A Model for Intermolecular Cooperativity in Conformational Relaxations near the Glass Transition

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ABSTRACT: Some of the basic molecular and thermodynamic factors that affect the relaxation behavior above and below the glass transition temperature are discussed. A model is proposed for segmental relaxation that requires *inter*molecular cooperativity. A domain of cooperativity is defined as a group of segments that must undergo relaxation simultaneously. As the density is increased by changes in temperature or pressure, the domain size, as specified by the number z of the interlocked segments, grows and the conformational entropy decreases more than it would in isolated chains. In the process, it becomes progressively more difficult to maintain thermodynamic equilibrium, and the glass transition ensues. It can be shown that for a given drop in temperature, the increase in the domain size z is greater for a polymer with a larger conformer, which as a result undergoes the glass transition at a higher temperature. Thus, this model employs the basic concepts of the theory of Adam and Gibbs, although the specifics vary. A relaxation function is formulated based on the domain size distribution. The resulting equation gives a better fit to the dielectric and viscoelastic data than the Kohlrausch–Williams–Watts equation, particularly at extremely high frequency or short times. The theory is extended into the *non*equilibrium glassy state by fixing the entropy at the fictive temperature. In the glassy state, the breadth of the relaxation spectrum increases because of the domain size-dependent spread in the activation energy for the segmental relaxation.

1. Molecular Model for Intermolecular Cooperativity

When a force is applied over a polymer chain through the surrounding medium, the molecular segments respond by readjusting themselves to relieve the stress. The momentarily raised free energy dissipates by a small amount every time a segment reorients to a new lower free energy state. The "stress" referred to here can also be in the form of an electrical potential acting on a polar segment. In polar polymers, the segmental dipoles react to the sudden imposition of an electric field by reorienting from the original random and isotropic orientational state to a state of orientation in the direction of the field. The orientation cannot take place at once, however, because the rate at which the molecules can reorient is limited by their ability to undergo configurational changes.

The angular dependence of the potential energy for rotating the carbon–carbon bonds in butane has been investigated by Abe and Flory.[1] The energy difference between the gauche and trans states is ca. 500 cal/mol, and the activation energy is ca. 3100–3500 cal/mol of bond. The relaxation time for the rotational motion of the C–C bond between two methylene units is $\sim 10^{-10}$ s at room temperature. In polymers the molecular segments undergo more complex motions involving triads as suggested by Helfand and co-workers,[2] but the basic barrier is that of the C–C rotation. The barrier energy weakly increases with the size of the segments, as will be discussed.

The smallest segmental unit of rotation (which we will call a conformer) is surrounded by other conformers in a solid or molten state. In order for a conformer to complete a rotational relaxation, its neighbors must also move *in cooperation*. The barrier for this process is intermolecular by nature. Under such restrictions a conformer can change its conformational state only if its close neighbors *cooperate* with it as if they are in a group of meshed gears. This is illustrated in Figure 1. A model incorporating meshed gears has been suggested by Adachi,[3] although his analysis is quite different from ours.

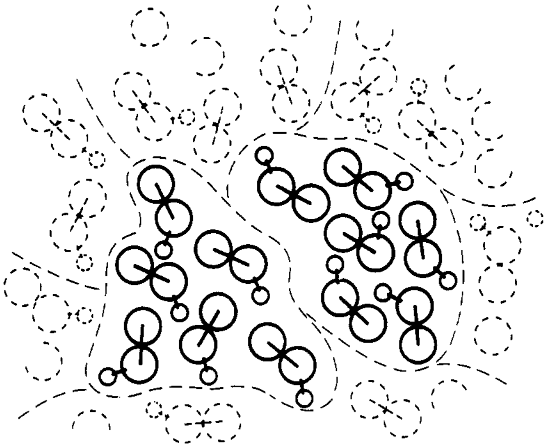


Figure 1. Model for the intermolecular cooperativity where molecular segments in a domain can only relax together.

The effective domain size increases with the overall density. If equilibrium can be achieved at a low-temperature limit we call T_0, every conformer becomes meshed with all others, the entire body of the polymer becomes one huge meshed domain, and the number of conformers in one domain is nearly infinite. This is the state of zero conformational entropy at temperature $T_0 \gg 0$ K. At the high-temperature limit we call T^*, on the other hand, the conformers are sufficiently far apart that each can relax independently from the neighbors, and only the intramolecular barrier must be overcome. The number of conformers in each domain is 1. Between these two extreme temperatures, the size of a domain is specified by the number z of conformers in the domain. In the example in Figure 1, z is shown to be 6. The basic concepts of this model are that of the theory of Adam and Gibbs,[4] though the specifics vary. Also, this model will incorporate a distribution of the relaxation times.

For illustration purposes only, we first assume that each conformer can take 3 different conformations. At the high-temperature limit T^*, where no cooperativity is at work among the conformers, 6 independent conformers are able to exhibit $W_z = 3^6$ conformational states. In the state

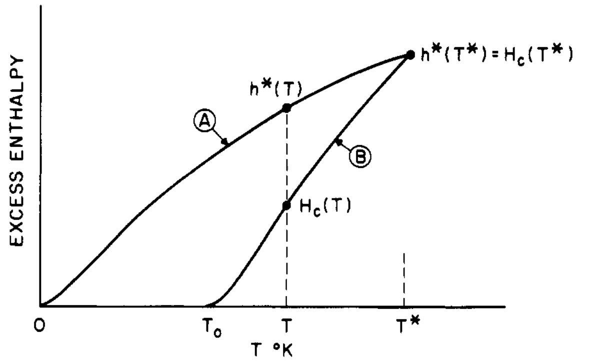


Figure 2. Excess enthalpy $h^*(T)$ without intermolecular cooperativity (curve A) and $H_c(T)$ with cooperativity (curve B). Curve A is obtained from the concentration of the high-energy conformation(s) through calculation of the rotational isomeric states.

illustrated where 6 conformers are meshed together, however, in order for one conformer to change its conformation, all others must change also. Thus, it makes no difference which conformer the observer disturbs, the results are always that every conformer in the domain of cooperativity must change its conformation. Thus, the total number of conformations available to the domain of 6 intermeshed conformers is only 3. A domain of z meshed conformers can take only the same number of states that one conformer can take, i.e., $W_z = 3$. We now generalize the above example by calling the number of states a conformer can take c_1 instead of 3. Since the conformational probability depends on the populations of gauche and trans conformations, the value of c_1 is temperature dependent. c_1 is also species dependent, as some bond angles are prohibited in certain polymer chains. For 1 mol (of conformers) in which there are N_z domains consisting of z conformers, the conformational entropy S_c for 1 mol of conformers is

$$S_c = N_z k \ln c_1 \tag{1}$$

where k is the Boltzmann constant. Because $z = N_A/N_z$, where N_A is Avogadro's number

$$z = N_A k \ln c_1 / N_z k \ln c_1 = N_A k \ln c_1 / S_c \tag{2}$$

Thus, the domain size z is inversely proportional to the conformational entropy. We now define s^* as the conformational entropy of 1 mol of conformers in chains that are not mutually restricted by each other, i.e., where each conformer relaxes independently:

$$s^* = N_A k \ln c_1 \tag{3}$$

s^* is the conformational entropy that corresponds to that calculated by rotational isomeric state theory, and it too is temperature dependent. Thus, we obtain the formula

