The glass transition temperatures of highly crosslinked networks: Cured epoxy resins

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The glass transition temperatures of a series of cured epoxy resins have been determined, using broad line proton n.m.r. and stress–strain measurements. The networks were prepared by curing bis-phenol-A epichlorohydrin epoxy resins, I, with the stoichiometric amount of diaminodiphenyl methane (DDM), II. The length of the network chains was varied by a factor of 17. The glass transition temperatures ranged from 367 to 410K and were found to be linearly related to the reciprocal of the number average molecular weight, $\bar{M}_n$, of the pre-polymer molecules. A theory is presented in which each component of the network has an associated thermodynamic transition in the pure state. Development of this theory predicts a limiting linear relationship between glass transition temperature and the reciprocal of the number average molecular weight of the network chains between the DDM crosslinks.

Keywords Glass transition; epoxy resins; highly crosslinked networks; nuclear magnetic resonance; stress–strain measurements

INTRODUCTION

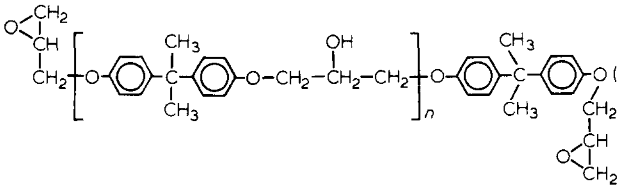
The behaviour of polymers in their glass transition regions is of central importance, because many of their properties change very rapidly with temperature through the glass to rubber transition. There have been several reviews of both the experimental features and the theories of the nature of this transition, to which reference may be made for the background relevant to this study[1–4]. This paper is concerned with the glass-transition behaviour of a series of cured epoxy resins; these resins may be regarded as highly crosslinked network polymers[5]. Despite the technological importance of thermosetting resins, especially the epoxies, the glass–rubber transition of highly crosslinked resins had been much less studied than has the corresponding transition in thermoplastics.

An important factor affecting the glass transition temperature, T_g, of cured resins is the so-called degree of crosslinking, which may be alternatively expressed as the number average molecular weight of the network chains, $\bar{M}_c$. Neilsen[6] has collated the results from a number of studies relating T_g to the degree of crosslinking, and, although there is not good agreement between these published results, he suggests that a rough estimate of $\bar{M}_c$ can be made by use of equation (1)

$$T_g - T_{g_0} = \frac{3.9 \times 10^4}{\bar{M}_c} \qquad (1)$$

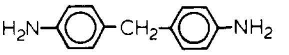
where T_{g_0} is the glass transition temperature of the uncrosslinked polymer. Neilsen points out that equation (1) accounts only for the effect of crosslink restriction on molecular motion, and does not account for the so called copolymer effect. However, it will be clear from the experimental results and the theoretical analysis presented in this paper that the form of equation (1) is inappropriate. More recently, Rietsch and co-workers[7,8] have determined the glass transition temperatures of crosslinked polystyrenes and proposed a theory to account for their results.

In the present work epoxy resin networks were prepared from blends of prepolymers, derived from the reaction of Bisphenol-A and epichlorohydrin, with the general structure, I.



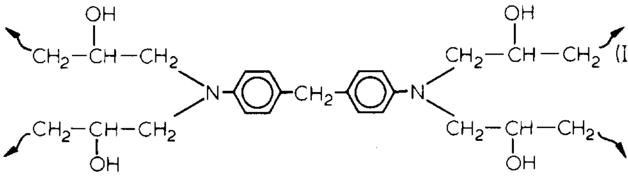
(I)

where *n* was varied between 0 and 16. The resins were cured with the stoichiometric amount of 4-4′ diaminodiphenylmethane, DDM, hardener, which has the structure II.



(II)

The resin prepolymer molecules, I, are difunctional and the hardener molecule, II, is effectively tetrafunctional, so that the structure of a fully reacted crosslink will be III:



(III)

A standard cure treatment was given, as specified in the experimental section.

For these resins the degree of molecular motion through the glass transition region was studied by measuring the proton n.m.r. linewidth, using a broadline n.m.r. spectrometer. On a similar set of resins the effect of temperature on the Young's modulus was determined

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from stress–strain measurements in tension. It was found that T_g determined from both types of measurements were in good agreement. The effect of network structure on the glass transition temperature was determined experimentally, and a theory is proposed which is in conformity with the experimental results.

