Cooperative Relaxation Processes in Polymers

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ABSTRACT: The basic mode of relaxation in polymer molecules involves the rotation of a conformer, with a time scale of the order of picoseconds. This fast relaxation process, however, cannot take place easily in the condensed state crowded by densely packed conformers, necessitating the intermolecular cooperativity among them. The domain of cooperativity grows at lower temperatures, towards the infinite size at the Kauzman zero entropy temperature, though the system deviates from the equilibrium as the glass transition intervenes at about 50°C above that temperature. From the temperature dependence of the domain size, the well-known Vogel equation is derived, which we consider is the basic origin of the empirical WLF and free volume equations. The molar volume is a crucial factor in determining molar free volume. The molecular weight of a conformer with a density correction, therefore, can be used as a parameter in determining the T_g of liquids and amorphous polymers. A larger size conformer means a higher glass transition temperature. A conformer at the chain end, on the other hand, has a higher enthalpy, i.e., a smaller effective size for that conformer. If a conformer is reacted trifunctionally, the resulting conformer is a combination of the two conformers and T_g increases, but a further addition of another conformer to that branch point reduces the average size of the conformers, so T_g decreases. The model for cooperative relaxation can be directly applied to predicting T_gs from the chemical structure of polymers, the kinetics and T_gs of thermosets during the crosslinking reaction, the distribution of relaxation times from the domain size distribution at a given temperature, the dynamics of the physical aging process, and other complex behaviors of polymers and liquids near the glass transition temperature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 77–93, 1997

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INTRODUCTION

The term "relaxation" may mean different things to different people, because many types of relaxation processes are observed by many different techniques. In the phenomenological viscoelasticity the term "relaxation" is defined in a very specific way. A stress relaxation experiment is conducted under a constant strain, and the relaxation modulus is defined as the time-decaying stress divided by the constant strain. However, the macroscopic "constant strain" should not be interpreted to mean that all molecules are immobile; they certainly are undergoing many modes of small but irreversible deformations, while the macroscopic strain is held constant. The relaxing stress being measured in this case is actually the energy decay while the macroscopic boundary is fixed. On the molecular scale, the energy level is raised initially when polymer molecules are instantaneously deformed, but that energy is dissipated with time as the stressed molecules change their shapes from

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their strained conformations. The dielectric relaxation is observed when the electrical energy is lost while the sample is subjected to the alternating electrical field. The dielectric loss factor is easily identified with molecular relaxation processes, as the measured loss arises from the motion of dipoles lagging the electric field. All experimentally observed relaxation processes originate in some form of molecular motions. Identifying the modes of relaxation with specific molecular motions will enhance our understanding of the structure-property relationships for polymers.

Because polymer molecules are capable of many modes of molecular motions, a spectrum of relaxation times extend to enormous ranges covering 10 to 15 decades. A relaxation process involves some form of energy loss under the imposed force field. For a polymer molecule, the dissipation of the raised energy is achieved through a change of its shape, i.e., the molecular conformation. The smallest unit for the conformational change is accomplished through a change of a bond angle along the main molecular chain. We call the smallest unit of conformational change the conformer. For example, a repeat unit in a vinyl polymer consists of two conformers along the main chain. If its substituent group is a long enough flexible branch, then the number of conformers per repeat unit will be more than two. When the force field is imposed on the chain, a conformer can respond by a change of the bond angle from one equilibrium angle to another in the direction toward lowering the raised energy. Such an irreversible change may be visualized as the bond angle shifting from a gauche to *trans* (or another gauche) conformation under the stress. During this process the energy is raised initially then irreversibly dissipated. Dielectric relaxation can also involve a conformational change, but if the dipoles are configured in the more perpendicular than parallel direction to the chain, the relaxation may occur from the *trans* to gauche conformation.[1]

To change a bond angle involves going through an energy barrier. The Gibbs free energy is higher at an intermediate temporary state between the gauche and the *trans* conformations. The height of the energy barrier for the bond angle rotation in the paraffin conformer is 3.3 Kcal per mol of conformers.[2] As each bond MUST go through this angle in order to change a conformation irreversibly, the relative population of this least favorable, highest energy state plays the decisive role in determining the rate of the conformer relaxation. The ratio of the relative probability of any

two thermodynamic states, p, is calculated from the energy difference $\Delta\mu$ between the two states, according to the equipartition principle of Maxwell−Boltzmann, i.e.,

$$p = \exp\left(-\frac{\Delta\mu}{kT}\right) \qquad (1)$$

As is well known, this is the origin of the theory of rate processes,[3] where the high energy state is termed the activated state, and the energy $\Delta\mu$ is termed the activation energy.

The shortest relaxation time, or the time constant for the conformational change involving one bond angle, is in the order of 10^{-10} s at room temperature and 10^{-12} s at 500°C. This is possibly the highest frequency end of the vast spectrum of many modes of relaxation a polymer molecule is capable of undergoing. The conformational change of a whole molecule apparently involves changes of only a few simultaneous rotations at a time; otherwise, the apparent activation energy would be in the millions of calories. These simultaneous rotations are necessitated not because of the nature of a polymer molecule but because of the interference from the conformers of the neighboring chains, necessitating the intermolecular cooperative relaxation. Though such cooperativity increases both the activation energy and the magnitude of the time constant, the long relaxation time exhibited by a whole polymer molecule arises from something else. For the whole molecule to undergo a "successful," i.e., irreversible, change, the conformational changes of smaller parts of a whole chain, the strands, must be coordinated. If many such strands are involved in the shape change of a length of a polymer chain, the probability for that process is small, and the relaxation time is long, in proportion to the length of the polymer molecule. For this type of molecular relaxation, the energy-restoring or elastic tendency arises from the tendency for the molecules to assume random conformations. The Gibbs free energy increases with deformation, which tends to orient the molecule and decrease the degree of randomness, with the logarithm of such a conformational probability being the entropy. It is interesting to note that the temperature dependence for this regime of the relaxation spectrum reflects the rotational energy barrier for simultaneous rotation of only several bonds, and the entire spectrum shifts with the same time−temperature shift factor indicating that the bond angle rotation

is the basic mode of all conformational relaxation processes.

As is well known, the viscoelastic relaxation spectrum of amorphous polymers go beyond the process that involves the entire molecule. Above a certain value of molecular weight, the relaxation time is no longer proportional to the molecular weight, but instead begins to depend on the 3.4th power, clearly indicating that some intermolecular coordination is being required for this regime of relaxation process. This relaxation process is variously known as the disentanglement or the reptation process. One might point out that, even in this case where the typical relaxation time may be minutes and hours as compared to 10^{-10} second, this portion of the spectrum shifts with the same time–temperature shift factor as that for the rest of the spectrum. Its temperature dependence still reflects the same energy barrier for the cooperative bond angle rotation involving a few conformers at a time, and this is one of the main subjects of discussion here.

Intermolecular Cooperativity

We restrict the term "cooperative" relaxation to the processes in which a number of conformers relax simultaneously. In the condensed liquid state, the rotation of a conformer can be interfered and frustrated by the presence of a neighbor. Two conformers, each with high enough rotational momentum to overcome the rotational energy barrier, can fail when they are close by and hit each other. The energy is not lost, as both molecules will return to the original conformations. Only if they cooperate with each other by making room dynamically can they both successfully assume new conformations, i.e., relax under the imposed force field. The probability for the cooperative relaxation by two conformers is the square of the probability for one, and the cooperative relaxation time is also the square of the relaxation time for one single conformer. In amorphous polymers, the crowded condition created by the neighbor conformers persists until a very high temperature is reached. In fact, the temperature at which the molecules can relax in the pico second range is where the vibration is in the low infrared range, and the bonds begin to disintegrate chemically even in the absence of oxygen. This temperature is about 500°C or 800 K. At this temperature the frequency and the magnitude of oscillations are such that a change to a new bond angle can be reversed in no time, and the theoretical meaning

of the relaxation process, as we understand it, is lost. We arrived at the value of 500°C for this temperature after analyzing data for a hundred polymers.[9]

