Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

VISCOELASTICITY AND THERMAL ANALYSIS

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Abstract

DMA is a tool for studying linear viscoelastic behavior of polymers over ranges of temperature and frequency. Viscoelasticity has its origin in the complex molecular behavior of the polymer. A theoretical master curve has been constructed, based predominantly on thermodynamic theories of polymer molecular conformations, and their intermolecular cooperativity.

Keywords: cooperativity, entanglement, entropy, free volume, glass transition, viscoelasticity

Conformation of a polymer molecule

Consider a polymer molecule to be a chain of segments like a string of pearls. In the chain, a segment is connected to the next neighbor by a covalent bond at an angle. This bond can rotate about the axis of the adjacent bond. Because these bonds are not straight, a polymer chain can take a large number of shapes, conformations. We call each 'pearl' a conformer; it is the smallest unit to make up the conformation of a whole chain. In a typical hydrocarbon chain, one of the three tetrahedral links can take three different angles of rotation. When these bonds are in the same plane, it is in the *trans* conformation. The two other angles are called *gauche*. A specific sequence of bond angles in the whole chain makes one specific conformation. If there are N conformers in a chain, each capable of assuming three different bond angles, then there are N^3 possible conformations this polymer chain can assume. For each conformation, there is one unique distance between the two ends of the chain. The statistical probability for the end-to-end distance is the statistical probability for the conformations of the chain. If the potential energy for the *gauche* is at the same level as that for the *trans* conformation, the distribution of conformations will be Gaussian, following the law of the normal distribution. The thermodynamic probability is at the maximum. The thermodynamic free energy to describe the probability is to take its logarithm. This is Gibbs free energy, $H - TS$, where H is the enthalpy, T is the temperature, and S is the entropy. The term entropy is in the form to describe the probability such that $S = k\ln P$, where k is the Boltzmann constant, and P the conformational probability. The mean of the square of the population for each conformation describes the most probable conformation in the Gaussian coil. The mean of the square of end-to-end distances, $\langle r^2 \rangle$, describes the most probable dimension of the random coil.

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The distribution of conformations is perturbed when an external force is imposed. Any disturbances will make the conformational probability less than the maximum, and the entropy is decreased. The distribution of the end-to-end distance is no longer spherically symmetrical, but is elongated in the direction of the applied force, accompanied by the contraction in the two directions perpendicular to the force. It can be shown that a polymer with N tetrahedral bond of length l will have the mean square end-to-end distance of $2Nl^2$ [1]. Some polymers have segments that are not tetrahedral. A paraphenylene linkage is co-linear. Even though it can rotate around the bond easily, the rotation does not change the molecular conformation, which is a rigid rod. Other polymers contain the ether linkage, –C–O–C–, which has a bond angle of 110°, so the rotation affects the molecular conformation. This link does not have definitive angles for low energy state like the tetrahedral bond, so the polymer is a classic freely rotating chain with a fixed bond angle. The mean square of this type of a chain molecule is also equal to $2Nl^2$. In thermal analysis (TA) and dynamic mechanical analysis (DMA), studies are made on how the molecular shapes or conformations depend on temperature and stress. The two techniques can complement each other for the analysis of the structure/property relationship in polymers.

Polymer molecule in solution

Only in the very dilute solution, a polymer molecule is in a truly unperturbed state. This is the state of maximum entropy. Strictly speaking, the solvent must be the theta solvent that has zero heat of mixing. In the theta condition, the interfacial potential energy between the solvent to polymer segments is equal to that between the polymer segments. This means there is only the entropy change during dissolution. The average volume or space occupied by a random coil of a polymer chain, as it is spread out in the dilute solution, is very large as compared to that in the condensed state. The relaxed state contains a large volume of solvent.