EXPERIMENTAL

Specimen preparation

The formulation of the resins is given in *Table 1*; all resins, with the exception of No. 2, were used as supplied by the manufacturers (Ciba-Geigy Plastics and Additives Company). Cured resins were prepared by heating the pre-polymer in a glass beaker to 110°C, at which temperature the viscosity was low enough to allow the powdered DDM to be stirred in until it had all gone into solution. The resins were given the manufacturer's recommended cure of one hour at 110°C followed by a further hour at 140°C. Films cured in this manner showed little residual infra-red absorption at 918 and 862 cm^{-1}, the positions of the epoxy bands, but, more importantly, no change in the T_g of resin 1 was found after an additional cure of 18 hours at 160°C: it was concluded that the cure was essentially complete after the recommended thermal treatment. However, for the purpose of this paper, all that is necessary is that the extent of reaction is the same for all resins. Although there have been reports of inhomogeneities in cured epoxy resins it has been established from electron microscopy[9] that for DDM cured resins any inhomogeneity must be at a scale of at the most 50 Å, which is about the length of 3 network chains for resin 1.

Specimens for the measurement of Young's modulus were prepared by cutting strips, with a cross-section of 5 × 10 mm from cast sheets of the cured resin. Powdered samples for the determination of n.m.r. spectra were obtained by crushing the cured resins at liquid nitrogen temperature, the cooling being required to make the resins brittle. The samples were stored in a vacuum desiccator until required, it having been previously shown that small amounts of absorbed water can drastically reduce T_g[10].

Experimental procedure

The temperature dependence of the proton n.m.r. spectra of the cured resins 1 to 5 was investigated over the temperature interval 200 to 450 K, using a JOEL JNH 3H60 spectrometer operating at 60 MHz. Temperatures were controlled to within ± 1 K. Six spectra were obtained at each temperature, and averaged to give the results used in this work.

The Young's moduli of resins 6 to 9 were investigated as a function of temperature over the range 280 to 450 K, using a bench top Instron Universal testing machine (model 1026) equipped with a temperature controlled cabinet. Sample temperatures were measured to ± 0.5 K by a thermocouple placed adjacent to the test piece. An initial grip separation of 120 mm was used. During the test a cross-head speed of 0.5 mm min^{-1} was used, resulting in an initial strain rate of 6.94×10^{-5} s^{-1}. The elongational strains were limited to less than 3%, and the Young's modulus was calculated from the initial slope of the stress–strain curve.

RESULTS AND DISCUSSION

N.m.r. linewidth

Broadline n.m.r. spectra are recorded as the first derivative of the absorption, as shown in *Figure 1*. The linewidth, δH, is defined in *Figure 1*. The change in linewidth with temperature is given in *Figure 2*; for the

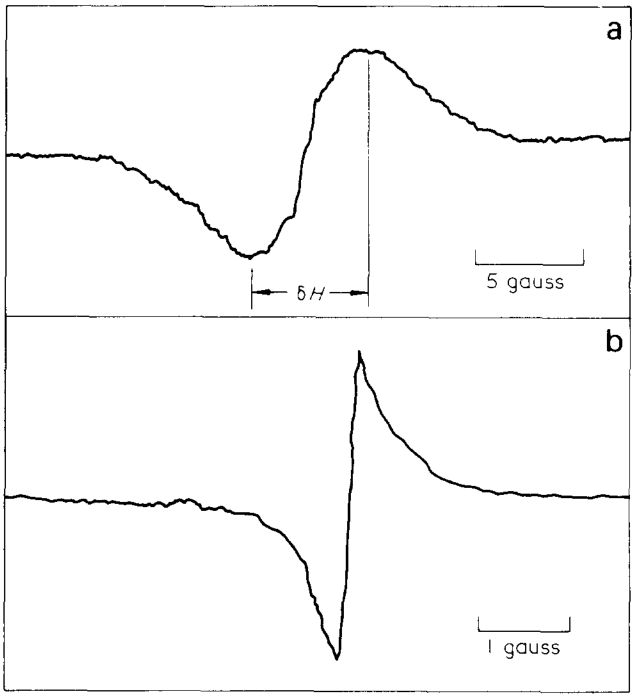

Figure 1 Broad line n.m.r. spectra of resin 1. (a) Broad line at 219 K; (b) motionally narrowed line at 449 K (T_g + 39 K)

