

# Theoretical Prediction of Physical Properties of Network Glasses versus Extent of Cure

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**ABSTRACT:** A theoretical model was developed for describing the behavior of isothermal properties vs. the extent of cure for thermosetting glasses. The consideration follows the two-state Gibbs–DiMarzio (GD) theory of the glass transition. Network formation is considered on the basis of only interconnected trifunctional crosslinked sites using the Flory's mean-field theory of gelation. Theoretically, the proposed model predicts that the fraction of hole volume ( $v_0$ ) in the glassy state and the difference of expansion coefficient ( $\Delta\alpha$ ) between glass and liquid pass through a minimum with increasing extent of cure for thermosetting materials. These results suggest that the isothermal density and modulus will pass through a maximum with increasing extent of cure. Experimental data support the theoretical results. A discussion of the mechanism is included. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 69–75, 1997

## INTRODUCTION

The basic physical properties of high- $T_g$  thermosetting materials, such as the density, modulus, water absorption, and creep, change anomalously with increasing extent of cure (as measured by time of cure, conversion, crosslinking density, and glass transition temperature). Recent studies on the cure and properties of thermosetting resins show that the shear modulus<sup>1,2</sup> and the density at 25°C (Ref. 3) pass through a maximum with increasing chemical conversion and that the free-volume fraction at 25°C (Ref. 4) and the physical aging rate at isothermal temperatures below  $T_g$  (Ref. 5) pass through a minimum with increasing chemical conversion. The anomalies and the relationships between isothermal physical properties of amorphous thermosetting polymers and chemical conversion can be summarized in the form of a  $T_g$ –temperature–property ( $T_g$ TP) diagram.<sup>1</sup> The common reason for these phenomena in terms of the free-volume fraction is not at all obvious. In

principle, an increased extent of cure will result in an increase of the fraction of covalent bonds compared to van der Waals bonds. The free volume is therefore expected to decrease with increasing extent of cure. The above anomalies have been phenomenologically related to each other<sup>1–5</sup>; however, the mechanism in which the anomalies may occur is not fully understood.

In this work, a theoretical model was developed for describing the anomalous behavior of isothermal properties vs. extent of cure for thermosetting systems. The consideration follows the two-state Gibbs–DiMarzio (GD) theory of the glass transition.<sup>6</sup> Network formation is considered on the basis of only interconnected trifunctional crosslinked sites using the Flory's theory of gelation.<sup>7</sup> This combination takes into account the specific features of monomers and the architectures of the resulting polymers, thus permitting one to express molecular parameters and internal parameters as a function of measurable thermodynamic quantities. Theoretically, the proposed model predicts that the fraction of the hole volume  $v_0$  (which corresponds to the fraction of the free volume) and the difference of the expansion coefficient ( $\Delta\alpha$ )

between glass and liquid pass through a minimum with increasing extent of cure for thermosetting materials.

## THEORETICAL MODEL

The criterion of glass formation, according to Gibbs and DiMarzio,<sup>6</sup> is that the temperature-dependent configurational entropy ( $S_c$ ) cannot decrease below zero with the decrease of temperature. For an undercured thermosetting system, the entropy ( $S_c$ ) can be expressed in terms of

$$S_c = S_c^{(0)} + \Delta S_c^{(1)} \quad (1)$$

where  $S_c^{(0)}$  is the configurational entropy for an uncrosslinked system and  $\Delta S_c^{(1)}$  is the change in configurational entropy due to adding crosslinks.<sup>8</sup> For the configurational entropy,  $S_c^{(0)}$ , related to 1 mol rotatable groups (or units) in a linear polymer at the condition of  $T > T_2$ , it follows that<sup>6</sup>

$$\begin{aligned} \frac{S_c^{(0)}}{R} = & -\frac{v_0}{v_p} \ln S_0 + \frac{z-2}{2v_p} \ln \frac{v_0}{S_0} - \frac{\ln S_p}{xn_r} \\ & + \frac{1}{xn_r} \ln \{ [(z/2 - 1)xn_r + 1](z - 1) \} \\ & + \frac{xn_r - 3}{xn_r} \left[ \frac{f\Delta\varepsilon}{kT} - \ln(1 - f) \right] \quad (2) \end{aligned}$$