The relative viscosity (normalized relative to the solvent viscosity) is proportional to this molecular volume, multiplied by the number of the molecules per cm^3 in the solution, according to the Stokes-Einstein formula. For the theta condition, the average volume occupied by a polymer molecule is proportional to $M^{3/2}$, as the average diameter is $\sim M^{1/2}$. In general, the diameter is proportional to M^{ν}, so the volume is proportional to $M^{3\nu}$. In good solvent, ν is greater than 0.5, as the molecule swells. The number of molecules in 1 cm^3 of the solution is c/M, where c is the concentration in g cm^{-3}. So the relative viscosity is proportional to $M^{3\nu-1}$. The intrinsic viscosity, $[\eta]$, is the relative viscosity divided by the concentration (the reduced viscosity) extrapolated to the infinite dilution. It is proportional to M^a as described by Mark-Houwink formula. Thus a in the latter is $3\nu-1$. The volume can be calculated from $c[\eta]$. This volume is called the hydrodynamic volume. The hydrodynamic volume divided by the molecular weight is the hydrodynamic specific volume of the random coil. The reciprocal is the concentration within the coil, c^*. When $c<c^*$, polymer hydrodynamic volume do not fill the solution, i.e., they are still isolated islands. But the polymer coils touch the neighbors from time to time, more often at higher concentrations.

Even at this low concentration, polymer conformation is no longer at maximum, and the entropic change is manifest in the increase of the reduced viscosity as described by the Huggins equation [2].

At the concentration of c^*, the islands of the chains begin to touch each other. There are no more islands of individual chains, but the solution is nominally homogeneously filled by polymer segments. Actually, the density of a random coil is not uniform but it is higher toward the center. The average density of the coil is proportional to $N^{-1/2}$ for the theta solvent, or $N^{-\nu}$ in general. The longer the chain, lower the density. At this point, the viscosity is no longer proportional to $M^{0.5} \sim M^{3\nu-1}$, but typically to $M^1 \sim M^{2\nu}$ [3, 4]. The latter is typical of the free-draining worms, such as the Rouse model. Below, we present a brief description of the analysis we completed and submitting for publication [5]. This worm is randomly shaped, and becomes more and more slender with increase in concentration. By so doing, the worms regain the entropy lost while being compressed by the increased concentration. This worm is fat at c^*, having the diameter of the random coil, but becomes skinnier with increased concentration. The worm is a string of connected 'blobs' which are individual random coils of submolecules. Higher the concentration, the smaller and more numerous are the blobs. The skinniest extreme is the *KP* worm, [6, 7], in which the blob is reduced to the equivalent bond length, Kuhn's unit of the entropic spring. The viscosity is proportional to $M^1 \sim M^{2\nu}$ until the entanglement takes place. The M^1 dependence follows the theory of Rouse-Bueche [8]. If the molecular weight is high enough, entanglement can occur even in the solution with a relatively low concentration, such as 1% or less for a polysaccharide called hyaluronan, with molecular weight exceeding a half million. The critical value of molecular weight for entanglement depends on concentration, chain stiffness, and the kind of solvent. Entanglement can occur when $c[\eta] > 7.5$, when the blobs have become the minimum size, below which they no longer would be able to behave as random coils. So, above this concentration, blobs would compress to a higher density than the law of the most probable radial conformational distribution would warrant for the molecular weight of the submolecule. The change in the molecular weight dependence from M^1 to $M^{3.4}$ could occur when the blobs are crowded together. This phenomenon could occur without the pre-requisite of flexible polymer chains, but could occur for rigid rods or micelles. Disentanglement would involve the disengagement of blobs from the neighboring molecules. A coordinated relaxation becomes necessary, which means a simultaneous relaxation of neighboring chains. The cooperative probability is the product of individual probabilities. When the molecular weight exceeds a critical value, a higher power of M for both relaxation time and the viscosity takes over. The reptation model [9, 10] is based on the coupling of three modes, each of which depends on $M^1 \sim M^{2\nu}$ which will bring to $M^3 \sim M^{3.6}$ dependence. Our model is based on the interaction of the partially overlapped neighbor molecules, so it is a power of the unperturbed specific volume $c[\eta]$. It involves the terms in polynomial up to $\{c[\eta]\}^4$. If $[\eta] \sim M^{0.85}$, the relaxation time and the viscosity would be proportional to $M^{3.4}$. The concentration-dependent shift factor for the relaxation time depends on the nature of solvent, and so does the critical mo-

lecular weight in our model. Our model also predicts the change in the relaxation spectrum with concentration. A polymer molecule exhibits not one relaxation time but a spectrum of relaxation times. Each mode of relaxation is related to a portion of a chain. The relaxation times with entanglement also show a distribution. G' and G'' are calculated based on a model for the modes of relaxation [11]. The low frequency part of the master dynamic moduli curves for polystyrene, shown in Fig. 1, was calculated from the distribution of relaxation times published by Matsuoka [11].