$$z = s^*/S_c \tag{4}$$

At T^*, S_c and s^* are equal. The value of T^* turns out to be 500 °C. As we shall show in Figure 7, the relaxation vs temperature plots for all polymers approximately converge to this T^* and 3×10^{-11} s. Below T^*, as the temperature is decreased, the conformational entropy S_c (and enthalpy) will drop more rapidly than does s^* and will reach 0 at T_0, while s^* depends on the equilibrium concentration of various conformations and will reach 0 at 0 K. The comparison between the corresponding enthalpies is illustrated schematically in Figure 2. Curve A denotes the excess enthalpy h^* without meshing of the conformers, and it is approximately proportional to the concentration of higher energy configurations calculated from rotational isomeric statistics. Curve B represents the conformational enthalpy H_c that incorporates the meshing or cooperativity concept, which raises the zero entropy temperature from 0 K to T_0. If we assume that curves A and B have similar shape but differ only in the temperature scale, curve B can be obtained by compressing curve A through a change in the temperature scale from $[0 \rightarrow T^*]$ to $[T_0 \rightarrow T^*]$, and we obtain the relationship

$$\frac{H_c(T)/H_c(T^*)}{h^*(T)/h^*(T^*)} \approx \frac{(T-T_0)/(T^*-T_0)}{T/T^*} \tag{5}$$

and since the free energy, enthalpy, and entropy all scale proportionately

$$H_c/h^* \approx TS_c/Ts^* \tag{6}$$

we obtain

$$\frac{S_c}{s^*} = \frac{T^*}{T^*-T_0}\,\frac{T-T_0}{T} \tag{7}$$

In order for the z meshed conformers in a domain to relax *simultaneously*, their combined transition probability is the zth power of the (independent) probability of one conformer, and the apparent activation energy must be z times the *intra*molecular activation energy for one conformer to relax. We define this energy barrier as $\Delta\mu$. $\Delta\mu$, for example, depends on the van der Waals force, which in turn depends on the packing density, as we shall discuss later. For non-polymers such as *o*-terphenyl, it is possible to arrive at a reasonable value for $\Delta\mu$ empirically. The relaxation time λ at T is related to the relaxation time λ^* at T^* by the formula

$$\ln \frac{\lambda}{\lambda^*} = \frac{\Delta\mu}{k}\left(\frac{z}{T} - \frac{1}{T^*}\right) \tag{8}$$

but, from eq 4

$$\ln \frac{\lambda}{\lambda^*} = \frac{\Delta\mu}{k}\left(\frac{s^*}{TS_c} - \frac{1}{T^*}\right) \tag{9}$$

Expectedly, this equation is identical in form with the Adam–Gibbs equation,[4] although our S_c is largely intermolecular in nature and therefore is not limited to polymers.

Substituting eq 7 into eq 9 will obtain

$$\ln \frac{\lambda}{\lambda^*} = \frac{\Delta\mu}{k}\,\frac{T^*-T_0}{T^*}\,\frac{1}{T-T_0} - \frac{\Delta\mu}{kT^*} \tag{10}$$

which is the Vogel–Fulcher equation[5]

$$\ln \frac{\lambda}{\lambda^*} = \frac{\Delta\mu^*}{k}\,\frac{1}{T-T_0} - \frac{\Delta\mu^*}{kT^*} \tag{11}$$

where $\Delta\mu^* = \Delta\mu(T^*-T_0)/T^*$. ($\Delta\mu/kT^*$ in eq 10 was simply changed to $\Delta\mu^*/kT^*$, as $\Delta\mu^*$ is the activation energy for an independently relaxing conformer.) In the equilibrium state, eq 11 is completely equivalent to the Williams–Landel–Ferry (WLF) equation:[6]

$$\log \frac{\lambda}{\lambda_r} = -\frac{C_1(T-T_r)}{C_2 + T - T_r} \tag{12}$$

where C_1 and C_2 are constants that depend on the choice of the reference temperature T_r, and to the free volume equation by Doolittle:[7]

$$\ln \frac{\lambda}{\lambda_r} = \frac{1}{\alpha_f(T-T_0)} - \frac{1}{\alpha_f(T_r-T_0)} \tag{13}$$

based on an arbitrary reference temperature, T_r. However, an important difference exists between the Adam–Gibbs

Table I
Vogel-Fulcher Energy

polymer	$\Delta\mu^*$, kcal/mol	polymer	$\Delta\mu^*$, kcal/mol
polyisobutylene	4.2	hevea rubber	4.2
polycarbonate	3.6	poly-1,4-butadiene	3.1
poly(vinyl acetate)	3.4	poly-1,2-butadiene	2.1
polystyrene	3.2	styrene-butadiene copolymer	8.3
poly(α-methylstyrene)	3.1	poly(dimethylsiloxane)	2.1
poly(methyl acrylate)	3.8	poly(oxymethylene)	1.8
poly(methyl methacrylate)	11.7	poly(propylene oxide)	1.8

Table II
Molar Heat and Volume of Fusion per Conformer

	E, cal/mol	V, mL/mol	M	E/M, cal/g
CH_2	680	21.8	14	48
C_6H_4	3900	83.9	76	51
$CH{=}CH$	1700	32.0	26	65
$C(CH_3){=}CH$	2400	53.8	40	60
$CH(CH_3)$	1360	42.8	28	49
$C(CH_3)_2$	1900	65.4	42	45
$CH(C_6H_5)$	4300	105.7	90	48
CCl_2	3100	53.4	77	40
$CHCl$	2360	37.6	45	52
COO	2900	28.9	44	66
O	1000	7.3	16	53
CH_3	1700	27.8	15	113
C_6H_5	5400	89.9	77	70
Cl	2800	21.8	35.5	79
$COOH$	5600	36.5	45	124
OH	5800	14.9	17	341

equation and the free volume equation. In the *non*equilibrium glassy state, the former correctly predicts the temperature dependence of the loss peak frequency, while the latter predicts temperature independence.[8-10]

When eqs 11 and 13 are compared, it is immediately clear that $\Delta\mu^*/k$ should be numerically equal to $1/\alpha_f$. α_f is the expansion coefficient of the Doolittle free volume fraction $f = V_f/V$, where V_f is the free volume $V - V_0$, and V_0 is the "occupied" volume, which is obtained by extrapolating the equilibrium liquidus line to T_0. The values of α_f are found experimentally to be nearly the same for many polymers, $\sim 3 \times 10^{-4}$ K^{-1}. This implies that $\Delta\mu^*$ should exhibit a "universal" value of 3–3.5 kcal/mol of *conformer*. The experimental values of $\Delta\mu^*$ shown in Table I were calculated from the shift of viscoelastic and dielectric relaxation spectra with temperature in the equilibrium state, most showing values close to 3 or 4 kcal. From the WLF coefficients, C_1 and C_2 in eq 12, $\Delta\mu^* = 2.3RC_1C_2$, is obtained. Some data in the table were derived from our own unpublished data, while others were taken from Table 11-II in ref 11. In fact $\Delta\mu^*$ is approximately equal to the *intra*molecular activation energy for the C–C bond rotation in butane. (For polymers with heteroatom backbones such as siloxanes and ethers, $\Delta\mu^*$ is smaller, as are the bond rotation activation energies.) This implies that $\Delta\mu^*$ does not depend on the polymer species. However, $\Delta\mu$ varies with the chemical structure, and as will be shown, the relationship between $\Delta\mu$ of a given polymer and the universal value $\Delta\mu^*$ is described by the equation

$$\Delta\mu = \Delta\mu^* \frac{T^*}{T^* - T_0} \tag{14}$$

Thus, the activation energy for the *intra*molecular relaxation of *one* C–C bond is greater with conformers that exhibit a higher T_0 and thus a higher T_g. As we shall discuss below, the differences in the packing densities among polymers of different conformer sizes affect the excess cohesive energy.

