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The Glass Transition Temperature (T_g) as a Parameter for Monitoring
the Cure of an Amine-Cured Epoxy System at Constant Heating Rates

by

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THE GLASS TRANSITION TEMPERATURE (T_g) AS A PARAMETER FOR MONITORING THE CURE OF AN AMINE-CURED EPOXY SYSTEM AT CONSTANT HEATING RATES

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ABSTRACT

A continuous heating transformation (CHT) diagram displays the time and temperature of events that a material encounters during the course of continuous heating at different heating rates. For thermosetting systems, these events include gelation, vitrification and devitrification. Analysis of isothermal data for a diglycidyl-type epoxy/tetrafunctional aliphatic amine system, which is initially liquid at room temperature, indicated that kinetic control applied prior to vitrification, i.e., for $T_g < T_{cure}$ (temperature of reaction). The parameters so obtained (i.e., order of reaction, Arrhenius pre-exponential term, and activation energy) together with a relationship between T_g and extent of reaction were used as a basis for modeling the onset of vitrification and devitrification in the CHT diagram. For heating scans from below T_{g0} (glass transition temperature of the reactants), the initially glassy material will devitrify when the temperature reaches T_{g0} , except for very low heating rates for which initial devitrification is not encountered. Vitrification is identified as the point at which T_g becomes equal to the increasing curing temperature. Diffusion control retards the reaction rate beyond vitrification. In the limiting case of complete retardation of the rate after vitrification, the reaction can proceed along the $T_g = T_{cure}$ path as long as the additional reaction with increasing temperature is sufficient to increase T_g at least at the same rate as the heating temperature; devitrification occurs thereafter. The critical heating rates at which the material does not devitrify at T_{g0} , and that at which no vitrification is encountered, are calculated.

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INTRODUCTION

The concept of the time-temperature-transformation (TTT) cure diagram (Figure 1) is useful for understanding the behavior of thermosetting systems under isothermal cure conditions [1,2]. The diagram displays the times to reach certain events during isothermal cure as a function of cure temperature. Events common to most liquid thermosetting polymers include gelation which corresponds to the incipient formation of an infinite network, vitrification which occurs when the glass transition (T_g) rises to the temperature of the cure reaction (T_{cure}), and devitrification which occurs when T_g falls below T_{cure} due to degradation. Reactions proceed to some degree after vitrification which leads to $T_g > T_{cure}$ [3].

Analogous to the TTT diagram is the continuous heating transformation (CHT) diagram (Figure 2) which displays the times and temperatures required to reach similar events during the course of continuous heating at constant heating rates [4,5]. For low heating rates, above the initial glass transition temperature of the unreacted material (T_{g0}), chemical reaction in the early stages can proceed such that the T_g of the material rises at a faster rate than the reaction temperature (T_{cure}). Vitrification occurs when T_g equals T_{cure} . After vitrification, the reaction rate is greatly diminished because diffusion control becomes more pronounced in the glass transition region ($T_g \geq T_{cure}$) [4,6-8]. However, immediately after vitrification, T_g increases at least at the same rate as the temperature. At high temperatures towards the maximum glass transition of the cured material ($T_{g\infty}$), the reaction rate is further reduced due to low concentration of the reactants at high conversion. Eventually, the cure temperature rises above T_g and devitrification occurs.

For high heating rates, the glass transition temperature of the material never reaches the cure temperature. Thus, the reaction can proceed to completion entirely in the rubbery state without encountering vitrification or devitrification.

When heating scans start well below T_{g0} , the starting material is in the glassy state. For higher heating rates, the material will pass through initial devitrification (to become a liquid) when the temperature reaches T_{g0} . However, for lower heating rates, the reaction

rate near T_{g0} can be sufficient to keep T_g rising at least at the same rate as the heating temperature. In such cases, the material need not devitrify below $T_{g\infty}$.

The principal technique used for determining the glass transition temperature in this laboratory has been Torsional Braid Analysis (TBA) [4,9]. T_g as measured in this technique corresponds to a state approximately halfway (but closer to the rubbery side of the transition region) between the rubbery and glassy states [1,10]. Thus, in a continuous heating situation after gelation and until vitrification (measured $T_g = T_{cure}$), the material is basically in the rubbery state and the reaction is predominantly kinetically controlled. Beyond vitrification, diffusion control dominates the reaction kinetics until the occurrence of devitrification.

This paper is an attempt to model the behavior of an epoxy/amine system under such continuous heating conditions. Vitrification and devitrification points in the CHT diagram are quantitatively calculated using the kinetic parameters determined from isothermal conversion data. The calculated CHT diagram is compared with the experimental data obtained from Torsional Braid Analysis [4]. A preliminary report has been published [8].

RESULTS

Isothermal Reaction Kinetics of an Amine-Cured Epoxy System

The chemical system used in this study was a stoichiometric mixture of a diglycidyl ether of bisphenol A (Epon 828, Shell Chemical Company) with a tetrafunctional aliphatic amine, bis(p-aminocyclo hexane) methane (PACM-20, Du Pont). T_{g0} and $T_{g\infty}$ for the mixture as determined by TBA are -19°C and 166°C , respectively [2]. The chemical structures of the two reactants are shown in Figure 3.

Conversion vs. time of isothermal curing data at different temperatures obtained using Fourier Transform Infrared (FTIR) spectroscopic analysis of the epoxy group absorption at 915 cm^{-1} are reproduced from reference [2] in Figure 4. These data were re-analyzed for this present report with an ordinary n-th order kinetic equation (1)

(assuming that the only reaction occurring is that between one epoxy and one amine hydrogen atom, and that the primary and secondary amine hydrogens have equal reactivity).

$$\frac{dx}{dt} = k(1-x)^n \quad (1)$$

where x = fractional conversion of epoxy

k = rate constant

n = order of reaction

It was found that different values of the reaction order can be chosen to best describe the reaction kinetics depending on which stage of the reaction is of interest. Figures 5 and 6 show plots of all of the original data in Figure 4 recast by assuming the reaction is first order and second order, respectively. Initially, the reaction can be best described by first order kinetics. Away from the initial stages, the reaction is more satisfactorily represented by second order kinetics. The parameters for first and second order kinetics are summarized in Table 1.

Table 1: Kinetic parameters [pre-exponential factor (A) and activation energy (E)] for assumed first and second order kinetics.

	A	E (Kcal/mol)
First order	4.51×10^6	12.61
Second order	3.18×10^8	14.83

The time to vitrify for isothermal cure versus temperature can be computed by calculating the time for the T_g to rise from its initial value to the temperature of reaction [2,11-13]. Experimental times to vitrify are marked in the isothermal data of Figures 4, 5 and 6.