As the temperature is decreased from this 500°C, the liquidus state densifies, shortening the average intermolecular distance. It soon becomes necessary, in order for a conformer to successfully rotate from one position to another, to wait for a neighbor to go through a rotation in unison to accommodate for simultaneous relaxation. The intermolecular cooperative relaxation time is, as in the example above, the square of the rotational relaxation of one uncrowded bond, i.e. 10^{-6} s instead of 10^{-11} s. The activation energy is twice as high, i.e., 6.6 Kcal instead of 3.3 Kcal per mol of conformer. The densification continues as the temperature is further decreased. The domain of cooperativity, defined by the number of cooperative conformers z, grows in size. The apparent activation energy is now $\Delta\mu z$. The number of the domains, N_z, is Avogadro's number divided by z. N_z decreases in proportion to the Doolittle free volume that vanishes at the zero entropy temperature, rather than the physically meaningful free volume that vanishes at 0 K; the relationship between the entropy and free volume will be discussed in more detail later. It will also be shown that the excess entropy, when the cooperativity concept is incorporated, is proportional to the number of domains, N_z, and the domain size z is inversely proportional to this entropy. This relationship will be used to obtain the temperature dependence of the cooperative relaxation time. This formalism follows exactly the theory of Adam and Gibbs.[4]

There exists a distribution of domain sizes at any given temperature, but it turns out that the most predominant is the maximum size domain, the rest being inversely proportional to the logarithms of the ratio of the pertaining relaxation times, for example, $\log(\tau_i/\tau_z)$, where τ_i is the relaxation time for the size of i at the thermodynamic condition where z is the maximum (major) domain size, and τ_z is the characteristic (major) relaxation time, i.e.,

$$\ln \frac{G_i}{G_z} = \frac{1}{\dfrac{\Delta\mu}{kT} \log \dfrac{\tau_i}{\tau_z}} \tag{2}$$

where G_i and G_z are the intensity of relaxation for the domain sizes of i and z, and z is the charac-

teristic domain size, whereas size i refers to the ith state of fluctuation.

The relaxation modulus $G(t)$ involving all conformational relaxation modes up to τ_z is, therefore,

$$G(t) = \sum_{i=1}^{z} G_i \exp\left(-\frac{t}{\tau_i}\right) \qquad (3)$$

and each G_i is governed by a different value of activation energy $\Delta\mu$ times i. Thus, the high frequency side from the loss maximum does change its shape with temperature, whereas the lower frequency side apparently maintains the same shape (which includes all of the melt viscoelasticity) and the same shift factor as for the domain size z.

The apparent activation energy $\Delta\mu z$ for this shift factor is an increasing function of $1/T$, rather than remaining constant, because z increases at lower temperatures. The domain size $z = N_A/N_z$, is unity at T^* and zero at T_0. N_z is proportional to the Doolittle free volume. Thus, for z, we obtain the formula

$$z = \frac{T^* - T_0}{T^*} \cdot \frac{T}{T - T_0} \qquad (4)$$

Substitution of $\Delta\mu z$ for the activation energy in the Arrhenius formula

$$\log \tau = \log \tau^* + \frac{\Delta\mu z}{kT} - \frac{\Delta\mu}{kT^*} \qquad (5)$$

will obtain the Vogel[5] equation,

$$\log \tau = \log \tau^* + \frac{\Delta\mu^*}{k(T - T_0)} - \frac{\Delta\mu^*}{k(T^* - T_0)} \qquad (6)$$

or with a chosen reference temperature,

$$\log \tau = \log \tau_{\text{ref}} + \frac{\Delta\mu^*}{k(T - T_0)} - \frac{\Delta\mu^*}{k(T_{\text{ref}} - T_0)} \qquad (7)$$

$\Delta\mu^*$ is related to $\Delta\mu$, i.e.,

$$\Delta\mu^* = \Delta\mu \cdot \frac{T^* - T_0}{T^*} \qquad (8)$$

A rationale for the above definition will be ex-

plained subsequently. Here T_{ref} refers to any reference temperature of choice, and T_0 is the temperature at which all conformers in the entire system become locked together, i.e., $N_z/N_A \approx 0$, and the equilibrium value of z reaches infinity, as will be explained subsequently. The fractional free volume $f = \alpha_f(T - T_0)$ used in Doolittle[6] and (indirectly) WLF[7] equations is related to the temperature dependence of $z = N_A/N_z$:

$$f = \frac{kT}{\Delta\mu^*} \cdot \frac{T - T_0}{T} \qquad (9)$$

and equating $R/\Delta\mu^*$ to α_f will result in

$$f = \alpha_f(T - T_0) \qquad (10)$$

The value of $R/\Delta\mu$ is about 6×10^{-4} K^{-1}, whereas the value of $\Delta\alpha = \alpha_l - \alpha_g$ or the difference in the thermal expansion coefficient between the liquidus and the glassy solid is typically 3 or 4 $\times 10^{-4}$ K^{-1}. The second coefficient in the Doolittle formula, B, is an empirical proportionality constant between $\Delta\alpha$ and α_f. The Doolittle free volume is thus an empirical parameter designed to behave like the domain population N_z. Because N_z is proportional to the volume in such a way that z changes from 0 to 1 between T_0 and T^*, the expansion coefficient for N_z is greater than the expansion coefficient for the excess volume that vanishes at 0 K. The proportionality constant B can be evaluated:

$$B = \frac{\alpha_f}{\Delta\alpha} = \frac{T^*}{T^* - T_0} \qquad (11)$$

which is in fact the factor that normalizes the domain size at T^* to be unity, i.e., there is 1 mol of excess volume (as with a mol of the ideal gas) per 1 mol of conformers at T^*. One mol of free volume is 0 cm^3 at 0 K and $\Delta\alpha T^* = \alpha_f(T^* - T_0)$ cm^3 or $0.25 \sim 0.3$ cm^3 at T^*.

The mass of 1 mol of conformer is M gram, where M is the average molecular weight of the conformers. If we assume the density of polymers to be 1 g/cm^3, the free volume at T^* is $\sim 0.3M$ cm^3. Thus, free volume per gram of conformer is the same for most polymers of the same density, but the free volume per mole varies greatly. Because T_g is affected by the molar entropy and not the entropy per gram, the glass transition temperature depends on the size of conformers, ca ln M. This dependence of free volume on the molecular
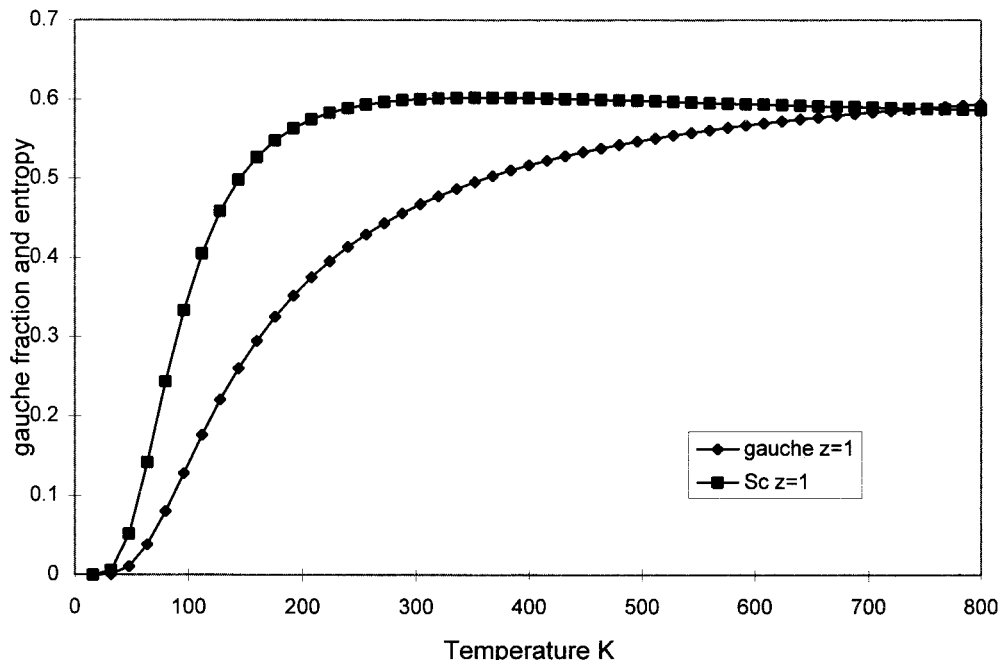
Figure 1 Mol fraction of the gauche conformation, and the entropy of mixing vs. temperature.

weight determines the dependence of T_g on the molecular volume of the conformer and, as will be explained subsequently, plays a key role in determining T_g of polymers from the chemical structure via the average size of conformers.

