

## Cationic Cure of Epoxy Resin by an Optimum Concentration of N-benzylpyrazinium Hexafluoroantimonate

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Received Jan. 5, 2002 ; Revised Feb. 2, 2002

**Abstract:** Cure behavior of an epoxy resin was investigated at different cure temperatures (110, 120, 130, 140, and 150 °C) and cure times in the presence of 2 wt% of an N-benzylpyrazinium hexafluoroantimonate (BPH) cationic catalyst by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The glass transition temperature ( $T_g$ ) and chemical conversion ( $x$ ) at the different temperatures were determined from DSC thermograms. The  $T_g$  and  $x$  vs.  $\ln$  time data were superposed up to  $T_g = 100$  °C and  $x = 0.70$  by shifting horizontally at a reference temperature of  $T_g = 130$  °C. It is interesting that the  $T_g$  and  $x$  of the superposed data increase rather slowly in the early stage of cure and rapidly thereafter. Therefore, the increase of the  $T_g$  and  $x$  can be divided into two regions;  $R_I = -18.4 (= T_{g0}) \sim 5$  °C and  $R_{II} = 5 \sim 100$  °C in  $T_g$ , and  $R_I = 0 \sim 0.24$  and  $R_{II} = 0.24 \sim 0.70$  in  $x$ . The  $R_I$  is closely related to the initiation reactions between BPH and epoxy and between hydroxy group and epoxy in this epoxy/catalyst system. From the kinetic analysis of the  $T_g$ -shift, activation energy was 12.5 kcal/mol. The relationship between  $T_g$  and  $x$  was also considered. The gelation and vitrification times for different cure temperatures were obtained from DMA curves.

**Keywords :** epoxy, cationic catalyst, glass transition temperature, conversion, cure kinetics.

### Introduction

Cationic latent cure system for epoxy resin is of interest since it can simplify cure processing and improve long term stability at room temperature and electrical properties, compared to the common amine and anhydride curing agent systems. Various cationic catalysts were introduced in the literature having photo and/or thermal latency for curing epoxy resins.<sup>1-7</sup> Recently, N-benzylpyrazinium salts showing thermal latency for epoxy resins have been synthesized<sup>8</sup> and used to study cure behavior, rheological and thermal/mechanical properties during and after cure.<sup>8-11</sup> The concentration of the latent catalyst ranging from 0.5 to 5 wt% has been used for the studies. It revealed that the optimum con-

centration of the catalyst was 1.5 or 2 wt% for various physical properties.

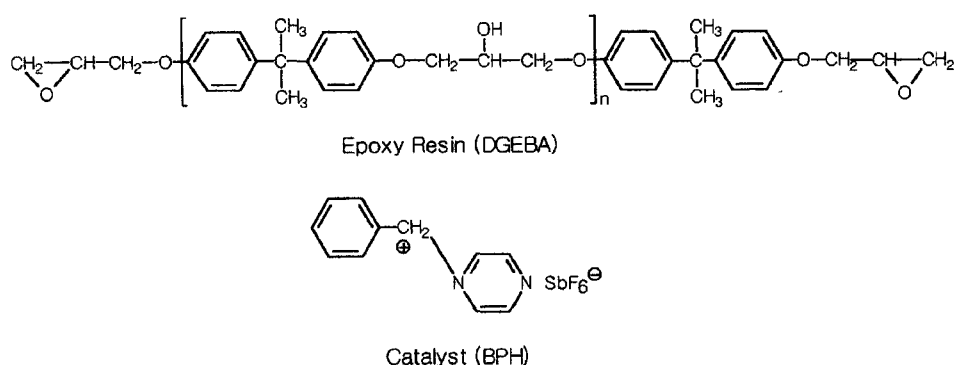
During cure of thermosetting materials, the glass transition temperature ( $T_g$ ) as an index of degree of chemical conversion increases greatly as low molecular weight liquid are transformed into high molecular weight solid. It is known that the  $T_g$  is an important parameter in analyzing cure behavior so that the variation of  $T_g$  with cure time has been studied for dicyanate ester-polycyanurate, epoxy/amine and epoxy/anhydride system.<sup>12-17</sup> It has also been described that  $T_g$  can be used to study the cure kinetics for various epoxy resin and curing agent systems.<sup>15-17</sup>