Table 1 Formulations and glass transition temperatures of resins used

Serial No.	Resin	M_n before cure	Epoxy value+ before cure	$\bar{n}$	Weight of hardener per 100 parts resin	T_g (K)	
1	MY750	355	5.15	0.06	25.5	410	Determined from n.m.r. experiments
2	MY750/6100	555	3.39	0.76	16.8	393	
3	6100	945	2.04	2.14	10.1	385	
4	6200	1460	1.17	3.95	5.8	376	
5	6400	4955	0.31	16.26	1.53	367	
6	GY250	360	5.24	0.07	25.9	416	Determined from Young's modulus experiments
7	GY280	518	3.86	0.62	19.1	398	
8	6100	952	2.10	2.14	10.4	381	
9	6150	1360	1.47	3.59	7.3	369	

The analytical values in this table were supplied by Ciba-Geigy Plastics and Additives Company
+ Epoxy value is equivalent to the number of moles of epoxy groups per kg

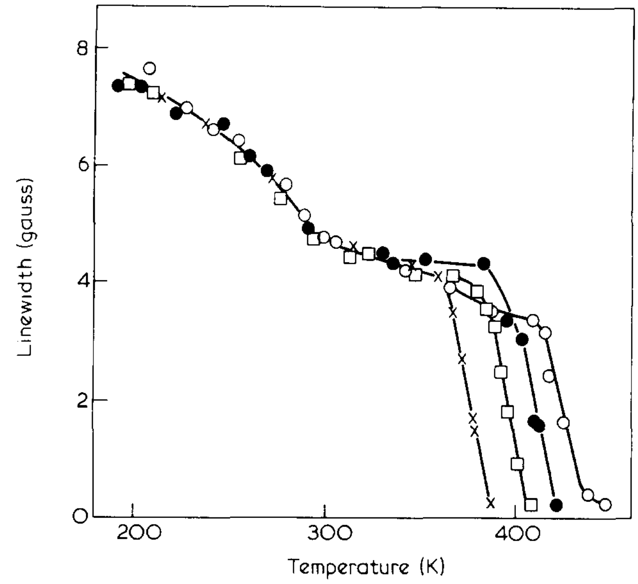

Figure 2 N.m.r. linewidth *versus* temperature: (○) Resin 1; (●) resin 2; (□) resin 3; (X) resin 5

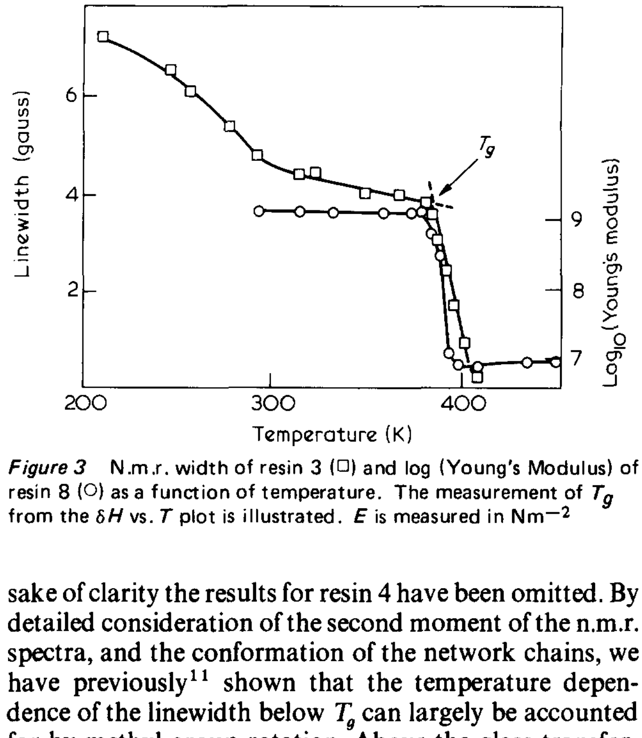

Figure 3 N.m.r. width of resin 3 (□) and log (Young's Modulus) of resin 8 (○) as a function of temperature. The measurement of T_g from the δH vs. T plot is illustrated. E is measured in Nm^{-2}

sake of clarity the results for resin 4 have been omitted. By detailed consideration of the second moment of the n.m.r. spectra, and the conformation of the network chains, we have previously[11] shown that the temperature dependence of the linewidth below T_g can largely be accounted for by methyl group rotation. Above the glass transformation range the linewidth is less than 0.2 gauss. As the temperature is reduced through the glass transformation range δH increases rapidly by about 4.5 gauss over a range of 30K.