where  $k$  is the Boltzmann constant;  $R$ , the gas constant;  $T$ , the absolute temperature;  $n_r$ , the number of rotatable groups per monomer; and  $x$ , the degree of polymerization.  $v_0$  is defined as the fraction of hole volume in the GD theory.  $v_p$  is the fraction of polymer volume and  $v_p = 1 - v_0$ .  $S_0 = zv_0 / \{ [(z-2)xn_r + 2]v_p / xn_r + zv_0 \}$  and  $S_p = 1 - S_0$ . The physical meaning of the parameter  $z$  is defined as that  $z - 1$  is the number of possible orientations of a rotatable group around a covalent bond.  $\Delta\varepsilon$  is the "flex energy."  $f$  is the fraction of the "flexed bond" and is given by  $f = [(z-2)\exp(-\Delta\varepsilon/kT)] / [1 + (z-2)\exp(-\Delta\varepsilon/kT)]$ . The change in configurational entropy due to adding crosslinks,  $\Delta S_c^{(1)}$ , is of the form

$$\begin{aligned} \frac{\Delta S_c^{(1)}}{R} = & -\frac{3}{2} X_d + \frac{3}{4} X_d \ln f \\ & + \frac{3}{4} X_d \ln X_d + \text{const } X_d \quad (3) \end{aligned}$$

where  $X_d$  is the crosslinking density and is defined as number of moles of crosslinked chains per mole of rotatable groups.<sup>8,9</sup>

The change in heat capacity,  $\Delta C_p$ , due to the glass transition, can be immediately obtained from the above expressions:

$$\begin{aligned} \frac{\Delta C_p}{R} = & \frac{T}{R} \left( \frac{\partial S_c}{\partial T} \right)_p \\ = & T \Delta\alpha \left\{ -\frac{1}{v_p} \left[ S_p + \ln \left( \frac{S_p^{z/2}}{v_0^{z/2-1}} \right) \right] + \frac{1}{v_0} \right. \\ & \times \left[ \left( \frac{z-2}{z} \right) \left( \frac{v_p - S_p}{v_p} \right) + \frac{S_0}{xn_r} \right] \left. \right\} + \frac{xn_r - 3}{xn_r} \\ & \times \left( \frac{\Delta\varepsilon}{kT} \right)^2 f(1 - f) + \frac{3}{4} X_d \frac{\Delta\varepsilon}{kT} (1 - f) \quad (4) \end{aligned}$$

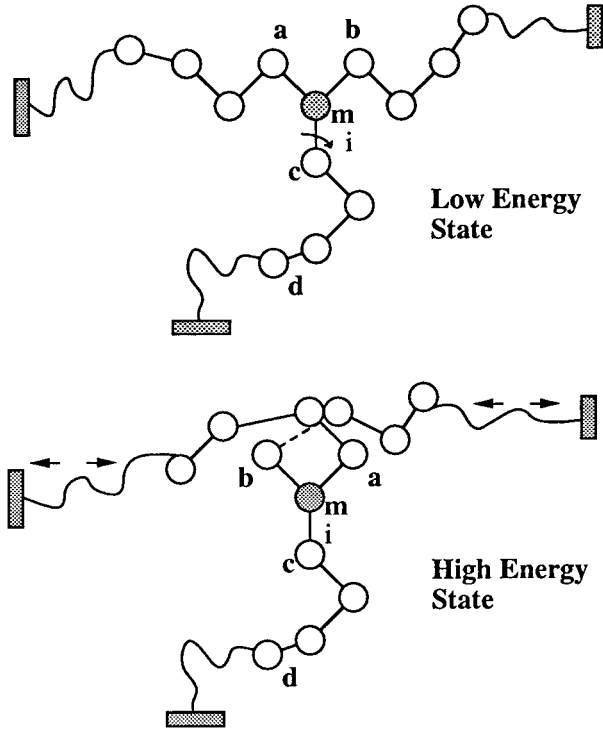
where  $T$  represents  $T_g$  and  $\Delta\alpha$  is the difference of expansion coefficient between glass and liquid and is given by<sup>6</sup>

$$\Delta\alpha = \frac{v_0 \ln(v_0^{z/2-1}/S_0^{z/2})/T}{zS_p/2 - 2S_0 \ln(v_0^{z/2-1}/S_0^{z/2}) - (z-2)v_p/2} \quad (5)$$

