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EFFECT OF PHYSICAL AGING ON GLASS TRANSITION TEMPERATURE OF POLYMETHYL-α-*n*-OCTYLACRYLATE

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Key Words: Physical aging; Glass transition; Polyacrylate derivatives

ABSTRACT

A simple structural relaxation model was applied to the physical aging of polymethyl-α-n-octylacrylate close to its glass transition temperature (T_g). By using differential scanning calorimetry, it was observed that varying aging temperature (T_a), aging time (t_a), heating rate (r), and providing the usual justified assumptions, overall aging parameters can be determined. These results allow us to foresee the thermal evolution of the polymer just below T_g. In particular, the activation enthalpy Δh = 237 kJ/mol and the calculated partition or structure parameter

$x = 0.7$, introduced by Narayanaswami, express a high temperature dependence of the relaxation time.

INTRODUCTION

In a previous paper we mentioned the synthesis of new poly(methyl-α-*n*-alkylacrylate)s with $n = 3, 5, 8, 10, 12$, and 18, and studied the influence of molecular weight and α-*n*-alkyl length on their physicochemical properties [1]. We showed that the glass transition temperature (T_g) decreases with the α-*n*-alkyl group length, according to free volume theory, and increases with molecular weight. However, other parameters are important on T_g measurement, and one of these is physical aging which leads to structural relaxation, a process by which amorphous materials in the glassy state reach the thermodynamic equilibrium state. The result is a variation of not only of such thermodynamic properties as enthalpy, entropy, or volume, but also all the properties depending on molecular mobility such as thermal, electrical, or mechanical properties. This process is detected through the time evolution of thermodynamic properties such as specific volume or enthalpy, as well as thermal, mechanical, or dielectric properties. For example, according to aging time, $Cp(T)$ curves exhibit particular peaks due to this structural relaxation (e.g., Fig. 1 for poly-α-*n*-propylacrylate).

In order to prevent and understand this phenomena, we have performed physical aging studies where a polymer initially in equilibrium at a temperature T_0 (higher than T_g) is cooled through the glass transition range at a constant rate ($r = dT/dt$) to a temperature T_a (aging temperature), maintained to this temperature during a time t_a (aging time), and finally reheated to T_0.

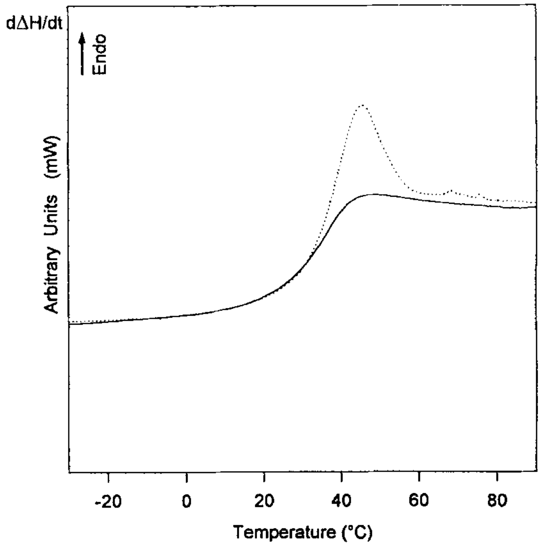


FIG. 1. DSC curves of polymethyl-α-*n*-propylacrylate: (· · ·) first heating run, (——) second heating run.

A great number of experimental works use differential scanning calorimetry (DSC) because of its high reproducibility and its convenience. Moreover, a variety of empirical equations agree with the results of DSC experiments of physical aging [2–4]. We therefore used this technique, and the characteristic peaks, observed on $Cp(T)$ curves after these thermal treatments, are related to T_a and t_a.

For this paper our purpose was to analyze the applicability and validity of a simple model, first on one of our new polymers to foresee its thermal evolution in order to enlarge afterward this study on the different polymers of our series and connect the results with the α-*n*-alkyl group. In this work, an intermediate term of the series, polymethyl-α-*n*-octylacrylate (P8M), was chosen for its T_g close to room temperature (Fig. 2).