The glass transition temperatures of resins 1 to 5 were determined from the δH vs. T plot by the method of linear extrapolation used previously[12], and illustrated in *Figure 3* for resin 3. This method of defining T_g means that the values obtained are a measure of the onset of the transformation range; alternative definitions of T_g applicable to broadline n.m.r. data have been discussed by Maklakov and Pimenov[13]. The present definition of T_g has the advantage that it is also readily adaptable to the measurement of T_g from the plots of log E vs. T, and that it is operationally well defined, offering an experimental procedure that can be applied consistently. The experimentally determined T_g's are given in *Table 1*.

Elastic properties

The temperature dependence of the Young's moduli, E, of resins 6 to 9 are shown in *Figure 4*. These results are in general agreement with those of Katz and Tobolsky[14], Misra *et al.*[15], and Bell[16], but differ in detail. The T_g of the resins were obtained from these plots by the same extrapolation method used for obtaining T_g from the δH vs. T plots, and are given in *Table 1*. The change in modulus from the glassy to the rubbery state can be represented by the ratio of the rubbery to the glassy modulus, Δ, that is $\Delta = E_r/E_g$. For the epoxy resin networks this ratio is a function of the network structure. Values of Δ obtained from the present work are given in *Table 2* together with values calculated from results given for epoxy resins by previous workers: also included in *Table 2* is the corresponding ratio for a highly crosslinked polyester[17]. It can be seen that the change in elastic modulus of the epoxy networks is much greater than that for the polyester, that is, Δ is numerically smaller for the epoxy resins.

The conclusion to be drawn from the effect of crosslink density on Δ is that in the epoxy resins the junction points are much more mobile than in the polyester. The present n.m.r. results confirm the mobility of the crosslinks in these epoxy resins. Thus the behaviour of highly crosslinked networks depends not only on the crosslink density but also on their detailed chemical structure.

The glass transition of highly crosslinked epoxy networks

The relationship between network chain motion and the glass transition. It has been found that the T_g and the glass

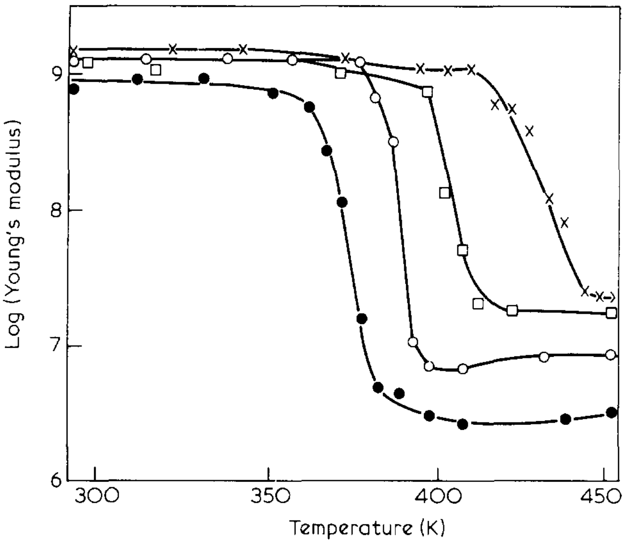

Figure 4 Log_{10} Young's modulus *versus* temperature: (X) resin 6; (□) resin 7; (○) resin 8; (●) resin 9. E is measured in Nm^{-2}

Table 2 Ratio of rubbery to glassy Young's modulus

Resin/Hardener	Δ
GY250/DDM	1.62×10^{-2}
GY280/DDM	1.35×10^{-2}
6100/DDM	7.4×10^{-3}
6150/DDM	3.5×10^{-3}
EPON 826/DETA[14]	2×10^{-2}
EPON 826/EDA[14]	2.6×10^{-2}
EPON 825/DDM[15]	2.04×10^{-2}
EPON 828/DDM[16]	3.8×10^{-2}
Ethyl acrylate/TEGDM[17]	1.45×10^{-1}