In this study, we investigated the cure behavior and cure kinetics of an epoxy resin in the presence of an optimum amount (2 wt%) of N-benzylpyrazinium hexafluoroantimonate (BPH) as a cationic catalyst in order to understand further the cure process of the system by means of a differential

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## Cationic Cure of Epoxy Resin



**Figure 1.** Chemical structures of the reactants for epoxy resin and catalyst used in this study.

scanning calorimetric technique. Dynamic mechanical properties were examined during curing isothermally.

### Experimental

A diglycidyl ether of bisphenol-A (DGEBA, YD 128 from Kukdo Chem. Co., Korea, equivalent weight = 185~190 g/eq.) epoxy resin and 2 wt% of an N-benzylpyrazinium hexafluoroantimonate (BPH) catalyst were mixed thoroughly in acetone for 10 min. The chemical structures of the reactants are shown in Figure 1. The unreacted mixture in a vial, covering with aluminum foil to protect from light, was stored in refrigerator.

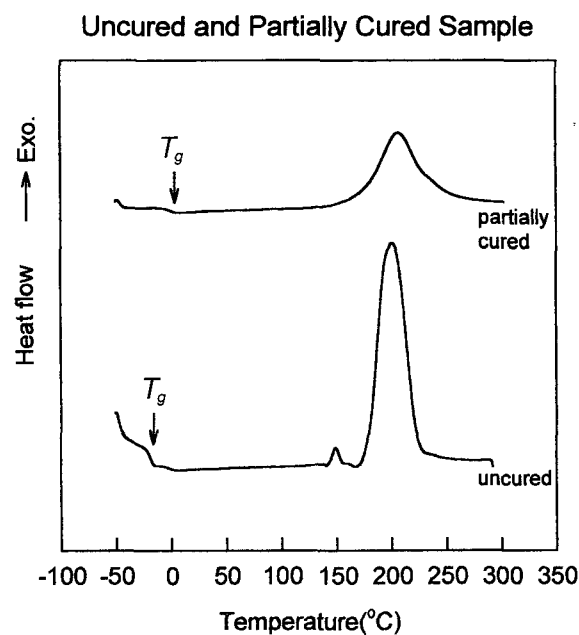
The cure of the epoxy resin was studied using differential scanning calorimetry (DSC, Du Pont 910). DSC measurements were made on the mixture containing approximately 10-15 mg in a hermetic pan. The glass transition temperature ( $T_g$ ) and the total exothermic heat of cure ( $\Delta H_T$ ) of the unreacted sample were determined from the DSC scan. The unreacted sample in the hermetic pan was partially cured in a dry oven for pre-selected periods (10 to 1,020 min) at different cure temperatures (110 to 150°C). DSC scans for the partially cured sample were taken to obtain  $T_g$  and residual heat of cure ( $\Delta H_R$ ). All experiments for the samples uncured and partially cured were performed in the temperature range from 60 to 300°C at a heating rate of 10°C/min in a dry nitrogen atmosphere. When the endothermic peak due to isothermal physical aging in a vitrified region was developed near  $T_g$  for partially cured samples, the peak was eliminated by heating the samples to just above the endothermic peak, quenching to room temperature. The sample was then subsequently reheated from room temperature to 300°C. This procedure is essential to determine not only the glass transition temperature but also the residual heat of cure accurately as used in other works.<sup>12,17</sup> A fully cured sample was prepared by curing at 140°C for 600 min and postcuring at 190°C for 120 min. The glass transition temperature ( $T_{g\infty}$ ) of the fully cured was 175°C.

Dynamic mechanical analysis (DMA, Du Pont 982) was employed to observe the cure behavior of the epoxy mixture

that is impregnated into glass mattress. The impregnated sample was placed in the heater after squeezing out the excess resin between aluminum foil. The cure of the sample was analyzed in terms of storage modulus and  $\tan\delta$ . The modulus obtained in this experiment is a relative value because of the composite nature of the specimen (resin mixture + glass mattress). Uncured samples were heated isothermally at the temperatures as in DSC experiments for times up to 2,000 min under a dry nitrogen atmosphere. Frequency and amplitude of the oscillation are 0.1 Hz and 0.2 mm, respectively.

