

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

THERMODYNAMIC THEORY OF VISCOELASTICITY

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Abstract

The relaxation spectra in polymers arise from the existence of many possible modes for dissipating the strain energy raised by the imposed force. These modes are made up by coupling the simplest and fastest mode of relaxation involving the rotation of a conformer, typically represented by the picosecond rotation of the carbon to carbon bond. This fast relaxation process cannot take place easily in the condensed state crowded by the densely packed conformers, necessitating cooperativity among them. The domain of cooperativity grows at lower temperatures, toward the infinite size at the Kauzmann zero entropy temperature. From the temperature dependence of the domain size, the well-known Vogel equation is derived, which is numerically equivalent to the empirical WLF and free volume equations. The molar volume is a crucial factor in determining the molar free volume and, therefore, in determining the T_g of a material. The molar ΔC_p is proportional to the logarithmic molar volume, and is greater for a polymer with a higher T_g , but ΔC_p per gram for it is smaller, as it is proportional to $(\log M)$ divided by M , where M is the molecular weight of the conformer.

From this theory, it is possible to predict the dependence of the characteristic relaxation time on temperature if either T_g or the conformer size is known, since one can be derived from the other. From the Vogel equation with all parameters thus derived, it is possible to obtain a master relaxation curve and the spectrum from one set of dynamic mechanical data taken at one frequency over a range of temperatures.

Whereas the linear viscoelastic principle is limited to small strains only, a real polymer is often deformed well beyond such a limit. Above a certain limit of strain energy level, linear viscoelastic deformation is no longer possible and the plastic deformation takes over. However, because a polymer typically manifests a spectrum of relaxation times, its behavior is a combination of viscoelastic and plastic behaviors. The ratio between the two behaviors depend on the rate of deformation, and can be precisely predicted from the linear viscoelastic relaxation spectrum. The combined behavior is termed viscoplasticity, and it applies to a wide range of practically important mechanical behaviors from the flow of the melt to the yield and fracture of glassy and crystalline solids.

Keywords: conformational relaxation, cooperativity, excess entropy, free volume, glass transition, viscoelasticity, viscoplasticity

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1. What do we mean by the 'relaxation process'?

1.1. On the experimental scale

When a mechanical test specimen is made to deform, work is done on each point in the body by the applied force over the distance that each point has traveled. Let us consider, for the sake of simplicity, that the material behaves as a perfectly elastic body, i.e., all of the work done on it is returnable when the application of the force is terminated. The stress is a force experienced within the body expressed as the force per unit area. The strain is the relative deformation experienced by the body expressed as the deformed distance per unit length. The integral of the stress over the strain is the mechanical work per unit volume, and in the elastic body it is equal to the strain energy density. At any point within the body, the type and the value of a stress depend on the plane of cross section. For example, a cross section perpendicular to the direction of the applied tension is under a uniform tensile stress without any shear component present. However, another cross section cutting the same body in a 45° angle to the direction of the tensile force would be under the shear stress with no tensile components present. In an arbitrarily chosen cross sectional plane, there are 9 components of stresses and strains, but the stored elastic strain energy is uniquely determined by a combination of the geometry and the boundary conditions for the applied forces. In thermodynamic terms, the stored elastic energy is a form of Gibbs free energy.

While a typical solid material behaves as an elastic body, a typical fluid flows as soon as the stress is applied. In fluids, the work of deformation is immediately dissipated and transformed into heat. Polymers exhibit viscoelastic behavior, a combination of the elastic and dissipative behaviors. Among the simple viscoelastic experimental methods is the stress relaxation test, in which the test specimen is suddenly deformed at onset and maintained throughout. The stress will rise initially, and will decay as the elastically stored energy will diminish as a consequence of the fluid-like dissipation mechanism. The time-dependent stress divided by the imposed (constant) strain is the relaxation modulus. In another simple experiment called the creep experiment, the stress is maintained constant while the strain continues to increase with time. To treat the viscoelastic behavior with an empirical and intuitive model for the continuum, often a combination of springs and dashpots are invoked for the elastic and dissipative responses, respectively. The relaxation modulus with a single relaxation time can be modeled by a spring and a dashpot in series (the Maxwell model), but this model would behave as a viscous fluid under a constant stress as in a creep experiment. A parallel combination of a spring and a dashpot (Voigt model) predicts the infinite initial stress in the relaxation experiment, while predicting a finite strain after infinite time of testing. Sadly, no combina-

tion of any numbers of springs and dashpots, including degenerate elements, e.g., dashpots alone, can describe a self-consistent linear viscoelastic behavior. This can be shown quite explicitly by requiring for the complex dynamic mechanical modulus to be equal to the reciprocal of the complex dynamic compliance, the condition that leads to a very important but not widely acknowledged relationship between the relaxation modulus, $G(t)$, and the creep compliance, $J(t)$:

$$\int_0^t G(t-x)J(x)dx = t \quad (1)$$

which must be true at any time t . The variable x in this equation is the so-called dummy variable of integration that sweeps from 0 to the real time t for the integral. No combination of springs and dashpots can satisfy Eq. (1), and so they disqualify as a model for linear viscoelasticity. An important corollary to this equation is that the form of the creep compliance is mathematically uniquely determined if the relaxation modulus is known, but the two as a rule are not reciprocals of each other, i.e.,

$$G(t)J(t) \neq 1 \quad (2)$$

It is customary to define the relaxation time as the time constant of a 'reaction' process in which the stress is allowed to decay under the rigidly held deformation, i.e.,

$$\frac{1}{\tau} = -\frac{1}{\sigma} \frac{d\sigma}{dt} \quad (3)$$

where σ is the time dependent stress at a given strain. Dividing σ by the experimental (time-independent) strain will obtain the relaxation modulus, and the solution of Eq. (3) is given by the formula:

$$G(t) = G_0 \exp\left(-\frac{t}{\tau}\right) \quad (4)$$

However, real experimental data seldom fit a simple equation such as Eq. (4). Instead, the stress relaxes over many decades gradually, as if the time constant τ is continuously shifting as time passes. One way of describing this type of behavior is to assume that there are not one but many relaxation mechanisms with varying degrees of intensity operating simultaneously within the body, so the overall modulus could be expressed in terms of a distribution, or a spectrum, of relaxation times, i.e.,

$$G(t) = \sum_i G_i \exp\left(-\frac{t}{\tau_i}\right) \quad (5)$$

In this equation, the relaxation modulus is assumed to consist of the sum of individually relaxing elements each with the relaxation time τ_i and the relative intensity G_i . It is important to note that Eq. (5) does not necessarily mean that the strains in a mechanically heterogeneous domains are equal and uniform. Nor does it require that the stress be the sum of $G_i \exp(-t/\tau_i)$ times the macroscopic (experimental) strain. Distributions of stresses and strains would have to be obtained usually through numerical computation. However, the strain energy tends to quickly become homogeneous. This is why Eq. (5) is found to be a good empirical formula in surprisingly many examples of heterogeneous systems, including such systems as semicrystalline polymers and polymer alloys [1].

A body of a homogeneous polymer consists of many relaxing units which can cooperatively relax as a larger relaxing unit with a longer relaxation time. Such a concept of multimode relaxation can be realistically modeled by considering the cooperative modes of relaxation among the smallest units of relaxation. The smallest unit of relaxation will be later described in molecular terms. Cooperativity is needed when these units are crowded into a dense space such that each unit can relax only if its neighbors can relax together. The probability for each unit to relax becomes smaller when such cooperation from a greater number of neighbors becomes necessary in a denser environment. In order for these units to synchronously relax, the cooperative relaxation time of n such individual units together must be the n -th power of each individual relaxation time, or τ^n , where τ is the relaxation time of each unit if it were able to relax independently. According to this model of cooperative relaxation, a domain consisting of n individual units will be able to exhibit n different modes of relaxation, exhibiting a spectrum of relaxation times starting with τ and all the way up to τ^n , the latter being the strongest, corresponding to the frequency for the loss maximum.