In addition, the internal parameter  $v_0$  (which represents the fraction of hole volume in the whole system) is related to the hole energy  $E_h/k$  by the equation<sup>6</sup>

$$\ln(v_0^{z/2-1}/S_0^{z/2}) - E_h S_p^2 / kT = 0 \quad (6)$$

In linear polymer chains, the number of rotatable groups  $n_r$  is usually considered to be constant. However, this consideration may not be true for a highly crosslinked system. First, a crosslinked site itself is difficult to rotate because rotation of a crosslinked site stretches two network chains, requires a number of interconnected rotatable groups to rotate simultaneously, and deforms the network (see Fig. 1). From the point of view of equilibrium thermodynamics, the flex energy ( $\Delta\varepsilon/kT$ ) for the rotation of a crosslinked site will be much larger than that of an ordinary group. Second, a crosslinked site may restrain the rotation of the groups that have been attached to the crosslinked site because of steric hindrance. This physical situation was first realized by Flory and



**Figure 1** Rotation of a crosslinked site around a bond  $i$  results in stretching two network chains and deforming the network.

Rehner<sup>9</sup> in their derivation of the structure entropy of network formation. Thus, the number of rotatable groups per monomer unit in the polymer chains, on average, must decrease with increasing crosslinking density ( $X_d$ ). For the present model,  $n_r$  is considered to vary proportionally to  $X_d$ ,

$$n_r = -\frac{m}{X_{d\infty}} X_d + n_r^{(L)} \quad (7)$$

where  $n_r^{(L)}$  is the number of rotatable groups per monomer unit in uncrosslinked polymer chains.  $X_{d\infty}$  is the crosslinking density for a fully cured system, and  $m$ , the number of the frozen groups per monomer unit due to the existence of crosslinked sites when the system is fully cured. The quantity  $m$ , in other words, is a measure of the chain stiffness introduced by crosslinks. It is noted that an alternative consideration is also possible that regards the average flex energy ( $\Delta\varepsilon/kT$ ) to increase with increasing  $X_d$  while  $n_r$  is kept constant. The result will be the same as that of using eq. (7).

The average degree of polymerization is defined as

$$x = \frac{\text{number of monomers } (Nm)}{Nm - (\text{number of total reactions} - N_{\text{intra.r}})} \quad (8)$$

where the parameter  $N_{\text{intra.r}}$  is the number of intramolecular reactions. This parameter can be calculated through computer simulations (e.g., based on a percolation model). If, however, intramolecular reactions are considered to become important only in the gel after gelation, mean-field theories can be applied. For example, since crosslinked sites arise from the intramolecular reactions, and one intramolecular reaction in a highly branched system is seen to introduce two trifunctional crosslinked sites,<sup>10</sup> therefore,  $N_{\text{intra.r}} = (X_d/2)xn_r$ . The crosslinking density  $X_d$  can be evaluated by using the method proposed by Scanlan<sup>11</sup> or that by the present author.<sup>10</sup> These methods, in general, require the knowledge of sol/gel fractions and chemical conversions in both sol and gel. To a good approximation, those quantities can be obtained from Flory's sol/gel fraction theory<sup>7</sup> or from its various new versions which have been developed by Miller and Macosko.<sup>12</sup> These theoretical derivations, based on mean-field statistical arguments, are not reproduced here. A detailed theoretical treatment on crosslinks and on intramolecular reactions has been published.<sup>10</sup>