EXPERIMENTAL

Materials

Synthesis of α-*n*-octylacrylic acid monomer was described elsewhere [1].

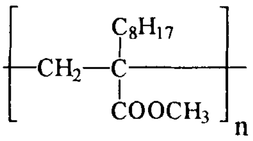
Poly-α-*n*-octylacrylic acid was prepared by radical polymerization in bulk at 50°C under N_2 with AIBN (0.5 mol%) as initiator for 24 hours. Purification was completed by two further reprecipitations into 50 mL methanol from 5 mL DMF solution. The precipitate was dried *in vacuo* at 40°C for 48 hours.

Quantitative methylation with CH_2N_2 led to polymethyl-α-*n*-octylacrylate (P8M). A 15-mL yellow diethylether solution of diazomethane, ready for use and prepared by adding an alcoholic solution of KOH to 300 mg Diazald, was poured on 0.5 g 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, the polymer was twice precipitated into methanol from chloroform solution and dried in vacuo at 40°C for 48 hours.

Molecular weight $\overline{M}_n$ = 24,400 was measured by using SEC in toluene with polystyrene standards for calibration.

Thermal Analysis

Measurements were achieved under nitrogen by using a differential scanning calorimeter (Perkin-Elmer DSC 4). The DSC 4 was calibrated with Indium (T_f = 156.6°C ΔH = 28.5 J/g). A sample of 6.96 mg polymer was sealed in an aluminum pan. The pan used in all measurements was always kept in the differential scanning calorimeter to obtain good reproducibility. The reported T_gs were taken as the onset of the $Cp(T)$ curves. The sample was annealed at 50°C for 5 minutes to erase



$$\left[-CH_2-\underset{COOCH_3}{\overset{C_8H_{17}}{\underset{|}{\overset{|}{C}}}}- \right]_n$$

FIG. 2. Structural formula of polymethyl-α-*n*-octylacrylate.

the effect of previous thermal histories. Two different types of experiments were performed.

1. The sample at 50°C was cooled at 320 K/min to $T_a = -15$°C, kept 5 minutes at that temperature, cooled again at 320 K/min to $T_1 = -40$°C, and heated back to 50°C at different heating rates r in order to determine the dependence of T_g upon r.
2. The sample at 50°C was cooled at 320 K/min to temperature T_a, kept at that temperature for time t_a, cooled again at 320 K/min to the starting temperature $T_1 = -40$°C, and heated back at 20 K/min to 50°C.

RESULTS AND DISCUSSION

Phenomenological Models of Structural Relaxation

Even if the elaborated models are described using a unique formalism, each parameter having a physical meaning [5-9], a number of empirical equations led to simple models that are phenomenological tools for a good description of the experimental results of physical aging [2-4, 10, 11].

In these models the main parameter which characterizes an aging process is the recovery time τ which occurs in the relaxation equation:

$$\frac{\partial H}{\partial t} = -\frac{H - H_e}{\tau} + Cp_g r \qquad (1)$$

where H is the current enthalpy, H_e is the equilibrium enthalpy (when aging is achieved), t is the time, $r = \Delta T/\Delta t$ is the heating rate, and Cp_g is the heat capacity in the glassy state.

General phenomenological models describe structural relaxation from a macroscopic point of view. These are based on Eq. (1) and on the existence of a distribution of recovery times which evolve when the temperature and/or the separation from equilibrium changes.

It has been shown [12, 13] that if the range of annealing temperatures used during relaxation process studies is close to T_g, a single average relaxation time is good enough to describe the phenomenon.

