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PII: S0032-3861(97)00201-2

Polymer Vol. 38 No. 26, pp. 6261–6266, 1997

0032-3861/97/$17.00 + 0.00

polymer papers

Why $C_1 = 16$–17 in the WLF equation is physical—and the fragility of polymers

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(Received 8 April 1996; revised 13 February 1997)

From the well-recognized equivalence of the Williams–Landel–Ferry (WLF) equation and the Vogel–Tammann–Fulcher (VTF) equation, $\tau = \tau_o \exp(B/[T - T_o])$, we shall show that the parameter C_1 in the former is just the number of orders of magnitude between the relaxation time at the chosen reference temperature and the pre-exponent of the VTF equation. Thus $C_1^g = \log(\tau_g/\tau_o)$ (a relation which is not found in the present polymer literature), measures the gap between the two characteristic time scales of the polymer liquid, microscopic and α-relaxation, at the glass transition temperature. For systems which obey these two equations over wide temperature ranges, τ_o is consistent with a quasilattice vibration period in accord with theoretical derivations of the VTF equation and also with the microscopic process of mode coupling theory. Thus for such systems, C_1^g is obliged to have the value 16–17 (depending on how T_g is defined), while C_2^g scaled by T_g will reflect the non-Arrhenius character, i.e. fragility, of the system. In fact when C_1^g has the physical value of 16–17, then $(1 - C_2^g/T_g)$, which varies between 0 and unity, conveniently gives the 'fragility' of the polymer within the 'strong/fragile' classification scheme. This is useful because it permits prediction from the WLF parameters of other properties such as physical ageing behaviour through the now-established correlation of fragility with other canonical characteristics of glassforming behaviour. Where the best fit C_1^g is not 17 ± 2, the corresponding best fit τ_o must be unphysical, and then the range of relaxation times for which the VTF or WLF equations are valid with a single parameter set will be limited, and the predictions of other properties based on that parameter set will be unreliable. © 1997 Elsevier Science Ltd.

(Keywords: WLF parameters; polymer fragility)

The Williams–Landel–Ferry equation[1] is one of the best known equations of polymer physics and for a long time it was believed to describe an approximately universal non-Arrhenius effect of temperature on viscosities and relaxation times in polymer systems. Its form is such that the molecular weight is factored out of the problem so that only the effect of temperature on the relaxation process has to be dealt with. The equation is written

$$\begin{aligned}\log a_T &= \log[\tau(T)/\tau(T^*)] \\ &= C_1(T - T^*)/[T - (T^* - C_2)] \qquad (1)\end{aligned}$$

where a_T is called the shift factor, τ is the relaxation time at temperature T, $\tau(T^*)$ is the relaxation time at some reference temperature T^* within the range of measurement, and C_1 and C_2 are constants. When the measurement range has included the glass transition temperature T_g (from calorimetry or dilatometry), it has been natural to choose T_g as the reference temperature T^*. When T_g was defined in some consistent way by measurement of thermal or volumetric changes at fixed scan rate Q, usually $\sim 1\,\mathrm{K\,min^{-1}}$, then the parameters C_1^g and C_2^g appeared to have universal values of 17.4 and 51.6 K, respectively[1].

An interpretation of these values in terms of the physically appealing free volume fraction, which is found to be approximately constant at the glass transition[2], quickly won widespread acceptance. This may in part explain why another physically meaningful interpretation of at least one parameter value has not, to the best of our knowledge, ever been pointed out. This other, not incompatible, accounting was hinted at in early compilations of the parameters. For instance, in ref. 2 (1st edn) it was noted that the universality suggested by the early measurements was only approximate, and that the C_1 parameter was much more constant than C_2. As examples, polyisobutylene (PIB) and polypropylene oxide (PPO), which have glass transition temperatures within 10 K of each other, have the same parameters C_1^g (16.5 and 16.2 respectively[2,3]) but C_2^g parameters which differ by a factor of 4 (104 vs. 24[2,3]), falling on either side of the original 'universal' value. The suggestion of such results, and others to be found elsewhere[2–6], is that C_1 should be constant for some fundamental reason while C_2, and in particular C_2/T_g, carries information on the character of the polymer. Indeed this is what we will show in the following analysis in which C_1^g will prove to be 16 for relaxation times of systems which obey equation (1) over the whole possible τ range with a single parameter set, and the corresponding C_2^g will be related to the strength parameter D of the strong/fragile liquids classification[7,8].