1.2. On the molecular scale

In the above discussion for the relaxation process in the continuum, a reference was made to a relaxing unit as the smallest unit that would exhibit the shortest relaxation time. Polymer molecules can undergo many different types of deformations involving many different size domains, but all kinds of changes in shapes can be interpreted in terms of the changes in their molecular conformations. The smallest unit that would contribute to the changes in the conformation of a polymer chain is termed a conformer, which Wunderlich chose to call a flexible bead [2]. In a vinyl polymer, a monomeric unit would consist of two conformers at least, and if endowed with a flexible side group the number may be greater. A rule for identifying individual conformers in a particular polymer will be introduced later in this article. The immediate question now is to ask what is the mechanical relaxation for one conformer and how does that relate to the macroscopic relaxation that can be measured in the laboratory?

The results of a molecular simulation study on deformation of atactic polypropylene, and later on other polymers as well, by Theodorou and Suter

[3], are very important. According to this study, the rotation of the main chain bond represents the softest degree of freedom and it is the overwhelmingly predominant mode of deformation. The relaxation of a conformer would involve mostly a bond rotation from one stable energy state to another under the influence of a stress field. It is not necessary to assume that the relaxation is always from the gauche to the trans conformation, although it is expected to be more prevalent in that direction than in the opposite direction from the gauche to trans conformation.

In order to rotate from one stable conformation to another, the bond between two conformers will have to be strained, causing the angular potential energy to rise. Abé, Jernigan and Flory [4] have shown that the inner bonds between methylene units in a butane molecule will have to pass through the energy maximum of about 3 to 3.5 kcal mol⁻¹ of bonds. A reaction process, in this case the relaxation of the conformational change, is controlled by the relative abundance (or scarcity) of those bonds which are in the highest energy state, as it makes up the bottleneck for the conformer to transit from one state to another. The methodology of calculating the process rate by invoking the statistical probability for the most scarce species in the path is the same as the classical methodology of calculating the nucleation rate from the statistical probability for the most scarce, critical size nuclei. The Boltzmann-Maxwell equipartition theory maintains that the population of a microstate is proportional to $\exp(-E/kT)$, where E is the energy, k the Boltzmann constant and T the absolute temperature. The energy difference between the stable conformation and the maximum twist energy of the bond between the two interior methylene units constitutes the energy for determining the relative abundance of the highest and least abundant energy state, and this highest energy state in the reaction path is called the activated state, and the energy level, in this case 3~3.5 kcal, is the activation energy or the energy barrier for the conformer relaxation. The classical rate constant, k , is formulated by the equation:

$$k = -\frac{1}{N} \frac{dN}{dt} = k^* \exp\left(-\frac{\Delta\mu}{kT}\right) \quad (6)$$

where N is the number of those conformers in the ground state. $\Delta\mu$ is the energy difference between the activated and ground states. The term k^* is the efficiency term which depends on the intensity of libration for the bonds in question.

The relaxation time τ is defined as the time constant for this 'reaction', and is the reciprocal of the rate constant k . The 'intensity' of the relaxation process is proportional to the relaxation modulus, hence

$$\frac{1}{\tau} = -\frac{1}{G(t)} \frac{dG(t)}{dt} \quad (7)$$

and Eq. (4) is a solution of Eq. (7).

At a high enough temperature, the rotational kinetic energy is so high that the reaction rate calculated from Eq. (6) reaches or exceeds the librational frequency, i.e., the most vibrating bonds can pass through the activated state back and forth. In such a state, the energy barrier is small enough in comparison to kT and the relaxation process as we know it no longer occurs. The critical reaction rate k^* is such a limiting frequency (in radians/s) and the critical relaxation time τ^* in seconds is set as the reciprocal of k^* . The critical temperature T^* , as will be empirically derived in the discussion to follow, turns out to be ca. 500°C, which is higher than the degradation temperature of most polymers, meaning that polymer chains will be destroyed before T^* is reached. The actual estimate for the value of τ^* turns out to be about 2×10^{-12} s or 2 picoseconds at 500°C, and about a decade longer at 100°C and 7×10^{-11} s at 25°C.

2. Intermolecular cooperativity

2.1 Free volume and excess entropy in the condensed state

The simple model of molecular dynamics has been presented above for the relaxation of polymer molecules as the conformer bond angles change from one position to another in presence of the force field [5]. The relaxation time based on this model, however, is in the picoseconds range, a far cry from the range of our interest. Moreover, this simple model involves a constant energy barrier, leading to an Arrhenius type dependence on temperature for the relaxation time, whereas the real polymers (and many nonpolymeric liquids) exhibit the Vogel-type dependence [6] characterized by the ever-increasing apparent activation energy as the temperature is decreased. Thirdly, the model predicts that all polymers would exhibit the same T_g . And finally, this model is a single relaxation time model, while real polymers exhibit a broad spectrum of relaxation times. The incorporation of the concept of intermolecular cooperativity among the conformers will correct all of the above shortcomings.

For polymer molecules, the complete rotational relaxation of a conformer without the interference from neighboring conformers would be possible at the temperature we define as T^* (ignoring for convenience a possibility of chemical degradation at such a temperature, which in real polymers would take place even in the inert atmosphere). At a progressively lower temperature below this T^* , the density increases, accompanied by a decrease in the intermolecular free space, and the rotational relaxation by a conformer becomes increasingly frustrated by the interfering neighbors, to such a degree that only through a well synchronized simultaneous relaxation with those neighbors, can the conformer undergo a conformational change that would permit to dissipate the elastically imposed energy. The probability of such cooperative relaxation among z conformers can be calculated by multiplying the probability of relaxation for each

conformer z times, hence the cooperative relaxation of z conformers together would be τ^z . In this model, the domain size, z , becomes greater as the temperature is decreased.

To compare the relaxation time of a conformer with and without the neighbors' interference, the two equations are shown below. The first is for the relaxation without the interference, i.e., no cooperativity is considered. This is an Arrhenius equation with the activation energy of $\Delta\mu$ cal mol⁻¹ of conformer,

$$\ln\tau = \ln\tau^* + \Delta\mu\left(\frac{1}{RT} - \frac{1}{RT^*}\right) \quad (8)$$

where T is the temperature, τ is the relaxation time, R the universal gas constant, and the asterisk $*$ is referred to the thermodynamic condition of the high temperature high frequency limit described above. When the cooperativity is introduced, the domain size, z , is determined by the state of intermolecular free space, or the free volume. The domain size z is a unique function of pressure and temperature unless, as in the glassy state, the thermodynamic equilibrium is broken. For the cooperative relaxation, then, we obtain

$$\ln\tau = \ln\tau^* + \Delta\mu\left(\frac{z}{RT} - \frac{1}{RT^*}\right) \quad (9)$$

Even though the difference between the above two equations seems insignificant at a first glance, they are really very different. Eq. (9) is no longer an Arrhenius equation because the domain size, z , is a function of temperature, growing larger at lower temperatures. The apparent activation energy increases at lower temperatures. The apparent activation energy is obtained from the slope of a straight line drawn between the points $(1/RT^*, \ln\tau^*)$ and $(1/RT, \ln\tau)$ in the plot for $\ln\tau$ vs. $1/RT$; it is not the changing slope of the plot of $\ln\tau$ vs. $1/RT$. The latter is $d(\ln\tau)/d(1/RT)$, which includes the values of dz/dT , and as a result an unreasonably large value in the range of hundreds of kcal's will be obtained.

The gauche conformation, being a higher energy state, has a larger average volume than the trans conformation. The population of a higher energy state will decrease with a decreasing temperature, while the population in the lower energy state will increase. If thermodynamic equilibrium can be maintained down to 0 K without 'freezing up' into the glassy state, the volume in excess of the lowest energy state will decrease to 0 at 0 K. In this context, the excess volume at some temperature T K would be T/T^* times the excess volume at T^* . No cooperativity has been considered, so the domain size is 1 at any temperature $0 < T < T^*$.