Hereafter, we consider a simple model in which the average relaxation time is given by

$$\tau = Ae^{F(T)+G(\xi)} \qquad (2)$$

where parameter A is a constant, $F(T)$ is a function characterizing the relative contribution of temperature to τ, and $G(\xi)$ is a function characterizing the relative contribution of structure to τ.

Different expressions are given in the literature for $F(T)$ and $G(\xi)$ [3, 4, 13, 14]. In the following, we used

$$F(T) = -bT \qquad (3)$$

or

$$F(T) = E_a/RT \qquad (4)$$

and

$$G(\xi) = -c(H - H_e) \tag{5}$$

where b and c are constants which depend on the material and E_a is an apparent activation energy.

Moreover, in a first approach we may assume that the difference between the equilibrium liquid and glass heat capacities ($Cp_e - Cp_g$) is constant over the experimental range of temperatures investigated. Then a linear relationship exists between the enthalpy and temperature variations:

$$H - H_e = \Delta Cp(T_f - T) \tag{6}$$

where T_f is the fictive temperature [4] and $\Delta Cp = Cp_e - Cp_g$.

Dependence of T_g on Heating Rate

During heating or cooling at different rates r for a sample of the same age, we can assimilate the continuous change of temperature in a series of instantaneous small temperature changes ΔT, each of which is followed by an isothermal time of duration $\Delta t = \Delta T/r$. The glass transition is reached when τ is of the same order as Δt ($\Delta t = k\tau$) [13]. Consequently, at T_g [15]:

$$r\tau(T_g) = \Delta T/k = \text{constant} \tag{7}$$

Combining Eqs. (2), (3) or (4), (5), and (7), we get:

$$\ln r = -\ln A + bT_g + c(H - H_e) + \text{constant}$$

or

$$\ln r = -\ln A' - \frac{E_a}{RT} + c(H - H_e) + \text{constant}$$

Taking into account Eq. (6):

$$\ln r = (b - c\Delta Cp)T_g + c\Delta CpT_f + \text{constant} \tag{8}$$

or

$$\ln r = -\frac{E_a}{RT_g} - c\Delta CpT_g + c\Delta CpT_f + \text{constant} \tag{9}$$

From Eq. (8), and for given T_a and t_a, T_f is constant, and the plot of ln r versus T_g must be a straight line with a slope of ($b - c\Delta Cp$). Figure 3 shows good agreement between the experimental results and this equation. A value of 0.31 K^{-1} is obtained for ($b - c\Delta Cp$).

Eq. (9) yields:

$$\frac{d(\ln r)}{d(1/T_g)} = -\frac{E_a}{R} + c\Delta CpT_g^2 \tag{10}$$

Rigorously, ln r versus $1/T_g$ is not linear. Nevertheless, to the extent that the variations of T_g are weak, these curves are similar to straight lines (Fig. 4) of average slope $(E_a/R) + c\Delta CpT_g^2 = -20.4 \times 10^3$ K.

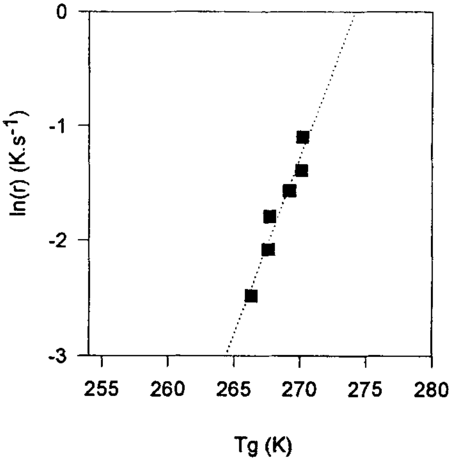


FIG. 3. Influence of heating rate (r) on T_g: ln r vs T_g for aging temperature T_a = −15°C and aging time t_a = 5 minutes.

Dependence of T_g on Aging Time

In this case, the heating rate (20 K/min) and the aging temperature are kept constant (e.g., Fig. 5 for T_a = 263 K).