In Figure 1, the temperature dependence of the concentration φ of the gauche conformation is shown, together with the entropy of mixing between the gauche and the *trans* conformations. It is obtained from the energy difference $\Delta\Gamma$ between the gauche and *trans* conformation through the formula:

$$\varphi = \frac{2\,\exp\left(\dfrac{\Delta\Gamma}{kT}\right)}{1 + 2\,\exp\left(\dfrac{-\Delta\Gamma}{kT}\right)} \qquad (12)$$

The factor 2 is placed in the formula because there are three possible angles that a conformer can assume per bond. In some polymers, the third position is forbidden by the geometrical interference; in such a case this factor 2 is replaced by unity. The entropy of mixing between the *trans* and gauche conformations is obtained through an approximation:

$$S_c = -R[\varphi \ln \varphi + (1 - \varphi)\ln \varphi] \qquad (13)$$

The conformational concentration φ and the conformational entropy S_c reaches zero at 0 K, although they appear to reach a very small value at 20 or 30 K. This behavior is affected by the choice of the value for $\Delta\Gamma$. For atactic polymers, the ground state should be higher than the *all trans* conformation, but we ignore these complicated possibilities here. In this instance we have taken it to be 500 cal/mol. If a greater value is assigned, this behavior will shift to a higher temperature. The domain size is always 1 for S_c, as no interference in relaxation of a conformers from their neighbors has been taken into consideration.

We now consider the case where the domain size does change with temperature. Since by definition all conformers in one domain relax together, the probability for the change of conformations by all conformers in that domain is equal to the conformational probability for one conformer. Thus, the conformational entropy decreases as the domain size z increases when the temperature is decreased. This is illustrated by the three curves for z of 1, 3, and 6, shown in Figure 2. When z increases, the conformational entropy decreases. The dotted line indicates the locus of the shrinking entropy with temperature, and this is the ex-
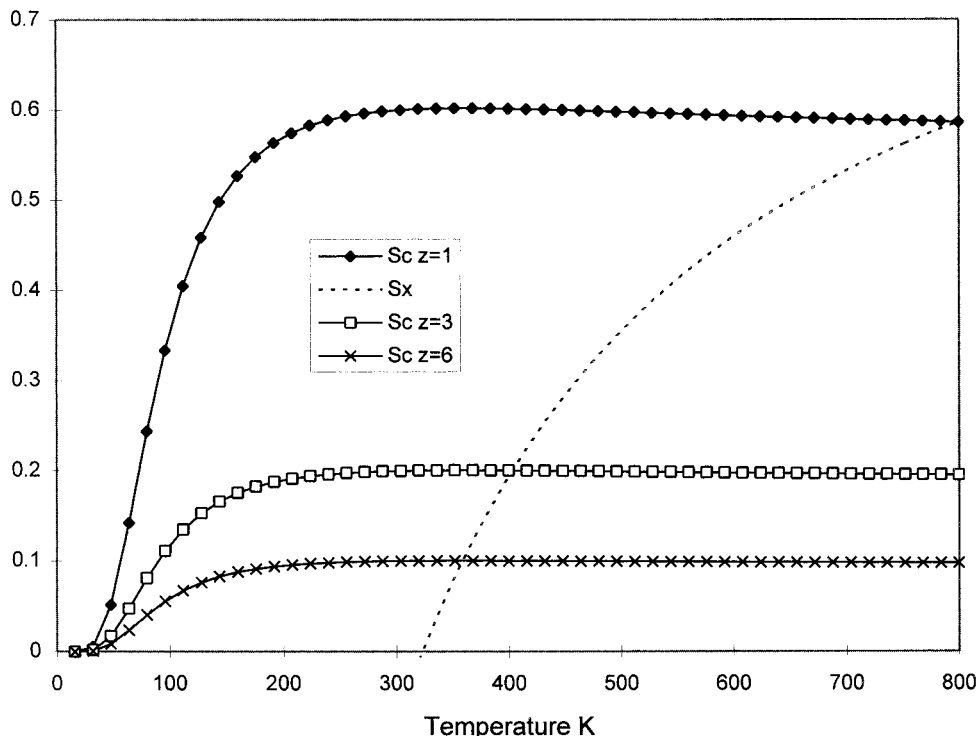
Figure 2 The conformational entropy for various domain sizes.

cess entropy, S_x, that goes to zero at T_0, for which the value of 325 K was chosen for this example. It will be shown later that T_0 is not empirically chosen, but it depends on the molecular volume; the greater the conformer size, the higher T_0.

The Gibbs free energy can be calculated by integrating the entropy with temperature. In comparing the three quantities, the enthalpy, entropy and free energy, the enthalpy is on the order of C_pT, the entropy on the order of C_p, and the free energy in an insignificant magnitude as compared to the enthalpy or T times entropy. In Figure 3, the quantity T times entropy is plotted for $z = 1$, 3, and 6, utilizing the entropy figure from Figure 2. In addition, the conformational enthalpy H_c for $z = 1$ is obtained from $TS_c + \int S_c \, dT$, and plotted in the same graph. H_c and TS_c superimpose on each other, indicating that they are indistinguishable from one another, i.e., the Gibbs free energy is negligible. The fifth curve in Figure 3 is the product of temperature and the (cooperativity) excess entropy, TS_x. Above T_0, it can be observed that the TS_c for $z = 1$ curve, i.e., the conformational entropy times temperature, and TS_x or the temperature times the excess entropy are nearly straight lines whose slopes can be scaled by the factor $T^*/(T^* - T_0)$. Thus, we arrive at the formula:

$$\frac{S_c}{S_x} = \frac{TS_c}{TS_x} = \frac{T^* - T_0}{T^*} \cdot \frac{T}{T - T_0} \cdot \frac{H_c^*}{H_x^*} \quad (14)$$

and $H_c^* = H_x^*$, so that eq. (14) is exactly equal to z, and from the Adam–Gibbs equation:

$$\log \tau = \log \tau^* + \frac{\Delta\mu}{kT} \frac{S_c}{S_x} - \frac{\Delta\mu}{kT^*} \quad (15)$$

one obtains the Vogel equation, eq. (6).

The excess entropy S_x with cooperativity decreases as the temperature is decreased, more rapidly than the conformational entropy S_c, following the domain size increase. We have shown that the product of the temperature T and entropy S is virtually equal to the enthalpy H, because the Gibbs free energy is much smaller than the enthalpy. Thus, the introduction of the cooperativity concept increases the slope dH/dT from what it is without. $(dH_x/dT)_p$ is the specific heat difference between the liquid and the solid states, ΔC_p, per mol of conformer, but not per gram, which is the usual unit, and the latter is obtained by dividing the former by M. The excess enthalpy (or, $\cong T$ times entropy) is shown vs. temperature in Figure 4. The curve denoted with filled circles is for the domain size of 1, without the cooperativ-
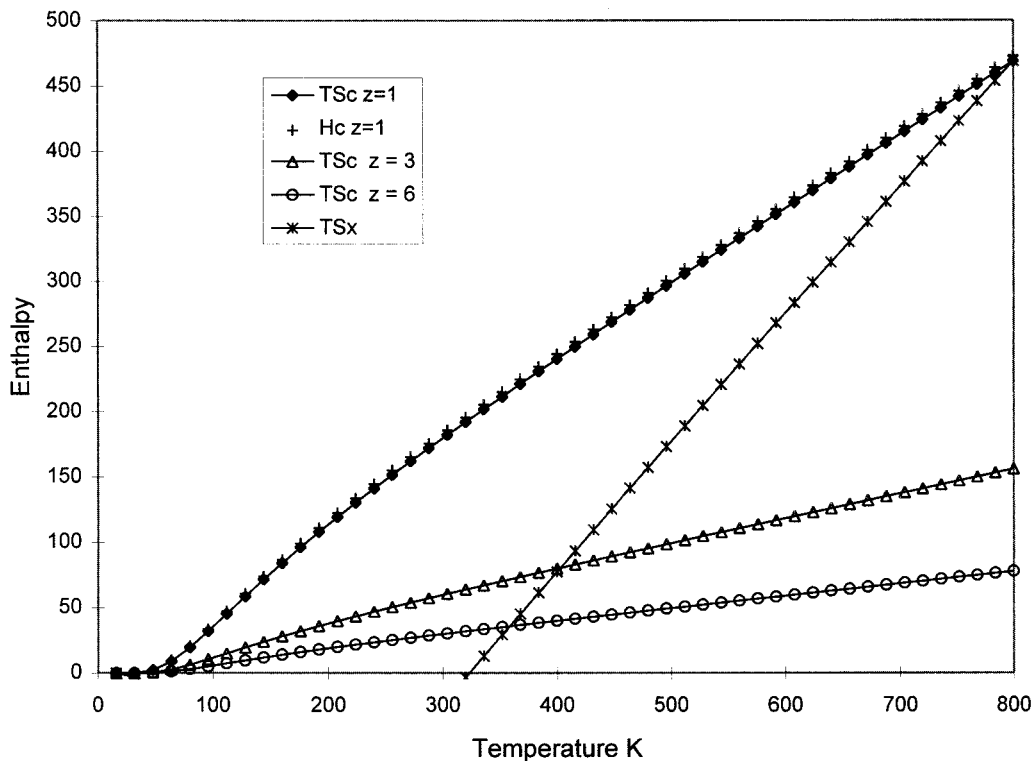
Figure 3   The product of the temperature and the conformational entropy shown in Figure 2, which is about equal to the conformational enthalpy.
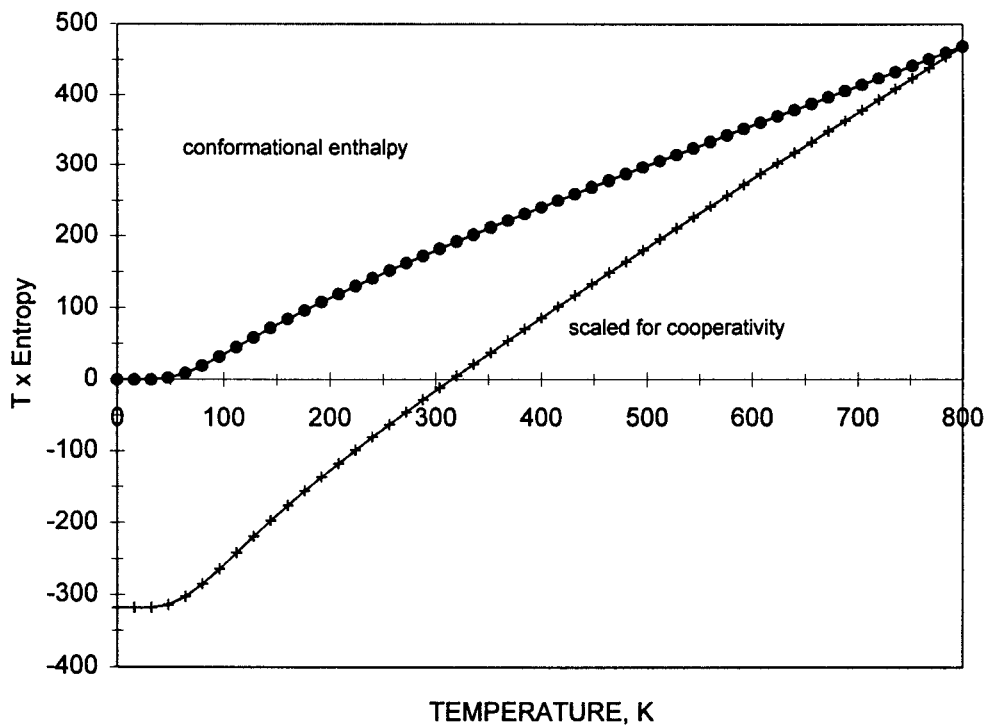