In real polymer systems, as the temperature is lowered, the domain size z increases and the relaxation time τ^z increases, until even the cooperative relaxation becomes so difficult that the system is no longer able to continue to densify with a typical dV/dT for the liquid, ca. 10^{-3} deg⁻¹. The V - T plot will depart

from that of the liquidus line with a solid like expansion coefficient, ca. 10^{-4} deg^{-1} . The new state of nonequilibrium is of course the well known glassy state. It is well known from the work of many investigators on physical aging phenomena [7] of the glassy state that the fictive temperature T_f depends on how long the glassy state has been held in a nonequilibrium state; the longer the aging, the closer the value of T_f to the aging temperature, but that waiting for an infinite period at below some limiting temperature will not lead to $T_f = T$, where T is well above 0 K. This limiting temperature, or the low temperature limit for the liquid-like behavior in equilibrium, is the Kauzman temperature [8], or the temperature that was extrapolated along the equilibrium liquidus line for the entropy to reach zero. It is about 50°C below the experimentally determined T_g by DSC. The C_2^g parameter in the WLF equation [9] is supposed to be 52°C , and this parameter corresponds to the difference between T_g and the Kauzman temperature. We believe that the Kauzman's zero entropy temperature is well above 0 K because the increasingly frustrated tendency to reach equilibrium results in the greater rate of entropy decrease than the rotational isomeric calculation would predict. If this is true, then at the zero entropy temperature somewhere 50°C below T_g , there would be still a substantial number of gauche conformers present, even though the excess entropy is extrapolated to be zero. Monnerie *et al.* [10] have shown for polystyrene that only 30% are in the trans conformation at T_g . In summary, if the aging is allowed at above the Kauzman temperature, thermodynamic equilibrium is eventually reached, and the fictive temperature will be equal to the aging temperature. If the aging is allowed at the Kauzman temperature, it will take an infinite time to reach equilibrium. The domain size will be infinite in this case. If aging is allowed at below the Kauzman temperature, the glassy state will never reach equilibrium.

At the Kauzman temperature, which we define as T_0 at this point, the equilibrium excess volume is zero, and the equilibrium relaxation time is infinity. There is a thermodynamic correspondence between the conformational state at 0 K obtained by the RIS (rotational isomeric systems) calculation and the thermodynamic state in the real liquids in equilibrium at T_0 K. Assuming the domain size z to be inversely proportional to the excess volume, scaled from T^* to T_0 instead of from T^* to 0 K, or we obtain:

$$z = \frac{T}{T^*} \cdot \frac{T^* - T_0}{T - T_0} \quad (10)$$

Substitution of Eq. (10) into Eq. (9) will obtain:

$$\ln \tau = \ln \tau^* + \frac{\Delta \mu}{R} \cdot \frac{T^* - T_0}{T^*} \cdot \left(\frac{1}{T - T_0} - \frac{1}{T^* - T_0} \right) \quad (11)$$

and by defining $\Delta \mu^*$ to be

$$\Delta\mu^* = \Delta\mu \cdot \frac{T^* - T_0}{T^*} \quad (12)$$

The Vogel equation is obtained:

$$\ln\tau = \ln\tau^* + \frac{\Delta\mu^*}{R} \cdot \left(\frac{1}{T - T_0} - \frac{1}{T^* - T_0} \right) \quad (13)$$

As it is well known, the Doolittle's free volume equation [11] calls for $\ln\tau$ to be inversely proportional to the fractional free volume f . It is another form of describing the temperature dependence of the relaxation time. The Vogel equation can be obtained from the Doolittle equation by assuming the fractional free volume $f = \alpha_f(T - T_0)$, where α_f is the thermal expansion coefficient of the fractional free volume, and setting it to be equal to $R/\Delta\mu^*$. The WLF equation, an empirical formula well known to polymer scientists, is another form of the free volume equation with two empirical parameters that can be evaluated in terms of α_f and T_0 . Therefore, it is another form of the Vogel equation. The meaning of the Doolittle free volume is slightly different from our excess volume that is associated with the higher energy conformations. The Doolittle formula predicts the relaxation time as the unique function of free volume, and the entire temperature dependence of τ is ascribed to the free volume. Our excess volume is different in that even at the same level of excess volume (and z), the relaxation time still depends on the temperature. Our excess volume enables us to successfully predict the relaxation behavior in the nonequilibrium state, where the volume is not uniquely dependent on the temperature. The Doolittle formula does not agree with those aging data taken over a wide range in temperature and aging time.

2.2. Excess entropy that drops faster than the conformational entropy

Another way of deriving the Vogel equation, Eq. (13), is to go through the calculation of the excess entropy. Let us assume for the moment that each conformer can take C_1 different conformations. The conformational entropy would be $N_A \ln C_1$, where N_A is Avogadro's number. If all z conformers in each domain are 'locked' together, however, the relaxation process would be z -th power times more difficult, and the effective conformational entropy would be $N_A/z \cdot \ln C_1$. In other words, the domain size z is inversely proportional to the effective conformational entropy, and substituting this into Eq. (9) we obtain:

$$\ln\tau = \ln\tau^* + \Delta\mu \left(\frac{s_c/S_x}{RT} - \frac{1}{RT^*} \right) \quad (14)$$

where s_c is the RIS conformational entropy that could relax independent of neighboring conformers, and S_x is the effective excess entropy in the coopera-

tivity environment. Equation (14) is essentially the equation introduced by Adam and Gibbs [12], though their implied cooperativity is among the conformers in the same chain and their S_x is simply called the conformational entropy. With the argument advanced for the temperature dependence of z above, the temperature dependence of S_x/s_c can be derived:

$$\frac{s_c}{S_x} = \frac{T}{T^*} \cdot \frac{T^* - T_0}{T - T_0} \quad (15)$$

which is substituted into Eq. (14) to obtain the Vogel Equation, Eq. (13).

Researchers familiar with thermal analysis of polymers are well acquainted with the important quantity ΔC_p , that is the difference between the liquid-like specific heat above T_g and the solid-like specific heat below T_g . This quantity is really related to S_x above, and not s_c . Thus,

$$S_x = \int_{T_0}^T \frac{\Delta C_p}{T} dT \quad (16)$$

is true above T_0 in the equilibrium state. Below T_0 , S_x takes up whatever the value it was at T_g , but the equilibrium value of S_x is zero. S_x is compared to the (RIS) conformational entropy, s_c , which is given by the formula:

$$s_c = \int_0^T \frac{c_p}{T} dT \quad (17)$$

where c_p is the specific heat associated with the conformational enthalpy. While s_c takes from 0 K to T^* K to reach the critical entropy at T^* , S_x arrives there starting from T_0 . A scaling scheme setting a relation:

$$\Delta C_p = \frac{T^*}{T^* - T_0} c_p \quad (18)$$

is true for all T 's from T_0 to T^* . Thus Eq. (12) is no longer a purely empirical equation at this point but it is now supported by a reasonable physical meaning, i.e., that $\Delta\mu^*$ is the rotational energy barrier calculated on the basis of the methylene bond rotation of butane, but $\Delta\mu$ is the real value which is greater than $\Delta\mu^*$ because of the added requirements for the intermolecular cooperativity. Thus $\Delta\mu^*$ and not $\Delta\mu$, is a universal number common to many polymers. $\Delta\mu$, on the other hand, depends on the kind of polymer, and higher the T_g , the greater is the value of $\Delta\mu$. The same statement can be made on ΔC_p per mol of conformer, but not per gram of polymer. Because the conformer sizes vary, the mass of a mol of conformers vary. A discussion on the relationship between ΔC_p per gram of polymer vs. T_g will have to wait until the relationship between the conformer size and T_g is discussed in the subsequent section.