The glass transition is reached when the relaxation times are equal. Then the variation of T_g with time can be described by the following relation [16], combining Eqs. (1) to (7):

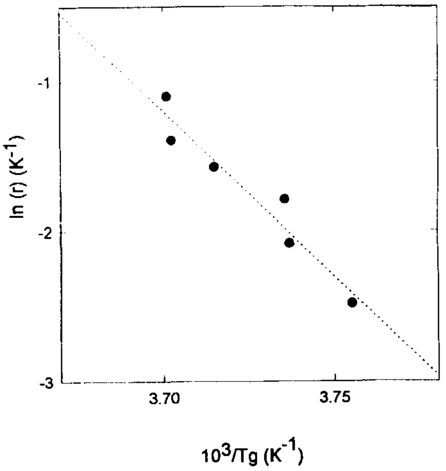


FIG. 4. Influence of heating rate (r) on T_g: ln r vs $10^3/T_g$ for aging temperature T_a = −15°C and aging time t_a = 5 minutes.

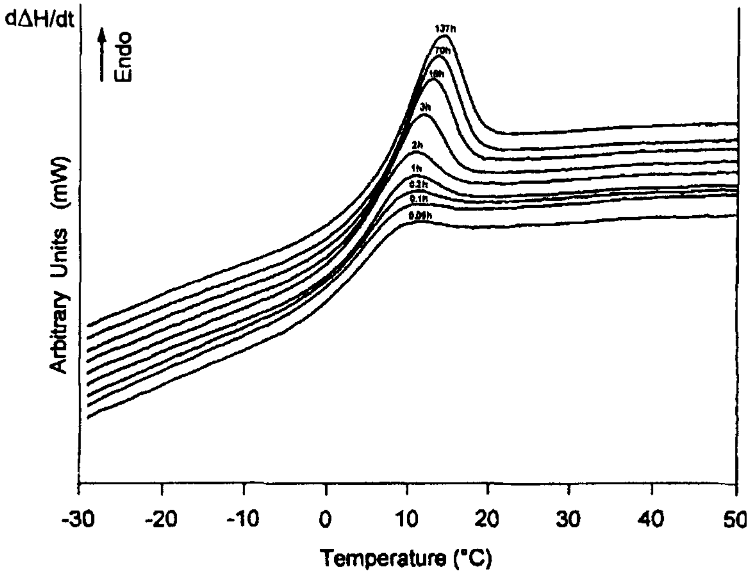


FIG. 5. DSC curves of P8M for aging temperature T_a = 263 K and different aging times t_a.

$$\frac{d(\Delta T_g)}{dt} = \frac{\Delta T_g \exp[(b - c\Delta Cp)\Delta T_g]}{\tau_e} \tag{11}$$

where $\Delta T_g = T_{g_e} - T_g(T_g$ and T_{g_e} are, respectively, the glass transition temperatures after an aging duration t and after complete aging) and

$$\tau_e = Ae^{-bT_f} = Ae^{-bT_a} \tag{12}$$

or

$$\tau_e = A'e^{E_a/RT_f} = A'e^{E_a/RT_a} \tag{13}$$

proceeding from Eq. (2) where $\tau = \tau_e$ when equilibrium is reached; that is, $H = H_e$ and $T = T_f = T_a$ (Fig. 6).

For four aging temperatures (258, 263, 265, and 268 K), the experimental data T_g versus log t_a lead to sigmoidal curves (Fig. 7). From these curves we estimated a T_{g_e} (ultimate value for an infinite aging time) and a T_{g_i} (ultimate value for zero aging time). Owing to Eq. (11) and the $(b - c\Delta Cp)$ value mentioned above, numerical analysis allowed us to infer a relaxation time τ_e for a given T_a (Table 1). The computed curves and experimental results reported in Fig. 7 attest to a satisfactory fitting.