There are two major modes of relaxation in the polymer melt. One is the normal mode that is associated with the intermolecular relaxation of the entanglement regime. The other is called α relaxation that is a much faster process related to the local motion of molecules in the segmental scale. In Fig. 1, the peak in G'' at 1 MHz range is this α process. The α process also is a cooperative relaxation, and the Vogel-Fulcher equation is a manifestation of cooperativity, as will be discussed.
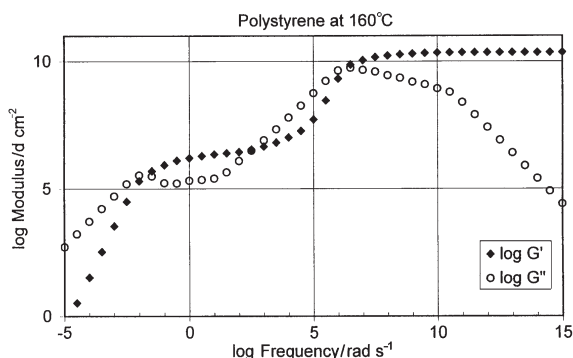
Fig. 1 The master dynamic moduli curves constructed from calculation for polystyrene with molecular weight of 330,000

Whereas the normal mode relaxation was the process of disengagement of the locked elastic blobs of the minimum size, as we proposed, the α process is the process of the conformational relaxation of polymer chains, the smallest and fasted unit of which is the conformer. A conformer is a bead in the polymer chain as a string of pearls. The total conformational change is a sum total of all changes in the rotational angles that occur at the conformer level. In the condensed state, the polymer chains are crowded, and rotation of a conformer is perhaps interfered by the presence of a neighbor(s). Intermolecular cooperativity in glass-forming liquids have been analyzed and theorized by many authors including ourselves [11]. All models are basically common in the feature of neighbor conformers relaxing simultaneously. According to these models, only when the rotations of the neighbors are synchronized, these conformers can relax simultaneously. The difficulty for the relaxation depends on the proximity of neighbor chains, involving more conformers for cooperativity. A lower temperature means less space for possible free rotation of conformers.

Let us visualize many conformers that are trying to rotate to a new angle but can't because the neighbors are in the way. Only once in a while, a lucky juxtaposition happens and several conformers are able to reach the new angles that are favored under the imposed force field. At a lower temperature, not a couple but several conformers must relax together. If z conformers must cooperate, the probability must be zth power of the probability for one conformer. The relaxation time of the rotation of one conformer is controlled by the population of the activated state, in this case the high energy state among the stable rotational angles, e.g., *gauche* and *trans* states. If we let the relaxation time of each conformer as τ_1, then the cooperative relaxation time, $\tau_z = \tau_1^z$. Since τ_1 is proportional to $\exp[\Delta\mu/kT]$, τ_z is proportional to $\exp[z\Delta\mu/kT]$, from the high temperature state at T^*, at which $z=1$ and $\tau=\tau^*$.