In Appendix I, we have shown that the conformational Gibbs free energy Ψ is much smaller than the excess enthalpy, i.e., $\Psi_X \ll H_X$, and, therefore, $\Psi_X \ll TS_X$ and $H_X \cong TS_X$. This is an important conclusion because it allows us to apply the same scaling factor, $T^*/(T^*-T_0)$, to the calculation of the excess enthalpy, entropy, ΔC_p , $\Delta\mu$, etc. in the cooperativity regime from the conformational (RIS) enthalpy, entropy, c_p , $\Delta\mu^*$, etc. This scaling scheme is crucial in predicting the glass transition temperature and related physical parameters, as we will be showing in the following section, while adding a meaning in physics to the equations such as Eqs (12, 15, 18) and now, the equation for the excess enthalpy as well:

$$H_x = \frac{T^*}{T^* - T_0} h_c \quad (19)$$

where H_x is the excess enthalpy and h_c is the conformational enthalpy corresponding to the RIS type calculation without accounting for the cooperativity aspect. The excess enthalpy H_x is an important thermodynamic quantity to the researchers familiar with thermal analysis, because the 'heat flow' in DSC is a direct measure of ΔC_p , which is the derivative, dH_x/dT . It follows that h_c is also nearly equal to Ts_c , and thus the temperature dependence of s_c is the same as that of c_p .

To summarize, at T^* ($\cong 500^\circ\text{C}$) all conformers can relax without cooperation from the neighbors, but as the temperature is lowered the excess enthalpy and entropy decrease faster than as predicted from the conformational probability by the factor z , the domain size. This increase in their temperature coefficients depends on the structure of a conformer, and can be scaled by the factor T^*-T_0 in place of T^* .

3. Chemical structure and T_g

All of the discussions up to this point have been based on a mol, rather than a gram, of conformers. It makes a great difference which unit is being taken because the molecular weight of conformers differs greatly. As a certain generalization can be made on the law on the molecular size dependence of the entropy of vaporization, our excess entropy depends on the molecular size of the conformer. Considering the liquid state to be composed of the van der Waals volume and the excess volume, the excess volume in one mol of a conformer can be compared with the volume of ideal gas with N_A massless molecules. (N_A is Avogadro's number.) The configurational entropy of one mol of ideal gas is equal to $k \ln V$, and in our case this V is equal to the excess volume. If we assume the fractional excess volume to be proportional to the molecular volume, we arrive at the proportionality between the excess entropy and $\ln M_c/\rho^*$, where M_c is the molecular weight of the conformer and ρ^* is the density extrapolated to T^* . The 'hole energy', our excess enthalpy, is also proportional to $\ln M_c/\rho^*$. Since

ρ^* does not vary much (at least not nearly as much as M_c) from polymer to polymer, we expect that:

$$H_x \propto \ln M_c \quad (20)$$

and that

$$\frac{T^*}{T^* - T_o} \propto \ln M_c \quad (21)$$

i.e., the smaller the conformer, the lower the Kauzman temperature T_o . We can extrapolate this principle to the smallest possible conformer with its $T_o=0$ K, i.e., the domain size is 1 all the way down to 0 K. We call this molecular weight M_o . If we can empirically determine M_o , then Eq. (21) can be replaced by the really useful equation for predicting T_o from the conformer size:

$$\frac{T^*}{T^* - T_o} = \frac{\ln M_c}{\ln M_o} \quad (22)$$

and, since T_o is about 50 K below T_g , we now have obtained a formula for predicting T_g from the chemical formula of a polymer.

In Tables 1 and 2 the conformer sizes of various polymers are compared with the experimental values of T_g . Assuming that T_g to be 50°C above the Kauzman temperature T_o , the best numbers for $\ln M_o$ and T^* in Eq. (22) were sought. It turns out that $T^*=773$ K and $\ln M_c=2.26$ are good choice, which would mean the last column termed 'Const' should be 1750.

The column titled ' M_c ' denotes the average conformer size and the value is entered as the molecular weight of the repeat unit divided by the number of conformers per repeat unit, e.g., 54/3 for polymer 3 means its repeat unit has the molecular weight of 54, and consists of 3 conformers. A conformer is a unit whose rotation will make a difference in the chain conformation. For vinyl polymers (polymers 1-14), a conformer can be a methylene unit or a methylene unit with a hydrogen substituted by a group. M_c is a number average molecular weight of all conformers that make up a polymer. A carbon atom with a rigid substituent group must rotate together as a unit, i.e., as one conformer. Thus the polypropylene (polymer 5) repeat unit consists of 2 conformers, not 3. 1,4-polybutadiene (polymer 3) consists of 3 conformers: two methylene units and one C=C unit. However, 1,2-polybutadiene (polymer 4) consists of two conformers, one methylene unit and the other a carbon atom with a double bonded ethylenic pendant. The latter having a much larger conformer than the former, exhibits a 65°C higher T_g . A similar consideration on comparing gutta percha (polymer 7) and *cis*-polyisoprene (polymer 8), both with the repeat units with the same molecular weight, leads to the T_g s separated by 59°C. Discussion of T_g for polyethylene will be postponed until after some aspects of the low-temperature relaxation has been discussed later.

Table 1 Conformer size and T_g aliphatic polymers

	Polymer	M_c	T_g	$T^* - T_0$	$\ln M_c$	Const.
1	Polyethylene (-C- as a unit)	14/1	-110	660	2.64	1742
2	Polyethylene (mix of -C- and -C-C-)	42/2	-25	580	3.02	1751
3	1,4-Poly(butadiene)	54/3	-55	605	2.85	1750
4	1,2-Poly(butadiene)	54/2	20	530	3.30	1749
5	Polypropylene	42/2	-30	580	3.04	1765
6	Polyisobutylene	56/3.5	-74	624	2.77	1728
7	Gutta percha	68/3	-10	560	3.12	1748
8	cis-Polyisoprene	68/4	-69	619	2.83	1753
9	Poly(4-methyl pentene)	85/3	29	521	3.34	1742
10	Polyvinyl chloride*	62/2	90	460	3.43	1577
11	Polystyrene	108/2	100	450	3.93	1769
12	Poly(α -methyl styrene)	119/1	180	370	4.78	1768
13	Poly(trifluoro-chloroethylene)	118/3	79	471	3.67	1728
14	Polyvinyl acetate	86/3	29	521	3.36	1748
15	VDCN-vinyl acetate**	164/2	179	371	4.41	1636
16	VDCN-vinyl formate	150/2	152	398	4.32	1718
17	VDCN-vinyl propionate	178/2	176	374	4.49	1678
18	VDCN-vinyl benzoate	225/2	186	364	4.72	1719
19	VDCN-methyl methacrylate	178/2	145	405	4.49	1818
20	VDCN-vinyl acetyl chloride	199/2	167	383	4.60	1761
21	VDCN-vinyl pivalate	206/2	171	379	4.63	1757
22	Polyoxymethylene	30/2	-73	623	2.71	1687
23	Polyoxyethylene	44/3	-67	617	2.69	1657
24	Polyoxypropylene	58/4	-75	625	2.67	1671
25	Polyoxybutylene	72/5	-88	638	2.67	1701
26	Polyvinylmethyl ether	58/3	-22	572	2.96	1694
27	Polyvinylethyl ether	72/4	-33	583	2.89	1685
28	Polyvinylisopropyl ether	86/4	-12	562	3.07	1724
29	Polyvinylbutyl ether	100/6	-56	606	2.81	1704
30	Polyvinylhexyl ether	128/8	-74	624	2.77	1730
31	Polymethyl methacrylate	100/2	105	445	3.91	1741
32	Isotactic PMMA	100/3	46	504	3.51	1767
33	Polyethyl methacrylate	114/3	65	485	3.64	1764
34	Polypropyl methacrylate	128/4	35	515	3.47	1784
35	Polymethyl acrylate	86/4	9	541	3.07	1660
36	Poly(<i>t</i> -butyl acrylate)	132/5	31	519	3.27	1698