CHT Diagram

The dynamic mechanical behavior of the material during the course of continuous heating at a constant rate displays changes when the material encounters various events similar to those observed in the isothermal case. These events can include the initial glass to liquid transition, gelation, vitrification, and devitrification. Figure 7A shows the TBA relative rigidity of the material during continuous heating from below T_{g0} to above $T_{g\infty}$ at different heating rates. The corresponding TBA logarithmic decrement data are shown in Figure 7B. Data are reproduced from reference [4]. The initial devitrification (the first glass transition encountered during temperature scanning), vitrification, and devitrification near $T_{g\infty}$, were identified, respectively, from the maxima of the first, fourth and fifth peaks (in the order of increasing temperature) in the logarithmic decrement spectra. The results are summarized in the form of a CHT diagram shown in Figure 2 [4]. (Gelation will not be discussed further in this report.)

Vitrification Calculation:

The vitrification points at various heating rates in the CHT diagram can be calculated from knowledge of the reaction kinetics and the relationship between the glass transition temperature and the extent of reaction. At a given constant heating rate, c , $T_{cure} = T_i + ct$, where $T_i = 223$ K (-50°C) is the starting temperature. The rate equation (1) becomes

$$\frac{dx}{dt} = A \exp\left(\frac{-E}{R(T_i + ct)}\right) f(x) \quad (2)$$

If E , A , and the form of $f(x)$ have been determined, the rate equation can be integrated numerically to give x as a function of time.

An empirical relationship between T_g and x is given by the Dibeneditto relation [14] adapted in the manner of Adabbo and Williams [13]:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(C_1 - C_2)x}{1 - (1 - C_2)x} \quad (3)$$

where C_1 and C_2 are constant parameters. For the epoxy-amine system in this study, C_1 and C_2 were determined to be 0.335 and 0.194 respectively [2]. Employing this relation, T_g can be calculated for each conversion x . Equation (2) together with equation (3) govern

how the T_g of the material increases as a function of time.

The time and temperature at which T_g becomes equal to the increasing curing temperature, T_{cure} , is identified as the vitrification point. These points at different heating rates make up the vitrification curve (the middle section of the S-shaped initial devitrification-vitrification-upper devitrification envelope) in the CHT diagram.

Upper Devitrification Calculation:

Beyond the vitrification point in the CHT diagram, the material is in the glass transition region and the reaction of the system is dominated by diffusion control. In the simplest limiting case, the reaction can proceed along the $T_g = T_{cure}$ path [13], i.e., T_g can follow the curing temperature as long as the additional conversion with each small temperature increment is sufficient to increase T_g to T_{cure} . However, eventually because of the high conversion at high temperature towards $T_{g\infty}$ or because of the relatively high rate of increase of temperature, the reaction rate is not sufficient to keep $T_g = T_{cure}$ and so devitrification occurs.

In order to quantitatively calculate the time to reach the devitrification temperature for a given heating rate, consider the time rate of change of T_g by chemical reaction which is given by

$$\frac{dT_g}{dt} = \left(\frac{dT_g}{dx} \right) \left(\frac{dx}{dt} \right) \quad (4)$$

The first term on the right hand side, dT_g/dx , is the rate of change of T_g with respect to conversion. This term can be derived from the Dibenedetto relationship:

$$\frac{dT_g}{dx} = \frac{T_{g\infty}(C_1 - C_2)}{[1 - (1 - C_2)x]^2} \quad (5)$$

The second term, dx/dt , is the rate of chemical reaction which can be calculated from the assumed reaction kinetics (equation 1).

When dT_g/dt is greater than the heating rate, c , the chemical conversion is sufficient to keep T_g at the reaction temperature. Eventually, the reaction rate decreases, and dT_g/dt falls below the heating rate, resulting in devitrification. Devitrification is identified in the

calculation as the point at which dT_g/dt equals the heating rate. The locus of this devitrification process at different heating rates constitutes the upper devitrification curve in the CHT diagram.

The calculation scheme to determine the devitrification point is as follows:

- 1) At the vitrification point, calculate the conversion, x , corresponding to T_g using the T_g vs. x relationship (equation 3).
- 2) For a small time increment from the vitrification point, determine the cure temperature from the heating rate (i.e., $T_{cure} = T_i + ct$)
- 3) Assuming that the reaction remains kinetically controlled, calculate dx/dt from the assumed kinetic rate law [equation (1)] and dT_g/dx from equation (5)
- 4) Evaluate dT_g/dt from equation (4)
- 5) If dT_g/dt is greater than the heating rate, the additional reaction in this time increment is sufficient to keep $T_g = T_{cure}$. Calculate the conversion corresponding to this T_g .
- 6) Repeat steps 2 to 5 for the next small time increment until the devitrification point is reached (i.e., the point at which dT_g/dt starts to fall below the heating rate).

It should be emphasized that the above procedure is only a limiting case since it assumes that the reaction proceeds along the $T_g = T_{cure}$ path after vitrification. It is apparent from the isothermal conversion data in Figure 2 that the reaction can proceed significantly in the glass transition region ($T_g > T_{cure}$), although its rate decreases markedly due to diffusion control. In the actual continuous heating situation, the non-zero reaction rate after vitrification can keep T_g higher than T_{cure} . Therefore, the actual devitrification point can be a few degrees higher than the computed devitrification temperature. A more realistic model for the material behavior after vitrification must take into account the fact that T_g can be higher than T_{cure} and can remain higher until devitrification. However, this requires knowledge of the diffusion controlled kinetics in the glass transition region.

Calculation Results:

The vitrification and upper devitrification points were calculated at different heating

rates (0.05, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0°C/min) for the two assumed kinetic rate equations using the kinetic parameters determined previously for each case. The results are shown in the form of the CHT diagram in Figure 8 and Figure 9 for first and second order kinetics, respectively. The calculations are compared with the experimental CHT diagram from Figure 2. It is apparent that second order kinetics can be considered to be a better representation of the reaction rate for this amine-cured epoxy system under continuous heating conditions.

Initial Devitrification:

In a similar manner to the above devitrification calculation procedure, the initial devitrification near T_{g0} (the lower branch of the S-shaped CHT curve) can also be determined as a function of heating rates. Assuming that the reaction is already in the kinetically controlled regime when $T_{cure}=T_{g0}$, the time rate of change of T_g at that point ($T=T_{g0}$, $x=0$) can be calculated as

$$\begin{aligned} \left(\frac{dT_g}{dt} \right)_{T=T_{g0}} &= \left(\frac{dT_g}{dx} \right)_{x=0} \left(\frac{dx}{dt} \right)_{T=T_{g0}, x=0} \\ &= [T_{g0}(C_1-C_2)] [k(T_{g0})] \\ &= [T_{g0}(C_1-C_2)] \left[A \exp \left(-\frac{E}{RT_{g0}} \right) \right] \end{aligned} \quad (6)$$

