Variation of Polymer Glass Temperatures with Molecular Weight

Fox and Flory[1] found that the glass temperature, T_g, varies with molecular weight, M, according to

$$T_g = T_g^\infty - K_g M^{-1} \qquad (1)$$

where T_g^∞ is the limiting T_g at high molecular weight and K_g is a constant. However, it is now known[2-5] that K_g is constant in many polymers only if $M > 10^4$, especially those of higher T_g. We have discovered an empirical correlation between K_g and T_g^∞ which is shown in Figure 1 for a variety of common polymers. In several instances two values are indicated for a given polymer. With poly(vinyl acetate) this represents two extremes which we have calculated from literature data. In the case of PVC and polystyrene, the lower value is the one found in the literature, the upper is what we have calculated from the same data by using only $M > 10^4$. Inclusion of data below 10^4 invites fitting the data points with a line of lesser slope, *i.e.*, smaller K_g. A double circle represents a datum point of higher weight, usually involving extensive tabulated data, especially above $M \cong 10{,}000$, which permits large-scale replotting of the data and a consistent assessment of K_g; or a good fit shown by the original authors.

$K_g = 0$ for hydroxyl-terminated poly(propylene oxide)[6] is probably indicative of strong end-group association. Such association has been observed in solutions of low molecular weight poly(ethylene glycols) in benzene and CCl_4.[7] Moreover, K_g is greater than zero when hydroxyl end groups are replaced with methyl ether groups.[8] However, hydroxyl-terminated ethylene adipate polymers have $K_g > 0$.[9]

When the complete set of molecular weight data for polystyrene from Ueberreiter and Kanig[2] is plotted according to eq 1, it can be represented by three intersecting straight-line sections having K_g's as follows

$M > 10^4$	$K_g = 20 \times 10^4$	(T_g = eq 1 values)
$10^3 < M < 10^4$	$K_g \sim 8 \times 10^4$	($T_g >$ eq 1 values)
$M < 10^3$	$K_g \sim 2 \times 10^4$	($T_g \gg$ eq 1 values)

We suggest that a decrease in free volume with molecular weight below $M = 10^4$ is in part responsible for T_g(obsd) > T_g(calcd) down to $M \sim 10^3$, below which the various styrene oligomers—the dimers, trimers, tetramers, etc., are no longer representative of the structure of higher molecular weight material. Bovey *et al.*[10] found that the nmr O-proton peak in polystyrenes first appeared with the octamer. Low molecular weight, nonmonomeric organic molecules follow eq 1 with K_g in the range of 0.25–1.0.

Calculations and numerical values are presented for the dependence of T_g on free volume, $\Delta T_g/\Delta V_f$. This quantity is in the range of 532–740°/cm^3 g^{-1} for poly(vinyl acetate), PVC, PMMA, and polystyrene. The pressure dependence of free volume, $\Delta V_f/\Delta P$, is shown to be smaller than but close to the coefficient of compressibility for these same four polymers.