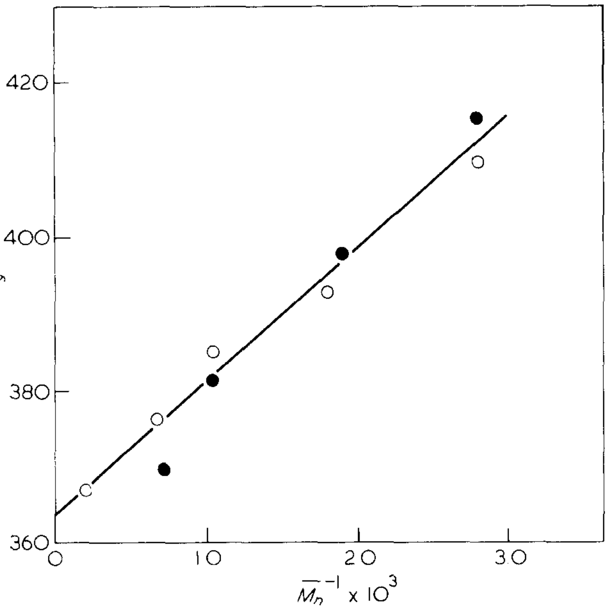

Figure 5 T_g as a function of the reciprocal of the pre-polymer number average molecular weight. (○) T_g determined from δH vs. T plots; (●) T_g determined from log (E) vs. T plots

transformation range of the cured 6100 resin determined from the δH vs. T plot agrees well with that determined by the precipitous decrease in Young's modulus as the temperature is raised; this is graphically illustrated in *Figure 3*. *Figure 5* shows a plot of the T_g of the cured resins determined either from n.m.r. or elastic measurements as a function of the reciprocal of the number average molecular weight, $\bar{M}_n$, of the original epoxy prepolymer. From this plot it can be seen that the determination of T_g from n.m.r. linewidth and Young's modulus *versus* temperature plots are mutually consistent. Also it can be seen that T_g is a linear function of $\bar{M}_n^{-1}$ and fits the empirical equation,

$$T_g = 365 + 17300\,\bar{M}_n^{-1} \qquad (2)$$

The coincidence of the T_g determined by these two methods is of some considerable interest.

The types of experiment which may be used for the determination of T_g can be divided into two classes: those that involve the measurement of the change in a bulk property with temperature, and those that are concerned with measuring the rate and nature of molecular motions. The Young's modulus experiments described above fall into the first class of experiment, along with the measurement of the coefficient of thermal expansion, refractive index, and hardness. The observed transition in the modulus occurs in the temperature range where the bulk relaxation of the test specimen occurs at a rate of the same order as the rate of strain (for the present measurements 6.94×10^{-5} s^{-1}). At temperatures above the transformation range the specimen relaxes at a rate much greater than the strain rate and so appears rubbery: below the transformation range the rate of relaxation is much less than the strain rate and the material is glassy. Thus the change in Young's modulus through the transition region may be explained in purely kinetic terms.

The n.m.r. experiment provides information on the extent and nature of the molecular motions that are occurring within the specimen at a particular temperature. The n.m.r. line narrowing occurs when the rate of motion becomes of the same order as the n.m.r. linewidth expressed in Hz (1G ≡ 4.25 kHz). The limiting value of the linewidth above the transition is governed by the fraction of protons in motion and the rate and nature of their motion. In the present case the linewidth of all the cured resins above their T_g is less than 0.2 gauss, which is as narrow as that of the uncured resins[12]. To obtain the time averaging of the local proton magnetic fields required to give such a narrow line there must be rapid reorientation of the network chains at a frequency of about 10^5 Hz. For this motion to occur the crosslinks must have considerable mobility about their mean positions; this is an essential feature of the theory of rubber like elasticity as presented by James and Guth[18,19,20] many years ago.

The glass transition temperature as determined by a particular experimental probe on a specific sample of material is a function of two types of rate effect. Often these two types of effects are confounded, but the one associated with the thermal history of the sample is not active in these experiments since the sample was allowed to reach thermal equilibrium before the n.m.r. spectrum or the stress–strain curve were measured. The time required to achieve thermal equilibrium is sufficient for an annealing to occur in which any thermal memory is lost. To obtain coincidence of the glass transition temperature obtained from the n.m.r. and the stress–strain measurements the rate of straining must be approximately equal to the photon spin–spin relaxation time at T_g, we have achieved this condition.

The effect of network structure on the glass transition temperature. The glass transition temperature may be a function of several variables; Gee[21] has shown that single parameter descriptions are not in general satisfactory and Roe[22] has used a multiple order parameter description to describe the glassy state. A fully general solution to the problem of finding functional relationships between T_g and variables such as composition has proved a continuing problem in polymer science but for the present set of resins which differ only in the average length of the network chains between DDM units it is possible to develop a theory based on the effect of this one variable on T_g; but as will be seen the functional relationship derived will be multiparametric.