Table 2 Conformer size and T_g aromatic polymers

	Polymer	M_c	T_g	$T^* - T_0$	$\ln M_c$	Const.
37	Polyphenylene sulfide	108/2	110	440	3.99	1755
38	Polyphenylene oxide	92/2	90	460	3.83	1761
39	Polyethyleneterephthalate	182/5	64	486	3.59	1746
40	Polycarbonate	254/3	147	403	4.44	1788
41	Polyether etherketone	288/3	158	392	4.56	1790
42	Polysulfone	444/4	187	363	4.71	
43	Polyether imide	596/4	200	350	5.00	1750
44	Polyimide (PMDA)	207/1	222	328	5.33	1749
45	Polyether sulfone	232/1	225	325	5.45	1770
46	Poly(tri-methyl phenylene ether)	172/1	210	340	5.15	1750
47	Kevlar	242/1	235	315	5.49	1729
48	B + F**	315/2.5	187	363	4.84	1755
49	C + F	376/2	210	340	5.24	1780
50	A + D	358/2.5	195	355	4.96	1762
51	B + D	420/1.5	243	307	5.63	1730
52	C + D	480/3	310	240	7.29	1750
53	A + E	434/5	148	402	4.46	1794
54	B + E	496/4.5	172	378	4.70	1778
55	C + E	540/3.5	205	345	5.04	1730
56	A + F	254/3	147	403	4.44	1788

** For the copolymers from 48 to 56.

A: bisphenol A

B: bisphenol AP

C: fluorene

D: terephthalate + isophthalate 50/50

E: 2,2'(m-biphenyl carboxylate)

F: carboxylate

Ph: phenyl group, bPA: bis-phenol A, slf: aromatic sulfone, Im: an imide group = 1 conformer; -O[bPA]O- = 2 conformers, and -OPh- = 1 conformer;

* For PVC, if the density is considered 10% greater than others because of chlorine, the value of the constant becomes 1750.

A repeat unit (the monomeric unit) in many vinyl polymers consists of two conformers. One is the methylene unit. The other is a carbon atom in the main chain plus a rigid substituent group. This carbon atom, being trifunctional, is not considered to be one conformer by itself but it is part of a large conformer in combination with the substituent group, that can participate in a conformational change of the main chain. Sometimes a substituent group itself is capable of conformational changes, such as the polyvinyl acetate (polymer 14) monomer units. Conformational changes within the acetate group are necessary in or-

der to rotate the bonds in the main chain because of the dense packing of chain segments. In this case, the conformers are three: $-\text{CH}_2-$, $-\text{CH}(-(\text{C}=\text{O})-)-$, and $-\text{O}-\text{CH}_3$ groups. The second conformer is a little difficult to see, but if one adheres to the rule that a trifunctional carbon cannot be a conformer by itself, it clearly is the structure. An independent check for the number of conformers in a repeat unit can be made from the data on its β transition. The β transition is a local mode relaxation process and is usually observed below the glass transition temperature, although the glassy environment is not a necessary condition for this to be observed. The glassy state is formed as the conformers become trapped by the neighbors, as a consequence of the increased packing density after the cooling. For polymers with conformers of mixed kinds, the largest conformer is the easiest to become pinned by the neighbors. Relaxation of all of these conformers, large and small, is possible in the glassy environment if all rotate simultaneously. The β transition as presented here involves intramolecular cooperation among conformers in the same chain molecule. The domain of intramolecular cooperativity is between the two nearest largest conformers along the chain, i.e., one complete repeat unit, typically. Unlike an intermolecular cooperative domain, this domain size remains fixed when the temperature is changed. The activation energy is constant and it is the activation energy of one bond, $\Delta\mu^*$, times the number of conformers in the repeat unit, z_β . The equation for the characteristic relaxation time for the β process, τ_β , is obtained:

$$\ln\tau_\beta = \ln\tau^* + \frac{\Delta\mu^*}{R} \cdot \left(\frac{z_\beta}{T} - \frac{z_\beta}{T^*} \right) \quad (23)$$

The β process in polyvinyl acetate exhibits a constant activation energy of 10 kcal over a wide temperature-frequency range. $\Delta\mu^*$ is 3.4 kcal for this polymer, and from Eq. (23) one obtains z_β of 3. We had estimated the number of conformers per repeat unit in polyvinyl acetate to be 3 from our analysis of the average size of conformers that would result in T_g of 29°C. At a high frequency and high temperature, the intermolecular cooperative relaxation process (α_n) crosses with the β process. Note an important difference in the T^* term for Eq. (21) and Eq. (13). The two formula will not meet at T^* ! This is because for the α process, it is a single conformer rotating at T^* , whereas for the β process it is z_β conformers rotating cooperatively in the same chain. The latter frequency being the slower, the two processes will merge at some temperature below T^* . Beyond the point where the α and β frequencies merge, the β process is the slower of the two and the β barrier looms as the main barrier, as it takes over as the rate controlling process. In polyvinyl acetate, only the β peak is observed above this temperature and frequency. The temperature dependence of the α and β processes for polyvinyl acetate are shown with a plot of the frequency for the dielectric loss maximum in Fig. 1 for the temperature range of the entire data points, and in Fig. 2 the crucial detail of the range where the two processes merge is shown. The lines have been calculated from Eqs 13 and 21.

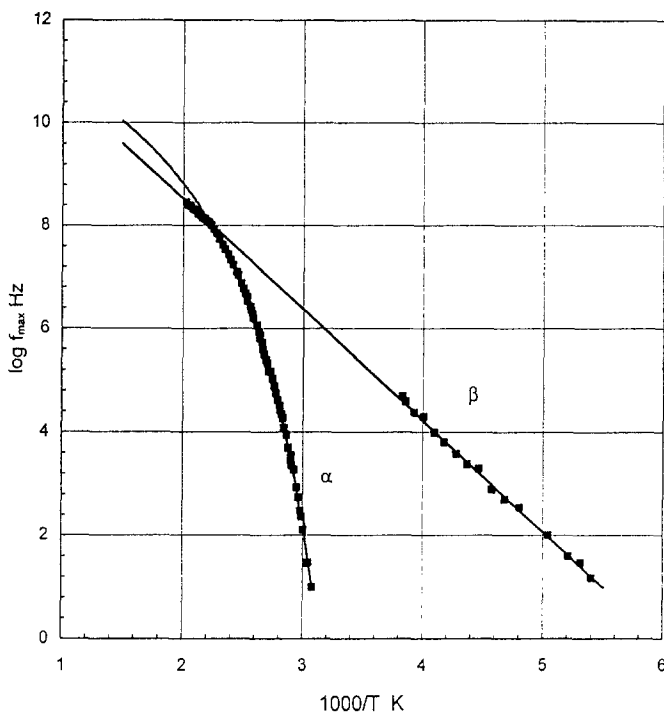


Fig. 1 The α and β relaxation processes in polyvinyl acetate; a plot of the frequency for dielectric loss maximum vs. temperature. The lines are calculated Vogel and Arrhenius plots with parameters as mentioned in the text

Even though the conformers in polyethylene are the simple methylene units, or perhaps because of their simple structure, many possible mechanisms of relaxation have been proposed, and they remain controversial. A prominent loss peak is observed at -110°C in both linear and branched polyethylenes and this relaxation is commonly known as the γ transition. The γ relaxation process has often been attributed to the local motion resembling a rotating crank shaft, advocating an intra-, and not inter-, molecular cooperativity. The supporters of this view often have advocated the assignment of the β transition at -25°C to be the (intermolecular cooperative) glass transition in the amorphous region. According to our model, the intramolecular cooperative relaxation involving two bonds simultaneously would bring the transition temperature to -110°C . In the crank shaft motion, for example, such a possibility exists. This would involve two methylene units as one conformer in the glass transition, and in fact a conformer with $M_C=28$ will obtain T_g of -25°C according to Eq. (22), which is the β temperature! There are a number of polymers with larger conformers than one methylene unit, such as polyisoprene, polyisobutylene and many other commercial rubber compounds, that exhibit T_g at much lower temperatures than -25°C , the fact that also supports that the β transition in polyethylene cannot be