As T is decreased from T^*, z continues to increase until the conformational rearrangement becomes so slow, that it cannot keep up with a further drop in temperature. Because of the apparent freezing up of the relaxation, the polymer appears to have become rigid. This is the glassy state. It is a non-equilibrium state, and the entropy or the volume cannot be specified by temperature and pressure alone. (It needs the time element, the history.) The slower the rate of temperature decrease, further down moves this freezing temperature. This freeze-up temperature is called the fictive temperature [12]. It is important to remember that the polymer glass is in equilibrium at its fictive temperature. Meanwhile, z grows to a larger number at lower temperature, if the equilibrium is maintained to that lower temperature by the extremely slow cooling. In the extreme, at least in theory, there is an extrapolated fictive temperature T_0 that corresponds to the infinitely slow cooling. z at this temperature is infinity, because $z\Delta\mu$ for τ_z must become infinity. To speculate on the formula for z as a function of T, there are certain conditions to be met: (1) $z=1$ at T^*, (2) $1/z=0$ at T_0, (3) thermodynamic extensive quantities such as entropy or free volume with and without cooperativity must be proportional to z, and (4) the cooperative relaxation stops at T_0, while the normal quantities such as conformational entropy and van der Waals free volume do not become zero until reaching 0 K. These four conditions are met by the following formula,

$$z = \frac{T^* - T_0}{T^*} \frac{T}{T - T_0} \qquad (1)$$

and when this z is substituted into τ_z, the Vogel-Fulcher formula [13] is obtained,

$$\ln\tau_z = \frac{\Delta\mu^*}{k(T - T_0)} - \frac{\Delta\mu^*}{k(T^* - T_0)} + \ln\tau_z^* \qquad (2)$$

where $\Delta\mu^*$ is $(T^* - T_0)/T^* \Delta\mu$, and τ_z^* is τ_z ($\sim\exp[z\Delta\mu/kT]$)at T^*. The reference temperature can be any temperature for the above equation, e.g., replacing T^* and τ_z^* by T_{ref} and τ_{ref}. This will be the Williams-Landel-Ferry equation [14] for the shift factor in time-temperature shift of viscoelastic data, such as the frequency dependent dynamic mechanical data,

$$\ln\tau_z = 2.3\frac{c_1 T - T_{ref}}{c_2 + T - T_{ref}} + \ln\tau_{ref} \qquad (3)$$

and if T_g is chosen as the reference temperature T_{ref} from which all experimental iso-thermal data are being shifted, then the two parameters c_1 and c_2 take on the universal values: $c_1^g = 13.7$ and $c_2^g \sim 50$ K [14]. $T_g - T_0$ is equal to c_2^g and should be ~ 50 K.

Up to this point, the fictive temperature at the infinitely slow cooling, T_0, has been treated as an empirical temperature. No rationale has been given why T_0 varies from polymer to polymer. We introduce a formula for calculating T_0 from the chemical structure of the conformer size.

The excess van der Waal's volume, V_f, and the conformational entropy, s, vanish, not at T_0 but at 0 K. When the cooperativity is introduced as an additional factor to affect the relaxation, however, the probability of the relaxation decreases. We consider that the *effective* entropy (the probability) and the *effective* free volume are smaller than the real entropy (conformational plus volumetric entropies), and the real (van der Waals) free volume, $V - V_c$, where V_c is the volume of the solid state, such as the crystalline volume. We define the minimum entropy S_0 and the minimum fractional free volume f_0, above which the cooperative relaxation becomes possible ($f = (V - V_c)/V_c = V_f/V_c$). The effective entropy is $S - S_0$, and the effective fractional free volume is $f - f_0$. It can be seen that $z = S/(S - S_0) = f/(f - f_0)$ will satisfy Eq. (1), which is the definition of z. The entropy criterion will lead to the well-known Adam-Gibbs equation [15], although our assumptions are different in that the real conformational entropy will not vanish at T_0. The *effective* free volume fraction, $f - f_0$, can be shown to be essentially the same as that fractional free volume introduced by Doolittle [16]. It can be seen that $\Delta\mu/RT \cdot f/(f - f_0) = \Delta\mu/R \cdot \alpha_f/(f - f_0)$, where $\alpha_f = df/dT$. If we let $B = \Delta\mu/R \cdot \alpha_f$, noting that $\Delta\mu \sim 3$ kcal per mol of conformer and that $\alpha_f \sim 6 \times 10^{-4}$ K, B is about 1, and the Doolittle's free volume equation, $\ln\tau \sim B/f_D$, us obtained, where $f_D = f - f_0$. Now, at T^*, $f^* - f_0 = \alpha_f(T^* - T_0)$, but the free volume fraction we invoke in this discussion, f, is $(V - V_c)/V_c \sim \ln V - \ln V_c$, so we obtain the proportionality that $\ln V^* \alpha (T^* - T_0)$, and this is expressed by the equation

$$T^* - T_0 \ln M = T^* \ln M_0 \qquad (4)$$

where $T^* \ln M_0$ is a constant for many polymers, empirically arriving at a value of 1750 K.