The present treatment of the effect of the network structure on the glass transition temperature is based on three basic postulates, which will be stated didactically, their validity will be discussed later. These postulates are:

(i) The definition of a glass transition temperature T_g identifies a temperature at which a specific material parameter, X, has a critical value, X_g*.

(ii) For a component i of a glass forming system the temperature dependence of X is given by

$$X_i = X_{g,i} + F(T - T_{g,i}) \qquad (3)$$

where $X_{g,i}$ is the critical value of X at the glass transition temperature, $T_{g,i}$ of pure component i, and $F(T - T_{g,i})$ is a function of these temperatures. That is, the glass transition temperature occurs at an iso-X state, as initially suggested by Flory[23] with the property X being free

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* Strictly the glass transition range should be specified but with an operationally well defined T_g this is unnecessary for the present purposes as will be seen.

volume. It is usually satisfactory to use a linear function for the temperature dependence of X_i above $T_{g,i}$ so that equation (3) can be replaced by

$$X_i = X_{g,i} + \gamma_i(T - T_{g,i}) \tag{4}$$

where γ_i is defined as $\frac{dX_i}{dT}$. If X is regarded as free volume then free volume increases linearly above T_g, which is regarded as experimentally established despite various definitions of free volume.

(iii) That the property X is both additive and freely redistributive amongst the components in the glass forming system, so that in an n component system

$$X_n = \sum_1^n \phi_i X_{g,i} + \sum_1^n \phi_i \gamma_i (T - T_{g,i}) \tag{5}$$

where ϕ_i is the fractional amount of component i in the system. Because X is redistributive

$$\sum_1^n \phi_i X_{g,i} = X_{g,n} \tag{6}$$

This is equivalent to assuming that the glass transition will occur when sufficient 'X' has been contributed by the components in that system so that 'rapid' chain segment motion can occur, i.e. in the proton n.m.r. experiment they will have a correlation frequency greater than 10^5 Hz. At the glass transition temperature for n-component system

$$X_n = X_{g,n} \text{ with } (T = T_{g,n})$$

so on substitution of equations (5) into (6) and setting $T = T_{g,n}$

$$\sum_1^n \phi_i \gamma_i (T_{g,n} - T_{g,i}) = 0 \tag{7}$$

which can be recast as

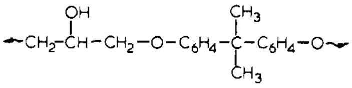
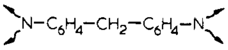
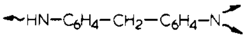
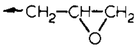
$$T_{g,n} = \frac{\sum_1^n \phi_i \gamma_i T_{g,i}}{\sum_1^n \phi_i \gamma_i} \tag{8}$$

This equation was derived by a less direct route by Chompff[24] (his equation 34) but with the critical property being stated specifically as free volume which is regarded as additive. Rietsch *et al.*[7] have shown Chompff's theory applies to the dependence of T_g of polystyrene networks on the molecular weight between crosslinks.

The results to be presented in this paper together with those of Rietsch show that provided the experimental variables can be kept to a minimum, in this case, is equivalent to $\bar{M}_n$, theories based on the additivity and redistributivity of free volume can describe the variation of T_g with molecular structure.

The difficulty in applying an expression of the form of equation (8) is that it contains too many unknowns to be used directly. However, it is possible with suitable simplification to re-arrange equation (8) into a simple form which relates T_g to $\bar{M}_n$ for crosslinked resins as will now be shown.

Table 3 Components of cured resins

No.	Component	Structure
1	Prepolymer repeat unit	 $\leftarrow CH_2-CH(OH)-CH_2-O-C_6H_4-C(CH_3)_2-C_6H_4-O\rightarrow$
2	Fully reacted DDM unit	
3	Partly reacted DDM unit	
4	Partly reacted DDM unit	$\leftarrow HN-C_6H_4-CH_2-C_6H_4-NH\rightarrow$
5	Unreacted epoxy ends	

The property, X, that is chosen to be critical at $T = T_g$ depends on the view taken of the relaxation processes that are occurring in the glass transition region. For polymeric materials the specific models that have been proposed for the glass transition have been reviewed by McCall[25]. More recently Holzmüller[26] has reviewed his particular model for segmented motion of polymer molecules and the 'algebraic manipulation' of the various definitions of free volume have been summarized by Lipatov[27]. Here X is an unspecified property and our argument is general; therefore it is only necessary to accept that relaxation processes are occurring and that each of these model theories consider one of the aspects of the same process.