Substituting in the Dibenedetto parameters and the kinetic parameters for both first and second order, the initial rate of change of T_g at $T=T_{g0}$ is found to be approximately 2×10^{-3} °C/min. Therefore, for heating rates greater than 2×10^{-3} °C/min, the unreacted material will devitrify when the reaction temperature reaches T_{g0} . For heating rates less than 2×10^{-3} °C/min., the material will not devitrify at T_{g0} since the reaction can raise T_g at least at the same rate as the cure temperature. As in the case after vitrification, T_g is assumed to follow the heating temperature as long as dT_g/dt is greater than the heating rate. Above T_{g0} , dT_g/dt is an increasing function, since the reaction rate increases exponentially with increasing temperature, while it only decreases as a power of n with increasing conversion. This follows directly from the n -th order kinetic rate expression. As T_g

approaches $T_{g\infty}$, near-depletion of the reactants causes the rate increment of T_g to decrease. Therefore, if dT_g/dt at T_{g0} is greater than the heating rate, then the material will not devitrify until the cure temperature is close to $T_{g\infty}$. Table 2 shows the calculated results of initial devitrification, vitrification and devitrification near $T_{g\infty}$ for the case of second order kinetics for heating rates between 1.94×10^{-3} and 2×10^{-3} °C/min. The results show that for heating rates less than 1.96×10^{-3} °C/min, the material does not encounter devitrification until $T_{g\infty}$. For these heating rates, the system will polymerize without liquifying; i.e., polymerization occurs under conditions of maximum density.

Table2: CHT results for second order kinetics for heating rate around 1.96×10^{-3} °C/min.

Heating Rates $\times 10^{-3}$ °C/min	Initial Devitrification Temperature (°C)	Vitrification Temperature(°C)	UpperDevitrification Temperature (°C)
1.94	-	-	$\sim 166 = T_{g\infty}$
1.95	-	-	~ 166
1.96	-19 = T_{g0}	-19.07	~ 166
1.97	-19	-19.14	~ 166
1.98	-19	-19.23	~ 166
2.0	-19	-19.41	~ 166

Limiting Heating Rate Without Vitrification:

The minimum heating rate at which the material will not encounter vitrification during a temperature scan can be determined by calculating the heating rate, c_L , at which vitrification ($T_g = T_{cure}$) and devitrification ($dT_g/dt = c_L$) occur simultaneously.

Let t_v and x_v be the time and conversion to reach vitrification for the limiting heating rate c_L . The vitrification condition combined with Debenedetto's relation can be expressed in terms of t_v , x_v and c_L as

$$T_g = T_{g0} + \frac{T_{g0} (C_1 - C_2) x_v}{1 - (1 - C_2) x_v} = T_i + c_L t_v \quad (7)$$

The devitrification condition becomes

$$\left. \frac{dT_g}{dt} \right|_{vit} = \frac{T_{g0}(C_1 - C_2)}{[1 - (1 - C_2)x_v]^2} A \exp\left(-\frac{E}{R(T_i + c_L t_v)}\right) f(x_v) = c_L \quad (8)$$

These two equations together with the rate expression (Equation 2) provide the necessary equations which can be solved simultaneously for the three unknowns t_v , x_v and c_L .

The calculations were performed numerically for the case of second order kinetics. The procedure assumes the heating rate, c_L , then calculates the time (t_v) and conversion (x_v) to reach vitrification for the assumed heating rate. The time rate of change of T_g is then evaluated at the calculated vitrification point according to equation (8). If dT_g/dt is greater than the heating rate c_L , the procedure is repeated for a new higher heating rate. If no vitrification is encountered, the guessed value of c_L is higher than the actual limiting heating rate. This trial and error procedure is repeated until the limiting heating rate is found. For second order kinetics, this value is found to be 2.94°C/min. Thus, for any heating rate greater than 2.94°C/min., the material will not encounter vitrification during the temperature scan. This critical heating rate has practical implications in molding technology. For example, it defines the minimum heating rate so as to obtain full conversion without the interference of vitrification. Conversely, vitrification can be an essential part of a cure cycle in order to control the reaction rates of highly exothermic reactions. The polymerization of 250 gallons of epoxy to encapsulate a magnetic coil in Princeton University's experimental Tokamak nuclear fusion reactor is accomplished by heating at a very low rate of temperature increase ($\sim 7 \times 10^{-3}$ °C/min); the reaction rate is controlled in the process by the T_g increasing in concert with the temperature until $T_{g\infty}$, i.e., full cure, is attained.

CONCLUSIONS

1) For isothermal cure, the initial stages of the reaction can be better described by first order than second order kinetics. However, away from the initial stages (0-30%

conversion) and up to the vicinity of vitrification, the reaction can be better represented by second order kinetics.

2) When this system is subjected to continuous heating conditions, its overall reaction kinetics in the liquid and rubbery states appears to be second order. Prediction of the CHT vitrification/devitrification envelope is much better when the second order rather than the first order rate equation and parameters are used in the calculation.

3) Initially in a continuous heating case, when the heating temperature passes through T_{g0} , the unreacted glassy material will devitrify. For very low heating rates, however, no initial devitrification will be encountered since the reaction rate at T_{g0} is sufficient to increase T_g at the same rate as the temperature. For second order kinetics, the minimum heating rate at which the material will devitrify at T_{g0} is $1.96 \times 10^{-3} \text{ } ^\circ\text{C/min}$.

4) After initial devitrification, the reaction proceeds in the liquid state, and vitrification is identified as the point at which T_g becomes equal to T_{cure} . After vitrification, the upper devitrification envelope was computed by comparing the rate of change of T_g with respect to time, dT_g/dt , with the heating rate dT/dt assuming that the reaction proceeds along the $T_g = T_{cure}$ path, as long as the former is greater. The upper devitrification point is identified as the point at which dT_g/dt starts to fall below the heating rate (due to low reaction rate at high conversion, or because of a relatively high heating rate). For second order kinetics, the critical heating rate at which vitrification and devitrification occur simultaneously is 2.94°C/min .

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FIGURE CAPTIONS

Figure 1. Schematic time-temperature-transformation (TTT) isothermal cure diagram for a thermosetting system, showing three critical temperatures, i.e., $T_{g\infty}$, $gelT_g$, T_{go} , and the distinct states of matter, i.e., liquid, sol/gel rubber, gel rubber (elastomer), sol/gel glass, gel glass, sol (or ungelled) glass, and char. The full-cure line, i.e., $T_g = T_{g\infty}$, divides the gelled glass region into two parts: sol/gel glass and fully cured gel glass. (Phase separation, in two phase systems, occurs prior to

gelation. Successive isoviscous contours which are shown in the liquid region for a neat system with no phase separation differ by a factor of ten.) The transition region approximates the half width of the glass transition. T_{g0} is the initial glass transition temperature of the reactants; $_{gel}T_g$ is the glass transition temperature of the reaction system at its gelation point.

Figure 2. Continuous Heating Transformation (CHT) diagram of EPON 828/PACM-20 which includes initial devitrification, vitrification and devitrification events (from reference [4]).

Figure 3. Chemical reactants.

Figure 4. Fractional conversion of epoxy vs. time during isothermal curing at different temperatures (FTIR results from reference 2). Experimental isothermal vitrification at each cure temperature is designated by an arrow.