From a parametric analysis of a number of polymers, we concluded that polymer conformers, of diverse species, can relax independently only at a very high temperature, 500°C. We assigned this value for T^*. Before reaching such a high temperature, most real polymers would have degraded chemically, so T^* is only a theoretical temperature for calculation for the states at much lower temperatures. It can be stated that, had they not degraded, then at 500°C, most polymer segments would be far enough apart from the neighbors, and they would have been able to rotate with their own relaxation time. That relaxation time is of the order of 3×10^{-12} s at T^* of 500°C, but rapidly comes down to nanoseconds at 100 to 200°C ranges. The extremely high

frequency state that allows relaxation without cooperative help from neighbors is in fact a state of infrared vibration that can jump over the energy barrier $\Delta\mu$ easily forward and back. It is the state in which the meaning of relaxation is lost.

Table 1 Conformer size and T_g

Polymer	Repeat unit/number	$T_g/°C$	ln$M$
Polyethylene (linear)	14/1	−110	2.64
Polyethylene (branch)	41/2	−30	3.02
1,4 poly(butadiene)	54/3	−55	2.89
1,2 poly(butadiene)	54/2	20	3.30
polypropylene	42/2	−30	3.04
Gutta percha	68/3	−10	3.12
cis-polyisoprene	68/4	−69	2.83
Polystyrene	104/2	100	3.95
PMMA	100/2	105	3.91

A partial list for the molecular weight of a conformer and the predicted T_g is shown in Table 1. The average molecular weight of conformers is calculated from the chemical formula of the repeat units. For most vinyl polymers, there are two conformers in a repeat unit. A polymer typically consists of conformers of various sizes, and the average is taken for the calculation of T_0 from Eq. (4). For example, for polystyrene, M is 52, whereas for polypropylene, M is 21. Many readers who have seen the table have raised a question why T_g of HDPE is at the γ transition, and T_g of LDPE is at the β transition. We have made an extensive analysis of the dielectric relaxation time for the both, and concluded that the temperature dependence of the HDPE near −110°C follows a Vogel-Fulcher equation, unlike the γ transition of the LDPE, which is Arrhenius. As for the T_g of LDPE being near that of polypropylene, rather than that of HDPE, all experimental evidence points to this T_β as a genuine T_g. Apparently, in the amorphous regions that have ample room to move around, two methylene units act as one conformer and, when pinned at T_g, the more restricted relaxation, such as a crank shaft-like motion, can take place only as a typical γ relaxation. The γ transition has a low Arrhenius type activation energy, and its intensity increases with the temperature. Neither of these attributes are observed at for HDPE at its T_g. 1,4 poly(butadiene) is a linear polymer with three conformers per monomer unit, while 1,2 poly(butadiene) consists of two conformers of uneven sizes, one with and one without the substituent group, and this results in very different values of T_g. The same principles can be applied to long branched polymers. In general, the β transition of amorphous polymers (γ for crystalline polymers) is the restricted relaxation, usually pinned at the largest conformer in the repeat unit. The activation energy of the β relaxation would indicate the total number of conformers relaxing together, so by dividing this activation energy by 3~3.5 kcal will obtain the number of conformers per repeat unit, providing a check for the estimated number for the glass transition from

the chemical formula. More extensive table and discussion on this subject are found in [11].

