Correlation of Polymer Segmental Chain Dynamics with Temperature-Dependent Time-Scale Shifts

In 1955 Malcolm Williams presented a single temperature-dependence curve with data from 17 polymers.[1] This correlation was rationalized by Williams, Landel, and Ferry utilizing the Doolittle free-volume equation in deriving the noted WLF equation[2]

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \qquad (1)$$

where a_T is the temperature shift factor that is the ratio of a relaxation or retardation time at the chosen reference temperature, T_0, to that at the temperature of measurement, T. When T_0 is chosen to be the glass temperature, T_g, the constants $C_{1,g}$ and $C_{2,g}$ were thought to be universally applicable to all polymers. Indeed $C_{1,g} = 15.9$ in fact does appear to be applicable for most polymers, but $C_{2,g}$ varies appreciably from polymer to polymer[3-5] due to the variation of $T_g - T_\infty$, where T_∞ is the temperature where according to the equivalent Vogel, Fulcher, Tamman, and Hesse (VFTH) equation[6-8] rates go to zero. Viscoelastic creep, stress relaxation, or dynamic data whose rates are usually fitted to the WLF equation are obtained over the entire softening glass-to-rubber dispersion.[3]

The molecular mechanisms that contribute to the short-time portion of this dispersion are believed to be local segmental motions, the same as seen by photon correlation spectroscopy measurements, local dielectrically active modes, NMR, etc. All the data monitoring these motions can be fitted by distribution functions of relaxation or retardation times or by an inherently nonexponential decay function such as a stretched exponential of the Kohlrausch[9] and Williams and Watts[10] function, which for the stress relaxation modulus is

$$G(t) = (G_g - G_e) \exp[-(t/\tau^*)^{1-n}] + G_e \qquad (2)$$

where G_g is the glassy modulus, G_e is the equilibrium modulus, t is the time after the application of a fixed strain, τ^* is a measured relaxation time, and n is the coupling constant, which ranges from 0 to 1.0. This kind of stretched exponential has been rationalized by Ngai with his coupling model,[11,12] which includes a second relationship of measured relaxation times τ^* to primitive or underlying relaxation times τ_0, which are governed by intramolecular interactions. It is assumed that the observed values have been enhanced by the interactions of the molecular processes

$$\tau^* = [(1 - n)\omega_c^{\,n}\tau_0]^{1/(1-n)} \qquad (3)$$

where ω_c is a cross-over frequency for the onset of coupling.

It is through the temperature and the molecular weight dependence of τ_0 that these variables are related to n, which is also a measure of the width of the effective distribution of material response times. Hence, temperature and molecular weight dependences are both affected by the coupling of molecular processes. The correlations (or cooperativity) between segmental motions of neighboring molecules under the crowded conditions existing near the glass temperature influence not only the functionality of the viscoelastic behavior but its temperature dependence as well.

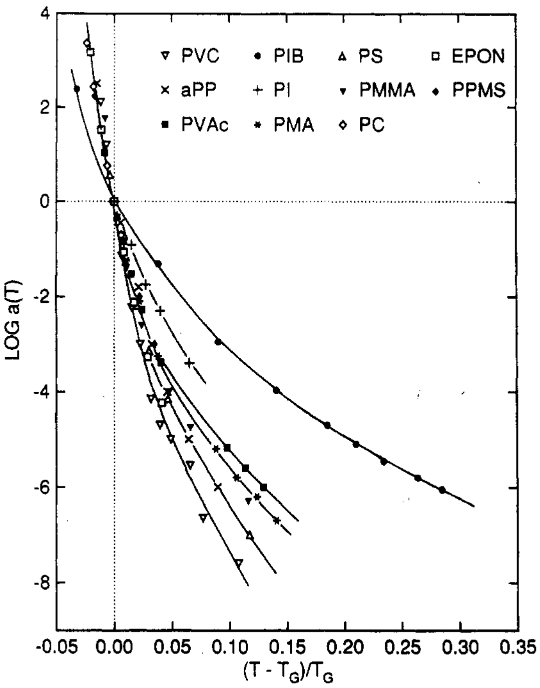

Figure 1. Logarithmic presentation of the temperature-dependent time-scale shift factors as a function of the fractional deviation from the glass temperature, $(T - T_g)/T_g$, for 11 polymers.