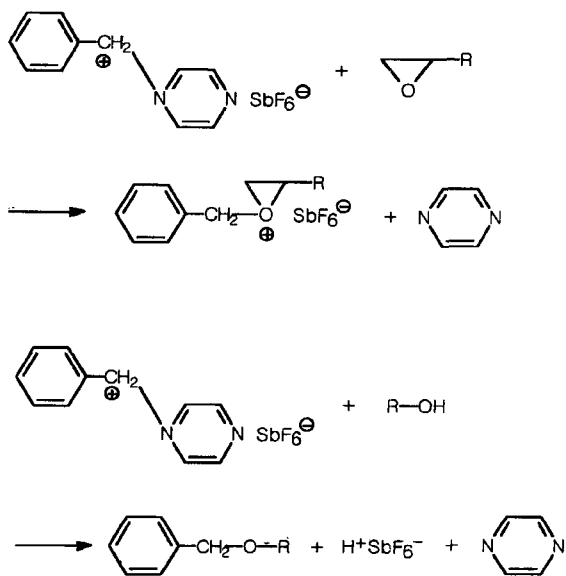
### Results and Discussion

Figure 2 shows typical DSC thermograms of samples



**Figure 2.** DSC thermograms of samples uncured and partially cured, showing the glass transition temperature ( $T_g$ ) and exothermic peak ( $\Delta H$ ).

uncured and partially cured at 140°C for 30 min in the epoxy resin/N-benzylpyrazinium hexafluoroantimonate (BPH) catalyst system. The glass transition temperature ( $T_{g0}$ ) and the total exothermic enthalpy ( $\Delta H_T$ ) of the uncured mixture determined from the DSC curve were -18.4°C and 400 J/g, respectively. For the partially cured sample, the  $T_g$  increased to 10°C and the residual enthalpy value ( $\Delta H_R$ ) decreased to 200 J/g. Multi-exothermic peaks on the DSC thermogram for the uncured sample were observed in this study; two small peaks at lower temperatures and one large peak at a higher temperature. According to the previous work,<sup>8</sup> it is considered that the small exothermic peaks at lower temperatures are due to the two different initiation reactions between BPH and epoxy and between hydroxyl group and epoxy as shown below.<sup>9</sup>



After curing at 140°C for 30 min, the small peaks are disappeared completely and the main peak at higher temperature becomes smaller. The 2 wt% of BPH in this study is considered to display rather pronounced small exothermic peaks, which disappear after curing at a short period of time before gelation.<sup>8</sup>

**Cure Characteristics.** The glass transition temperature, which is one of the important parameters in analyzing cure behavior, was determined from the inflection point of the step transition on DSC thermogram. The variations of  $T_g$  with  $\ln(\text{time})$  during isothermal curing at different temperatures ( $T_c = 110, 120, 130, 140,$  and  $150^\circ\text{C}$ ) are shown in Figure 3. The  $T_g$  increases rather slowly in the beginning of cure, rapidly in the middle, and levels off thereafter at lower cure temperatures (i.e. 110, 120, and  $130^\circ\text{C}$ ), while the  $T_g$  increases rapidly from the beginning at higher cure temperatures (i.e. 140 and  $150^\circ\text{C}$ ). Figure 4 shows the corresponding conversion ( $x$ ) with  $\ln(\text{time})$  calculated by the following equation from the total ( $\Delta H_T$ ) and residual heat of cure