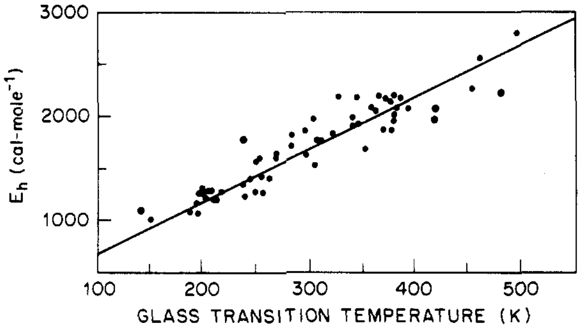


Figure 3. Hole energy,[11] or the excess enthalpy at T_g described by eq 17.

It can be shown from thermodynamics that the specific heat related to the configurational entropy with cooperativity is

$$\Delta C_p = T\frac{dS_c}{dT} = T\left(\frac{\partial S_c}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p \tag{15}$$

where $\Delta C_p = C_{p,\text{liquid}} - C_{p,\text{glass}}$, hence

$$T\left(\frac{\partial S_c}{\partial V}\right)_p = \frac{1}{V}\frac{\Delta C_p}{\Delta\alpha} \tag{16}$$

where the thermal expansion coefficient, $\Delta\alpha = \alpha_{\text{liquid}} - \alpha_{\text{glass}}$. For convenience, we shall take T_g to be the temperature at which the characteristic relaxation time has a chosen value λ_g, even though we are aware that the glass transition temperature is not a thermodynamic temperature. λ_g turns out to be 2 h for $T_g = T_0 + 50$ °C, as will be discussed. This is similar to defining T_g to be the equilibrium temperature at which the shear viscosity has an arbitrary value, e.g., 10^{13} poise.

Consider now that we increase the volume at T_g from V_0 to V_g. The total increase in the enthalpy E_h is T_gS_{cg} and

$$E_h = T_gS_{cg} = \frac{\Delta V_g}{V_g}\left(\frac{\Delta C_p}{\Delta\alpha}\right)T_g \tag{17}$$

The above E_h has been designated as the "hole energy" by Kanig,[12] since it is the energy required to create the free volume fraction $f_g = \Delta V_g/V_g$ at T_g. E_h (in calories per mole of repeat units) calculated from the experimental data for over 70 polymers shows, in Figure 3, a clear tendency to be greater for polymers with a higher T_g. (Kanig actually derived an equation with van der Waals volume in place of V_g in eq 17 and introduced a correction that ends up essentially the same as eq 17.)

Equation 17 should be, according to our model, on the basis of a mole of conformer. The hole energy E_h per mole of conformer is the cohesive energy per mole. However, this relationship should also hold between E_h per gram and ΔC_p per gram, since the volume ratio and the thermal expansion coefficients do not depend on the chosen amount of mass. Bunn[13] published in 1955 his observation that the molar heat of fusion for conformers of various sizes and shapes can be scaled with their molecular weights, drawing an analogy to Trouton's rule that the ratio of the heat of evaporation to the temperature of vaporization proportionality between the molar heat of fusion and the molecular weight with a proportionality constant of ca. 50 cal/g for conformers that are *in the middle* of a chain rather than at the end. (Chain ends are at a higher energy level.) These values of cohesive energy in his Table I were divided by the molecular weight of the corresponding unit and are shown in Table II. Bunn finds, however, the proportionality to be only an approximate relationship,

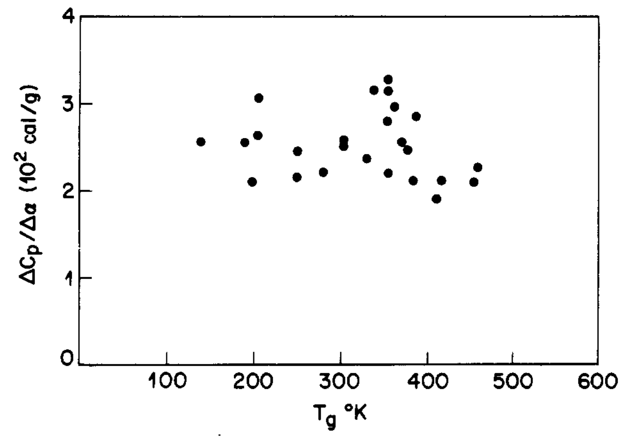


Figure 4. Ratio of ΔC_p over $\Delta\alpha$ in eq 17 vs T_g. Unlike the hole energy, there is no trend indicative of a temperature dependence.

and in order to be applicable to structures composed of a group of these conformers, a correction factor for the packing density must be taken into consideration. The quantity $\Delta C_p/\Delta\alpha$ per gram is essentially independent of T_g, as shown in Figure 4.

When segments are packed together, according to Bunn, the molecular volume is actually smaller than the sum of individual segments, and the cohesive energy is therefore greater than the sum. Corrected values for the molecular volume and the cohesive energy can be made following the equation

$$\frac{E_1 - E_2}{E_2} = 1.73\frac{V_2 - V_1}{V_1} \tag{18}$$

for segmental species 1 and 2. This has been shown to hold for the substance in which intermolecular forces are of the van der Waals type, whether or not there is a phase-change from liquid to solid. (This is exactly the correction factor that Kanig introduced for the difference between the van der Waals volume and V_g. Thus the fractional free volume defined by V_f/V_g, rather than $V_f/V_{0,0\,\mathrm{K}}$, should be regarded as the universal constant.)

We can apply this formula to obtain a correction for the intermolecular energy when the molar volume is increased from V_1 to V_2 by increasing the molecular weight from M_0 to M:

$$\frac{E - E_0}{E_0} \propto \frac{M - M_0}{M_0} \approx \ln M - \ln M_0 \tag{19}$$

Thus, the hole energy per gram increases with ln M, whereas from simple additivity, E_h per gram should be independent of the conformer size.

The conformational entropy S_{cg} at T_g in eq 17 can be substituted with the entropy without cooperativity, s_g^*, using eq 7 to obtain

$$(T_g - T_0)s_g^* \frac{T^*}{T^* - T_0} = E_h = E_{h_0} + C(\ln M - \ln M_0) \tag{20}$$

where E_{h_0} and M_0 refer to a hypothetical polymer with T_0 = 0 K. (T^* = 773 K as mentioned earlier.) From the Vogel equation, $T_g - T_0$ must be a constant for various conformers to satisfy the iso-λ_g condition. The entropy s_g^* is for no meshing from the neighbors to interfere. For that polymer with $M = M_0$ and T_0 = 0 K, $T_g s_g^* = E_{h_0}$. Thus, eq 20 states that among various species the following relationship should hold:

$$(T^* - T_0) \ln M = C_3 = T^* \ln M_0 \tag{21}$$

In Figure 5, we have shown that T_g is higher for repeat units with greater molecular weight. Because a repeat unit may consist of one to several conformers, the scatter of the data points is not surprising. However, there is a trend suggesting the proportionality between the log molecular weight of repeat units vs T_g. With our model, a repeat unit in a typical vinyl polymer consists of two conformers. If eq 20 should hold for the conformers, then eq 21 should also hold and C_3 should be a universal constant. We find this to be true with $C_3 \approx 1750$ for many of the common vinyl polymers, when half of the monomer molecular weight is taken as M for the average size of the conformers. Examples are shown by polymers 1–14 in Table III. For these entries and others to follow, M is the molecular weight of the repeat unit, and the number after the / is the number of conformers per repeat unit, which in the majority of cases is simply the number of "beads". T_g is the experimental value. T_0 is simply T_g – 50 K. C_3 is calculated from these numbers. T^* is 500 °C. The universal value 1750 for C_3 translates to M_0 of 9.6 (or $^2/_3$ the size of a methylene unit) for the previously mentioned hypothetical polymer with T_0 of 0 K, in which the domain size remains 1 down to 0 K with no intermolecular meshing. In the following exercise of estimating the number of conformers per repeat unit in polymers, one should keep in mind that the local relaxation we are interested is essentially the "unkinking" of segments in the main-chain arrive at the conclusion that the glass transition temperature of linear polyethylene (polymer 1) is the γ transition temperature. The β transition in polyethylene, according to the same rule, would involve three carbons as two conformers. For poly(vinyl chloride) (PVC; polymer 10) with strong dipoles, C_3 is substantially smaller, but a density correction to M will result in $C_3 \approx 1750$. Two notable exceptions to the simple rule of two conformers per repeat unit are polyisobutylene (6) and *cis*-polyisoprene (8). In both cases, the most suitable conformer size to be consistent with their experimental T_g values is 16 or 17, which is a size only slightly larger than a methylene unit; i.e., each methyl and methylene unit is a conformer.