For simple liquids and oxide melts, deviations from Arrhenius temperature dependence have most commonly

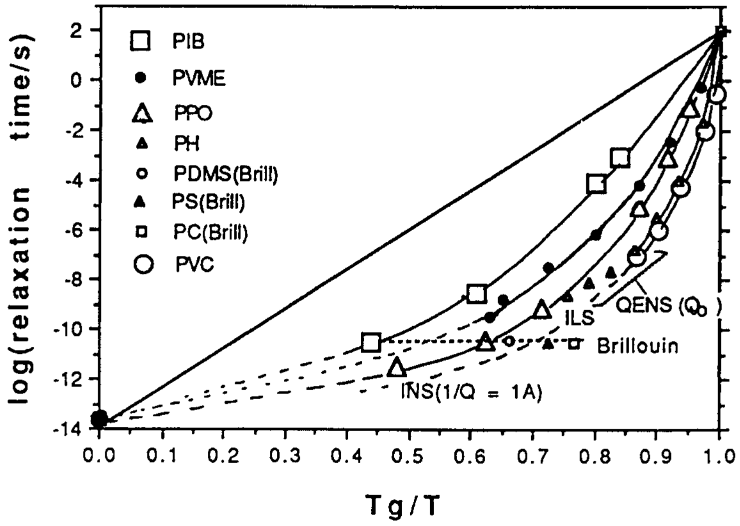

Figure 1 T_g-Scaled Arrhenius plots of segmental relaxation times for linear chain polymers based on mechanical relaxation, light scattering, and n.m.r. ^{13}C segmental relaxation time data. T_g is defined by the temperature at which $\tau = 10^2$ s. The data extrapolations suggest an infinite temperature value of about 10^{-4} s, consistent with Raman modes associated with short wavelength acoustic phonons which, in the absence of selection rules, dominate the Raman spectrum in this frequency range[48]. The identifications of data sources on the diagram are as follows: INS = inelastic neutron scattering for the inverse wave vector, $Q^{-1} = 1$ Å[49]; QUENS (Q_o) = quasielastic neutron scattering at peak of structure factors, Q_o[50]; ILS = impulsive light scattering[51]

been described by the well known Vogel–Tammann–Fulcher (VTF) equation[1–11] which is exemplified by

$$\eta = \eta_o \exp\,[B/(T - T_o)] \qquad (2)$$

or

$$\tau = \tau_o \exp\,[B/(T - T_o)] \qquad (3)$$

Here η is the viscosity, τ a relaxation time, and η_o, τ_o, B and T_0 are constants. The success of this equation for simple liquids has been comparable with that of the WLF equation for polymers. While there has been no suggestion of even approximately universal behaviour, the equation also describes the behaviour of a wide variety of systems, though there are systematic failures of the equation form at short relaxation times in the case of very fragile liquids[12,13], i.e. for liquids which deviate most strongly from Arrhenius behaviour. The deviation from Arrhenius behaviour may be quantified by the parameter D in a modified form of equation (3)

$$\tau = \tau_o \exp\,[DT_o/(T - T_o)] \qquad (4)$$

where D is a 'strength' parameter. A convenient parameterization of fragility would be $F = D^{-1}$, which varies between 0 and 1. An alternative parameterization related more closely to the WLF parameter C_2, comes out of the present analysis.