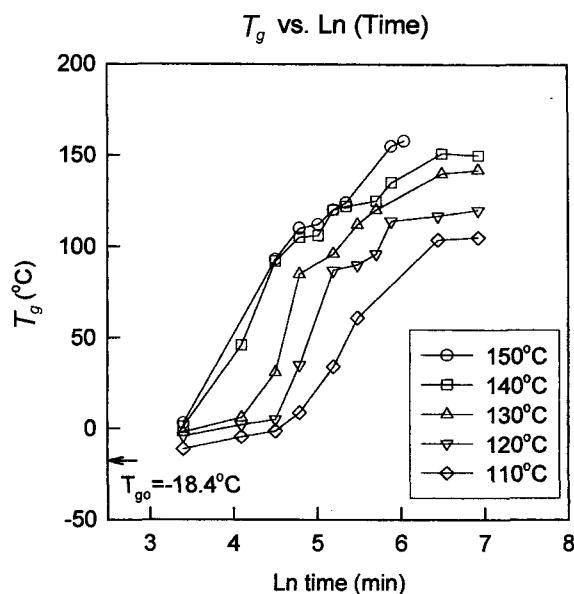


Figure 3. Glass transition temperature ( $T_g$ ) vs  $\ln(\text{time})$  during curing at various cure temperatures from 110 to  $150^\circ\text{C}$ .

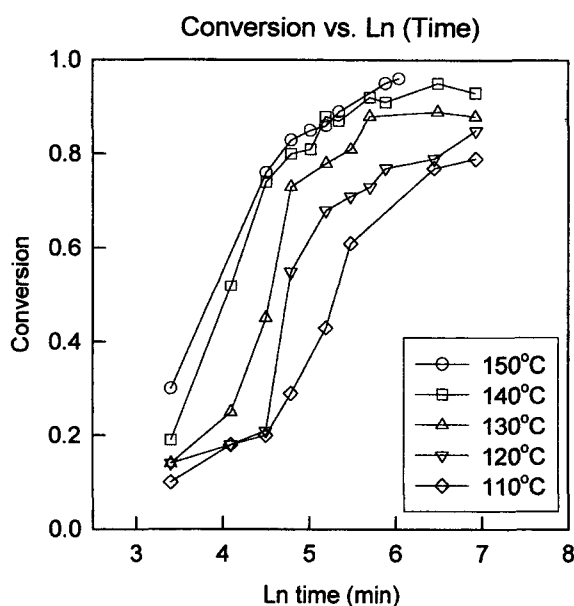
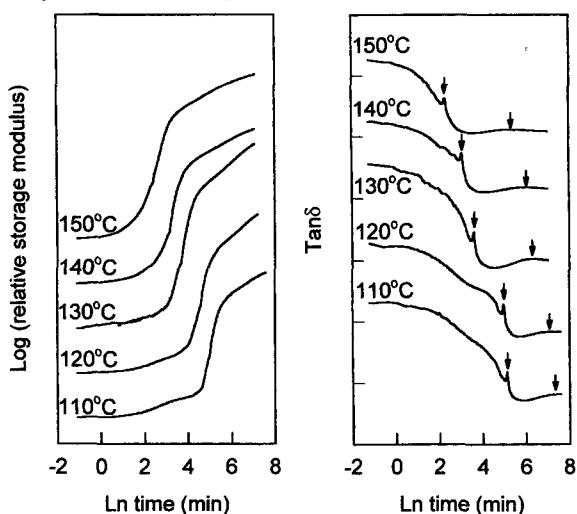


Figure 4. Corresponding conversion ( $x$ ) vs  $\ln(\text{time})$  during curing at various cure temperatures from 110 to  $150^\circ\text{C}$ .

( $\Delta H_R$ ).

$$x = 1 - \frac{\Delta H_R}{\Delta H_T} \quad (1)$$

The increasing trend of conversion with cure time is similar to that of  $T_g$  in Figure 3. After curing for 1020 min, the  $T_g$  and conversion increased up to  $105^\circ\text{C}$  and 0.79 at  $T_c = 110^\circ\text{C}$  and  $150^\circ\text{C}$  and 0.93 at  $T_c = 140^\circ\text{C}$ , respectively.