In this research, network formation is modeled on the basis of only interconnected trifunctional crosslinked sites using Flory's mean-field theory.<sup>7</sup> The number of crosslinked sites in a thermosetting system during cure,  $X_d$ , is considered to be the number of crosslinked sites at 100% conversion in the gel fraction minus the number of crosslinked sites that do not form because of incomplete reactions in the gel.<sup>10</sup> For an  $A_a$ - $B_b$  thermosetting system at a stoichiometrical ratio,

$$X_d = \frac{3}{2} \left[ \frac{N_a(a-2) + N_b(b-2)}{xn_r} G - 2 \frac{aN_a G_a (1 - P_{Ag})}{xn_r} \right] \quad (9)$$

where  $N_a$  is the number of  $A_a$  monomer;  $N_b$ , the number of  $B_b$  monomer;  $P_{Ag}$ , the fractional conversion of the functional group A in the gel;  $G_a$ , the weight fraction of monomer  $A_a$  in the gel; and  $G$ , the total gel weight fraction in the system. In

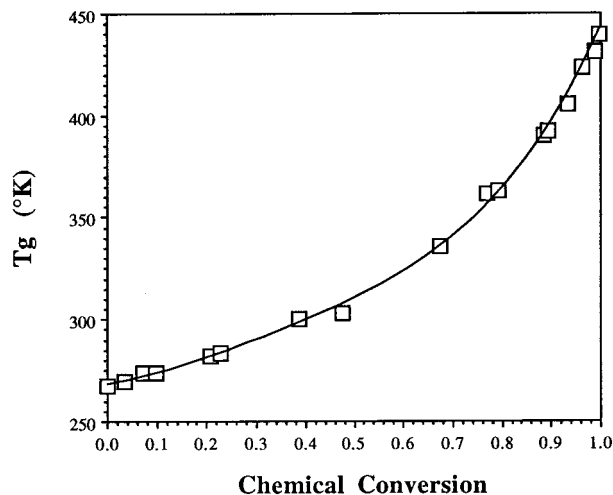
our computation, the values of  $P_{Ag}$ ,  $G_a$ , and  $G$  are evaluated from the sol/gel fraction theory.<sup>12</sup>

## EXPERIMENTAL

The purpose of this work was to investigate the effect of crosslinks in a polymeric system; therefore, a highly crosslinkable system is chosen, i.e., a liquid difunctional epoxy (diglycidyl ether of bisphenol A, DGEBA) with a tetrafunctional aromatic diamine (trimethylene glycol di-*p*-amino-benzoate, TMAB) at a stoichiometrical ratio. This system is a typical  $A_a-B_b$  thermosetting system.<sup>12</sup> Here,  $A$  represents the epoxide group in DGEBA,  $B$  represents the amine hydrogen in TMAB,  $a = 2$  is the functionality of DGEBA, and  $b = 4$  is the functionality of TMAB.

The thermoanalysis was performed on a TA instrument modulated DSC 2920 using a nitrogen-purged cell at a flow rate of 80 mL/min. Modulated DSC provides the unique ability to measure heat capacity continuously even during the exothermic curing process with high stability and reproducibility. The heat-capacity signal is calibrated using a sapphire at a 5°C/min, 40 s period, and a 0.5°C modulating amplitude. The same conditions are then applied for all sample experiments. Chemical conversion of the undercured sample is calculated from the residual heat that appears in the nonreversible heat flow vs. temperature. This determination of chemical conversion eliminates the effects which come from the change of heat capacity of the sample with increase of temperature. The values of  $T_g$  and  $\Delta C_p$  are obtained from the reversible heat flow curve alone.

Thermal expansion coefficients are determined below and above the  $T_g$  for fully cured samples using an automated dynamic mechanical analyzer (Rheometric RDA-2). Cast buttons with a diameter of  $\sim 6$  mm and thickness of  $\sim 11$  mm are used for this experiment. A specimen is made by gluing a button between a pair of parallel metal plates. The same epoxy resin is used as an adhesive for the sandwich specimen. The specimen is fully cured before testing. The instrument is set at an automatic adjustment mode with 0 g of tension and 0.5 g of sensitivity. In this mode, the instrument automatically adjusts the relative positions of the two plates to keep the specimen under 0 g tension. Temperature change is programmed to be a 3°C step change and 10 min soak time. Such a soak time is necessary for getting