Since $a_T \equiv \tau^*(T)/\tau^*(T_0)$, eq 3 yields

$$(1 - n) \log a_T = \log \frac{\tau_0(T)}{\tau_0(T_0)} \equiv \log a_T^{\circ} \qquad (4)$$

where $\tau_0(T_0)$ is a primitive characteristic time constant at an arbitrary reference temperature, T_0, and $\tau_0(T)$ is the value at the temperature of measurement.

To fit shear creep deformation arising from the local segmental motions, we have used

$$J(t) = J_g + (J_e^{\,s} - J_g)[1 - \exp(-(t/\tau^*)^{1-n})] \qquad (5)$$

where J_g is the glassy compliance and $J_e^{\,s}$ is the long time limit of the contribution of the local segmental motions to the compliance. These modes are followed by Rouse modes. This kind of equation has been used by Dean, Read, and Tomlins to decompose contributions to the creep compliance.[13]

It is generally assumed that the temperature dependence of τ^* is the same as the other viscoelectric mechanisms throughout the softening dispersion from glasslike to rubberlike consistency.[3] Because of the frequent failure of thermorheological simplicity at compliances above 10^{-7} Pa^{-1} and the discrepancies found between reduced viscoelastic functions for poly(vinyl acetate) and poly(methyl acrylate),[14-17] in the analysis reported here only data from smaller compliances (or the equivalent) are utilized. Greater compliances are believed to arise from modified Rouse-like modes for undiluted polymers.

Since dependable corresponding glass temperatures, obtained properly in cooling experiments, are not yet available, for our analysis we have estimated T_g's from isothermal stress relaxation moduli, $G(t)$, storage $G'(\omega)$ moduli or creep, $J(t)$, or storage, $J'(\omega)$, compliance curves. The temperature where $J(100\ \text{s}) - J_g = 10J_g$ or $G_g - G(100\ \text{s}) = G_g/10$ was chosen to be T_g. The glassy compliance is J_g; the glassy modulus, G_g, and $t = 1/\omega$. We believe this procedure yields values that are equivalent to those obtained with a fixed rate of cooling. The T_g's obtained

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Table I
Characterizing Parameters

polymer[a]	T_g, K		n			Q, apparent activation energy, kcal/mol	$S, -T_g\left[\frac{d \log a_T}{dT}\right]_{T_g}$	refs
				calcd				
	this work	lit.	measd	restricted	all			
PIB	201	203	0.45 ± 0.5	0.382	0.355	42.3	46	19, 26, 39
cis-PI	200	200	0.50	0.461	0.483	56.7	62	27, 28
PPMS	243	240	0.56	0.607	0.64	112.1	100	20, 36, 37
PVAc	310.5	310	0.57	0.576	0.576	134.9	95	15, 31, 34
PMA	287.4	287	0.59	0.598	0.596	134.1	102	17, 30, 32
PP	262.5	263	0.65	0.644	0.656	164.4	137	16, 33
PC	418	415	0.65	0.603	0.668	252.4	132	29
PS	375	373	0.65	0.654	0.660	238.4	139	21, 22, 34, 35
a-PMMA	379	378	0.66	0.628	0.631	246.5	145	24
Epon 1004	389.2	385	0.67	0.676	0.707	268.8	151	25
PVC	352	353	0.76 ± 0.03	0.726	0.750	307	190.5	38, 40, 41

[a] Polyisobutylene, PIB; 1,4-*cis*-polyisoprene, *cis*-PI; poly(methylphenylsiloxane), PMPS; poly(vinyl acetate), PVAc; poly(methyl acrylate), PMA; amorphous polypropylene, PP; Bisphenol A polycarbonate, PC; polystyrene, PS; ideally atactic poly(methyl methacrylate), a-PMMA; epoxy resin, Epon 1004; poly(vinyl chloride), PVC.