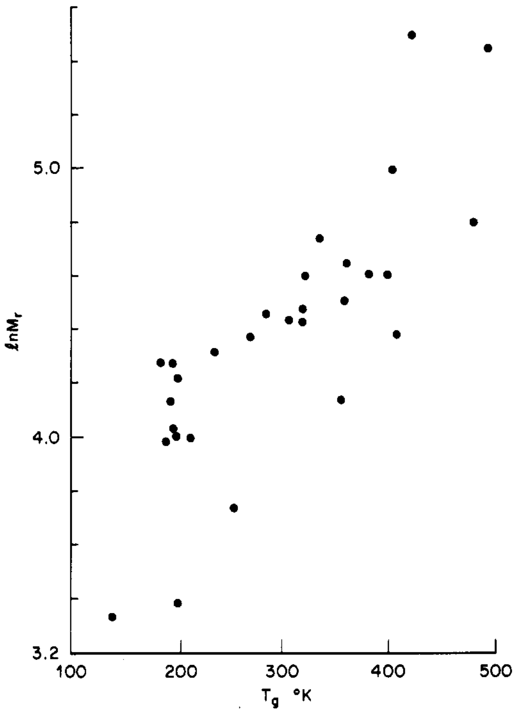


Figure 5. log molecular weight of the repeat unit vs T_g. A possible linear relationship exists if a proper choice for the conformer size is made instead of simply using the repeat unit as the segmental unit.

Table III
The Relationship between Conformer Size and T_g

		M	T_g	$T^* - T_0$	ln M	C_3	conformers
				Aliphatic Polymers			
1	PE	14/1	−110	660	2.64	1742	[CH$_2$] 1
2	PE(branch)	41/2	−30	580	3.02	1751	[CH$_2$][CHCH$_3$] 2
3	1,4-PB	54/3	−55	605	2.85	1750	[CH$_2$][CHCH][CH$_2$] 3
4	1,2-PB	54/2	20	530	3.30	1749	[CH$_2$][CHCH$_2$CH$_3$] 2
4	PP	42/2	−30	580	3.04	1765	[CH$_2$][CHCH$_3$] 2
6	PIB[a]	56/3.5	−74	624	2.77	1728	[C(CH$_3$)$_2$[CH$_2$] 3.5
7	gutta percha	68/3	−10	560	3.12	1748	[C(CH$_3$)][CH=CH][CH$_2$] 3
8	PIsoprene[a]	68/4	−69	619	2.83	1753	[C(CH$_3$)][CH=CH][CH$_2$] 4
9	PMP	85/3	29	521	3.34	1742	4-methylpentene 3
10	PVC[a]	62/2	90	460	3.43	1577	[CH$_2$][CHCl] 2
11	PS	108/2	100	450	3.93	1769	[CH$_2$][CHPh] 2
12	PMS	119/1	180	370	4.78	1768	α-methylstyrene 1
13	PTE	118/3	79	471	3.67	1728	triF Cl eth 3
14	PVA	86/3	29	521	3.36	1748	[CH$_2$][CH(CO)OCH$_3$] 3
15	VDCN–VAc	164/2	179	371	4.41	1636	[C CN$_2$CH$_2$][CHCOOMeCH$_2$] 2
16	VDCN–VFo	150/2	152	398	4.32	1718	VDCN–[CHCOOH CH$_2$] 2
17	VDCN–VPr	178/2	176	374	4.49	1678	VDCN–[CHCOOEtCH$_2$] 2
18	VDCN–VBz	225/2	186	364	4.72	1719	VDCN–[CHCOOPhCH$_2$] 2
19	VDCN–MMA	178/2	145	405	4.49	1818	VDCN–[CMeCOOMeCH$_2$] 2
20	VCDN–VAcCl	199/2	167	383	4.60	1761	VDCN–[CHCOOCH$_2$ClCH$_2$] 2
21	VDCN–VPiv	206/2	171	379	4.63	1757	VDCN–[CHCOOCMe$_3$CH$_2$] 2
22	POM	30/2	−73	623	2.71	1687	oxymethylene 2
23	POE	44/3	−67	617	2.69	1657	ethylene 3
24	POP	58/4	−75	625	2.67	1671	propylene 4
25	POB	72.5	−88	638	2.67	1701	butylene 5
26	PVME	58/3	−22	572	2.96	1694	vinyl methyl ether 3
27	PVEE	72/4	−33	583	2.89	1685	ethyl 4
28	PVIE	86/4	−12	562	3.07	1724	isopropyl 4
29	PVBE	100/6	−56	606	2.81	1704	butyl 6
30	PVHE	128/8	−74	624	2.77	1730	hexyl 8
31	PMMA	100/2	105	445	3.91	1741	[CH$_2$]-[C(CH$_3$)COOCH$_3$] 2
32	I-PMMA[a]	100/3	46	504	3.51	1767	isotactic PMMA 3
33	PEMA	114/3	65	485	3.64	1764	ethyl methacrylate 3
34	PPMA	128/4	35	315	3.47	1784	propyl methacrylate 4
35	PMAC	86/4	9	541	3.07	1660	methyl acrylate 4
36	PBA	132/5	31	519	3.27	1698	*tert*-butyl acrylate 5
				Aromatic Polymers[b]			
37	PPS	108/2	110	440	3.99	1755	[Ph][S] 2
38	PPO	92/2	90	460	3.83	1761	[Ph][O] 2
39	PET	182/5	64	486	3.59	1746	[OPh]O(CO)(CH$_2$)(CH$_2$) 5
40	Pcarbonate	254/3	147	403	4.44	1788	O[bPA]O[CO] 3
41	PEEK	288/3	158	392	4.56	1790	[OPh][OPh][COPh] 3
42	Psulfone	444/4	187	363	4.71	1709	O[bPA]O[Slf] 4
43	PEI	596/4	200	350	5.00	1750	O[bPA]O[Im][PhIm] 4
44	PMDA	207/1	222	328	5.33	1749	[Im = Im] 1
45	PES	232/1	225	325	5.45	1770	[OSlf] 1
45a	PPE	172[a]/1	210	340	5.15	1750	[OPh(CH$_3$)$_3$] 1
46	Kevlar	242/1	235	315	5.49	1729	[NHPhNHCOPhCO] 1
47	A + F	254/3	147	403	4.44	1788	O[bPA]O(C=O) 3
48	B + F	315/2.5	187	363	4.84	1755	[OPh]$_2$CPhMe(C=O) 2.5
49	C + F	376/2	210	340	5.24	1780	O[C(Ph)$_4$]O(C=O) 2
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[c]	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	

[a] These special cases are explained in the text. [b] Ph, phenyl group, bPA, Bisphenol A; Slf, aromatic sulfone PhSO$_2$Ph; Im, imide N(=O)$_2$; O[bPA]O, 2 conformers; OPh, 1 conformer. 45A poly(phenylene ether) is considered as a mixture of head–tail and head–head structures; the latter is a larger conformer and the average was taken. [c] It seems that 3 repeat units makeup 1 conformer for this exceptionally bulky structural unit.