Any cured resin formed by the reaction of a prepolymer with a hardener can be thought of as a copolymer of the following components: (1) prepolymer repeat units, (2) fully reacted hardener units, (3) partly reacted hardener units, with one or more unreacted functionality, and (4) unreacted prepolymer ends. The major components in the cured resins investigated here are given in *Table 3*. From the work of Bell[28,29] the curing of an epoxy resin with DDM can be regarded as the reaction of primary and secondary amine hydrogens with the epoxy groups. Very few of the primary amine groups will remain in the cured resin as they have a faster rate of reaction (~ × 6) than the secondary amines, and cure is essentially complete.

When the extent of reaction is the same in all the cured resins, components 2 to 5 in *Table 3* can be treated as equivalent to a single component with average properties determined by the degree of reaction, and equation (8) can then be simplified to

$$T_{g,n} = \frac{\phi_1 \gamma_1 T_{g,1} + \phi_2 \gamma_2 T_{g,2}}{\phi_1 \gamma_1 + \phi_2 \gamma_2} \tag{9}$$

without any approximation, the subscripts 1 and 2 refer to the prepolymer repeat units and the hardener units. Initially we will regard ϕ_1 and ϕ_2 as number fractions but as will be seen later they could equally well be taken as weight, or volume fractions without altering the form of the final result. The number of repeat units per prepolymer chain is equal to $\bar{M}_n/M_R$ where M_R is the molecular weight of the repeat unit. There are 0.5 hardener units per prepolymer chain so the number fraction of hardener units, N_H, is given by

$$N_H = 0.5(\bar{M}_n/M_R + 0.5)^{-1}$$

$$= (1 + 2\bar{M}_n/M_R)^{-1} \qquad (10a)$$

Then the number fraction of repeat units, N_R, is

$$N_R = 1 - (1 + 2\bar{M}_n/M_R)^{-1} \qquad (10b)$$

Equation (9) can now be rewritten as

$$T_{g,n} = \frac{\gamma_1[1-(1+\kappa\bar{M}_n)^{-1}].T_{g,1} + \gamma_2(1+\kappa\bar{M}_n)^{-1}.T_{g,2}}{\gamma_1[1-(1+\kappa\bar{M}_n)^{-1}] + \gamma_2(1+\kappa\bar{M}_n)^{-1}}$$

$$T_{g,n} = \frac{T_{g,1} + f.T_{g,2}}{1+f} \qquad (11)$$

where

$$\kappa = 2/M_R$$

and

$$f = \frac{\gamma_2(1+\bar{M}_n)^{-1}}{\gamma_1[1-(1+\bar{M}_n)^{-1}]} = \frac{\gamma_2}{\gamma_1}.\frac{1}{\kappa\bar{M}_n}$$

It should be noted here that if a different definition of ϕ_1 and ϕ_2 was used, equations (10) and (11) would have the same form but the constant κ would have a different value: for example, if volume fractions had been used κ would equal $2V_R/(M_R.V_H)$ where V_R is the volume of a repeat unit and V_H the volume associated with the hardener units. A direct test of equations (11) is not possible as they contain too many variables, but as f gets smaller with increasing pre-polymer molecular weight, $\bar{M}_n$, equation (11) can be approximated by

$$T_{g,n} = T_{g,1} + fT_{g,2}$$

when f is small compared with 1, substituting for f yields

$$T_{g,n} = T_{g,1} + \varepsilon.\bar{M}_n^{-1} \qquad (12)$$

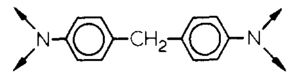
where

$$\varepsilon = \frac{\gamma_2}{\gamma_1}.\frac{M_R}{2}.T_{g,2}$$

Thus, if equation (12) is correct the variation of the glass transition with $\bar{M}_n^{-1}$ should approximate to a linear function as $\bar{M}_n$ gets large. *Figure 5* shows a plot of T_g vs. M_n^{-1} for the resins investigated here; a straight line has been fitted to the experimental results and equation (12) appears sufficient to describe all our results, including resins 1 and 6 in which $\bar{M}_n$ is lowest and f is largest. But this does not prove the correctness of the model presented above; in the following paragraphs we will try to indicate a physical interpretation of the parameters in equation (12).

When $\bar{M}_n$ is equal to infinity ϕ_2 is zero and $T_{g,n}$ will equal $T_{g,1}$. $T_{g,1}$ is the glass transition temperature of an infinite molecular weight linear polymer with the same repeat unit as our epoxies. From *Figure 5* the experimental value of $T_{g,1}$ is 365K, which is near to the glass transition temperature of phenoxy resins (373K)[30].