Figure 5. Isothermal conversion data of Figure 4 analyzed according to first order kinetics. An Arrhenius plot of the reaction rate constants (obtained from the slopes of the straight lines) against $1/T(K)$ yields an activation energy (E) and a preexponential factor (A). Experimental isothermal vitrification at each cure temperature is designated by an arrow.

Figure 6. Isothermal conversion data of Figure 4 analyzed according to second order kinetics. Experimental isothermal vitrification at each cure temperature is designated by an arrow.

Figure 7. TBA dynamic mechanical behavior of EPON 828/PACM-20 during continuous heating from below T_{g0} to above $T_{g\infty}$ at different rates: (A) relative rigidity and (B) logarithmic decrement (from reference [4]). The events relevant to this work are the times to reach T_{g0} , vitrification and devitrification which are identified by the first, fourth and fifth peaks, respectively, in the logarithmic decrement in the order of increasing temperature (see, for example, the marked spectra at $1.0^\circ\text{C}/\text{min}$). These events are summarized in the CHT diagram in Figure 2.

Figure 8. Calculated CHT (vitrification and upper devitrification) diagram from first order kinetics ($\square$), also included: experimental data (x) (from Fig. 2).

Figure 9. Calculated CHT (initial devitrification, vitrification and upper devitrification) diagram from second order kinetics: initial devitrification limit ($\blacktriangle$), vitrification (+) and upper devitrification (x). Experimental data (from Fig. 2): initial devitrification(Δ), vitrification (O) and upper devitrification near $T_{g\infty}$ ($\square$). Note the critical heating rates: $2.94^{\circ}\text{C}/\text{min}$ is the maximum heating rate that the material will encounter vitrification, and $1.96 \times 10^{-3}^{\circ}\text{C}/\text{min}$ is the minimum heating rate that the material will encounter initial devitrification (at T_{go}).

FIGURE 1: THE THERMOSETTING PROCESS:
TIME-TEMPERATURE-TRANSFORMATION
ISOTHERMAL CURE DIAGRAM

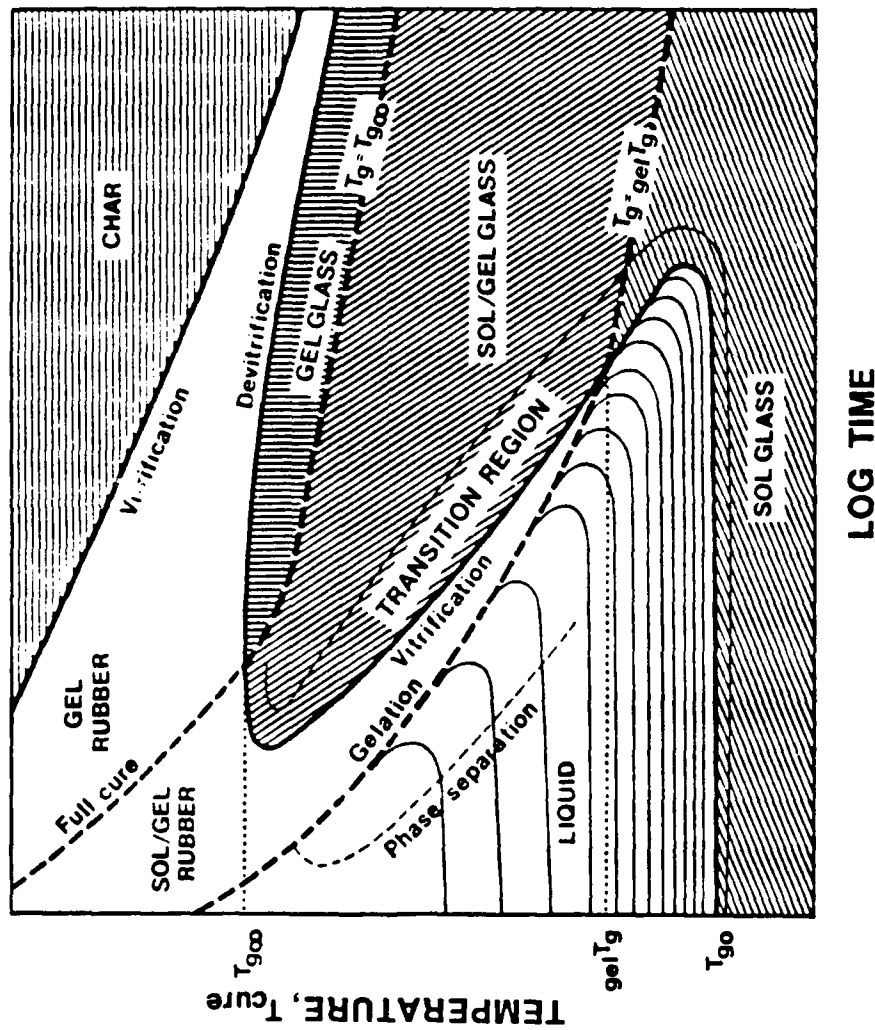
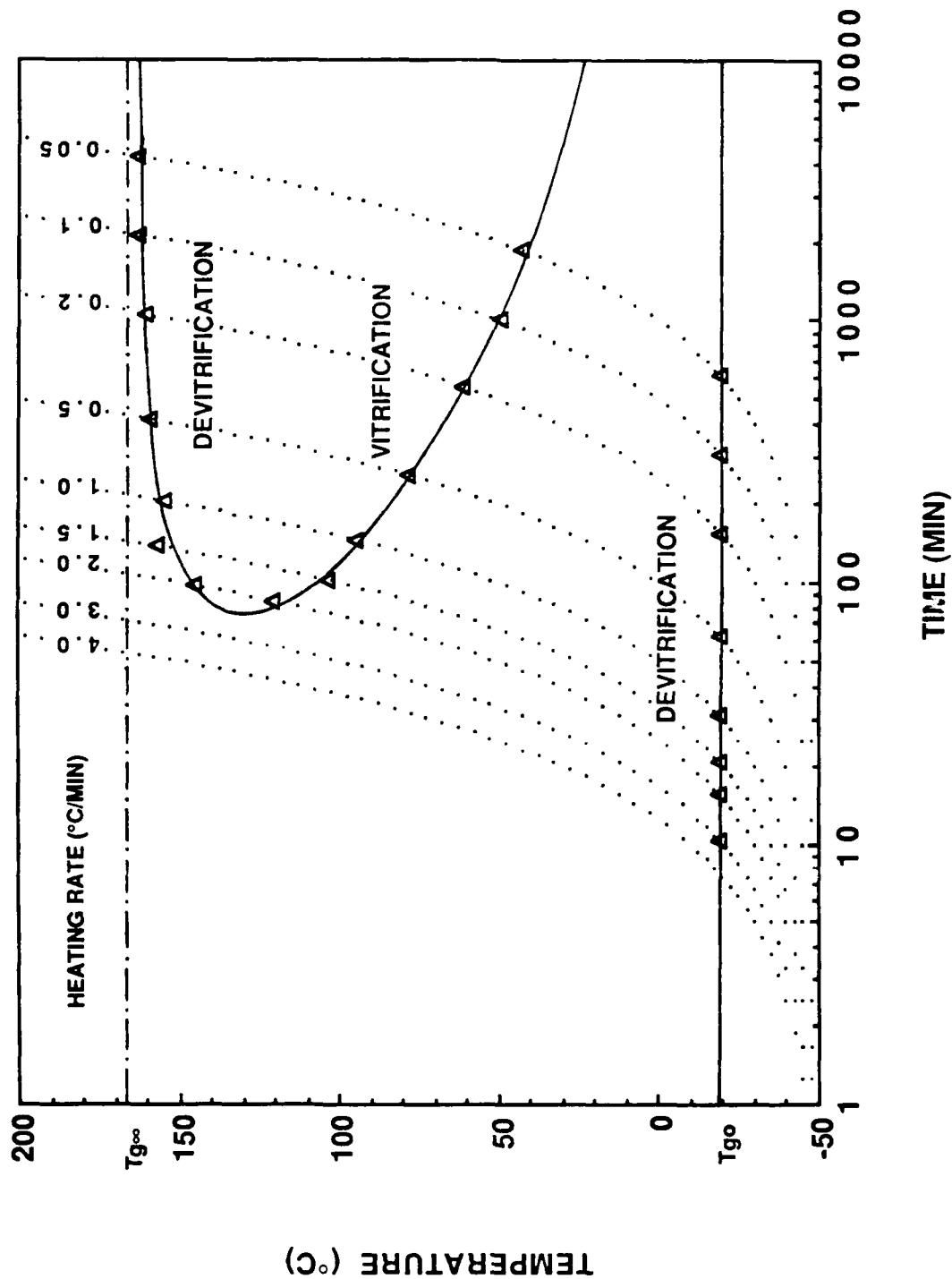