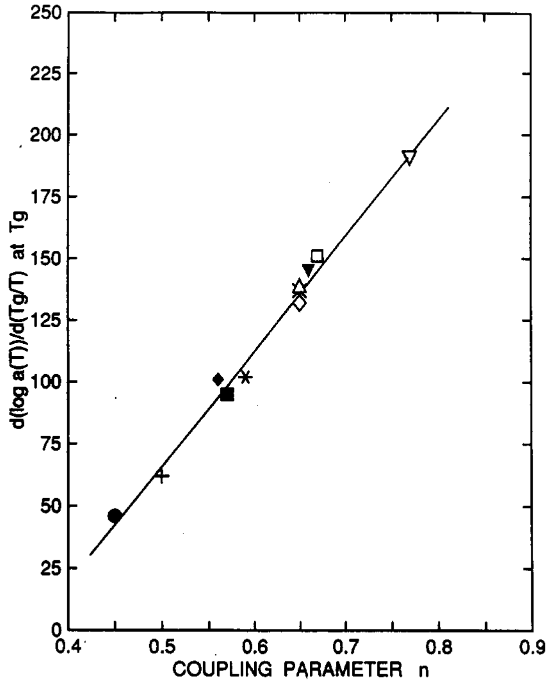

Figure 2. Temperature sensitivity d log a_T/d(T_g/T) determined at T_g correlated with the coupling parameter, n, for 11 polymers. This derivative is equal to -T_g(d log a_T/dT) and is referred to as the steepness index.

are presented in Table I, where they are compared with common literature values.

Temperature shift factors, a_T, obtained from the references also listed in Table I are plotted logarithmically in Figure 1 as a function of $(T - T_g)/T_g$. This plot is close in appearance to a mirror image of the related plot of log τ^* vs T_g/T due to Angell[18] where τ^* values for several polymers were obtained from photon correlation spectroscopy (PCS) measurements. The dimensionless normalized variable $(T - T_g)/T_g$ represents the change in rates as functions of the relative fractional increase in available thermal kinetic energy, whereas the explicit temperature difference $T - T_g$ directs attention to the influence of free volume, as in the WLF equation. Plotted simply against $T - T_g$, the log a_T curves fan out less but do not superpose onto a single line. The significance of the divergence displayed in Figure 1 can be seen in Figure 2 where the values T_g(d log a_T/dT) determined at T_g are plotted as a function of the coupling factors for the 11 different polymers. This derivative, which we will call the steepness index S, is equivalent to d log a_T/d(T_g/T)

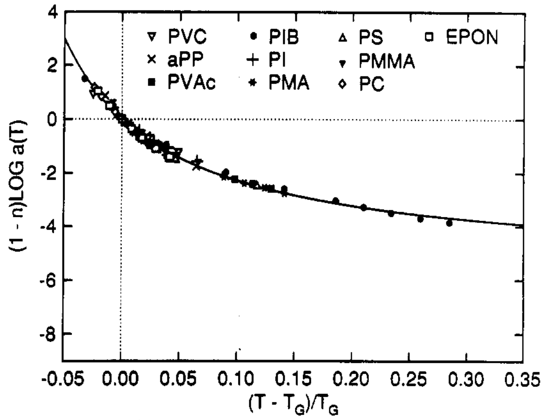

Figure 3. Logarithm of the temperature-dependent time-scale shift factor $(1 - n)\log a_T = \log a_T^{\circ}$ for the 10 indicated polymers shown as a function of $(T - T_g)/T_g$.