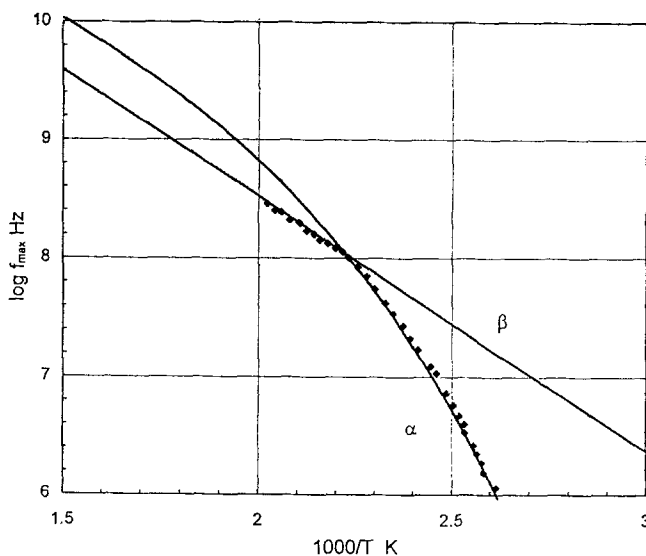


Fig. 2 The detail of Fig. 1 in the vicinity of the temperature and frequency that α and β processes merge, above which point the intramolecular cooperative β process takes over

the glass transition of the methylene units, but it is more likely to be the T_g for two methylene units acting as one conformer. Utilizing Eq. (22), T_g of -110°C is obtained for a conformer consisting of one methylene unit. This complicated picture is supported from the dielectric data [13] that the apparent activation energy for the -110°C transition of linear polyethylene is much greater than that of branched polyethylene. We believe that the confusion arises from the fact that T_g of linear polyethylene and the local relaxation of crank shaft rotation (intramolecular cooperative relaxation) overlap in the region of 1 kHz and -100°C . To reiterate, methylene units can relax through the intramolecular cooperative motion (crank shaft rotation), and at the temperature-time regime of the γ transition, this and the intermolecular cooperative (α_a) relaxation involving the methylene units in the different chain compete. Here again, above the frequency and temperature where the α and β processes merge, the β process must take over.

The conformer dangling at the end of a polymer chain has a higher energy than those in the middle of the chain [4]. A list of heats of fusion, estimated by Bunn [14], that includes species some of which are in the chain and some are at the end, show that those at the chain end have much higher values. Thus the melting point of the same conformer is lower if placed at end, and its T_g is expected to be lower. We believe this to be the primary reason for the low T_g for polymers with very low molecular weight. The chain ends act as if they are solvent molecules in bringing down the overall T_g . A short branch attached to the chain molecule contains a high concentration of the end conformer, whereas with a longer chain the effect becomes less, just as the high concentration of the

ends in a low molecular weight specimens resulted in the lower T_g of the whole polymer. An increase in the number of smaller conformers in a branch will decrease T_g by decreasing the overall average conformer size, reducing the effect of one large conformer at the trifunctional carbon atom. This is exemplified in examples 26–30, a series of polyvinyl alkylethers. Starting with T_g of -22°C for methyl ether, it goes down to -74°C for hexyl ether. With simple alkyl branch, T_g does not decrease indefinitely with increasing molecular weight. At about 10 carbon atoms, T_g levels off. A presence of conformers other than C–C bonds would have to be analyzed with care. The ether linkage, for example, is known to have much smaller energy barrier, $\Delta\mu^*$, ca. 1.5 kcal. Because we are averaging $\Delta\mu^*$ times z , a smaller $\Delta\mu^*$ of the oxygen link should show a smaller effective conformer size. A smaller conformer size assignment is also taken for the end group; in this case the effective z being smaller. Looking at a series of alkyl ethers, 22–25, at the first glance, they seem to conform to Eq. (22) without requiring a modification. However, one notices that the constants at the last column are consistently lower than 1750. In fact, the value of 1750 will be obtained if we change the numbers for M_C for Polymer 22 to 25 to the following: 30/1.8, 44/2.6, 58/3.5, 72/4.6. Note the conformer numbers have been reduced by ~ 0.4 , which would imply that $\Delta\mu^*$ for the ether link is almost half that of one C–C link. A similar exercise on the vinyl ethers we discussed earlier will also indicate that the numbers such as 2.7, 3.6, 3.8, 5.6, 7.8 will obtained 1750 for the constant. Polymers 15–21 are an interesting group. VDCN stands for vinylidene cyanide and it has strong dipole interactions within the unit such that the whole group acts as a huge conformer, and this induces the alternating whole vinyl copolymer to also behave as one conformer. This is an excellent example to obtain high T_g values by making the effective conformer size large.

Table 2 is a similar list for aromatic polymers. The aromatic ring has a large molecular volume, but its $\Delta\mu^*$ is about the same 3 kcal, so it can rotate easily at low temperature if given the necessary space, but when incorporated in the chain, the T_g of the polymer is high. The values of the constants in the last column are about the common value of 1750, indicating that $\Delta\mu^*$ is about the same. An interesting challenge was presented when we tried to figure out how many conformers are in the repeat unit of the bis-phenol polycarbonate chain. Note that the ‘constant’ is a bit high. In order to obtain the value 1750, the conformer size would have to be 3.3 instead of 3. This was rationalized by saying that there are 4 linkages with 2 ether-like oxygen atoms in the main chain which will bring $4-2 \times 0.3 = 3.4$. The activation energy for the β transition is 8 kcal, which can be divided up to $3+3+1+1$ kcal. Apparently the limited movements at the bis-phenol links do not contribute into breaking the group into two conformers, though such a degree of freedom may play a significant difference in allowing for the classical plastic deformation. This is an interesting and useful subject from a practical view point but obviously it is not within the scope of this article.

The theory of conformer sizes affecting the relaxation and T_g is also applicable to thermosetting polymers. Hale *et al.* [15] point out that a multifunctional epoxy moiety, for example, would tend to form linear chains first, then crosslinks between the already large polymer chains at a later stage. This is completely consistent with the concept that a unit in the chain that have reacted trifunctionally to grow a side group has become a much larger conformer as a combined unit, exhibiting a higher T_g . This is a much more 'difficult' reaction, so it is slower. The kinetics of crosslinking reaction has been analyzed in such a light in Matsuoka's book [16]. At the later stage in which the real interchain bridging reaction takes place, the reaction rate is restricted by the ever decreasing entropy in a remarkably similar way that a physical aging takes place in glassy polymers (and nonpolymers). The climbing T_g in the early reaction stage has been analyzed by Hale *et al.* as a consequence of the polymer molecules growing linearly. Gelation occurs at about the point of transiting from the stage 1 to the stage 2.

In summary, the incorporation of larger conformers in a polymer chain will raise T_g , and vice versa, opening a useful way for creating a recipe for many candidate conformers of different sizes to arrive at a desired overall T_g , while controlling the average molecular weight between crosslinking points to maintain the desired modulus and toughness in the rubbery state above T_g . Both T_g and ΔC_p (per mol of conformer) increase with a larger size conformer. The value of ΔC_p obtained by the calorimetry is always in units of calories per degree per gram, and not per mol. Since ΔC_p per mol is proportional to $\ln M_C$, ΔC_p per gram is proportional to $(\ln M_C/M_C)$, and is smaller for the larger conformers with higher T_g . For a more thoroughly crosslinked system with a higher T_g , ΔC_p per gram has been observed to become less. The theory presented here predicts that a polymer with T_g of 550°C will have ΔC_p (per gram) of zero. This rule applies to both thermosets and uncrosslinked polymers.

4. Viscoelasticity data analysis

Relaxation behavior is measured dielectrically or mechanically. There are many methods associated with either of the techniques. Viscoelastic properties of polymers are measured either by imposing a constant stress or strain to produce the creep or relaxation data, or by measuring the steady state cyclical response to the cyclical strain or stress to obtain dynamic modulus or compliance. One additional useful method is to obtain stress-strain data under a constant deformation rate. Usually linear viscoelastic data are obtained under a very small strain amplitude. The stress relaxation and the dynamic mechanical tests are among the most common techniques for easily maintaining a small strain amplitude.