Figure 4   The filled circles are the conformational enthalpy, and the + marks are calculated by scaling the former by the factor $T^*/(T^* - T_0)$ but matching at $T^* = 800$ K. $T_0 = 325$ K.

ity, and the other curve, denoted by +, is obtained by scaling the first curve by the factor: $T^*/(T^* - T_0)$. It is meant to mimic the curve for TS_x in Figure 3, that is, the equilibrium conformational enthalpy for the cooperative domain size that changes with temperature, such that the entropy and enthalpy reaches zero at about 325 K. The zero entropy temperature is called the Kauzmann[8] temperature. To reiterate, physically it means that, starting from the very high temperature, T^*, down, the entropy drops faster than is suggested by the conformational probability. Thus, the enthalpy and entropy are directed toward zero at T_0. The excess volume, however, seems to point toward zero at 0 K, though the glass transition would intervene well above 0 K to make it impossible to reach the equilibrium at 0 K. The concentration of the higher energy state such as the gauche conformation also points toward zero at 0 K as expected, but when the glass transition intervenes near T_0, the gauche concentration is far above zero.[9]

The scaled curve in Figure 4 is obtained by the equation:

$$H_x = \frac{T^*}{T^* - T_0} \cdot \frac{T - T_0}{T} H^* \qquad (16)$$

where H_x is the excess enthalpy with cooperativity and H^* is the conformational enthalpy as well as the excess enthalpy at T^*. H_x/H_c ($= TS_x/TS_c$) is $(T^* - T_0)/T^*$, and so should the Gibbs free energy. Thus, $\Delta\mu^*/\Delta\mu$ takes on the same value and results in the relationship shown with eq. (8).

To summarize, a scaling scheme has been proposed[10] to calculate the characteristic relaxation time for the cooperative conformational relaxation, by multiplying the conformational enthalpy (the first curve in Fig. 4) by the factor $T^*/(T^* - T_0)$ starting from T^* down, as shown by the second curve in Figure 4. The following results are derived from this scaling scheme:

1. The specific heat for the conformational enthalpy ΔC_p per mol of conformer, is scaled from that of the rotational isomeric states by the same scaling factor, $T^*/(T^* - T_0)$. ΔC_p per gram is the more common form of the data, and it is smaller for polymers with higher T_g, whereas the per mol quantity is greater. For a given polymer, ΔC_p is approximately proportional to $1/T$.

2. The domain size z is equal to the ratio of the enthalpy without cooperativity over that with cooperativity, and $z = (T^* - T_0)/T^*(T/(T - T_0))$.

3. The enthalpy and entropy reaches zero at T_0, that is, about 50 K below the experimentally determined T_g, for example, by dielectric, dynamic mechanical, or thermal analyses. Van der Waal's free volume does not extrapolate to 0 at T_0, but toward 0 at 0 K.

4. The apparent activation energy for the characteristic relaxation time increases with z as the temperature is decreased. The Vogel equation is obtained for the temperature dependence of the characteristic relaxation time associated with the maximum domain size at each temperature.

Glass Transition

It is well known that the glass transition is not a thermodynamic transition, because the glassy state is not a thermodynamically definable equilibrium state. Rather, the glassy state is a non-equilibrium state created by the inability of a material to maintain the equilibrium with the surroundings at the same temperature and pressure. However, a solid-like state at T_0 can, in theory, reach a thermodynamic equilibrium, though in practice it cannot because the relaxation time is infinite there. Another point can be raised about the equilibrium state above T_0 but below the empirical T_g. In this region the equilibrium can be reached within a finite length of time. The appearance is glassy, so one may call it the equilibrium glassy state, but the thermal expansion coefficient is that of a typical liquid than of a glassy solid. It is preferable to call it a highly vitreous equilibrium liquid.

The TS_x curve in Figure 3 is the equilibrium liquidus line. As mentioned already, when the temperature is decreased approaching the zero entropy temperature, ca. 325 K in the figure, the domain size continues to increase. If an equilibrium could be maintained all the way to 325 K, T_0 for this polymer, then the domain size would have grown to infinity, and the relaxation time would also be infinity. All conformers would have been locked together. It is intuitively obvious that a realistic rate of cooling will induce the material to apparently freeze up before reaching this true zero entropy state; by then the relaxation time will have grown to so large a value that internal rearrangements will become practically impossible. This apparent freezing typically occurs at about 50 K above T_0. 50 K is the value of c_2^g in the "universal" WLF equa-

tion.[6] All thermodynamic quantities appear to freeze, but if the temperature and pressure are held constant, they will seek lower values until reaching the equilibrium state. This is known as the physical aging process.[11] It turns out that the apparent time constant for physical aging is much greater than the characteristic relaxation time τ. This is true because the relaxation time τ continually changes with aging such that the apparent time constant for the volume change is much greater than if τ were to remain fixed.