FIGURE 2: CHT DIAGRAM: EPON 828/PACM-20



$$\left[\begin{array}{c} \text{CH}_2\text{CH}_2\text{O} \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{C}(\text{CH}_3)_2 \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O} \end{array} \right]_{0.15} \left[\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}(\text{CH}_3)_2 \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{OCH}_2\text{CH}_2\text{O} \end{array} \right]$$
N[C@H]1CCCC[C@H]1C[C@H]2CCCC[C@H]2N

BIS(p-AMINOCYCLOHEXANE) METHANE (PACM-20)

FIGURE 4: CONVERSION OF EPOXY (EPON 828/PACM-20) VS. TIME

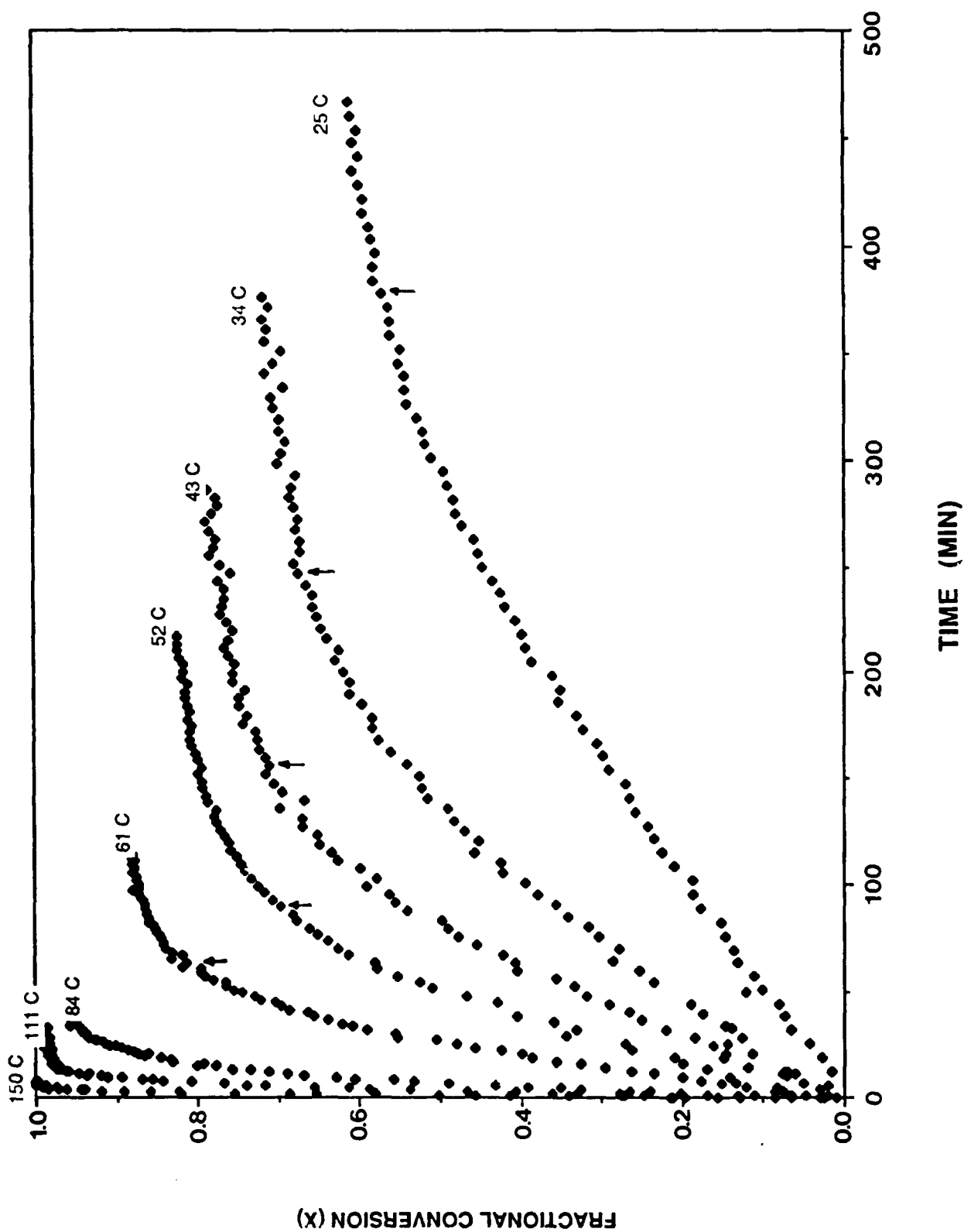


FIGURE 5: FIRST ORDER KINETICS

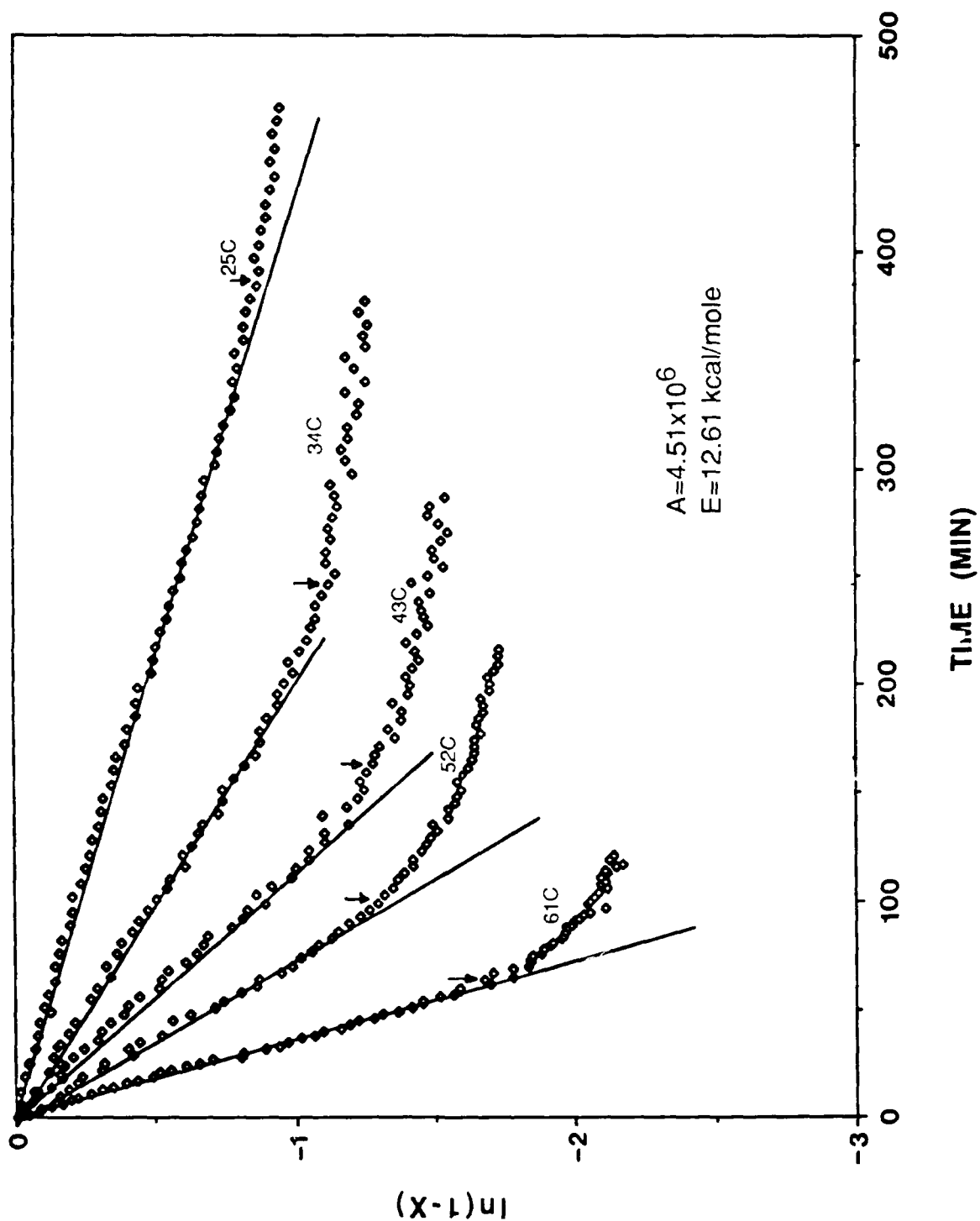


FIGURE 6: SECOND ORDER KINETICS

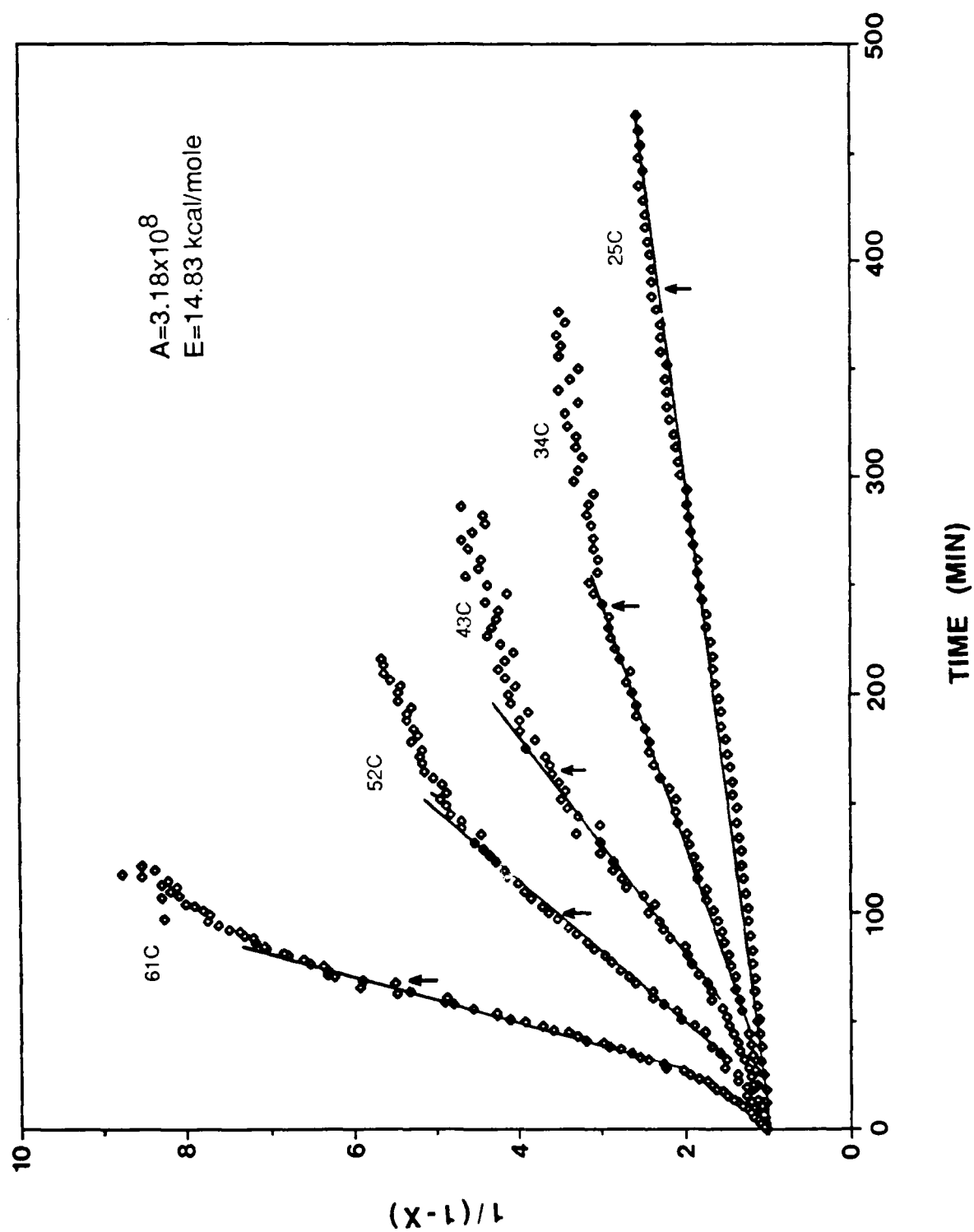
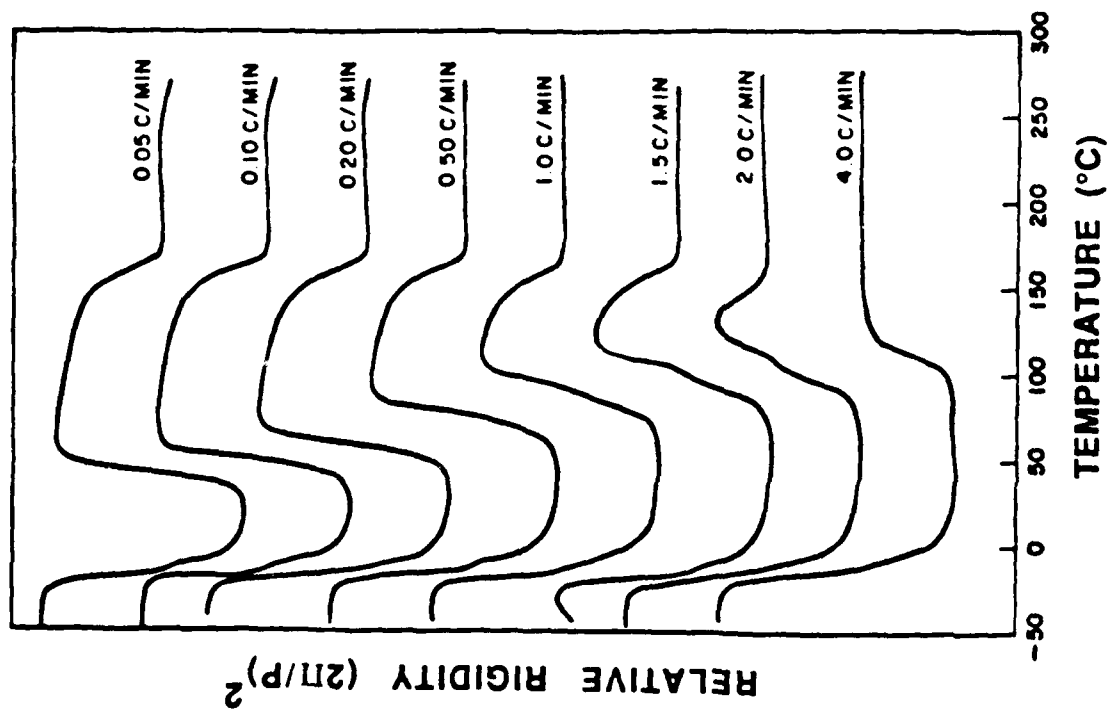