An example of dynamic mechanical data is shown for a commercial polyisoprene in Fig. 3. The data were obtained by subjecting the sample to the temperature from -100 to 70°C under the constant frequency of 1 radian/s.

Usually additional data are taken at several other frequencies, and analyzing how much each of the curves has been shifted from one frequency to another, the temperature dependence of the relaxation times is calculated, and the 'master curve' for the relaxation modulus vs. frequency or time over a wide range is constructed at a chosen reference temperature, e.g., 25°C. In the real practice, the limited available range of frequencies makes the accurate determination of the shift factor difficult. Then there is the question of what to do with the portion of data taken at temperature below T_g . These problems are substantially reduced and the confidence limit expanded when the thermodynamic theory behind the relaxation behavior is utilized. In fact only one set of isochronal data obtained at one frequency, such as shown in Fig. 3, is needed to produce a master relaxation curve over a wide range of frequency or time.

The glass transition as measured by DMA at 1 rad/s takes place at -58°C as noted by the maximum in E'' . The loss modulus closely reflects the relaxation spectrum, while $\tan \delta$ (E''/E') is affected by the temperature dependence of E' and as a rule the maximum is shifted to a higher temperature than for the maximum E'' . The master curve for the relaxation modulus vs. log time can be constructed by replacing the value of the temperature in the original isochronal data with log time at -58°C , the temperature that divides the equilibrium and nonequilibrium regimes. The values of the temperature in the original isochronal data, which will be termed the variable X from this point, will be first converted to log time by invoking the Vogel equation, Eq. [13]. This can be easily achieved with a spread sheet program such as Microsoft Excel or Lotus 123.

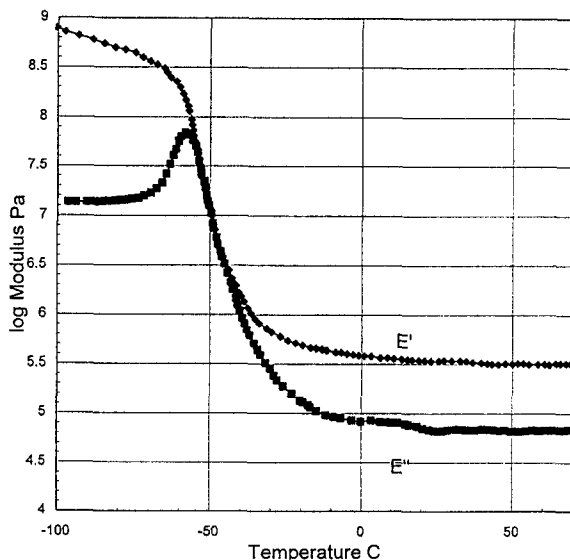


Fig. 3 The elastic (E') and loss (E'') moduli data taken at 1 radian/s for a commercial polyisoprene sample

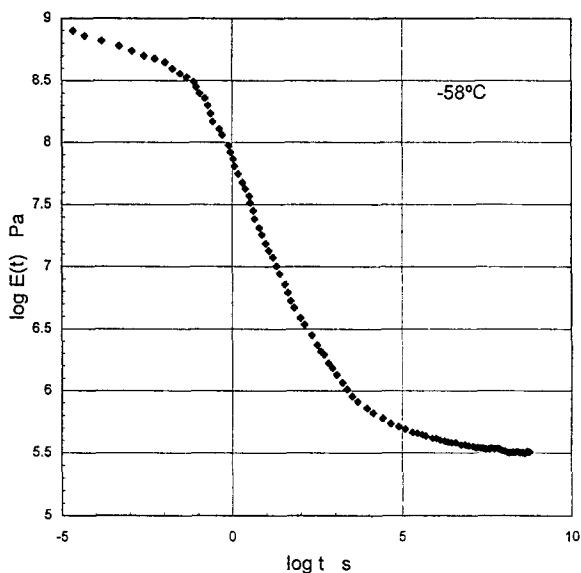


Fig. 4 The master relaxation modulus curve calculated from the isochronal data shown in Fig. 3, with the reference temperature set at $T_g = -58^\circ\text{C}$

The values of T_0 of 165 K, $\log \tau^*$ of -11.4 s, T^* of 773 K and $\Delta\mu^*$ of 3 kcal were used. For these values to be correct, the calculated time at T_g must agree exactly with the data. If not, the value of $\Delta\mu^*$ is the first to be adjusted. The tried values gave an almost perfect agreement. The formula for $\log t$ in seconds is $11.4 - 653^*(1/X - 1/608)$ above $X = -58^\circ\text{C}$ or 215 K. Below T_g , the activation energy for the Arrhenius formula is obtained from the slope of a straight line between the points $(1/773, -11.4)$ and $(1/215, 0.57)$ and multiplying it by 2 times 2.3 to obtain the value of 16.4 kcal. Thus the formula for $\log t$ below $X = -58^\circ\text{C}$ is $-0.57 - 3565^*(1/X - 1/215)$. The master curve for the relaxation modulus at -58°C is constructed from these time temperature converting scheme and by assuming the $E(t) \sim E'$ ($\omega = 1/t$); the calculated results are shown in Fig. 4. To obtain a master curve at 25°C from the one at -58°C , the entire curve is shifted to a shorter time scale. For those $\log t$ points originating from the isochronal data above $X > -58^\circ\text{C}$, the shift factor is the -8.14 resulting from the Vogel equation, Eq. (13). For those $\log t$ point originating from $X < -58^\circ\text{C}$, however, must be calculated with the Arrhenius formula, i.e., $-0.57 - 8.14 + 3565^*(1/215 - 1/X)$. The master curve calculated for 25°C is shown in Fig. 5. The 'transition region' between the glassy high modulus and the rubbery plateau shows the slope of $3/5$, which is a typical value observed in the similar master curves [12]. This polyisoprene specimen is crosslinked, so there will be no thermal drop in modulus for the entanglement/reptation relaxation. If it were

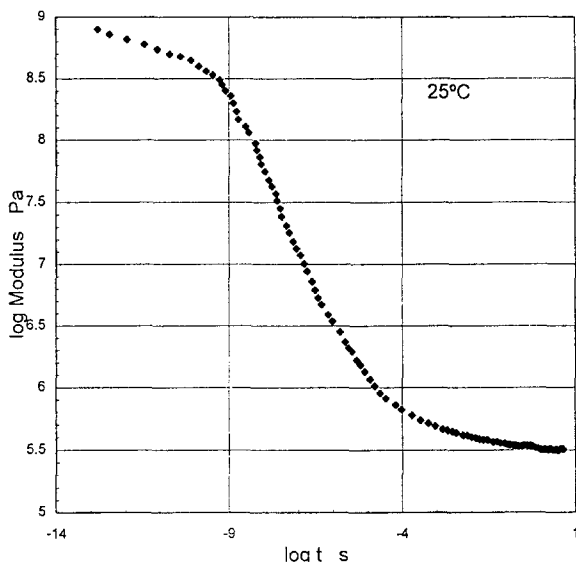


Fig. 5 The master curve at 25°C obtained by shifting the calculated master curve for 58°C shown in Fig. 4

not crosslinked, it would have been observed when data were taken up to a sufficiently high temperature and the instrument is capable of measuring extremely low stress levels. If the molecular weight of such a polymer is with a very narrow distribution, the approximation of equating E' to $E(t)$ breaks down, so the final master curve should be presented as E' vs. frequency rather than $E(t)$ vs. time, but this is a minor point.