Log (Relative Storage Modulus) and  $\tan\delta$  vs. Ln (Time)

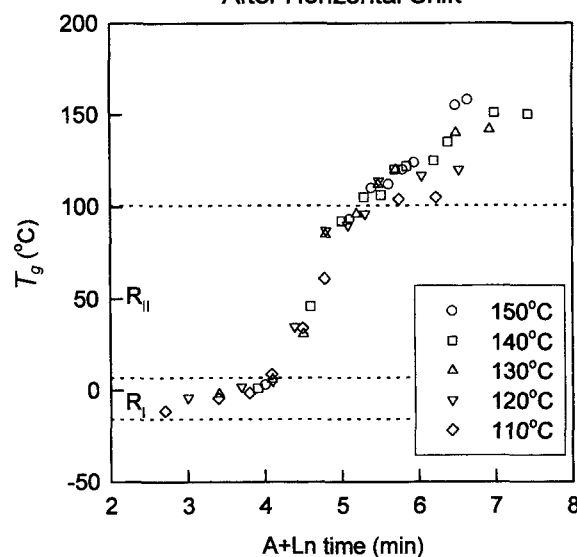
**Figure 5.** Log(relative storage modulus) and  $\tan\delta$  vs Ln(time) at various cure temperatures from 110 to 150 °C.

Cure of thermosetting polymers, especially epoxy, can be characterized by the variations of the storage and loss modulus (or  $\tan\delta$ ) by means of dynamic mechanical analysis. Figure 5 has the variations of (a) relative storage modulus and (b)  $\tan\delta$  during isothermal curing at isothermal temperatures, ranging from 110 to 150 °C. For all the temperatures, the storage modulus increases slowly and then rapidly, and levels off vs Ln(time). Whole curve shifts to a shorter time scale with increase of cure temperature, meaning that cure reaction is accelerated. All  $\tan\delta$  curves show two peaks as marked by arrows, which correspond to gelation at a shorter cure time and vitrification at a longer cure time. At gelation, viscosity increases dramatically by the formation of branched molecules with infinite molecular weight. A glassy material is formed as a consequence of the network becoming tighter through further chemical crosslinking reaction at vitrification. As in the modulus, the  $\tan\delta$  curves move to a shorter time scale. Gelation and vitrification time of 145 and 1,355 min at  $T_c = 110^\circ\text{C}$  are shortened to 12 and 230 min at  $T_c = 150^\circ\text{C}$ , respectively. The times for the gelation and vitrification are

**Table I. Gelation and Vitrification Times Obtained from DMA**

Cure Temperature (°C)	Gelation Time (min)	Vitrification Time (min)
110	145	1,355
120	96	984
130	40	593
140	23	420
150	12	230

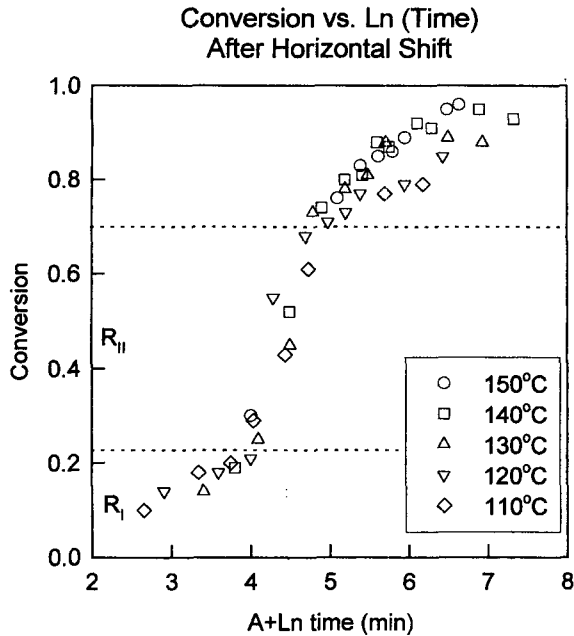
$T_g$  vs. Ln (Time)  
After Horizontal Shift



**Figure 6.** Horizontal shift of  $T_g$  vs Ln(time) data ( $T_c = 130^\circ\text{C}$ ), showing superposition below  $T_g = 100^\circ\text{C}$ . Note the break in the increasing slope at  $T_g = 5^\circ\text{C}$ .

listed in Table I.