Equation (4) was based on the idea that the cooperativity entropy is the conformational entropy divided by z. If T_g were calculated on the basis of conformational entropy per mol of conformers, then the molecular size would have made no difference to the value of T_g. The reason why a larger conformer exhibits a higher T_g, as stated in Eq. (4), is because a greater free volume is trapped at higher T_g for a larger conformer size. A straight expansion or contraction, without a change in conformation, can also mean an increase or decrease in the probability. For the ideal gas, the entropy related to the volume is $k \ln V$. In the liquid, the comparative volume is van der Waals free volume. The free volume, V_f is proportional to the molecular volume and hence to the molecular weight of the conformer. This is the basis of the proportionality in Eq. (4). Like for the entropy, enthalpy, and ΔC_p, the fractional free volume of cooperativity has a coefficient of expansion that is $T^*/(T^*-T_0)$ times greater than the true van der Waals free volume. Starting down from the same value at T^*, the former drops more rapidly than the latter, and reaches zero at T_0, even though there is plenty of van der Waals free volume still left at T_0. A similar situation exists between the cooperativity entropy and the conformational entropy. The conformational entropy is still very high near T_0, as can be seen from the infrared analysis of polystyrene by Monnerie *et al.* [17]. The same trend can be cited for the value of ΔC_p at T_g. It is $T^*/(T^*-T_0)$ times greater than $\Delta C_p(=dH/dT)$ for the conformational enthalpy, on the basis of mol of conformers. However, if ΔC_p is expressed on the per gram basis, it is ΔC_p times $T^*/(T^*-T_0)$ divided by M, in joules per g, which is essentially ln M/M, so ΔC_p *per gram* is smaller than ΔC_p *per gram* for the high T_g polymer. An example of calculation is shown for polycarbonate in Fig. 2. ΔC_p at 420 K is about 0.33 J (K g)$^{-1}$, which agrees with data by Bair [18].

ΔC_p can be calculated, starting with the conformational probability, from which the conformational entropy, s, can be calculated. The cooperativity entropy, S, can be calculated from $dS/dT = T^*/(T^*-T_0) \cdot ds/dT$ and $S=s$ at T^*. The free energy Ψ is obtained from $-\int T \cdot dS/dT dT$, and the enthalpy is obtained from $\Psi + TS$. ΔC_p per mol (of conformer) is obtained from dH/dT. ΔC_p per gram is obtained by dividing it by M, the
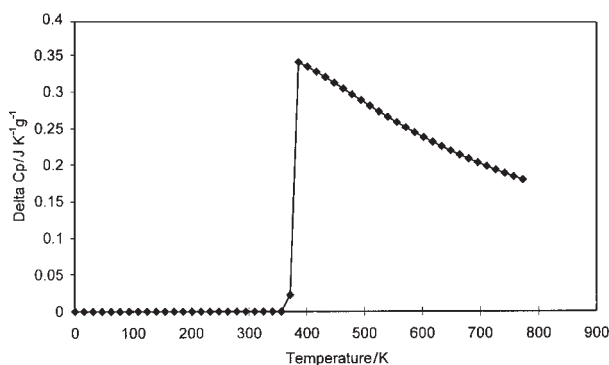

**Fig. 2** Theoretical ΔC_p based on the cooperativity parameters of polycarbonate

molecular weight of the conformer. ΔC_p is at maximum at T_0. For a real polymer the equilibrium cannot be realized near T_0, but the glass transition intervenes at $T_g > T_0$. In thermoanalysis, T_g is measured by heating the glassy state from well below T_g upward. The enthalpy of the glassy state can continue on the glassy line for some time above the fictive temperature, because the relaxation time is very long. How far above the fictive temperature the apparent glassy state will remain depends on the aging history. The more extensively it has been aged, the higher the apparent T_g. Thus, the fictive temperature of a glassy state is lower when its T_g is higher. It is the fictive temperature that must be used to estimate the relaxation properties, rather than T_g. The former is an equilibrium parameter, which the latter is not.

From the information on the relaxation characteristics of a polymer in the amorphous state, it is possible to predict its dynamic mechanical behavior. Figure 3 is an example of the isochrone for G' at 0.1 radians per s for polystyrene with molecular weight of 330,000. The fictive temperature of 90°C has been used. This is compared to the data obtained by Tobolsky and Yu [19].