The parameters ln A and b can be determined by plotting ln τ_a (Eq. 12; Fig. 8). A value of ΔCp was calculated from the $\Delta Cp(T)$ curves for each experiment. An average value of 0.27 (J/g/K) was obtained. These results enabled us to deduce c, the last parameter of the model, using the $(b - c\Delta Cp)$ value.

As above, a plot ln τ_e versus $1/T_a$ (Eq. 13; Fig. 9) gives ln A' and E_a. The overall aging parameters are reported in Table 2.

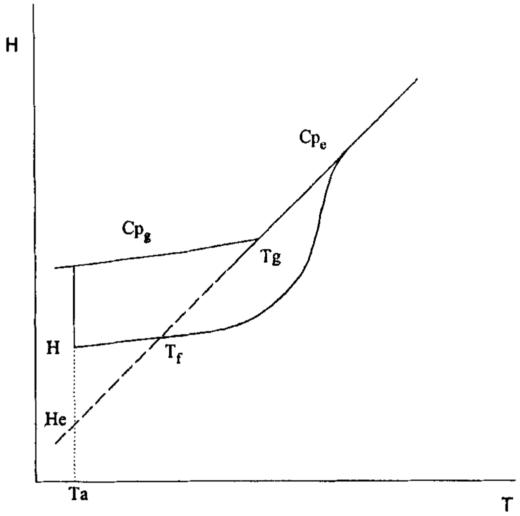


FIG. 6. Theoretical curve $H = f(T)$ at aging temperature T_a for aging time t_a.

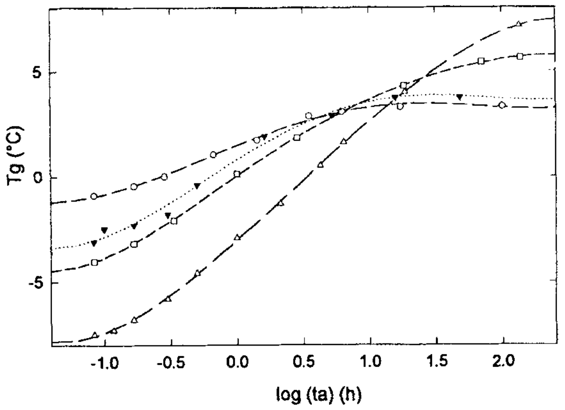


FIG. 7. Evolution of T_g with aging time t_a for different aging temperatures (r = 20 K/min): (○) T_a = 268 K; (▼) T_a = 265 K; (□) T_a = 263 K; (△) T_a = 258 K.

TABLE 1. τ_e Values Using Eq. (11) with Estimated T_{g_i} and T_{g_e} from Fig. 7 at Different Aging Temperatures T_a

T_a(K)	258	263	265	268
T_{g_i}(K)	263.5	268.1	269	271.6
T_{g_e}(K)	281	278.5	277	276.3
τ_e(h)	165	19	6	3

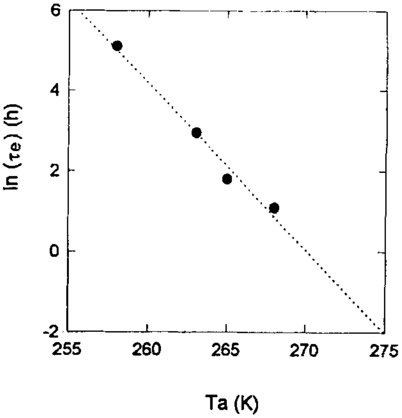


FIG. 8. Linear relation between ln τ_e and T_a according to Eq. (12).

