e$  = Relaxation times (h).
- $H, H_e$  = Enthalpy and enthalpy at equilibrium (J).
- $a$  = Material constant (h).
- $b$  = Material constant ( $\text{K}^{-1}$ ).

- $b'$  = Material constant ( $K^{-1}$ ).  
 $c$  = Material constant ( $g/J$ ).  
 $\Delta C_p$  = Difference between  $C_{pl}$  and  $C_{pg}$  ( $J/gK$ ).  
 $C_{pl}$  = Heat capacity of liquid ( $J/gK$ ).  
 $C_{pg}$  = Heat capacity of glass ( $J/gK$ ).  
 $T_i$  = Onset temperature of the endotherm peak associated to the glass transition ( $^{\circ}C$ ).  
 $T_{ie}$  = Onset temperature of the endotherm peak associated to the glass transition after infinite aging ( $^{\circ}C$ ).

### Thermal Cycle

- $T_a$  = Aging temperature ( $^{\circ}C$ ).  
 $t_a$  = Aging time (h).  
 $q+$ ,  $q-$  = Heating (+) or cooling (-) rate ( $^{\circ}C/min$ ).  
 $T_r$  = Rejuvenation temperature ( $^{\circ}C$ ).

### REFERENCES

1. L. C. E. Struik, *Physical Aging In Amorphous Polymers and Other Materials*, Elsevier Publishing Company, Amsterdam (1978).
2. A. Q. Tool, *J. Am. Ceram. Soc.*, **29**, 240 (1946).
3. J. M. Hutchinson, *Prog. Polym. Sci.*, **20**, 703 (1995).
4. I. M. Hodge, *J. Non-Cryst. Solids*, **169**, 211 (1994).
5. J. Grenet, J. P. Larmagnac, P. Michon, and C. Vautier, *Thin Solid Films*, **76**, 53 (1981).
6. J. M. Hutchinson and M. Ruddy, *J. Polym. Sci. B. Polym. Phys.*, **26**, 2341 (1988).
7. O. S. Narayanaswamy, *J. Am. Ceram. Soc.*, **54**, 491 (1971).
8. C. T. Moynihan, A. J. Easteal, M. A. DeBolt, and J. Tucker, *J. Am. Ceram. Soc.*, **59**, 12 (1976).
9. C. T. Moynihan, A. J. Easteal, J. Wilder and J. Tucker, *J. Phys. Chem.*, **78**, 2673 (1974).
10. A. Q. Tool and C. Eichlin, *J. Am. Ceram. Soc.*, **14**, 276 (1931).
11. J. P. Larmagnac, J. Grenet, and P. Michon, *J. Non-Cryst. Solids*, **45**, 157 (1981).
12. J. P. Larmagnac, J. Grenet, and P. Michon, *Phil. Mag.*, B, **46**, 627 (1982).
13. J. M. Saiter, A. Assou, J. Grenet, and C. Vautier, *Phil. Mag.*, B, **64**, 33 (1991).
14. A. J. Kovacs, J. J. Aklonis, J. M. Hutchinson and A. R. Ramos, *J. Polym. Sci., B., Polym. Phys.*, **17**, 1097 (1979).
15. G. Bartenev, *Dokl. Akad. Nauk., SSSR*, **76**, 227 (1951).
16. H. N. Ritland, *J. Am. Ceram. Soc.*, **37**, 370 (1954).
17. A. J. Kovacs, J. M. Hutchinson, and J. J. Aklonis, *The Structure of Non-Crystalline Materials*, p. 153, P. H. Gaskell, Taylor & Francis, London.
18. A. J. Kovacs and J. M. Hutchinson, *J. Polym. Sci. B. Polym. Phys.*, **17**, 2031 (1979).
19. J. M. Hutchinson, *Lecture Notes in Physics*, **277**, 172 (1987).
20. F. Burel, J. P. Couvrecelle, C. Bunel, J. M. Saiter, and M. E. Godard, *J. Macromol. Sci., A*, **33(1)**, 1 (1996).