Before we proceed any further, however, it is important to recognize that, despite their popularity and the amount of theoretical effort devoted to their interpretation, neither the WLF equation nor (necessarily) the VTF equation are very successful except for liquids which do not deviate much from Arrhenius behaviour. For fragile liquids the parameters of either equation depend very much on the particular range of data fitted. This is manifested by the wide variations recorded for C_1. Values for individual property fittings of limited data sets swing from 6.1 for PDMS to 34 for PMMA[2] (though the latter value is not confirmed in the compilation of parameters by Sanchez[6] and the small values are found only for selected silicones[6]). Furthermore, the small value for PDMS is not consistent with the series of (very short relaxation time) Brillouin scattering-based data presented below. As will be seen later, the errant values correspond, in VTF-equation terms, to systems with respectively far too much and far too little curvature to be physically interpretable in terms of microscopic models such as have been developed to account for the form of the VTF equation. We will return to this matter later in this paper.

In theoretical efforts to account for the provocative form of the VTF temperature dependence[14–17], τ_o is seen as a microscopic quantity related to the frequency of attempts to cross some barrier opposing the rearrangement of particles involved in relaxation[15,17], or the time a molecule needs to move into some free space[14,16], and it is expected to have phonon-like time scales, 10^{-14} s. Indeed, T_g-scaled Arrhenius plots of structural relaxation times for simple liquids[18], and for segmental relaxation times for polymers[8], are consistent with this assignment. For instance, a collection of relaxation time data for polymers, updated since the original presentation[8], is shown in *Figure 1*. For this presentation, the scaling temperature T_g was chosen as the temperature at which $\tau = 10^2$ s, on the basis of various analyses[19,20] of enthalpy and structural relaxation data obtained at the common d.s.c. scan rate of 10 K min^{-1}. The assignment is consistent with the common observation[3,21], usually by an equation (3) extrapolation, that $\tau_{\text{dielectric}} = 10^2$ s (or $f_{\max} = 10^{-3}$ Hz) at the 10 K min^{-1} calorimetric T_g (onset definition). A plot of the same form as *Figure 1* for the viscosities of simple liquids[7] which was earlier used as the basis for the strong/fragile classification of liquids, also suggested an approximately constant value for the pre-exponent for the viscosity equation, equation (2). This plot is reproduced in *Figure 2*.

The observation may be made from *Figure 1* that the number of orders of magnitude between the relaxation time at T_g and the inverse attempt frequency (τ and $1/T = 0$) is ~ 16. In *Figure 2* the corresponding number is 17: both are reminiscent of the 'universal' value of C_1^g