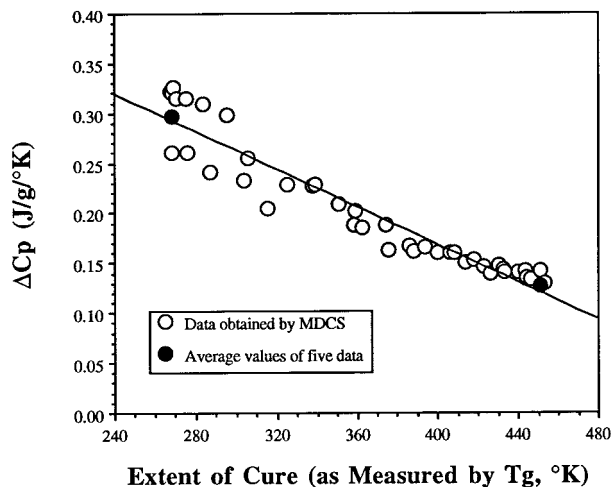
**Figure 2** Nonlinear relationship between  $T_g$  and chemical conversion for the DGEBA-TMAB system.  $T_g$  can be regarded as an index for measuring conversion.

thermal equilibrium. The change in positions of the parallel plates are recorded vs. temperature. The determination of the thermal expansion coefficient is made using the data during cooling. For fully cured DGEBA-TMAB, it is found that  $\Delta\alpha = (3.0 \pm 0.4) \times 10^{-4} \text{ K}^{-1}$  (based on three samples). This method, however, is not suitable for measuring an undercured specimen because of chemical reactions above  $T_g$ .

## RESULTS AND DISCUSSION

The glass transition temperature,  $T_g$ , is a good index for monitoring the chemical conversion for thermosetting systems. The fact that  $T_g$  increases nonlinearly with conversion in the crosslinking system makes it more sensitive for monitoring the extent of cure at higher extents of reaction than chemical conversion, as shown in Figure 2. This nonlinear relationship is expected from eq. (1): Crosslinking raises the glass transition temperature so effectively because it decreases the configurational entropy over what it would be in a linear polymerization. When  $T_g$  is used as an index for monitoring the extent of cure,  $\Delta C_p$  is found to be a linear function of  $T_g$ . As shown in Figure 3,  $\Delta C_p$  decreases with increasing chemical conversion.

In this work, the number of rotatable groups of a monomer unit in a polymer chain,  $n^{(L)}$ , is determined according to Havlicek's method,<sup>13</sup> i.e.,

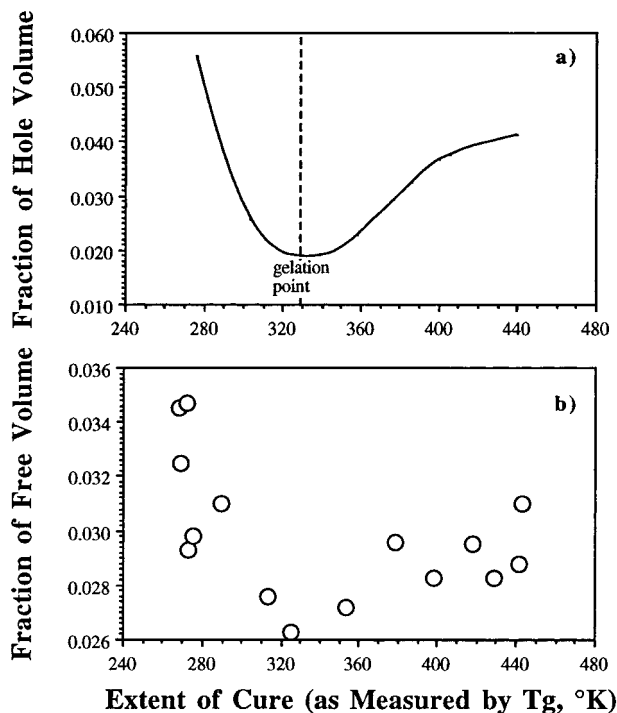


**Figure 3** Linear behavior of heat capacity ( $\Delta C_p$ ) of the DGEBA-TMAB system vs. extent of cure (as measured by  $T_g$ ).