Those points that originated below T_g in Fig. 3 were obtained in the non-equilibrium glassy state. As such, the time-temperature superposition does not apply, because the slope of $\log E(t)$ vs. $\log t$ in the glassy state is dependent on temperature. For example, the $E(10^{-13} \text{ s})$ at 25°C in Fig. 5 has been assumed to be equal to $E(-100^\circ\text{C})$ at 1 rad/s in Fig. 3 but, in reality, being in the equilibrium state at 25°C the modulus at the high frequency extreme should be higher. We have a method for deriving the exact values based on irreversible thermodynamics in the glassy state [13], but DMA is not the most suitable method to explore this frequency regime anyway.

5. Beyond linear viscoelasticity

Because linear viscoelasticity holds for the strain levels of only a few percent for polymer melts, and even less for the solid polymers, a direct application of these data to engineering problems is limited. However, the time dependent mechanical properties of polymers in the nonlinear range can be predicted from

viscoplasticity. Viscoplasticity is a combination of viscoelasticity and plasticity. It exhibits linear viscoelastic behavior when the stored elastic energy is small but diverts to the classical plasticity when the energy reaches a critical yield level. The classical plastic behavior is observed in metals when the elastic energy exceeds the level that the polycrystalline grain boundaries can sustain. These metals are initially elastic until this limit is reached. Polymers, on the other hand, are viscoelastic under small strains, and are capable of dissipating energy even below that yield limit. So what is the difference between the viscoelastic flow and the plastic flow?

When a viscoelastic material is deformed at a constant rate, the increasing stress eventually reaches a plateau. The value of this plateau is proportional to the product, the relaxation time times the strain rate. This is purely a consequence of the nature of linear viscoelasticity and it is not the yield phenomenon we have in mind. The viscoelastic plateau stress can in theory increase indefinitely as the strain rate is increased. In real polymers, as in any materials, surely there is a limiting strength beyond which the structure must break down. A mechanism of flow other than the viscoelastic flow is needed at such high stress levels. A viscoelastic 'solid' tends to break down when it is made to deform faster than its own pace characterized by the relaxation time. It can still be deformed at a rate exceeding $1/\tau$, but it is now undergoing a viscoplastic deformation. For the material with a greater τ value, the easier is the transition to plastic flow at a slower rate of deformation. If there is a spectrum of many relaxation times within one material, as it is the case with polymers, some part will undergo plastic flow while other parts remain linearly viscoelastic. As the plastic flow stress is the limiting maximum for the viscoelastic flow at each limiting speed, the sum total of the stresses arising from a mixture of viscoplastic and viscoelastic flows depends on the viscoelastic relaxation spectrum and the imposed deformation rate. The overall stress increases with the strain rate, and the behavior can be theoretically and quantitatively predicted from the linear viscoelastic data. The classical plastic flow is, being the strength behavior, independent of the strain rate. A log-log plot of the stress divided by the strain rate, i.e., the flow viscosity, vs. the strain rate will have a slope of exactly -1 for the pure plasticity. The similar plot for the viscoplastic flow will have a less steep slope than -1 , e.g., -0.8 . A linear viscoelastic flow would show the slope of 0 , and this is called a 'Newtonian' behavior, though the physics involving the analogy between this and the flow behavior of a typical fluid is very limited, to say the least. The melt viscosity obtained in a large deformation flow in viscoplasticity typically closely agrees with the magnitude of the complex dynamic viscosity obtained in the linear viscoelastic range with a very small maximum strain. This is known among the rheologists as the Cox-Merz rule [17].

The theory of viscoplasticity is also useful in polymers in the glassy and crystalline states for predicting the stress strain behavior at all temperatures and strain rates. In glassy polymers, the behavior is affected by the physical aging, but thermodynamic predictions can be carried out with this theory. The possi-

bility for predicting the large deformation behavior from the linear viscoelastic data extends the usefulness of the linear viscoelastic data on the practical applications enormously, making it possible to predict the creep behavior over the period of years from DMA data taken only at 1 rad/s. The application of thermodynamics to the understanding of viscoelasticity further realizes the usefulness of not only the DMA data but data taken by DSC. From the values of T_g and ΔC_p alone, we will not only know how to adjust T_g of a newly formulated compound but we can also construct a master relaxation curve for such a compound at any use temperatures in the glassy, crystalline, and molten states.

Nomenclature

Conformer: Smallest unit of relaxation, typically one carbon atom in the chain rotating from gauche to trans conformation under the influence of the imposed force field.

Excess entropy: The effective available conformation entropy S_x , smaller than the statistical conformational entropy s_c , because of the frustration from the neighbors in the condensed state.

Excess enthalpy: The effective available enthalpy H_x ; it is smaller than the statistical conformational enthalpy, h_c , and is approximately equal to TS_x .

Excess volume: Free volume available for cooperative relaxation of the conformer. Its value is slightly different from the conventional free volume in the Doolittle-WLF equations.

Viscoelasticity: A rheological behavior characterizable in terms of combined elastic and viscous response to imposed stress. Linear viscoelasticity means that all viscoelastic coefficients, e.g. moduli, compliances, $\tan \delta$, etc. are the functions of time only, and not on the stress or the strain magnitude.

Viscoplasticity: A class of rheological behavior which combines the classical plasticity and linear viscoelasticity.

α relaxation: We mean the cooperative relaxation by the conformers in polymer chains that lead to the glass transition by cooling.

β relaxation: Intramolecular cooperative relaxation along several consecutively placed conformers along a polymer chain; usually identified as the low temperature relaxation below T_g , but it can occur above T_g at high frequencies.

M_c : Conformer molecular weight.

T^* : High temperature limit of relaxation above which the barrier energy loses its meaning because of large kT .

T_o : Extrapolated temperature for zero entropy along the equilibrium liquidus line.

ΔC_p : The step change in the specific heat near T_g , usually reported in units per gram. The value is smaller for polymers with higher T_g .

$\Delta\mu$: $\Delta\mu^*$ with the added effect of intermolecular interference to relaxation.
 $\Delta\mu^*$: Energy barrier for the relaxation of a conformer without interference from neighbors.

Appendix

The entropy associated with the domains of cooperative relaxation

From thermodynamics, we write for the Gibbs free energy $\Delta\Psi$,

$$\Delta\Psi = \Delta H - T\Delta S \quad (\text{A-1})$$

where Δ refers to the difference between the liquidus and glassy states, and

$$\frac{d\Delta\Psi}{dT} = -S_x \quad (\text{A-2})$$

and with definitions in Eqs (15) and (18) we obtain:

$$\begin{aligned} \frac{d\Delta\Psi}{dT} &= \Delta C_p - \frac{d}{dT} \left[s_c \frac{T^*}{T^* - T_0} \cdot (T - T_0) \right] \\ &= \Delta C_p - \left[\frac{ds_c}{dT} \cdot \frac{T^*}{T^* - T_0} (T - T_0) + s_c \frac{T^*}{T^* - T_0} \right] \\ &= \Delta C_p - \Delta C_p \frac{T - T_0}{T} - S_x \frac{T}{T - T_0} \\ &= \Delta C_p \frac{T_0}{T} - S_x \frac{T}{T - T_0} \\ &= -S_x \end{aligned} \quad (\text{A-3})$$

from which we obtain the relationship:

$$\Delta C_p = S_x \frac{T}{T - T_0} \quad (\text{A-4})$$

and

$$\frac{d\Delta\Psi}{dT} = -\Delta C_p \left(\frac{T - T_0}{T} \right) \quad (\text{A-5})$$

and finally, in the limited temperature range where ΔC_p is not a strong function of temperature, as we often assume that the thermal expansion coefficient stays constant over a range of temperature for liquids, we can approximate:

$$\Delta\Psi = - \int_{T_0}^T \Delta C_p \left(1 - \frac{T_0}{T}\right) dT$$

$$\approx - \Delta C_p (T - T_0) + \Delta C_p T_0 \cdot \ln \frac{T}{T_0} \quad (\text{A-6})$$

From Eq. (A-6), it can be said that the excess free energy $\Delta\Psi$ is zero at T_0 , and increases toward T^* but always much smaller than either ΔH or $T\Delta S$ alone, hence the excess enthalpy is relatively close to the value of T times the excess entropy, particularly near (but above) T_g .

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