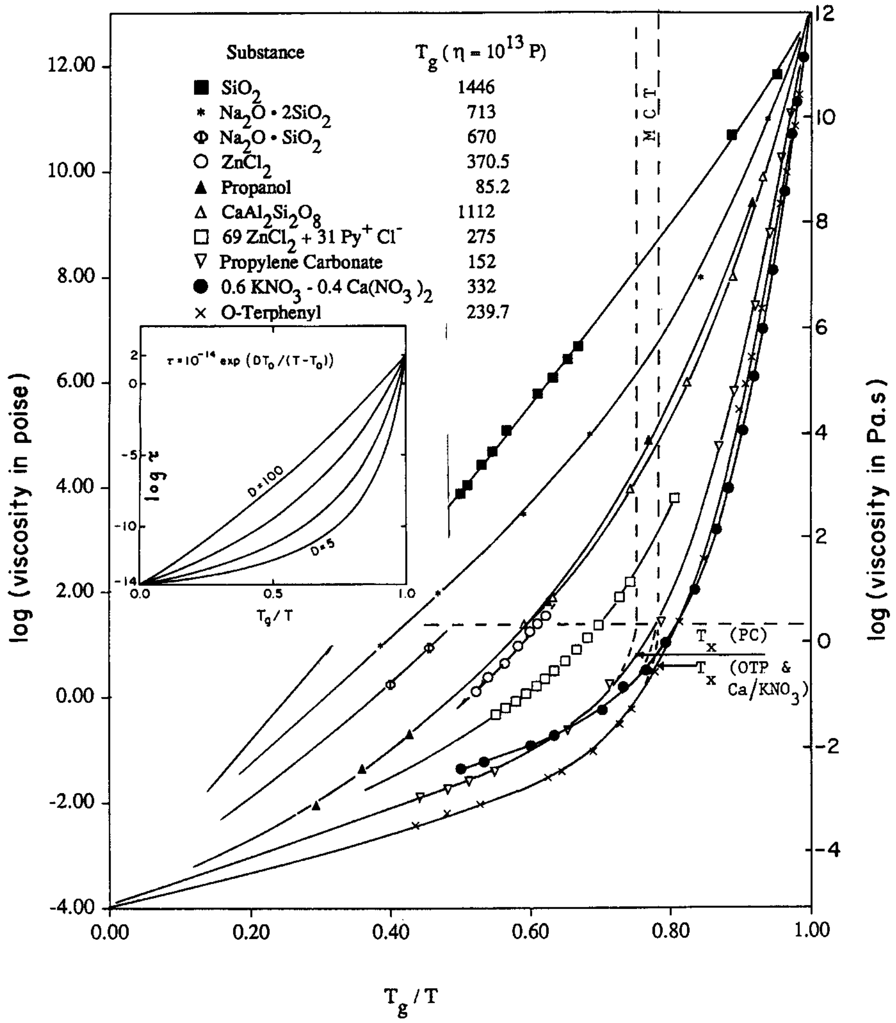

Figure 2 Viscosity data for a variety of molecular liquids and ionic liquids (some inorganic polymers in nature) showing extrapolations to a common high temperature value of 10^{-4} poise[52]. The predictions of a power law fit to high temperature data of fragile liquids suggested by mode coupling theory, are shown by dashed lines. The manner in which the actual pattern is reproduced by equation (4) with variable D parameter is shown in the insert. (From *J. Phys. Chem. Solids*, by permission)

which was obtained using a reference temperature T_g defined on a time scale about one order of magnitude longer than used in *Figure 1*. To show that this is indeed the origin of the value of C_1^g, we turn to the mathematical equivalence of the WLF and VTF equations.

The equivalence of the WLF and VTF equations was first pointed out by Kovacs[22]. The well-known identities are

$$C_2 = T^* - T_0 \qquad (5)$$

$$2.303C_1C_2 = B \qquad (6)$$

Our identification of C_1^g with $(\log\tau_g - \log\tau_0)$ hence, according to *Figure 1*, with the number ~ 16, is shown from equations (3), (5) and (6) by algebra so trivial that we consign it to a footnote[23]. Yet for reasons not very obvious, this relation

$$C_1^g = \log(\tau_g/\tau_0) \qquad (7)$$

has never found its way into any of the textbooks or other literature of polymer science[24,25]. For viscosity, one obtains

$$C_1^g = \log(\eta_g/\eta_0) \qquad (8)$$

However, for polymers of high molecular weight (beyond entanglement), the viscosity at T_g is too high to measure because of the molecular weight factor in the pre-exponential of equation (2). This factor ($M^{1.0}$ for pre-entanglement molecular weight and $M^{3.4}$ for high polymers[2]) should apply to η_g and η_0 equally, so in cases where measurements can be made at T_g, the value of C_1 should be unaffected. The pre-exponent for the shear viscosity relaxation time will, however, no longer be an inverse phonon frequency in high MW polymer cases.

According to *Figure 2*, C_1^g for viscosity data should be 17 rather than 16. The difference arises from the fact that η is connected to the shear relaxation time τ_s through the Maxwell equation

$$\eta = G_\infty \tau_s \qquad (9)$$

where G_∞ is the high frequency shear modulus, and this has a weak temperature dependence.