This can be shown by realizing that the relaxation time τ in the following differential equation for the volumetric aging for the Doolittle free volume fraction, $f = \alpha_f(T - T_0)$:

$$\frac{df}{dt} = -\frac{f}{\tau} \qquad (17)$$

is changing with time. Now, all viscoelastic functions such as the relaxation modulus or dynamic mechanical compliance are formulated with (t/τ) as one variable. This is possible because the entire spectrum shifts with temperature with the same shift factor for τ. If the changing τ also results in a shift for the entire viscoelastic spectrum with the same shift factor, then the aging phenomena can be characterized by (t/τ) where t is the aging time. This means that the time elapsed and the increasing τ are always proportional, such that

$$\frac{d \log \tau}{d \log t} \cong 1 \qquad (18)$$

Equation (17) is further developed by using eq. (18) and the Doolittle equation for $\tau(f)$:

$$\frac{df}{dt} = \frac{df}{d\tau} \cdot \frac{d\tau}{dt} = -f^2 \frac{d \ln \tau}{d\tau} \frac{d\tau}{dt} = -\frac{f^2}{t} \quad (19)$$

which implies that the volume contraction during aging will proceed with the ever increasing apparent "time constant" t/f, and τ does not even appear in the equation, at least directly. It means that if the viscoelastic relaxation takes τ second to relax, the aging process would take τ/f seconds. Because f is a small number, for example, 0.025, it takes 40 times longer for aging process than for viscoelastic relaxation. This can be observed in Figure 5, which depicts the stress relaxation data for polystyrene taken while the polymer was un-
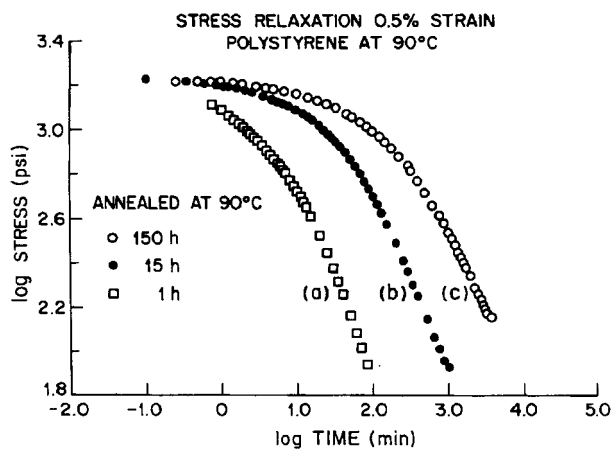

Figure 5 Stress relaxation of polystyrene while it undergoes through physical aging at 90°C.

dergoing aging. If the curve is for a single relaxation process, $1/e$ of the initial modulus can be taken for the characteristic time for the viscoelastic relaxation. For the polymer relaxation, the "stretched exponential" would make the relevant $\Delta \log(\text{stress})$ smaller. On the graph, $\Delta \log(\text{stress})$ of -0.43 corresponds to the decay of the stress to $1/e$, or the level of 2.9 for $\log(\text{stress})$. The ratio of aging over the viscoelastic τ is typically about 20. The curve for the longest aging time results in a greater ratio because in this case the polymer reached equilibrium volume, after which τ did not increase as the time continued to elapse. In fact, eq. (18) is valid only when τ is increasing at steady state. At the initial stage of aging τ is too long for the short t, and that condition is not met until the time has elapsed to be equal to the value of the initial τ/f. When the equilibrium is reached, the right side of eq. (18) is $-\infty$. Also, even at steady state, because there is a distribution of domains sizes, there is a distribution of τ. This means that the right side of eq. (18) is less than 1. In our study on polyvinyl acetate, the value of 0.85 was observed. A rule of thumb for the rate of aging would be about 10 to 30 times slower than the viscoelastic relaxation.

When $T < T_0$, such as for most commercial glassy polymers at room temperature, the equilibrium will never be reached so eq. (18) will prevail indefinitely once the steady state is reached.

T_g and Chemical Structure

So far, we have shown that the zero entropy temperature is at T_0 rather than at 0 K because of the cooperativity. The cooperative domain z de-

pends on the amount of free volume, where we accept the concept of free volume to be the volume in excess of the van der Waals volume, rather than the Doolittle-WLF free volume, which is the empirical parameter for fitting relaxation data. The free volume does not vanish at T_0, unlike the Doolittle's free volume, but it extrapolates toward zero at 0 K just as the RIS enthalpy does. Thus, there will be more free volume at T_0 for polymers with higher T_0. If the T_0 is higher, so is T_g. Therefore, a polymer with higher T_g would have a greater amount of free volume "frozen in" at the glass transition. Now, the configurational entropy, S_f, of the molar free volume, V_f, can be considered to be equal to the configurational entropy of the ideal gas of the same volume V_f, i.e.,

$$S_f = k \log V_f \qquad (20)$$

This entropy should scale for the cooperativity consideration in the same manner as the conformational entropy was shown in the preceding discussion, so that the scaling factor $T^*/(T^* - T_0)$ is proportional to $\log V_f$, which in turn, is proportional to $\log M/\rho$, where M is the molecular weight of the conformer and ρ is the equilibrium density at T^*. Thus, we have obtained a way to describe the dependence of T_0 on the size of the conformer. In practice, a polymer consists of many conformers of different sizes, but an algebraic average can be taken of those sizes. This procedure works because the molar entropy of mixing different size molecules can be estimated on the molar fractions, according to Hildebrand.[12] Thus, we have a formula:

$$\frac{T^*}{T^* - T_0} \propto \log \frac{M}{\rho} \qquad (21)$$

where T^* is 773 K, at which the conformational relaxation can proceed without necessitating the cooperation from the neighbors. T^* is the temperature above which the relaxation time exceeds the librational frequency. Above T^*, the meaning of the term relaxation is lost, because no sooner a conformer relaxes it is back to the previous unrelaxed position and back and forth. In this temperature/frequency range, we suspect that the relaxation spectrum would be flat as if exhibiting the white noise.

Ignoring the density variations among the amorphous polymers (in comparison to the molecular weight variations), the proportionality constant $C = (T^* - T_0) \log M$ can be evaluated through introduction of a virtual polymer with
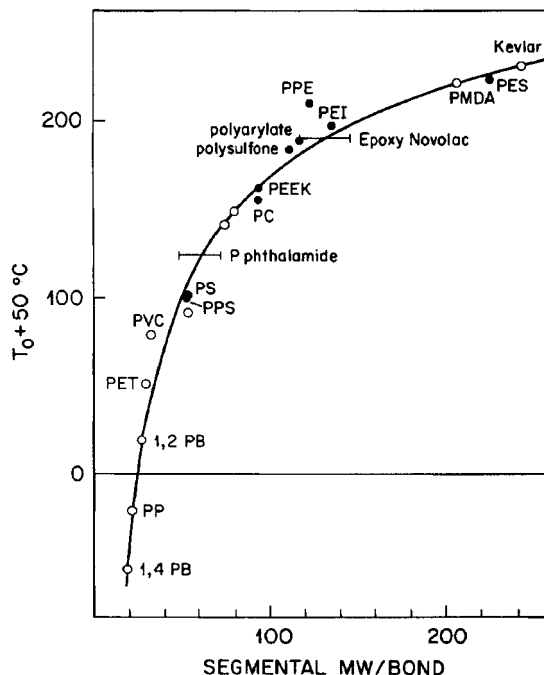

Figure 6 $T_0 + 50$ K, or T_g, vs. $\ln M$; M is the molecular weight of a conformer.

low molecular weight M_0, that its T_0 is at 0 K, i.e., the curve marked as $z = 1$ in Figure 3, and we obtain the formula:

$$C = (T^* - T_0)\ln M = T^* \ln M_0 \qquad (22)$$

The empirically arrived value for C is 1750 for many polymers, and this means M_0 is 9.6, not even as large as one carbon atom. For the methylene unit as a conformer, T_0 of $-160°C$, or T_g of $-110°C$ is obtained. This is near the γ transition temperature of branched (low density) polyethylene, but the apparent activation energy of the two seemingly similar transitions, i.e., the glass transition in linear polyethylene and the γ transition in branched polyethylene, differ distinctly. The γ transition for branched polyethylene is definitely a local relaxation process involving a fixed number of intramolecular cooperative conformers, exhibiting a constant activation energy, just as in the case of the β transition in amorphous homopolymers, as will be discussed subsequently.

The size dependence of T_g, or $T_0 + 50°C$, is shown in Figure 6, where the curve is calculated from eq. (22). The general rules for estimating the conformer size from chemical structure is elaborated below:

1. A conformer with a branch.

(a) When another conformer is attached as a branch to a conformer in the main chain, the new combination attains the combined size of the two. When a methyl group is attached to a carbon in the main chain, this combined conformer consists of $CHCH_3$ and its molecular weight is 28. However, polypropylene has a methylene unit as the other conformer along the main chain. Averaging the two, $(28 + 14)/2 = 21$ is obtained, and T_0 of $-75°C$, or T_g of $-25°C$ is obtained from eq. (22).

(b) When the branch contains more than one conformer so the branch itself can undergo its own conformational relaxation, the number of conformers per monomeric unit increases and the average conformer size decreases again. For polyvinyl acetate, the monomeric unit consists of three conformers instead of 2. The average conformer molecular weight M is $86/3 = 28.7$, and from eq. (22), T_g of $29°C$ is obtained. Whether a further addition of conformers will raise or reduce the T_g depends on the size of a conformer to be added. Simply, if it is larger than the present average size, the T_g will rise, but if smaller, T_g will fall. On the other hand, the concentration of the end group also decreases the T_g, such that a dangling group will have a smaller conformer at the end.