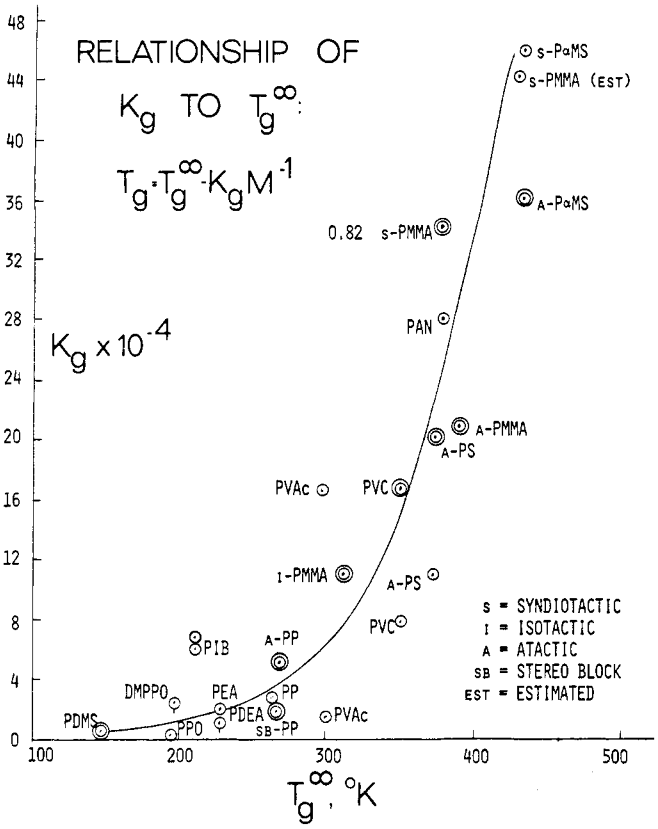

Figure 1. Correlation of eq 1 parameters, K_g and T_g^∞. The polymers from left to right are: polydimethylsiloxane, poly(propylene oxide), the dimethylether of PPO, polyisobutylene, poly(ethylene adipate), poly(diethylene adipate), polypropylene, poly(vinyl acetate), poly(methyl methacrylate), poly(vinyl chloride), polyacrylonitrile, polystyrene, and poly(α-methylstyrene). K_g was calculated for $M > 10^4$ except for two polymers with pips.

Polydimethylsiloxane on which data were published after this note was submitted[11] not only provides a gratifying anchor point for the lower end of Figure 1, but the data are remarkable in that eq 1 is followed down to $M_n = 162$. Quite recent data on polypropylenes of varying tacticity shows dependence of K_g on tacticity.[12]

We have found some advantages in plotting eq 1 in an alternative form, namely

$$\log (T_g^\infty - T_g) = \log K_g - \log M \qquad (2)$$

in addition to, and as a check on, the conventional $T_g - M^{-1}$ method of plotting. With the log-log representation, the high molecular weight data must be fitted to give a slope of -1 while intersecting the molecular weight axis at K_g when $T_g^\infty - T_g = 1$. The entire molecular weight range is easily handled, and the several regions mentioned previously are readily apparent. Moreover, a relatively sharp intersection is seen between the three molecular weight regions, in contrast to continuous curvature which is sometimes suggested.[2-5,9,11-13]

Figure 1 thus provides a useful correlation for checking old and new literature data as well as for estimating an approximate value of K_g for any new polymer for which $T_g \sim T_g^\infty$ is known. Figure 1 naturally invites at least a provisional attempt at rationalization. The simplest one is that shown in Figure 2 which assumes that monomeric species of different polymers will all have low T_g's only

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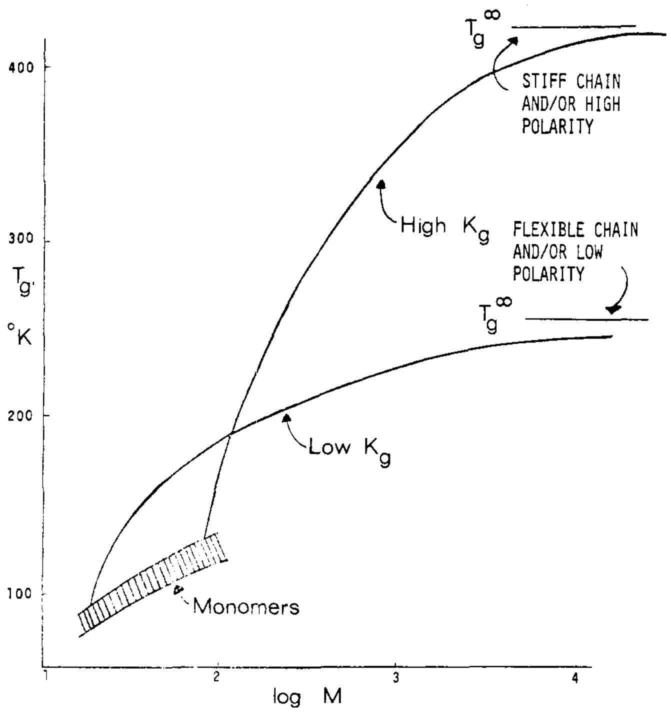

Figure 2. Schematic interpretation of results shown in Figure 1 using a T_g-log M plot. The shaded region shows the expected variation of monomer T_g's with molecular weight judged from data on low molecular weight, nonmonomeric compounds.

slightly dependent on molecular weight ($K_g \sim 1 \times 10^4$ as already stated). If T_g^∞ is very high because, for example, of chain stiffness, it is obvious that K_g must be higher than for a polymer of low T_g^∞.