What conclusion can be drawn from the equation (8) identity? Since τ_g has the value 10^2 s by assignment, the approximately universal value of $C_1^g = 17$ found empirically for 'well-behaved' polymers [implying τ_0 of equations (3) and (4) = 10^{-14} s], can be seen as support within the polymer class of material for the theoretical supposition that the VTF pre-exponent is a microscopic dynamical quantity, such as an inverse attempt frequency for barrier crossing. It suggests that only phonons of frequency near the Debye frequency (hence of short wavelength) have enough anharmonic character to localize and participate in the 'phonon-configuron'[26] exchanges (configurational rearrangements) responsible for relaxation. The closely related 'soft phonon' approach to interpreting the onset of mobility in glasses during warm-up is currently the focus of much activity[27–29].

We now return to the matter of deviant C_1^g values. A small C_1^g value is now seen to imply a small VTF pre-exponent as a consequence of the excessive curvature in the data in the range of measurement[30]. Likewise a large C_1 implies reduced curvature in the range of measurement, such as has been reported for viscosities of the fragile liquid CKN[31] and the strong liquid B_2O_3[32], in the range of temperature just above T_g ('return to Arrhenius behaviour')—and of course C_2 must change to compensate.

In the case of simple liquids, a check is available through the thermodynamically derived Kauzmann temperature T_K[33]. It is found[34] that when the relaxation time temperature dependence is such that T_o of equations (2) or (4) $\approx T_K$, then the VTF pre-exponent has a physically sensible (phonon-like) value, and accordingly C_1 must be the 'normal' value. If, on the other hand, the data being fitted tend back to Arrhenius behaviour near T_g, then T_o will fall well below T_K, and τ_o and C_1 will assume 'deviant' values. It is here that the now-popular graphical presentation of relaxation or viscosity data in a T_g-scaled Arrhenius plot finds its strength. The observer's eye classifies a liquid's fragility based on its overall behaviour between T_g and a high temperature limit regardless of whether the data conform well or otherwise to a particular viscosity equation. The definition of fragility via the slope of the *Figure 1* plot at $T_g/T = 1.0$ obtains the same ordering[35,36].

This line of thought suggests the following as a profitable approach to treating data obtained over a limited range if the object is either to make predictions of behaviour outside that range or to classify the liquid in order to take advantage of other known correlations with fragility (e.g. ageing behaviour[37]). It requires a recognition that conformity of relaxation data covering some 15 orders of magnitude to a simple three parameter equation is intrinsically unlikely for liquids of very different structural complexities, but that, nevertheless, all viscous liquids at T_g have in common the same gap in time scales between microscopic (phonon-like) dynamics and α-relaxation dynamics. Then, on the basis of the general pattern of *Figure 1*, one would input a fixed microscopic time scale, i.e. set τ_o at $\sim 10^{-14}$ s, and force-fit the data to the remaining two parameter equation to get the most probable behaviour far from the fitting range. The equivalent in WLF terms is fixing C_1^g (at 16 for the assignment $\tau_g = 10^2$ s), and then utilizing the remaining 'force-fitted' parameter C_2^g to characterize the liquid and predict out-of-range behaviour[38]. The frequency of occurrence of $C_1^g = 16$–17 strongly suggests that the degree of forcing required for polymer is much less than in the case of glass-forming molecular liquids.

With C_1^g fixed at 16 for relaxation time data, C_2, as the gap between T_g and the divergence (or Vogel) temperature, T_o, should decrease with increasing melt fragility for liquids or polymers of the same T_g. This is why C_2 is so small for polypropylene oxide which is quite fragile and why C_2 is so large for polyisobutylene, which is the 'strongest' chain polymer known[8,35] (possibly excepting poly-L-asparagine[39]). In fact, the fragility can be quantified, in terms of WLF parameters, by $1 - C_2/T_g$. From equation (5), $1 - C_2/T_g$, is just T_o/T_g which conveniently varies between 0 and 1.0 with increasing fragility. Indeed, the use of T_o/T_g as a fragility index has been suggested by both Donth[40] and Hodge[41]. We stress, however, that it is only useful if the accompanying τ_o parameter is physical. We note that T_o/T_g is related inversely to the previous strength parameter D of equation (4)—which orders the liquids in *Figures 1* and *2*—by the expression[42]