Even though methyl group rotation occurs in an intramolecular barrier, the extremely crowded structure of polyisobutylene is considered to require its rotation to accompany the unkinking relaxation of the main-chain backbone. Thus, we suggest that the methyl groups participate in the conformational changes in these two polymers. If each methyl group is counted as one conformer, there are 4 conformers per monomer unit in polyisobutylene, and also in *cis*-polyisoprene. If $\Delta\mu^*$ for the methyl group is less than for the methylene unit, the number would be less than 4.

The universality of the value of C_3 has also been tested with a number of other polymers, and some additional guidelines for defining conformer size have been determined. For vinylidene cyanide copolymerized with various vinyl monomers, shown as polymers **15–21** in Table III (data obtained through the courtesy of Dr. I. Seo of Mitsubishi Petrochemical Co.), again the value of ca. 1750 (or slightly less because of the dipoles) is obtained when each *monomer* is considered as one conformer. The strong dipole to dipole interaction within the co-mer unit of these piezoelectric copolymers results in the large bulky conformers with high T_g's. The intensity of dielectric relaxation for these polymers has been found to be enormous, substantiating the theory that the whole comer unit rotates as a dipole. For the four linear polyethers **22–25**, the rule can be applied successfully by counting each "bead" in the main chain as a conformer, though the value of C_3 is slightly lower than 1700, this time because the ether bond with a smaller value of $\Delta\mu^*$ is in the chain. If the conformer of –O– unit is scaled as 0.7 of the –C– unit, $C_3 = 1750$ is obtained. For poly(vinyl ethers) **26–30**, each bead in the branch as well as in the backbone is counted as a conformer, as was the case with polyisobutylene. This results in the uniform value of C_3, though it is less than 1700 if the –O– conformer is counted as 1. If it is counted as 0.7, however, the approximate value of 1750 is obtained. When T_g goes *down* with each additional C in the branch it is an indication that each –C– unit on the branch is participating in the relaxation by rotating simultaneously with the conformational change in the backbone. When the above rule is applied to methacrylates **31**, **33**, and **34**, a C_3 of ~1750 is obtained. For isotactic PMMA (**32**), 3 conformers instead of 2 conformers per monomer had to be assumed, possibly because a cooperative conformational change with the ester group is needed in the more densely packed isotactic polymer system. For the two acrylates **35** and **36**, the greater number of conformers also reflects the conformational changes within the ester groups when the α-methyl group in the methacrylate is removed.

In aromatic polymers, we find that a phenylene group alone cannot be counted as one conformer. A *p*-phenylene unit can rotate about its own longitudinal axis without disturbing the immediate neighbors on either side. Such a rotational mode does not contribute toward the relaxation of an applied stress, as it does not help unkink twisted segments. The rotation of the same phenylene group about a bond once removed, however, would be accompanied by a change in the shape of the local structure. Thus, if an ether or a carbonyl group is in the adjacent position in the main chain, it should be included as part of the conformer, i.e., a phenyl O or phenyl CO group should be counted as one conformer, and this leads to a C_3 of 1750, as shown by the 10 examples, polymers **37–46**, in Table III. If one follows this rule, a Bisphenol A with O in both sides should be considered as two conformers. Thus, the repeat unit of Bisphenol A polycarbonate consists of three conformers. The case of Kevlar is an exceptional one. It can be shown with molecular models that the rotation of the whole repeat unit can be achieved without a change of the conformation, the feature analogous to that of the rotating *p*-phenylene group, so the whole unit is counted as one conformer.

A group of high-temperature aromatic copolymers prepared by Mr. T. Tanaka of Unitika Ltd. have also been examined. These are included as polymers **47–55** in Table III. The chemical structures of the basic groups as well as that of the copolymers are shown in Table IV. They are polyarylates combining (A) Bisphenol A, (B) Bisphenol AP, or (C) fluorene with (D) a 50/50 mix of tere- and isophthalate, (E) 2,2′-biphenyl carboxylate, or (F) carboxylate. The numbers of conformers per monomer are (A) 2, (B) 1, (C) 1, (D) 0.5, (E) 3, and (F) 1, for which again C_3 of ca. 1750 is obtained. The curious number of 0.5 is assigned to the D group is perhaps because the terephthalate half does not participate in the conformational change independently, while the isophthalate half will, but we have no proof at this point. The conformer size is thus a measure of the molar cohesive energy of a chain segment, which increases with the larger conformer size for the reasons stated above. Equation 21 with $C_3 = 1750$ is plotted in Figure 6, together with the points corresponding to various polymers, some of which are included in Table III. The data point for PPE moves onto the curve if it is considered to be a half head-to-head and half head-to-tail mixture.

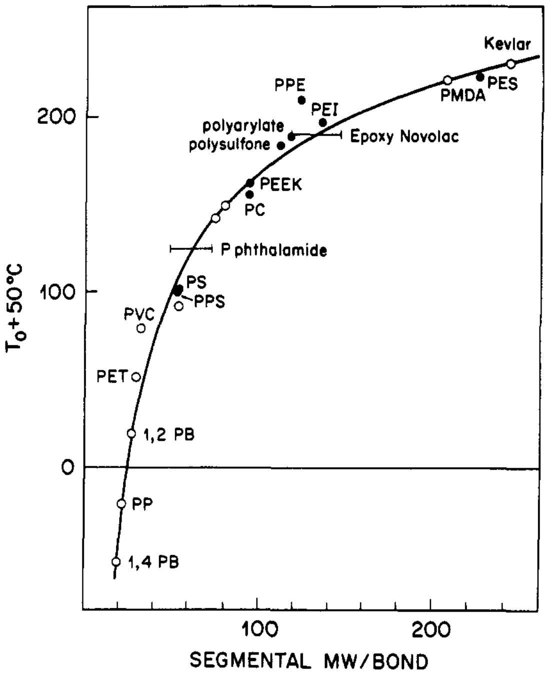


Figure 6. T_g vs the "conformer size" as determined by following the rule described in Table III. The theoretical curve from eq 21 is plotted. This plot is useful in estimating the conformer size when T_g is known, providing the insight for the relevant intramolecular motion for the segmental relaxation.

Finally, we summarize the useful features of this model by showing the so-called "transition map" for polycarbonate and poly(ethylene terephthalate) in Figure 7. A transition map is a plot of the frequency for the maximum rate of relaxation vs $1/T$ K.

The term including λ^* and T_0 in eq 11 can be further reduced to a universal value by considering again the hypothetical polymer with a conformer size of M_0, which exhibits $T_0 = 0$ K and the relaxation time λ_0^* at T^*:

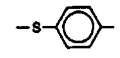
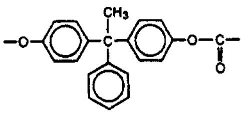
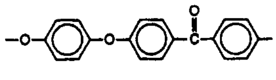
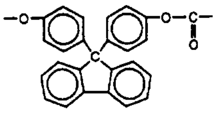
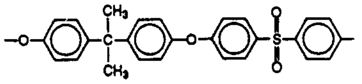
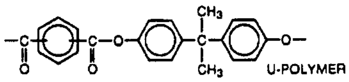
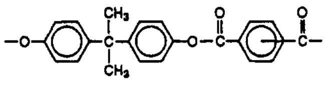
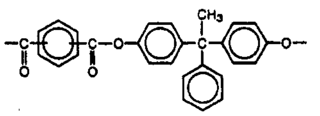
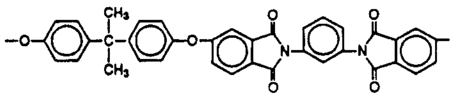
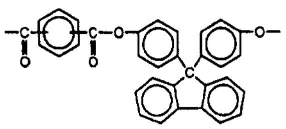
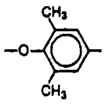
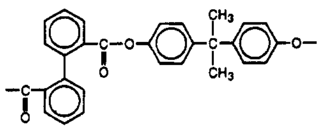
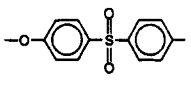
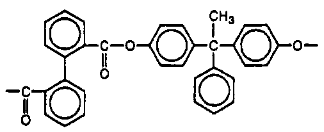
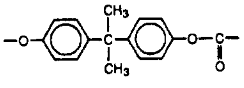
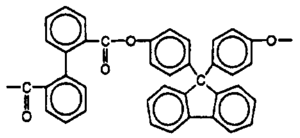
$$\ln\frac{\lambda}{\lambda_0^*} = \frac{\Delta\mu^*}{kT}\,\frac{T}{T-T_0} - \frac{\Delta\mu^*}{kT^*} \qquad (11')$$