$n_r^{(L)}$  is a group of bonds about which rotation is possible with the exclusion of bonds of end atoms and of rotationally symmetrical groups. In the determination of the coordination number,  $z$ , however, there is an ambiguity in the application of the GD theory for polymer chains that contain  $-\text{CH}_2-$ ,  $-\text{O}-$ , and  $-\text{C}_6\text{H}_4-$  links because these rotatable groups may have different flex states. In this regard, the molecular parameter,  $z$ , is considered to be a certain average property of the rotatable groups of polymer chains. Havlicek et al.<sup>13</sup> investigated a large number of polymers that includes poly(methyl methacrylate), poly(2-hydroxyethyl methacrylate), and polycarbonate of bisphenol A. What they found is that the coordination number  $z$  for these polymers<sup>13</sup> is nearly constant, in agreement with the value of 4. In the light of the result and of that these polymers are close relatives of the DGEBA-TMAB polymer, a value of  $z = 4$  is therefore used in our model computation. The molecular parameter,  $\Delta\varepsilon/k$ , is another average property of rotatable groups of polymer chains. Experimentally, it has been found<sup>4</sup> that for a partially cured DGEBA-TMAB glass of  $T_g = 300$  K the fraction of the free volume of the glass = 0.029. By use of the relationship of  $T_g$  vs. conversion, the relationship of  $\Delta C_p$  vs.  $T_g$ , and eqs. (4) and (8), we get  $\Delta\varepsilon/k = 614.3$  K. For the fully cured material, we have  $\Delta\alpha$ ,  $\Delta C_p$ ,  $T_g$ , and chemical conversion values that have been measured by means of the experiments described above. By using eqs. (4)–(9), we get  $m = 3.5$ . This value is reasonable in the light of stud-

ies of steric hindrance of a crosslinkage in the system.

For our model computation,  $T_g$ ,  $\Delta C_p$ , and the chemical conversion are used as input data; eqs. (4)–(9) are used for theoretical prediction. It is of interest to probe the relationship between the internal parameter ( $v_0$ ) and the extent of cure, which, in turn, indicates the mechanism of the anomalous behavior of the isothermal density or modulus vs. the extent of cure. Figure 4 shows that the fraction of the hole volume in the glass state passes through a minimum with increasing extent of cure, as calculated based on the present model. Experimental data of the free-volume fraction obtained by Venditti et al.<sup>4</sup> (as measured using positron annihilation spectroscopy) is also displayed. The agreement, although only qualitative, is satisfactory in view of the difficulties of the experiment and the simplicities of our model. It is also noteworthy that the fraction of the hole volume calculated and plotted in Figure 4(a) is the hole volume at  $T = T_g$ , whereas in Figure 4(b), the experimental data of the fraction of the free volume are measured at 25°C. The importance is



**Figure 4** (a) Fraction of hole volume  $v_0$  vs.  $T_g$  (obtained from model computation). (b) Fraction of free volume vs.  $T_g$  (obtained from Ref. 4). The gelation line marks the change from sol glass to sol/gel glass.

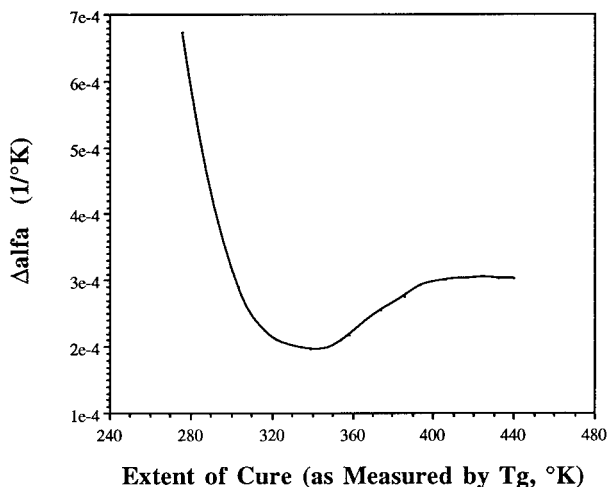
that the present model indicates the mechanism of the anomalous behavior of  $v_0$  vs.  $T_g$ .