$$
\begin{aligned}
(T_o/T_g)^{-1} &= (1 - C_2/T_g)^{-1} \\
&= 1 + D/17\ \ln(10) \quad \text{(viscosity)} \\
\text{or,}\quad &= 1 + D/16\ \ln(10) \quad \text{(relaxation time)} \quad (10)
\end{aligned}
$$

from which

$$C_2 = DT_o/C_1\ \ln(10) = DT_o/39.1 \quad \text{(viscosity)} \quad (11)$$

In other words, C_2 measures the liquid 'strength' almost as directly as does the D parameter of equation (4) (see *Figure 2*), but is moderated by T_o. The $(1 - C_2/T_g)$ index, which uses only data from the WLF fitting, conveniently gives the place of the polymer within the 'strong-fragile' classification scheme (provided $C_1 \approx 17$). It is useful to have an estimate of polymer fragility because Plazek and Ngai[35] have correlated polymer fragility (their 'steepness index') with *non-exponentiality* of relaxation, and Hodge[37] has correlated it with *non-linearity* of relaxation, hence with ageing behaviour, which is of major concern in polymer technology.

The common finding that C_2^g tends to be ~ 50 K must then mean that polymers with higher T_g values tend to be the more fragile ones. A reason for such a trend is not obvious to the present author, and it will be interesting to find if counter examples exist among chain polymers. Certainly they exist amongst inorganic polymers such as the common oxide glassformers. For instance, a WLF fitting of the shear relaxation data for a commercial silicate glass of high T_g yielded[43] the parameters $C_1^g = 14.5$, $C_2^g = 300$ K. The first is close to the 'universal' 16 expected from relaxation times according to our analysis[44], but the second is enormously in excess of 50 K. This is as expected since liquid silicates are 'strong' liquids (*Figure 2*). In this particular case $1 - C_2/T_g = 0.35$, which may be compared with the value for a typical chain polymer ($C_2 = 50$, $T_g = 300$ K) for which $(1 - C_2/T_g) = 0.83$. The most fragile system found to date is thought to be polyvinyl chloride[35,37] for which $1 - C_2/T_g = 0.9$, though it appears unexceptional in the compilation by Sanchez[6] (data of Saito[45]), in which polyacetaldehyde (dielectric data in ref. 2) appears to be the most fragile $(1 - C_2/T_g = 0.90)$.

Finally, when the fitting of relaxation time data yields a C_1^g value rather different from 16 despite correct referencing[30], then there is reason to suspect some additional phenomenon is present. An example would be ion pairing and its effect on WLF fitting of ionic conductivity data. The temperature dependence of ion pairing in polymer solutions affects the high temperature (short relaxation time) curvature of Arrhenius plots[46,47] and leads to WLF or V–F parameters ($C_1^g = 11$)[46] which cannot predict behaviour near T_g.

ACKNOWLEDGEMENTS

This work was supported by NSF DMR Solid State Chemistry Grant No. DMR9108028-002. I am grateful to Prof. J. D. Ferry for helpful comments on this contribution and for pointing out ref. 22 which first recognized the equivalence of the WLF and VTF equations.

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$$C_1^g = B/2.303[T_g - T_o] \qquad \text{(i)}$$
Rearrange the base 10 logarithmic form of equation (3) to
$$\log(\tau/\tau_o) = B/2.303[T - T_o] \qquad \text{(ii)}$$
and set $T = T_g$, $\tau = \tau_g$. This yields the same expression on the RHS as (i)
$$\log(\tau_g/\tau_o) = B/2.303[T_g - T_o] \qquad \text{(iii)}$$
which means,
$$C_1^g = \log(\tau_g/\tau_o) \qquad \text{(iv and 7)}$$
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vary up to three orders of magnitude from the value of 10^2 s assigned in the *Figure 1* plot, we believe later evaluations of the fragility/steepness index [38] to be more reliable.

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