**Horizontal Shift of  $T_g$  and Conversion.** The data of  $T_g$  vs Ln(time) in Figure 3 were horizontally shifted at a reference temperature ( $T_r$ ) of 130 °C and the result is displayed in Figure 6. All the glass transition temperature data are superposed and formed a master curve below  $T_g = 100^\circ\text{C}$ . The superposition is known to occur in a kinetically-controlled regime where the reaction mechanism changes to a diffusion-controlled (above  $T_g = 100^\circ\text{C}$  in this study) as observed in other studies.<sup>15-17</sup> In this Figure, it is very interesting that there is a distinct change of slope in the increase of  $T_g$  in the superposed region. Therefore, the master curve can be divided into two regions in term of  $T_g$ :  $R_I(T_g) = -18.4$  to  $5^\circ\text{C}$  and  $R_{II}(T_g) = 5$  to  $100^\circ\text{C}$ , as marked in the figure on a vertical axis. The horizontal shift of the data of  $x$  vs Ln(time) in Figure 4 were also made at the same reference temperature ( $T_r = 130^\circ\text{C}$ ) and the result is shown in Figure 7. The shift produced a master curve and the break in the conversion increase was observed as shown in the shift of  $T_g$ . The two regions in terms of  $x$  are  $R_I(x) = 0$  to  $0.24$  and  $R_{II}(x) = 0.24$  to  $0.70$ . The  $R_I$  where  $T_g$  or  $x$  increases gradually with isothermal cure time appears to be closely related to the small cure exotherms at lower temperatures on the DSC thermogram for uncured samples shown in Figure 2. The slope change in the  $T_g$  and  $x$  confirms the existence of the initiation reactions (epoxy/BPH and epoxy/hydroxyl group) involved in the cure, proposed in earlier reports.<sup>8,9</sup> Consequently, the initiation reactions were found to take place in the early stage of cure below  $T_g = 5^\circ\text{C}$  or  $x = 0.24$ .



**Figure 7.** Horizontal shift of  $x$  vs  $\ln(\text{time})$  data ( $T_c = 130^\circ\text{C}$ ), showing superposition below  $x = 0.70$ . Note the break in the increasing slope at  $x = 0.24$ .

**Cure Kinetics.** Among the methods in analyzing experimental results for the cure kinetics, a time-temperature superposition method has been used to determine the activation energy ( $E_a$ ).<sup>18</sup> When the rate of reaction is kinetically-controlled, the rate is given by the Arrhenius rate equation.

$$\frac{dx}{dt} = A \exp\left(\frac{-E_a}{RT_c}\right) f(x) \quad (2)$$

where  $E_a$  is the apparent activation energy for the overall reaction,  $T_c$  is the cure temperature, and  $f(x)$  is a function of conversion ( $x$ ) independent of temperature. Rearranging eq. 2 and integrating yields,

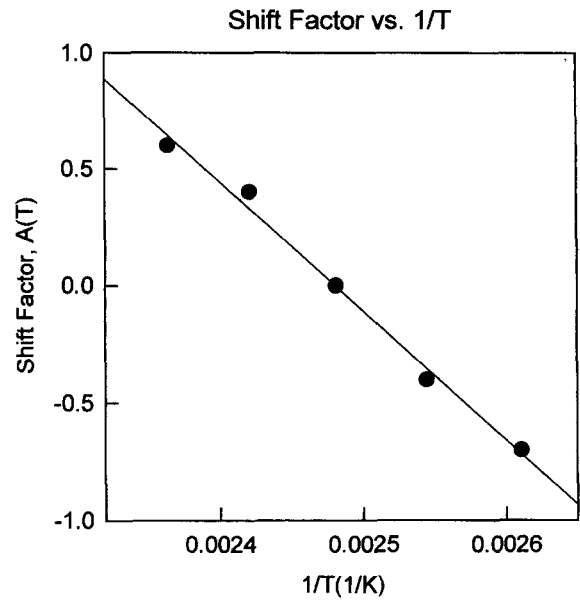
$$\ln \int_0^x \frac{dx}{f(x)} = \ln A + \ln t - \frac{E_a}{RT_c} \quad (3)$$