According to the model, increasing the degree of polymerization of a system usually reduces the fraction of the hole volume because it reduces the number of free ends. However, adding crosslinks into the system may increase the fraction of the hole volume. The reason is that adding crosslinks will reduce the total configurational entropy [see eq. (1)] by reducing the conformation number of linear chains and by reducing the number of rotatable groups in the polymer chains. For the cases after the gelation point when  $xn_r$  is much larger than 1, eq. (4) can be simplified as

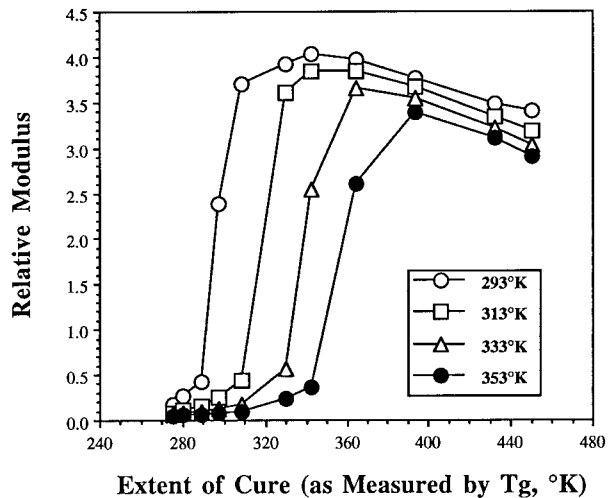
$$[\Delta C_p - \text{const } X_d] \propto -\ln v_0 \quad (\text{for } v_0 \ll 1) \quad (10)$$

where the quantity  $[\Delta C_p - \text{const } X_d]$  is always positive. Accordingly, increasing  $X_d$  will result in an increase of  $v_0$  because increasing  $X_d$  decreases the value of  $[\Delta C_p - \text{const } X_d]$ . Relation (10) illustrates the underlined reason that the fraction of the hole volume may increase with an increasing extent of cure for postgel glasses. In the light of the mechanism, the anomalous behavior of  $v_0$  vs.  $T_g$  may generally exist in highly crosslinked systems.

Figure 5 shows that the difference of the expansion coefficient ( $\Delta\alpha$ ) between glass and liquid, for the DGEBA-TMAB system, also passes through a minimum with increasing extent of cure, as obtained from the model computation. The results



**Figure 5** The difference of the expansion coefficient ( $\Delta\alpha$ ) between glass and liquid vs.  $T_g$  (obtained from model computation).



**Figure 6** Isothermal shear modulus vs.  $T_g$ . Experimental data were obtained by using torsional braid analysis.<sup>1</sup>

of Figures 4 and 5 suggest that the isothermal density of the system will pass through a maximum with increasing extent of cure. The data of Pang and Gillham<sup>3</sup> provides experimental support for this prediction.

Relationships of the isothermal modulus vs.  $v_0$  are much more complex than that of density vs.  $v_0$ . If intermolecular forces can be approximately described by the Mie potential function, one can show that<sup>14</sup>

$$B = \frac{C_1}{V^{p+1}} - \frac{C_2}{V^{q+1}} \quad (11)$$

where  $B$  is the bulk modulus;  $C_1$  and  $C_2$ , constants that depend only on temperature;  $p$  and  $q$ , constants in the Mie potential; and  $V$ , the specific volume. Since  $V$  varies linearly with  $v_0$ , and  $v_0$  change anomalously with extent of cure, the modulus is therefore expected to pass through a maximum with increasing extent of cure. The maximum in the isothermal modulus vs.  $T_g$ , however, will change with the change of temperature in view of the nonlinear relationship between modulus and  $V$  [e.g., eq. (11)]. Experimental data on isothermal shear modulus vs.  $T_g$  support these predictions (Fig. 6).

In summary, increasing the degree of polymerization of a system reduces the fraction of the hole volume. However, adding crosslinks into the system increases the fraction of the hole volume. The reason is that adding crosslinks will reduce the

total configurational entropy by reducing the conformation number of linear chains and by reducing the number of rotatable groups in polymer chains. The anomalies which have been found in the density, modulus, water adsorption, creep, etc., are considered to be related to this mechanism. The so-called anomalies are not anomalous since they generally exist in highly crosslinked glasses.

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