Beyond equilibrium amorphous state

Below T_g, an amorphous polymer is in a non-equilibrium state. This is manifest by the physical aging of the glassy state. Physicists argue that the glassy state is not a state because it is not in equilibrium, at which extensive quantities such as volume, enthalpy and entropy continue to change under constant temperature and pressure (the intensive variables). The rate for the aging process can be estimated by the use of a rate equation in which the time constant τ is continuously changing with time. The resulting solution is an exponential integral that resembles a stretched exponential from a broad distribution of relaxation times, although the apparent similarity comes about for the entirely different reasons.
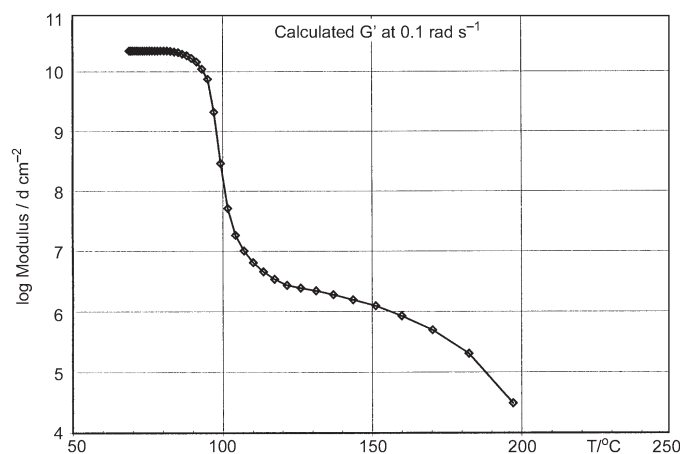
Fig. 3 The master curve of Fig. 1, replotted *vs.* temperature at the frequency of 0.1 rad s^{-1}. This plot was made to compare with the data in [19]

The relaxation process in the glassy state manifest the relaxation time that follows the Arrhenius formula rather than the Vogel-Fulcher formula, because the domain size z is independent of temperature (neglecting the aging).

Many polymers exhibit additional transitions below T_g, that are called β, γ, etc, in the order of the descending temperatures. Low temperature relaxation processes occur in the restricted environment of the glassy state. It may occur in the form of intramolecular cooperative relaxation in the case of polycarbonate. It may occur in the form of cooperativity with short substituent groups in copolymers. The general rules of the conformer size can be applied to these cases also.

Heterogeneity

Dynamic properties have been studied in many kinds of composites. How each component contributes to the overall behavior can be very complex, because a simple additivity law for the stresses or strains is not convincing. However, the weighted *recoverable* strain energy has been used as the basis for predicting the behavior of composites and blends [11]. Copolymers are heterogeneous in the nanometer scale. In most cases, they are treated as the homogeneous body with the weighting of relative fractions in the relaxation spectrum. The rheological data suggest that there are two scales of heterogeneity. One is in the nanometer scale related to z, and the other is for the normal mode, M^*, the minimum blob size in the high concentration.

Crystalline polymers contain various types of amorphous regions and defects, so they are a kind of composites. DMA of a typical semicrystalline polymer shows the α loss peak that is a transition of the crystalline region into a liquid crystal-like state, the β peak which is typically the glass transition of the amorphous region, and the γ peak that is related to the local motion like the β relaxation in the amorphous regions.

Conclusions

The time-dependent mechanical behavior of a polymer is a manifestation of the relaxation behavior at the molecular level. Molecular motions are complicated by the presence of interactions between the molecules as well as within the molecule. The time scale of the relaxation process is longer if larger parts of molecules are involved. The detailed aspects can be studied by thermal analysis and by dynamic mechanical (and dielectric) analysis that complement each other.

Personal tribute

For many years, Dr. Turi has organized and ably administered her well-known short courses in thermal analysis. For the last several years I have been honored to lecture for Dr. Turi on dynamic mechanical analysis in the context of thermal analysis. Understanding of viscoelastic behavior of polymers requires knowledge of their thermal behavior. Viscoelastic properties cannot be fully understood without thermal data.

In this manuscript written to celebrate Dr. Turi's outstanding contributions to the science of thermal analysis, it is my intention to submit my thoughts on the temperature dependence of the viscoelastic and rheological behavior of polymer molecules that is one of the objects of study in thermal analysis.

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