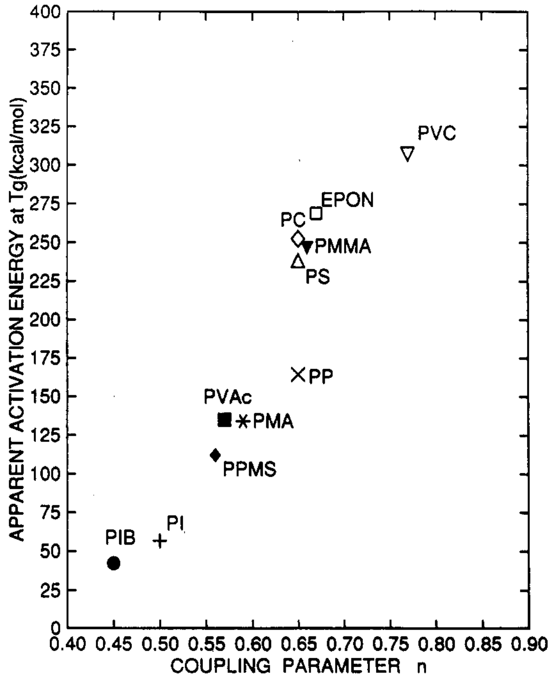

Figure 4. Correlation of the apparent activation energy, Q, with the coupling constant, n.

at T_g, which in turn is equal to $Q/2.303RT_g$ where Q is the apparent activation energy at T_g and R is the gas constant. Values for S and Q are listed in Table I. This reduced temperature dependence at T_g shows a remarkable correlation with the coupling constant n, which confirms the relationship between the time and the temperature dependences. This correlation suggests that the temperature dependences of the primitive segmental motions a_T° are similar if not the same for the polymers being examined. The logarithm of a_T° is shown in Figure 3 as a function of the fractional deviation from T_g, $(T - T_g)/T_g$. The line shown has been statistically fitted through the data with the exception of that from PIB and PVC, which are the extremes that are considered the least reliable. The equation fitted

$$(1 - n) \log a_T = \frac{-C_1(T - T_g)/T_g}{C_2 + (T - T_g)/T_g} = \frac{-C_1(T - T_g)}{C_2 T_g + T - T_g} \qquad (6)$$

resembles the WLF equation.

The fit with the restricted data set yields $C_1 = 4.723$ and $C_2 = 0.1073$. When all of the data available is included in the statistical fit $C_1 = 5.49$ and $C_2 = 0.141$. Using the first and second pairs of constants with the shift factors displayed in Figure 3, two values for n for each of the 11 polymers being examined here were obtained by the best least-squares fit of the data to eq 6. The two sets of n values are listed in Table I for comparison with the originally determined ("measured") values. Apparent activation energies at T_g, steepness factors, and data references are also listed in Table I.

The references given in Table I identify the source of the data analyzed to obtain n. Compliance data were analyzed with eq 5 and relaxation data with eq 2. Literature values for n were used from the given photon correlation papers. The remaining n values were either determined by the authors previously[28,33,34,41] or for this paper. With the exception of PIB the value of n is not sensitive to the value of J_e^s used. For PIB it was necessary to extract n from dielectric data[39] since there is a negligible component of the dipole moment parallel to the chain backbone and Rouse modes are dielectrically inactive.

Equation 6 can also be cast in the VFTH form

$$\log a_T^\circ = -C_1 + D_0 T_\infty/(T - T_\infty)$$

where $D_0 = C_1 C_2/(1 - C_2)$ and $T_\infty = (1 - C_2)T_g$.

The correlations shown above are evidence for fundamental relationships involving molecular structure, strength of coupling of molecular motions, the magnitude of the glass temperature, and time or frequency dependence with the temperature dependence of the molecular chain motions. Their convoluted interrelationships are reflected in the fact that a strong correlation exists between the product $T_g[\mathrm{d} \log a_T/\mathrm{d}T]_{T_g}$ and the coupling constant n, while a plot of the temperature sensitivity at T_g alone (as reflected by Q) against n shows a much degraded correlation in Figure 4. Differences of Q approaching 100 kcal/mol can be seen for polymers with nearly the same n. Polarity, symmetry, and steric hindrance to rotation appear to play strong roles in the determination of both T_g and n. Further work is necessary with n, a_T, and T_g determined on the same polymer samples to confirm the quality of the correlations observed.

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