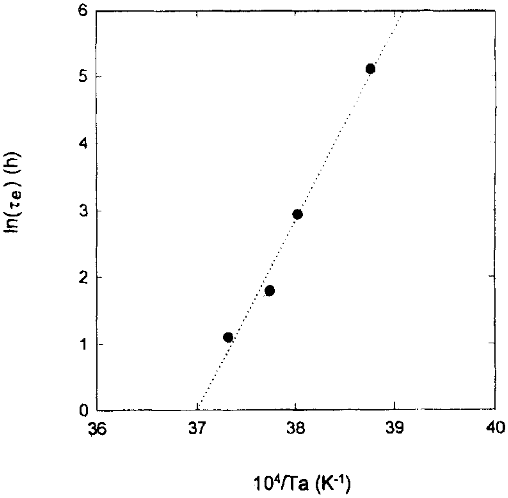


FIG. 9. Linear relation between ln τ_e and T_a according to Eq. (13).

TABLE 2. Aging Parameters

ln A	ln A'	E_a(kJ·mol^{-1})	b(K^{-1})	c(g·J^{-1})	ΔCp(J·g^{-1}·K^{-1})
112	−106	237	0.41	0.42	0.27

Finally, if we take into account that T_{g_i} and T_{g_e} are the maximum range of T_g with the annealing temperature T_a, a fictive temperature T'_f, which corresponds to the limit of no aging at all, can be estimated as the intersection of the two plots T_{g_i} and T_{g_e} versus T_a. Theoretically, this temperature squares with $T_{g_i} = T_{g_e} = T'_f = T_a = 275$ K in our case (Fig. 10).

Analogy with Narayanaswami's Model

The relaxation time expression used, $\tau = A' e^{E_a/RT} e^{-c(H-H_e)}$, may be expressed differently by using Eq. (6):

$$\tau = A' \cdot e^{\frac{E_a}{RT} - c\Delta CpT} e^{c\Delta CpT_f} \tag{14}$$

This relation is of the same form as that of Narayanaswami:

$$\tau = A'' e^{x\Delta h/RT} e^{(1-x)\Delta h/RT'_f} \tag{15}$$

where A'' is a constant, Δh is an activation enthalpy, and x is a partition or structure parameter. For the particular fictive temperature T'_f, Eqs. (14) and (15) lead to

$$\tau = A' e^{E_a/RT'_f} = A'' e^{\Delta h/RT'_f}$$

Assuming that preexponential factors A' and A'' are identical, we assimilate E_a and Δh. Identifying the T_f terms, for example, of Eqs. (14) and (15), gives, for $T_f = T'_f$

$$c\Delta CpT'_f = \frac{(1-x)\Delta h}{RT'_f}$$

and leads to $x = 0.7$ for $T'_f = 275$ K.

According to the theory, the limiting values of x express either a pure structure dependence ($x = 0$) or a pure temperature dependence ($x = 1$). In our case, we can conclude there is a highly temperature dependence.

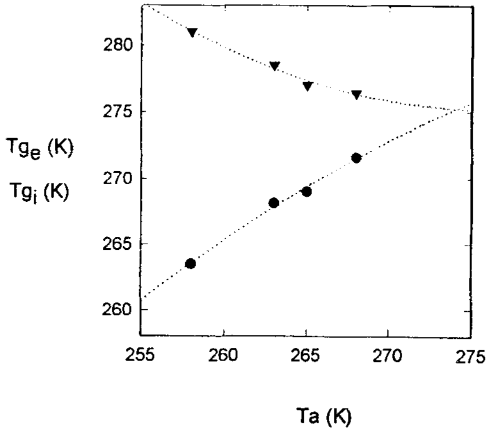


FIG. 10. Evolution of estimated zero (●: T_{g_i}) and infinite (▼: T_{g_e}) aging glass transition temperatures with the aging temperature T_a.

CONCLUSION

The structural relaxation model used in this work allowed us to determine the overall physical aging parameters, just below T_g, and to foresee the thermal evolution of polymethyl-α-*n*-octylacrylate, one of our series of polymethyl-α-*n*-alkylacrylates. This approach enabled us to carry on this study for other derivatives and thus enlarge our knowledge about the influence of the length of the α-*n*-alkyl group on thermal properties.

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