FIGURE 7: MECHANICAL BEHAVIOR OF EPON828/PACM-20 DURING
CONTINUOUS HEATING AT CONSTANT HEATING RATES.

(A)



(B)

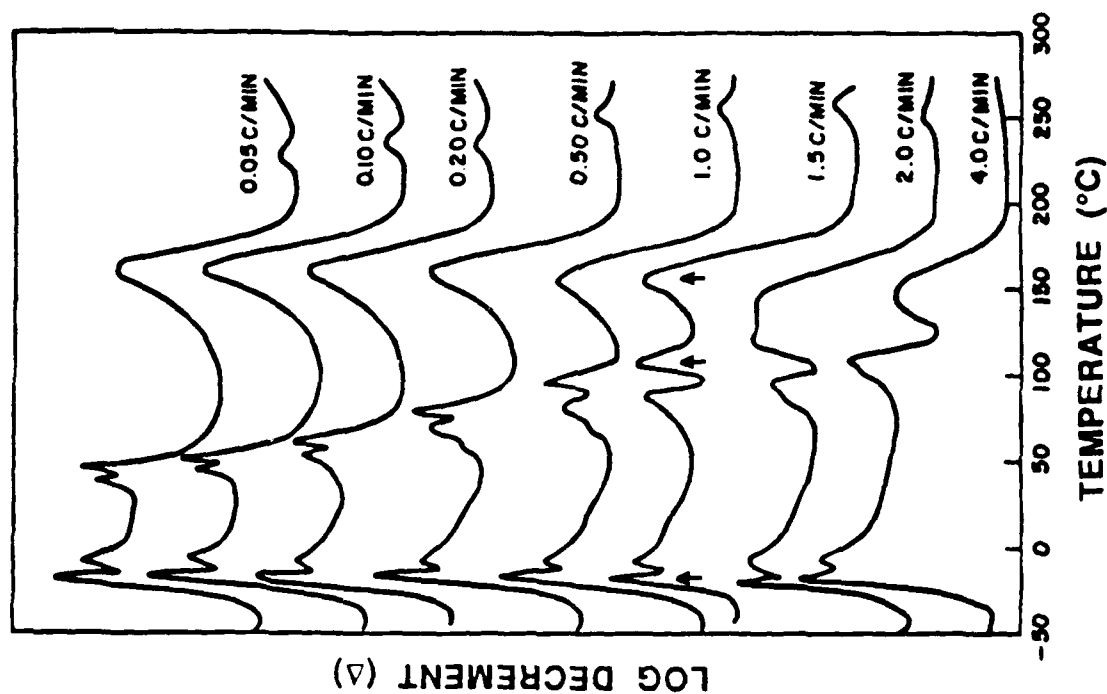


FIGURE 8: CALCULATED CHT DIAGRAM (VITRIFICATION AND DEVITRIFICATION):
FIRST ORDER KINETICS