Although $T_{g,2}$ is not accessible to direct measurement, it is analogous to $T_{g,1}$ and can be thought of as the glass transition temperature of a highly crosslinked three-dimensional network composed of the following units:



A resin of this type would be a thermoset with such a high T_g that degradation may take place at a temperature below its T_g so that it would not be possible to determine T_g directly. The more rigid the crosslink unit the higher will be $T_{g,2}$ and the steeper the slope of plots such as that given in *Figure 5*.

The term κ has been discussed already, its value depends on the weighting that is used in determining ϕ_1 and ϕ_2. The correct weighting to use depends on the mechanism that leads to the relaxation occurring in the transition region, for example, for the free volume theories volume fraction is the obvious choice but if the heat content or the degrees of freedom in the network are being considered a number fraction would seem more appropriate. If number fractions are used $\kappa = 2/M_R = 7.1 \times 10^{-3}$.

The remaining term in equation (12), $\frac{\gamma_2}{\gamma_1}$, is also a term that is dependent on the mechanism of the glass transition. Thus, the ratio of γ_2/γ_1 represents the relative rates of increase of X_2 and X_1 with temperature. If a large amount of thermal energy is required to change X_i by a small amount then γ_1 will be low. For the present system with rigid crosslinking units $\gamma_1 > \gamma_2$. It is possible to estimate $\frac{\gamma_2}{\gamma_1}$ from the slope of the graph if we make an estimate of $T_{g,2}$, say at about 600K, then

$$\frac{\gamma_2}{\gamma_1} = \frac{\text{gradient} \times \kappa}{600} = \frac{17300 \times 7.1 \times 10^{-3}}{600} = 0.2$$

and would not be very different if $T_{g,2}$ were somewhat lower (0.23) if $T_{g,2} = 500$).

With use of the present definition of T_g the glass transition occurs when molecular motion reaches a critical frequency of 10^5 Hz. Thus the property X which is critical at T_g must be closely related to this average correlation frequency. For instance with a given set of degrees of freedom, X could be the heat content. This is the basis of the approach used by Wunderlich[31]. The linearities of the free volume temperature relationship have been well established by the work of Kovacs[32,33], and is obviously sufficient for the behaviour of the present system.

Previously it has been usual to consider free volume as additive but this alone is not sufficient; it is essential for the present treatment that the property X is redistributive. It is possible that this condition does not hold for all systems, in which case it might be possible to detect two or more transition temperatures. However, it is more likely that the transition will become more diffuse as is the case with cured unsaturated polyester resins[34].

The treatment of the glass transition presented here is very general and might be expected to predict the variation of T_g with structural variations other than crosslink density. Rietsch[7,8] and coworkers have followed a similar procedure to Chompff[24] to predict the effect of molecular weight on the glass transition temperatures of linear and crosslinked polystyrene. In each case they have found experimentally that the T_g of the polymer is given by

$$T_g = A + B\bar{M}_n^{-1} \qquad (13)$$

where A and B are constants. The physical interpretation that Rietsch places on the constant B is different from that which we have proposed. However, the present derivation of the relationship between $\bar{M}_n$ and T_g is both physically more meaningful and more direct.

The postulates used for the derivation of equation (8) require that the glass transition be regarded as an iso-X state. Haward[35] has pointed out that the concept of the glass transition as an iso-free-volume state cannot be correct in its most elementary form. However, Cohen and Grest[36] have developed a sophisticated free volume theory of the glass transition, in which they deal specifically with the additivity and redistributivity of free volume which is a particular case of our postulate (iii) that leads to equation (5). However, even if the postulates used for the derivation of equation (8) are not accepted it is clear that the equation does have value in describing the variation of T_g with polymer structure. Thus, equation (8) may be regarded as a useful empirical equation from which it is possible to obtain a relationship between T_g and the average molecular weight of network chains in some highly crosslinked epoxy resins.

Finally, it is of interest to note that the parameters in equation (12) can be considered as falling into three classes:

(a) properties of the components ($T_{g,1}$, $T_{g,2}$)

(b) compositional variable ($\bar{M}_n$)

(c) parameters affected by the processes which control the relaxation occurring at T_g (κ, γ_1, γ_2)

Thus, although the present treatment starts formally with a definition of the glass transition as an iso X state the final result shows that the glass transition demands a multi-parametric description.

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