All curves, including the β transition, seem to start at $T^* = 500$ °C, $\log \lambda_0^* - \Delta\mu^*/2.3kT^* = -11.4$ (seconds). The limiting relaxation time λ_0^* of ca. 3×10^{-11} s corresponds to the range of the dielectric relaxation time for heptane extrapolated to T^*.[14] Recently, Kaji et al.[15] reported the quasielastic neutron scattering on the local motions of *cis*-1,4-polybutadiene with a characteristic time of $\sim 5 \times 10^{-11}$ s with an activation energy of 2–3 kcal/mol. The corresponding frequency $\log f_0^*$ is the upper limit that a relaxation process is observable for any polymer. Similarly, $T^* = 500$ °C is the upper limit of temperature for T_0. As was mentioned earlier, λ_g of 1.8 h is obtained for $\Delta\mu^*$ of 3.5 kcal and $T_g = T_0 + 50$ °C. From eqs 14 and 11′, the following equation is obtained:

$$\Delta\mu\frac{s^*}{S_c} = \Delta\mu z = \Delta\mu\frac{T^*-T_0}{T^*}\,\frac{T}{T-T_0} \qquad (22)$$

from which the domain size z (which depends on the temperature) can be estimated. The slope of the α process curves in Figure 7 divided by the gas constant is not the

Table IV
Chemical Formulas for Polymers in Table III[a]

compound		structure	T_g, °C	compound		structure	T_g, °C
37	poly(phenylene sulfide)		100	48	B + F		183
41	poly(ether ether ketone)		158	49	C + F		210
42	polysulfone		187	50	D + A		195
50	polyarylate		192	51	D + B		243
43	poly(ether imide)		200	52	D + C		310
45a	poly(phenylene ether)		210	53	E + A		148
45	poly(ether sulfone)		225	54	E + B		172
47	A + F		147	55	E + C		205

[a] A, Bisphenol A; B, Bisphenol AP; C, fluorene; D, terephthalate + isophthalate 50/50; E, 2,2′-biphenyl carboxylate; F, carboxylate.

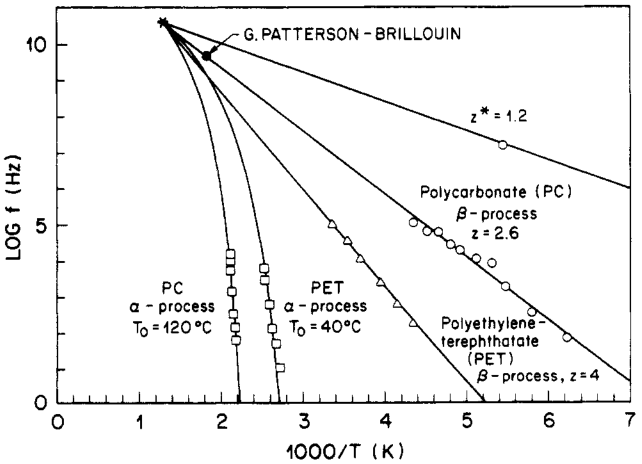


Figure 7. Transition map - log frequency at which the dielectric loss maximum is observed vs $1/T$ K, for polycarbonate and poly(ethylene terephthalate).

above quantity, $\Delta\mu z$. The derivative of eq 11′ with respect to $1/T$ is $\Delta\mu^* T^2/k(T - T_0)^2$, which is usually a large value in the range of 200 kcal near T_g, but it is not a meaningful entity from the physics viewpoint. For the apparent activation energy in the glassy state where z is constant, a reasonable value of ca. 40 kcal/mole is obtained. Since $\Delta\mu \approx$ 4–6 kcal/mol (of conformer), the domain size z_g at T_g is typically ca. 7–10 conformers. Generally, a sudden decrease in the slope of the shift factor from 200 to 40 kcal is observed as the liquid departs from the equilibrium state and enters the nonequilibrium glassy state.

The β relaxation process typically is a constant activation energy process. The process can be considered as due to molecular segments trapped (like gas molecules trapped in clathrates) but able to continue liquidlike, though local, motions even after the rest are vitrified. The apparent activation energy is a few times greater than $\Delta\mu^*$, which leads to the speculation that a chain is "pinned" at the bulkiest conformer, and intramolecular coordination is needed for this relaxation process. The number of conformers in the β process must be equal to or smaller than the domain size for the α process at the glass transition. For polycarbonate, the size of a unit of relaxation for the β process is between 2 and 3 conformers, whereas for poly(ethylene terephthalate) (PET) the size is 4 or 5 conformers. These values correspond to the number of conformers per repeat unit in the α transition. This suggests that one of the conformers within a repeat unit is especially easier to be pinned by the neighboring chains, and this leads to the result of one repeat unit as a typical size for the β relaxation. The larger number of conformers for the β relaxation in PET is related to many C–C links, each acting as a conformer within the repeat unit, while the terephthalate is the likely site where the

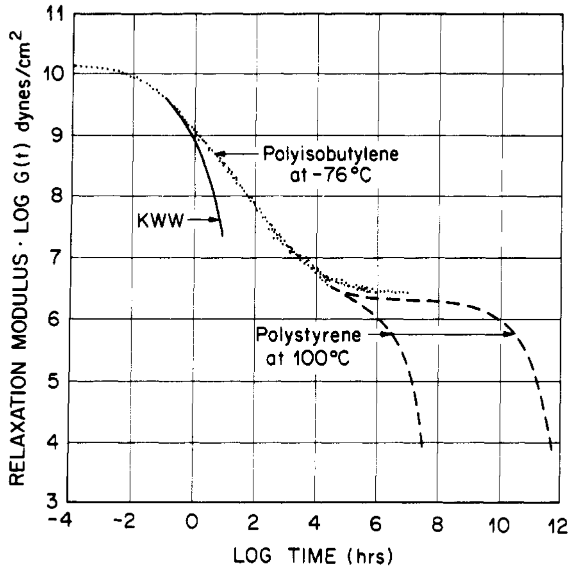


Figure 8. Master curve for viscoelastic relaxation modulus for amorphous polymer in the equilibrium state, from Catsiff and Tobolsky[24] for polyisobutylene, and Marin and Graessley[25] for polystyrene data.

group is pinned. When the β relaxation involves the conformers in the main chain as these examples do, the β process merges with the α process at T^*, and the molecular weight of the repeat unit divided by these numbers typically agrees with the molecular weight of the respective conformers used for calculation in eq 21. Thus, even though polycarbonate has a higher T_g than poly(ethylene terephthalate), its β temperature is lower. This feature should be useful for designing a polymer molecule with a high T_g but a low T_β, which has perhaps better low-temperature fracture properties. If a side group is responsible for the β relaxation, as in PMMA, the β process will merge with the α process at a substantially lower temperature than T^*, and the two curves will not appear as tangentially touching each other. One point shown on the straight line labeled $z = 1.2$ corresponds to the frequency and the temperature of the methyl group rotation, which we think is a good example of the unhindered conformer; i.e., z is always 1. This is neither α nor β transition, but it represents a limit of the shortest relaxation time for all kinds of polymers and olefins.