The functional form of the curve in Figure 1 is still open to precise determination pending additional data and/or a suitable theory. Omitting the single point for $K_g = 0$, a plot of log K_g *vs.* T_g^∞ is a reasonable straight line. We originally believed that K_g *vs.* $(T_g^\infty)^2$ was a reasonable good fit but one reviewer of this paper is convinced that (a) K_g varies as $(T_g^\infty)^4$ and (b) that K_g may well depend on some factor(s) other than T_g^∞.

Several authors[3-5,9,11-13] have tried to interpret K_g in terms of molecular parameters arising from theory, the most common being those of Bueche, Gibbs-DiMarzio, Kanig, and Somcynsky and Patterson. We have not noted any expression for K_g that would lead to a semilogarithmic or a quartic relation between K_g and T_g^∞. The closest is that of Somcynsky and Patterson[14] who give the expression

$$K_g = SM_0T_g^\infty \quad (3)$$

where S is a chain stiffness factor and M_0 is the segment length. It is generally recognized that T_g^∞ increases with chain stiffness. There is also a strong tendency for T_g^∞ to increase with M_0 if one avoids long alkyl side-chain polymers. Hence Somcynsky-Patterson could lead to a K_g-$(T_g^\infty)^3$ correlation but we do not wish to emphasize such a point at this time. We recognize that many other factors affect T_g^∞ such as polarity, symmetry, and tacticity.

Full details, with appropriate literature documentation, are currently being written up. The K_g-T_g^∞ relationship in Figure 1 can be verified provisionally with data assembled by Pezzin *et al.*,[5] which tabulation does not include all of the examples in Figure 1[6,8,9,11,12] nor our modification of literature values of K_g.

Finally, we note that eq 1 is obeyed by a series of lactones with molecular weights ranging from 72 to 240, and leading to a $K_g = 0.45 \times 10^4$. Since these ring compounds lack end groups, it is apparent that molecular weight itself can lead to a lowering of T_g (at least for low molecular weight compounds), possibly through a free volume effects. T_g's of these lactones (but not K_g) have been reported.[15]

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A Double Thermal Helix-Coil Transition

The great majority of thermally induced conformational transitions in polypeptides in mixed organic solvents investigated to date have been found to be of the so-called "inverse" type, in which the ordered conformation is stable at the higher temperature.[1] Nevertheless it has been recognized for many years that in such cases a second transition in the "normal" (helix-to-coil) direction should in principle be observed at a relatively still higher temperature.[2] Up to now such a double transition has not been reported in spite of investigations over quite wide temperature ranges: for example, optical rotation studies of poly(γ-benzyl L-glutamate) have been made in several solvents up to 200° without gaining unequivocal evidence for even the onset of the expected second transition before degradation,[3] attesting to the high stability of the ordered conformation of this particular polypeptide. Such studies are, of course, always limited by the chemical and physical integrity of the polypeptide and solvent system.

Recently the calculation of the effect of solvent composition on helix-coil transition temperatures has been extended in a quantitative manner that has made it possible to delineate polypeptide-solvent combinations in which the possibility of observing a double transition in an experimentally accessible temperature range would be maximized.[4] These results predict that the requirement was for an intrinsically weak polypeptide (*i.e.*, one with a relatively low helix-to-coil transition temperature in pure inert solvents) in combination with a fairly strongly interacting active solvent component which is needed to provide an "inverse" transition in a normally accessible temperature range. These requirements are met by the system poly(β-benzyl L-aspartate) ($(\mathrm{BzlAsp})_n$) and $HCCl_2COOH$. The relative weakness of the $(\mathrm{BzlAsp})_n$ helix is suggested by two observations: (1) the fact that $(\mathrm{BzlAsp})_n$, alone amongst polypeptides of this class, has been shown to undergo both "normal" and "inverse" thermal transitions according to the solvent system used,[5] and (2) the relatively low $HCCl_2COOH$ concentration necessary to induce an isothermal transition from the helical to the random-coil conformation (about 7.5 mol % in $HCCl_2COOH$-$CHCl_3$ mixtures at 25°.[6]) The instability has been attributed to the atypical left-handed chirality of the α-helical

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