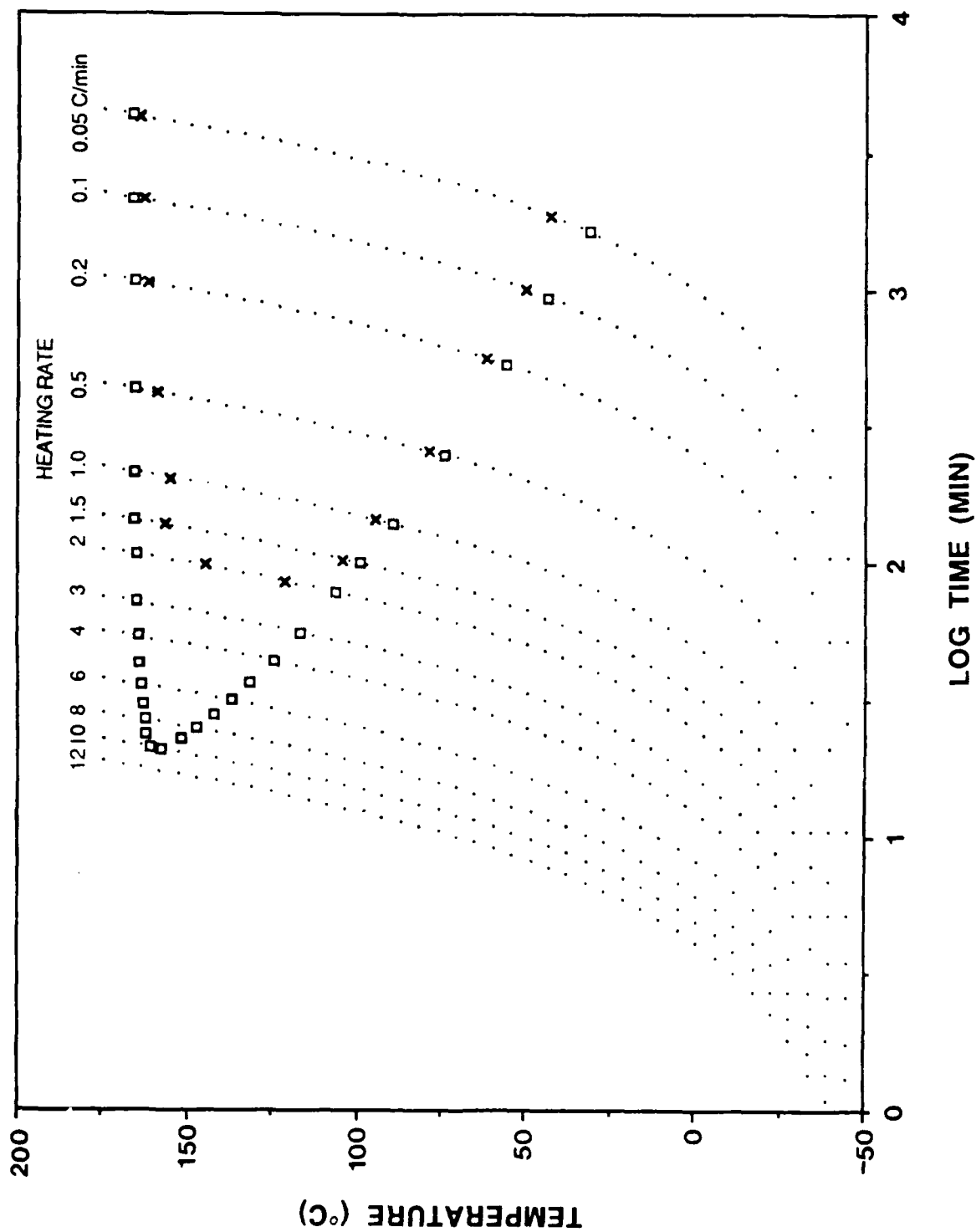
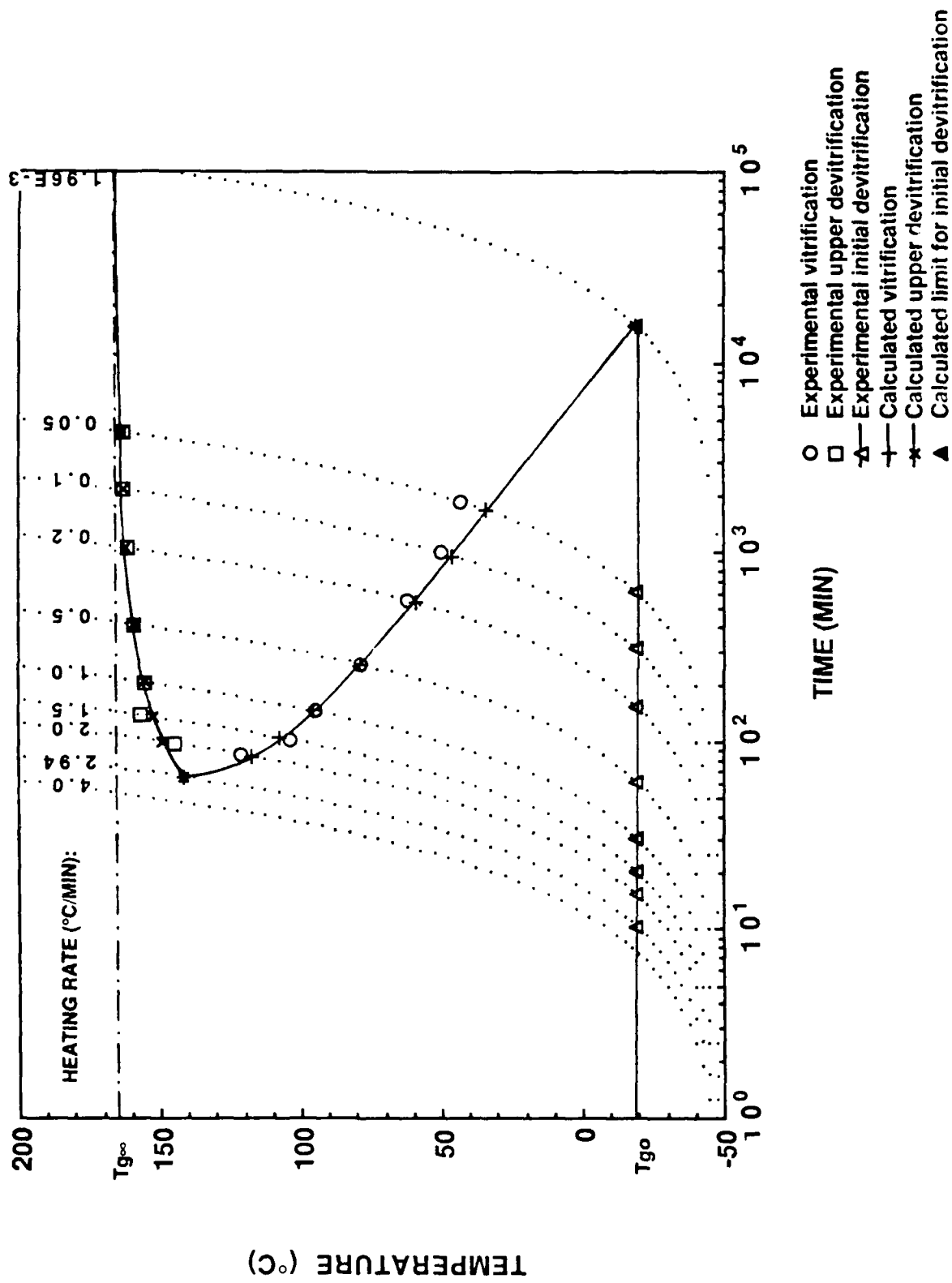


FIGURE 9: CALCULATED CHT DIAGRAM (INITIAL DEVITRIFICATION-VITRIFICATION
-UPPER DEVITRIFICATION): SECOND ORDER KINETICS



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