2. Distribution of Relaxation Times near the Glass Transition

A "master" curve for the relaxation modulus of an amorphous polymer in the equilibrium state is shown in Figure 8. The wide range of the relaxation spectrum is divided into three stages, stage 1 being the comparatively fast-relaxing stage observed at low temperatures, stage 2 being the transition zone between the solidlike stage 1 and the much slower stage 3 observed in a typical melt.

We will discuss only stage 1. This stage is observed in the solidlike state where the characteristic relaxation time λ_c is in the order of hours. (A benchmark can be set at λ_c of 1 h at T_g − 5 °C with G(1 h) of 10^9 dyn/cm².)

Our cooperative domain model has dealt up to this point with a single relaxation time associated with the characteristic domain size. In fact, the theory of Adam–Gibbs considers equivalent and identical cooperative rearranging regions, i.e., a single relaxation time. However, the possibility of a variation in domain size must exist. The well-known memory effect in the volume recovery experiment conducted by Kovacs[16] is a point in case. It could best be explained by the existence of different size domains having different relaxation times. At a given temperature T, the cooperative domain with size z will exhibit a relaxation time λ following the equation

$$\ln \frac{\lambda}{\lambda_c} = \frac{\Delta\mu}{kT}(z - z_c) \tag{23}$$

where the subscript c refers to the characteristic (maximum or "cutoff") size, or the Adam–Gibbs domain size. (This λ is the size-dependent relaxation time, whereas λ in eq 10 is approximately equal to λ_c above.) The logarithm of the modulus is related to the population of domains with size z. The population ΔN_z of domains whose size falls between z_1 and z_2 can be described by the difference between the modulus $G(\lambda_1)$ at time $t = \lambda_1$ and $G(\lambda_2)$ at time $t = \lambda_2$:

$$\Delta N_2 \propto \frac{G(\lambda_2) - G(\lambda_1)}{G(\lambda_1)} \approx \ln G(\lambda_2) - \ln G(\lambda_1) \tag{24}$$

The maximum size z_c is uniquely determined by the pressure and temperature. The energy per domain is proportional to the number of conformers in that domain, as we discussed earlier in relation to Table II. The entropy per domain is, by definition, equal to the entropy of one conformer. Thus, Gibbs free energy is proportional to the size of the domain. From the equipartition principle, the total free energy per each ensemble of domains with a given size should be the same, and this is accomplished by making product zN_z constant. Moreover, since the total number of conformers residing in all of the various size domains is Avogadro's number N_A, we obtain

$$\sum_{z=1}^{z_c} zN_z = N_A \tag{25}$$

from which the following relationship should hold:

$$N_z = \frac{N_A}{z_c}\frac{1}{z} \tag{26}$$

and N_z/N_A is the fractional number of domains of size z. The proportionality sign of eq 24 can be replaced by the equality sign if N_z is taken to be such a fractional number. From eq 23 and 24, if we let $z_2 = z_c - 1$ and $z_1 = z_c - \zeta$

$$\ln G(\lambda_2) - \ln G(\lambda_1) = \frac{1}{z_c}\left(\frac{1}{z_2} - \frac{1}{z_1}\right) = \frac{1}{z_c}\left(\frac{1}{z_c - 1} - \frac{1}{z_c - \zeta}\right) = \frac{1}{z_c(z_c - 1)} + \frac{1}{z_c}\frac{\Delta\mu}{kT}\left[\frac{1}{\ln (t/\lambda_c)}\right] \tag{27}$$

where ζ is a parameter that varies with time such that $\ln (t/\lambda_c) = \Delta\mu(\zeta - z_c)/kT$. For the relaxation modulus

$$\ln G(t) = \ln G(0) + \frac{1}{z_c}\frac{\Delta\mu}{kT}\left[\frac{1}{\ln (t/\lambda_c)}\right] \tag{28}$$

where $t < \lambda_c$. We now compare this equation with the frequently quoted, well-known Kohlrausch–Williams–Watts (KWW) equation:[17]

$$\ln G(t/\lambda_c) = \ln G(0) - \left(\frac{t}{\lambda_c}\right)^{\beta} \tag{29}$$

The KWW formula has as a convenient feature that is characteristic relaxation time corresponds to the dielectric loss maximum frequency (for the polymers with dipoles perpendicular to the chain direction) as well as the time at which the relaxation modulus has decreased to $1/e$ of the initial value. It turns out, however, that, while the KWW formula is very good when t or ω^{-1} is near λ_c, it is

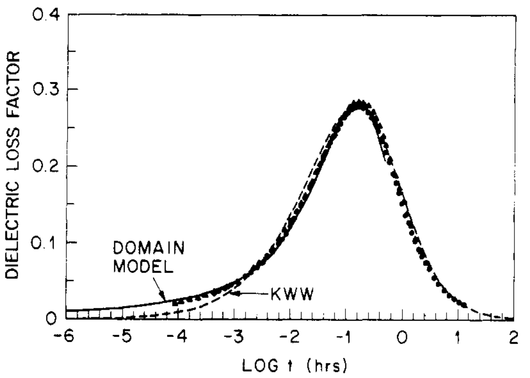


Figure 9. Dielectric loss vs log time (−log circular frequency) for poly(vinyl acetate). Data by G. E. Johnson (private communication); the circles and triangles denote sets of data obtained at 49 and 53 °C and were shifted to superimpose; the dotted line is calculated from the KWW equation by using $\beta = 0.6$ and $\lambda_c = 0.3$; the solid line is from eqs 28 and 29, with $\lambda_c = 0.6$. The cutoff at long time for the latter is because the calculation limit was set there, and for no other reason.

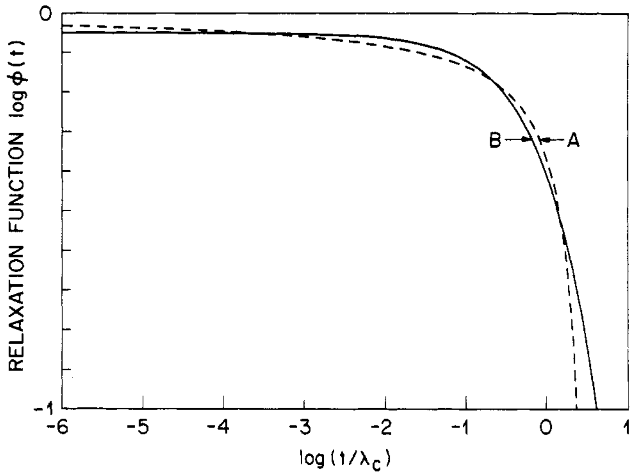


Figure 10. Comparison of the relaxation functions, the KWW equation (curve B) with $\beta = 0.5$ and $\log \lambda_c = 0.3$, and eq 28 with $\Delta\mu = 3$ kcal/mol, $T = 300$ K, $z_c = 10$, and $\log \lambda_c = 0.6$ (curve A).

poor at extremely short times such as 5 decades shorter than λ_c. This is illustrated by comparing the dotted line in Figure 9 against the dielectric loss data points for poly(vinyl acetate).