From a one-to-one relationship between  $x$  and  $T_g$ , eq. 3 can be written as:

$$F(T_g) = \ln A + \ln t - \frac{E_a}{RT_c} \quad (4)$$

At the arbitrary reference temperature ( $T_r$ ), eq. 4 becomes

$$F(T_g) = \ln A + \ln t_r - \frac{E_a}{RT_r} \quad (5)$$



**Figure 8.** Shift factor vs  $1/T$  to obtain activation energy.

**Table II. Activation Energies for Epoxy Systems Obtained by a Time-temperature Superposition Method**

Materials	Activation Energy (kcal/mol)	References #
Epoxy Novolac/DDS <sup>a</sup>	14.6	15
DGEBA/TMAB <sup>b</sup>	15.2	16
DGEBA/Anhydride/Imidazole	15.2	17
DGEBA/BPH	12.5	This work

<sup>a</sup>DDS, 4,4-diaminodiphenylsulfone.

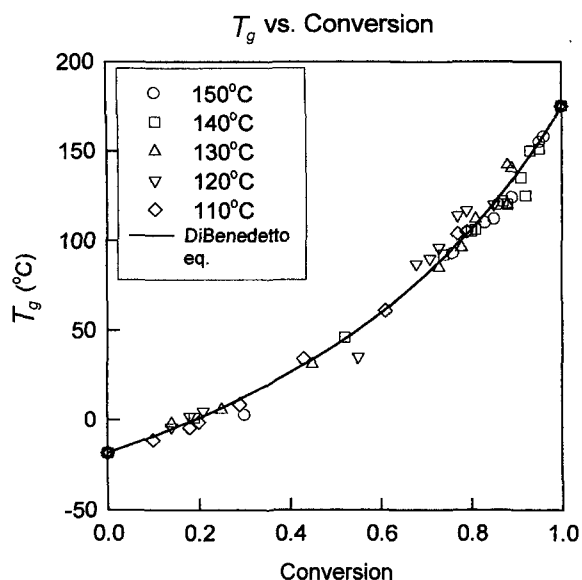
<sup>b</sup>TMAB, trimethylene glycol di-p-aminobenzoate.

The shift factor,  $A(T)$ , is defined as  $\ln$  time difference at constant  $T_g$ , subtracting eq. 4 from eq. 5,

$$A(T) = \ln t_r - \ln t = \left(\frac{-E_a}{R}\right) \left(\frac{1}{T_c} - \frac{1}{T_r}\right) \quad (6)$$

The shift factor at a reference temperature (i.e.  $T_r = 130^\circ\text{C}$ ) in Figure 6 was obtained and plotted against inverse of absolute temperature in Figure 8. The shift factor varies linearly with  $1/T$ . Using eq. 6, activation energy was determined from the slope of the figure. The activation energy was 12.5 kcal/mol in this epoxy/BPH system, and compared with other values obtained by the same method in Table II. The result shows that the activation energy of the catalytic system is smaller than that of amine or anhydride systems, meaning that the curing may proceed readily at the cure temperatures tested.

**Relationship between  $T_g$  vs Conversion.** For many thermosetting systems, there is a unique relationship between  $T_g$



**Figure 9.** Relationship between  $T_g$  and conversion for all isothermal cure temperatures.

and conversion independent of cure temperature.<sup>12</sup> The relationship can be described by the empirical DeBenedetto equation:<sup>19</sup>

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad (7)$$

where  $T_{g0}$  and  $T_{g\infty}$  are the glass transition temperatures of the unreacted and the fully cured material, respectively, and  $\lambda$  is a material constant. All the data for  $T_g$  were plotted vs conversion in Figure 9 with the best fitted line of the DiBenedetto equation. The material constant value ( $\lambda$ ) was 0.45. Note that the  $T_g$  vs conversion relationship in the figure is not influenced by the presence of the initiation reactions (i.e., epoxy/BPH and epoxy/hydroxyl group).

**Acknowledgement.** This paper is supported by a 2000

Research Fund from Kumoh National University of Technology.

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