2. The end group in a polymer chain has a higher enthalpy and entropy than a similar conformer inside the chain. The end group lowers T_g as would the solvent molecules. The contribution of the chain ends to the overall enthalpy can be estimated by mixing them with those conformers along the chain, and the average T_g can be obtained.

3. When compatible polymers are mixed, a value of T_g between the two individual values is found. One approach for estimating the T_g from the individual concentrations of the two polymers is to invoke the principle of isentropic state at $T_g = T_0 + 50$ K. The entropy S_g for cooperative relaxation determines the domain size z at T_g, so the same value for S_g means the same z value at T_g for all polymers and their mixtures. The entropy S_g can be derived by the formula:

$$S_g = \frac{dS}{dT} \cdot (T_g - T_0) \qquad (23)$$

but $T_g - T_0$, the WLF parameter c_2^g, is 50 K, and dS/dT at T_g is ΔC_p, so we have:

$$S_g = \frac{50\Delta C_p}{T_g} \qquad (24)$$

and ΔC_p per mol is proportional to $T^*/(T^* - T_0)$ or to $\ln M$, hence

$$S_g \propto \frac{\ln M}{T_g} \qquad (25)$$

is obtained. The mixture containing x mol of conformer A and $1 - x$ mol of conformer B will exhibit the T_g:

$$\frac{\ln M}{T_g} = x \frac{\ln M_A}{T_{gA}} + (1 - x) \frac{\ln M_B}{T_{gB}} \qquad (26)$$

When a thermosetting resin monomer is cured, the chain ends are converted to conformers in the interior of the chain. Here is the case that the molecular weight is the same but T_g is not. Earlier, we discussed using a smaller value of M for the chain end as it has more free volume. The amount of free volume, however, will not account for a nearly one-third reduction in molecular weight. In such a case, we let the molecular weight be the same but use a lower T_g as with the solvent molecules. Equation (26) above will be simplified to the equation below:

$$\frac{1}{T_g} = \frac{x}{T_{gA}} + \frac{1 - x}{T_{gB}} \qquad (27)$$

which is the well-known Fox–Flory[13] formula.

There is another case when M remains the same but T_g is different. It is the case of conformers in a tightly crosslinked network. In this case the new T_g is higher, rather than lower as was the case with chain ends. The idea for the rising T_g with decreasing entropy is the core of the well-known Gibbs–DiMarzio[14] theory. We follow the concept, but we cannot use the statistics of rubbery molecules, as the tight molecular bridge between the three way branching points are too short. The molecular motions are comparable to the β relaxation in the restricted environment of the glassy state, rather than a taught entropy spring. When the bridging molecule is long and rubbery, then Fox–Flory equation above is adequate. Actual calculation will be shown subsequently during the analysis of thermoset curing.

The β Relaxation

When some conformers, usually the largest one in the repeat unit in the polymer chain, are pinned

by neighbors at glass transition, there still remains a possibility for the limited and local relaxation by the smaller conformers along the chain. This process does not require total chaotic rearrangements that are typical of the liquid state. The local relaxation process in the glassy matrix is the β relaxation. As a rule, the β relaxation requires the intramolecular cooperation among the conformers located between the pinned conformers. The number of these conformers corresponds to that of the repeat unit minus one, assuming that each repeat unit contains one large conformer that is most easily pinned. The rest will relax, not independently, but through the cooperative efforts by all consecutive conformers. The size of the intramolecular cooperative domain z_β for the β relaxation, therefore, is fixed and does not change with the temperature, unlike the α transition discussed above. The value of z_β should be equal to the ratio of the molecular weight of the repeat unit over the average molecular weight of the conformers used to calculate T_g. For polycarbonate, z_β is 3.3, the fraction being due to the oxygen bonds with much smaller rotational energy barrier, and this number obtains the correct T_g when substituted into eq. (22), i.e., $M = 254/3.3$ will obtain T_g of 147°C. The cooperative relaxation among 3.3 conformers will lead to the activation energy of 3.3 × 3.3 = 10.9 Kcal, which agrees with the data.[9]

It is also well known that some side branches are responsible for a β relaxation. In as much as the conformational changes in a flexible side chains provide the possibility of enabling the main chain to relax in the α relaxation, it is entirely possible that these flexible branches will undergo a local relaxation after the main chain motion has been frozen. Figure 7(a) is an illustration of the relaxation frequency and the temperature relationship for polyvinyl acetate and glucose, a nonpolymer. Polyvinyl acetate is able to go through the β relaxation, as noted by the straight line in the plot vs $1/T$, and merges with the Vogel-type α relaxation at about 10^8 Hz. From the slope for the β transition the activation energy of 9.8 Kcal is obtained, or the multiple of 3 over 3.3 Kcal. This means all three conformers are involved in local relaxation of polyvinyl acetate. Similar data are shown for α glucose, with the β relaxation that is parallel to that of polyvinyl acetate. The three carbon bonds cooperatively involved in this case have to do with the conformational change in the six-member ring of glucose.

An enlarged detail of Figure 7(a) at the point of merging α and β relaxations is shown in Figure 7(b). Apparently, the β relaxation takes over above the merging temperature, indicating that the intramolecular cooperativity persists even in the liquid state free of the intermolecular interference seen in the glass transition. If the intramolecular cooperativity were not needed as in some polymer molecules, the α and β process would have met at T^*. Then the activation energy for the β process would be just $\Delta\mu^*$, or 3.3 Kcal.

The Glass Transition in Crosslinked Polymers

In the light of what has been discussed above, we will now attempt to analyze a crosslinking reaction in thermosets. In calculating T_g of the reacting mixtures, some of the concept from a previous study by Hale, Macosko, and Bair[15] has been incorporated.

We will take a thermosetting resin of commercial importance for which a respectable set of data exists, namely an epoxy-amine system studied by Wisanrakkit and Gillham.[16] Diglycidyl ether of bis-phenol A (DGEBA) will be called component A, and trimethylene glycol di-p-aminobenzoate component B. Each end of A has an epoxy group, and each end of B has an amine group. The amine can react either monofunctionally with one epoxide or bifunctionally with two epoxides. The primary and secondary amines are equally reactive, according to Wisanrakkit and Gillham. We now define the concentration of the DGEBA molecules with two unreacted ends as A_0, the ones with one reacted end as A_1, and ones with both reacted ends as A_2. Diamino deibenzoate can react monofunctionally to form a R—NH— link, or difunctionally to form R—N . Because there are two amines for each diamine, there are five stages for B. The molar fraction of unreacted monomers will be B_0, molecules with one reacted end will be B_1, the bifunctionally linked will be B_2, the three of four reacted will be B_3, and all ends with reacted links will be B_4.

Because this is a stoichiometrically matched mixture, we can estimate the molar concentrations of these reactants in terms of the molar conversion ϕ as the following:

$$A_0 = (1 - \phi)^2;$$
$$A_1 = 2\phi(1 - \phi);$$
$$A_2 = \phi^2; \text{ and}$$
$$B_0 = (1 - \phi)^4,$$
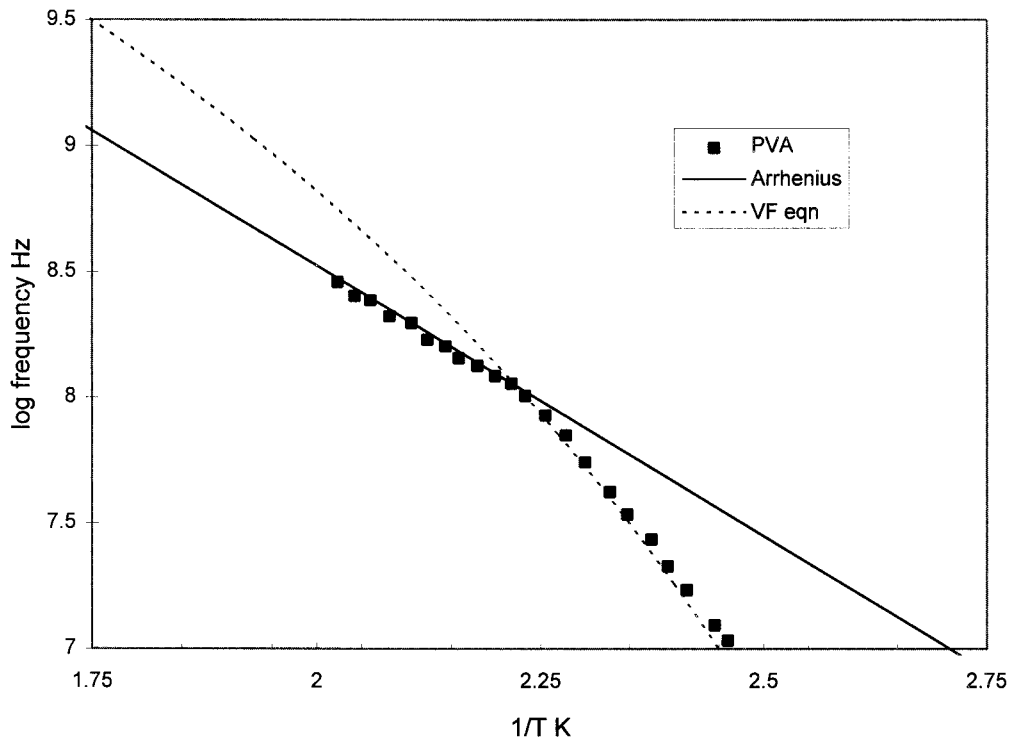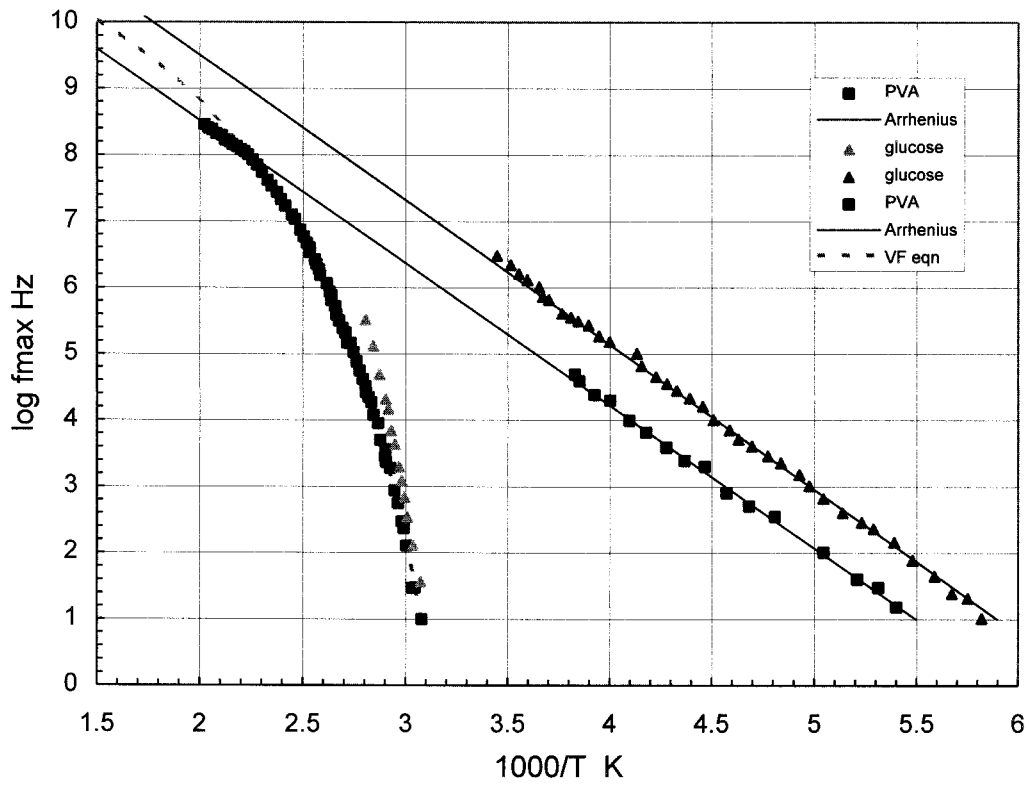$$B_1 = 4\phi(1 - \phi)^3,$$

Figure 7   The transition map, log frequency for the maximum dielectric loss vs. $1/T$, for polyvinyl acetate and glucose. (a) The detail of Figure 7 in the vicinity where the α and β relaxations merge.
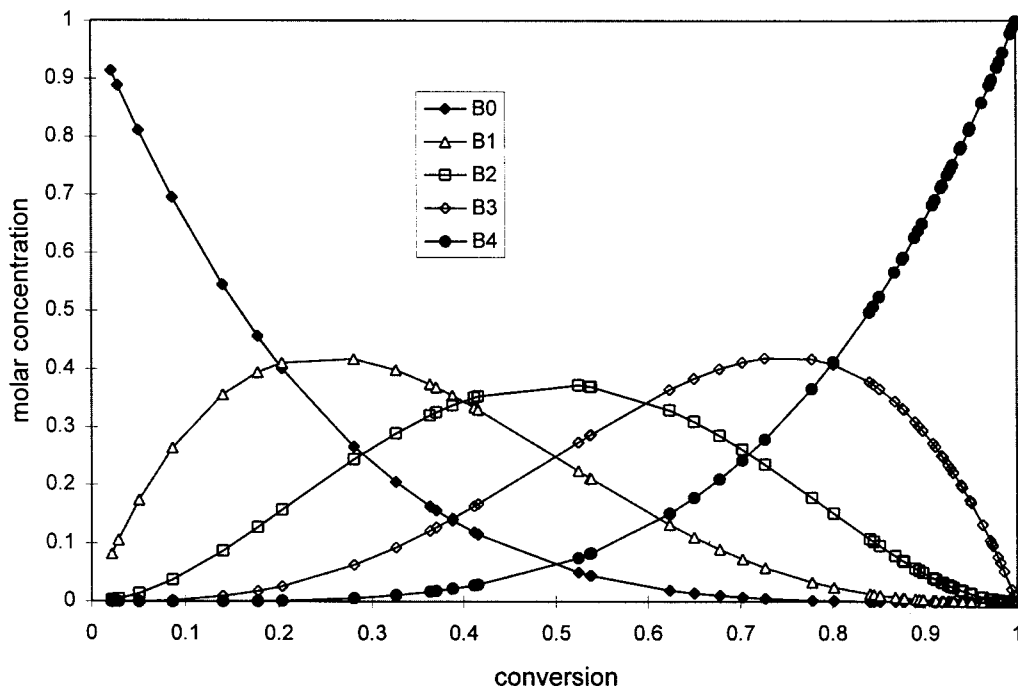
Figure 8 The relative concentrations of the trimethylene glycol di-p-aminobenzoate component B in the five different states of reaction vs. the overall extent of reaction.

$$B_2 = 6\phi^2(1 - \phi)^2,$$

$$B_3 = 4\phi^3(1 - \phi), \text{ and}$$

$$B_4 = \phi^4.$$

The concentration of the five B components are shown against conversion, or the extent of reaction, in Figure 8. A plot for the A components would also be symmetrical, though there are only three curves.

First, we attempt to estimate T_g of the A and B components with both ends reacted but the conformers are free to rotate as they would in a linear chain. This means that no chain ends and no bifunctionally reacted amine group R—N= are present, but only the reacted epoxides and monofunctional R—NH— groups. The molecular weight of DGEBA is 341, and the number of conformers is estimated as 9.5 from its chemical structure. The fractional value is a result of counting —O— conformers as 0.6 as was done in ethers and polycarbonates. This gives average M of 35.9 conformer in A, and from eq. (22), T_g of 61.3°C is obtained. For diaminobenzoate, the molecular weight is 318 and 10.3 conformers are counted. From this, M of 30.9 and T_g of 39.8°C are obtained. By applying eq. (26), we obtain T_g of the linear chain to be 50.3°C if B_3 and B_4 species are assumed to 39.8, i.e., all amines are bifunctionally reacted. For

B_3, three of the four arms are linked to three A species. A and B are about the same in length and molecular weight. The three-way Y will have about the same conformational probability as two linked end to end, so we guessed the conformer molecular weight to be half as much, or M of 46.8. If we include these B_3 and B_4 amines hanging as trifunctionally reacted branches, T_g will be higher, and the value of 77.3°C is obtained. The tetrafunctionally reacted B_4 should be almost "immobile," i.e., it will not be able to relieve stress by undergoing any conformational rotation. Then its T_g ought to be 550°C! We determined T_g for B_4 by curve fitting the data with a computer program. The result was 400°C. If this high T_g were to be attributed to the increased molecular volume of the conformer, its molecular weight would have to be over 100,000! This clearly shows that the high T_g is the result of the constrained tertrafunctional crosslinkers. T_g is plotted against the conversion in Figure 9. The parameters are tabulated in the Appendix.