The relaxation spectrum $H(\ln \lambda)$ is approximately

$$H(\ln \lambda) \approx -\left.\frac{\mathrm{d}G(t)}{\mathrm{d}\ln t}\right|_{t=\lambda} \qquad (30)$$

The loss factor for the domain model was calculated from the spectrum derived from eq 28 and is also included in Figure 9 as the solid line. The fit with our equation is better than with the KWW equation at the high-frequency (short-time) end, reflecting the feature of our model that smaller domains are responsible for the persistent tail of the stretched exponential function at the high-frequency limit, which even the KWW equation underpredicts.

Even though eq 28 appears to be very different from the KWW equation, they can be made to nearly coincide by the suitable choice of constants. Figure 10 is such an example. In this case, the choice of $\Delta\mu/z_c kT = 0.5$ ($\Delta\mu = 3$ kcal, $T = 300$ K, $z_c = 10$) for eq 28 (curve A) gives the slope of −0.5 at $t = \lambda_c/e$. The slope for the KWW formula (curve B) is $-\beta$ at $t = \lambda_c$. The greater slope of our model at the short times is, again, an important improvement over the KWW equation in predicting the creep and relaxation behavior of polymers in the glassy state for $t \ll \lambda_c$, where the KWW equation typically underestimates the itensity of relaxation. If these "stretched" exponential functions are in fact a reflection of the distribution of the size of cooperative domains, this may be the reason for the apparent success of the universal scheme created by Ngai and co-workers[18] that makes a connection between the KWW exponent β and the value of the apparent activation energy. When applied to local segmental relaxation of amorphous polymers, the mechanism of the coupling scheme is also intermolecular coupling, which was called crowding coupling by Ngai and Plazek.[19]

Both the KWW equation and our eq 28 cutoff fairly abruptly beyond $t \geq \lambda_c$, whereas the experimental viscoelastic relaxation modulus continues on into stage 2 (the "transition zone") for many more decades, due to the so-called *external* viscosity rather than the *internal* viscosity with which we have been concerned here. The behavior that is identified with the external viscosity is unique to polymers as it depends on the molecular weight, whereas the stage 1 behavior we have discussed involves only the local segmental relaxation observed by dielectric, volumetric, thermodynamic, and viscoelastic measurements. The values of the dielectric and viscoelastic λ_c for the stage 1 are nearly the same.

So far we have discussed only the *equilibrium* state above T_g. In the *nonequilibrium* state, the spectrum broadens at lower temperatures. This has been observed in both the viscoelastic[20] and dielectric[21,22] relaxation. The broadening occurs[23] because the relaxation times of the larger domains exhibit a greater temperature coefficient than those of smaller domains. We can use the KWW formula (which is good in the range $t \approx \lambda_c$) to predict this broadening quantitatively. The slope of a $\log G(t)$ vs $\log t$ plot such as shown in Figure 11 is $-\beta(t/\lambda_c)^\beta$ according to the KWW formula. At $t = \lambda_c$, $\log G(t) = \log G(0) - \log e$, or $\ln G(t) = \ln G(0) - 1$, and the slope is exactly $-\beta$. We define the time t_0 as shown in Figure 11 such that

$$1/\beta = \ln \lambda_c - \ln t_0 \qquad (31)$$

Now, we change the temperature from $T_A = 90$ °C to $T_B = 57$ °C in Figure 11 without changing the domain size distribution so that z_c remains unchanged. The characteristic relaxation time changes from λ_A to λ_B, and

$$\frac{1}{\beta_B} = \ln \lambda_B - \ln t_0 = \ln \lambda_A + \frac{\Delta\mu}{k} z_c \left(\frac{1}{T_B} - \frac{1}{T_A}\right) - \ln t_0 \qquad (32)$$

Thus

$$\frac{1}{\beta_B} - \frac{1}{\beta_A} = \ln \lambda_A - \ln \lambda_B = \frac{\Delta\mu^*}{k}\frac{T_f}{T_f - T_0}\left(\frac{1}{T_B} - \frac{1}{T_A}\right) \qquad (33)$$

One condition required for the above equations is that the thermal history be the same for comparing the temperature dependence, because both t_0 and z_c are dependent on the physical aging. The two curves in Figure 11 are not exactly for the same physical aging, but t_0 are close enough to allow the assumptions to stand.

When the polymer is quenched from the initial equilibrium state at T_f to a new glassy state at temperature $T < T_f$, the nonequilibrium glassy state is specified by the fictive temperature T_f. The relaxation time has changed from the initial value λ_{cf} to the new λ_c, while z_c remains unchanged. The broadening of the spectrum is given by the decrease in β from β_f by the formula

$$\frac{1}{\beta} - \frac{1}{\beta_f} = \ln \lambda_c - \ln \lambda_{cf} = \frac{\Delta\mu^*}{k(t_f - T_0)}\left(\frac{T_f}{T} - 1\right) \qquad (34)$$

which pertains to the *nonequilibrium* states only. The fictive temperature T_f is typically 5–10 °C below the

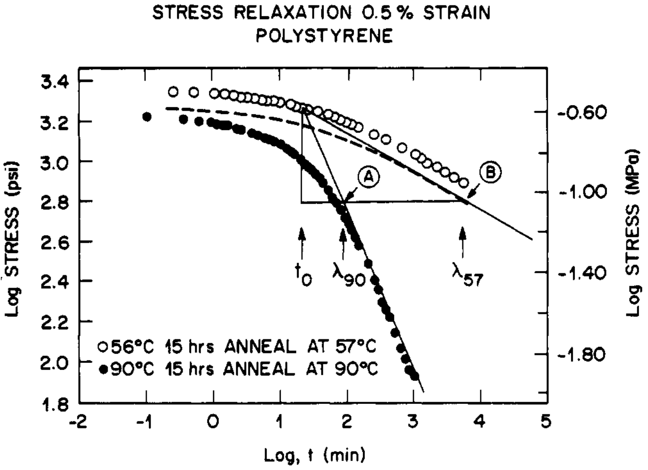


Figure 11. Plot of log $G(t)$ vs log t. The relaxation spectrum broadens with a drop in temperature. This is *not* a result of a simultaneous physical aging process. The broadening is the indication of the multiple values of apparent activation energy that depend on the size distribution of the cooperative domains. ln t_0 is equal to ln $\lambda_c - \Delta\mu z_c/kT$, which remains constant *for a given thermal history*.

experimental T_g. The value of β is smaller and the spectrum broader in the glassy state as described by eq 36.

Summary

The features of the cooperative domain model and its implications are summarized as follows:

(1) A model for the glass transition has been proposed that incorporates restrictions on individual segments from relaxing independently of their *inter*molecular neighbors. A domain of cooperativity is defined as a group of segments that must undergo relaxation simultaneously. The model has been used to explain several universal aspects of relaxation phenomena in polymers. The Adam–Gibbs formula is a natural consequence of the temperature dependence of the domain size.

(2) Whereas the Adam–Gibbs theory considers equivalent and identical cooperative rearranging regions, we consider a distribution of domain size and that the origin of the distribution of relaxation times in "solids" is the size distribution of the cooperatively relaxing domains.

(3) The KWW equation is a simple and convenient formula that approximates the dielectric relaxation near λ_c but not where $t \ll \lambda_c$. Our model leads to eq 28, which exhibits better fit to data.

(4) For short-time (stage 1) relaxation, the dielectric relaxation time λ_c is in general about equal to the viscoelastic λ_c, and their Vogel parameters $\Delta\mu^*$ and T_0 are also about equal.

(5) The distribution of relaxation times broadens markedly in the nonequilibrium glassy state as the temperature is lowered from T_g because of the different activation energies for different domain sizes.

(6) On the basis of the thermodynamic aspects of the domain model, we have introduced a simple formula that enables one to calculate T_g, and temperature dependence of the characteristic relaxation time λ_c, from the average conformer size. From these, we have succeeded in unifying the relaxation behavior of amorphous polymers both above and below their glass transition temperatures.

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