Because the T_g is known for conversion ϕ at each step, the relaxation time at any temperature at any extent of reaction can be calculated from the Vogel equation, eq. (6). The kinetics for the crosslinking reaction can be calculated using the overall T_g of the mixture of reacted and unreacted monomers. When these units react to become part of a growing polymer
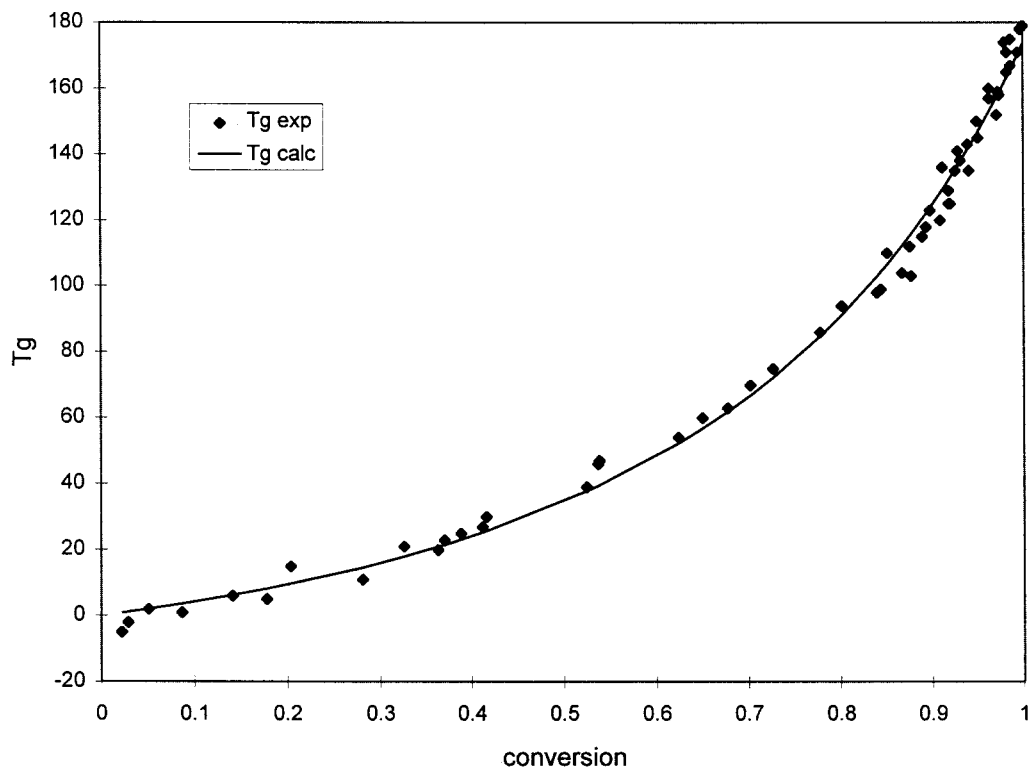
Figure 9 T_g for the epoxy-amine system, the data from ref. 14, and the line is calculated according to the procedure described in the text.

chain, the concentration of the high T_g units increases at the expense of the low T_g units. Ultimately, all reactants will have reacted if the stoichiometry has been set exactly, and all diamine joints will have reacted bifunctionally so that at every strand of monomer will have been connected.
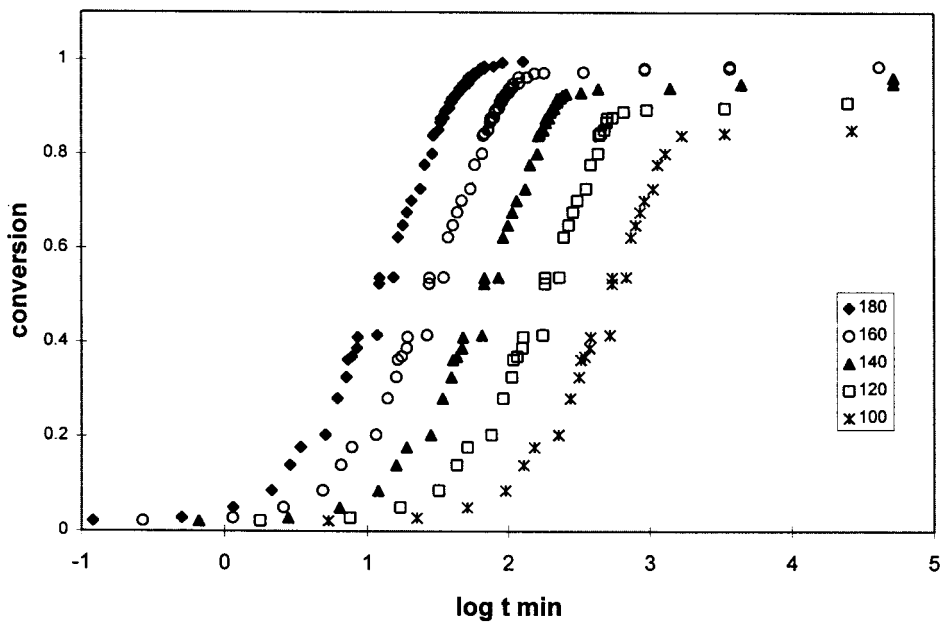

Figure 10 The kinetics of the crosslinking reaction recreated by calculation as described in the text.

The rate of reaction for thermoset resins is distinguished from the ordinary chemical reaction by its diminishing "rate constant," which does not remain constant but is affected by the changing state of the reacting system. In order to continue the reaction, the unreacted ends of A and B must meet. This will become more and more difficult as the reaction continues. The overall reaction time constant, then, is a combination of the chemical term, τ_a, and the bulk relaxation time τ_c. As mentioned earlier, the latter is not equal to the characteristic viscoelastic or dielectric relaxation time but is the apparent time constant for the bulk relaxation that is germane to the volume change such as observed in physical aging, and its value is about 30 times greater $(= 1/f)$ than the characteristic relaxation time. Thus, the τ^* at T^* for the Vogel equation, eq. (6), should be offset from the universal $\log \tau^* = -11.4$ (s), by about 1.5. We have set $\log \tau_c^*$ for the bulk relaxation to be -10 at $T^* = 773$ K. The rest of the parameters are as follows: $\Delta\mu^*$ for the bond angle rotation: 3 Kcal, the activation energy for the chemical reaction: 16 Kcal, and the time constant for the reaction at 140°C: 1 min. The results are shown in Figure 10.

The amount of free volume trapped at T_g is greater for a polymer with a higher T_g, the theory of the iso-free volume at T_g notwithstanding. The Doolittle free volume fraction, f_g, is a measure of free volume in excess of the free volume at T_0.

That value is, in principle, universal because $T_g - T_0 = 50$ K for all materials. A more meaningful free volume, however, should extrapolate to zero at 0 K and not at T_0. There is more of the latter type of free volume for the higher T_g material, everything else being equal. This is not limited to thermosets, but seems to apply to all glassy polymers, if normalized with respect to the density of conformers in the liquid state. The glassy (unrelaxed) modulus for a polymer with higher T_g tends to be lower, reflecting the less densely packed state at vitrification.

CONCLUSION

We have demonstrated that the theory of cooperative relaxation can lead to a number of useful predictions for the mechanical and thermal properties of polymers as related to the chemical structure of the conformers. T_g of polymers can be estimated, and the shift factors for the amorphous polymers can be predicted. The density and the unrelaxed modulus of the glassy state are lower if the T_g is higher, because the vitrification takes place at a higher level of free volume. A master relaxation curve can be constructed by knowing all these parameters. Furthermore, we have demonstrated how the reaction kinetics for thermosets can be predicted by knowing the chemical formula and a few key data points on the T_g of the product.

APPENDIX
DATA for PARAMETERS for Figs. 8, 9, 10

	GDEBA A	DABenzo B			Wisanrakkit & Gillham 1989			T cross	T linear
unreac T_g	0	0							
T_g linear	61.3	39.8						171.9194	60.93721
conversion	Tg exp	A0	A1	A2	B0	B1	B2	B3	B4
MW	341	318							
bonds	9.5	10.3							
Mc	35.894	30.873							
LN Mc		3.181	3.240	3.580	3.181	3.271	3.430	3.846	11.666
Mc		24.090	25.552	35.906	24.090	26.338	30.877	46.812	116618.
T_g°C		0	10	61.3	0	15	39.8	95	400
T_g K		273	283	334.3	273	288	312.8	368	673

relaxation	$\log \tau^*$	-10 sec
relaxation	$\Delta\mu^*$	3000 cal/mol
chemical	H	16000 cal/mol
reaction	Temp	100°C
	initial $\log t$	0 minutes
chemical	$\log \tau$ reac	0 min Tref
chemical	at T ref	150°C
chemical	$\log \tau$ ref reac	1.10225 min at T

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