Glass transition temperature and molecular parameters of polymer

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A new relationship, which correlates the glass transition temperature (T_g) with other molecular parameters, is developed by using Flory's lattice statistics of polymer chain and taking the dynamic segment as the basic statistical unit. The dependences of T_g on the chain stiffness factor (σ^2), dynamic stiffness factor ($\beta = -\mathrm{d} \ln \sigma^2/\mathrm{d}T$) and molecular weight of polymer are discussed in detail based on the theory. The theory is compared with experimental data for many linear polymers and good agreement is obtained. It is shown that T_g is essentially governed by the chain stiffness factor at T_g. Moreover, a simple correlation between the parameter K_g of the Fox–Flory equation ($T_g = T_g^{\infty} - K_g/M_n$) and other molecular parameters is deduced. The agreement between theoretical predictions and experimental measurements of K_g has been found to be satisfactory for many polymers.

(Keywords: glass transition temperature; chain stiffness factor; dynamic stiffness factor; molecular weight; conformation)

INTRODUCTION

Over the past 30 years there has been strong interest in deriving an equation to predict T_g as a function of either fundamental thermodynamic or molecular parameters. In the molecular interpretation of the glass transition of polymers, two different views have been adopted. One is directed at the non-equilibrium character of structural relaxation and physical ageing. The other considers the conditions when the relaxation processes take place so slowly that the glass transition can be treated as a time independent phenomenon, i.e. T_g measured under such conditions is presumably a 'true' value independent of experimental artefacts[1]. The theories have been developed by using the free volume concepts[2], the principle of corresponding states[3] and thermodynamic approaches[4]. These works have been the basis for understanding the thermodynamic behaviour of polymers. However, a theoretical equation, which can correlate T_g directly with molecular parameters measurable by independent experiments, has not so far been derived.

It has been shown that the free volume concepts, although very useful from the qualitative point of view, cannot be used quantitatively to describe glass transition phenomena even for polymers with the same chemical nature but a different physical structure. In the glass transition phenomena of polymers, intermolecular forces, chain flexibility and chain geometry play a principal role. The free volume theory, however, has not taken these three important variables into account. On the other hand, the thermodynamic theory of Gibbs and DiMarzio (GD)[4] seems to be more theoretically sound; in this theory the interaction and flexibility of chains have been considered quantitatively in terms of hole energy (E_h) and flex energy (ε), respectively. In principle, GD theory can be used to predict the T_g of a polymer if the parameters E_h and ε are known. Unfortunately, ε is an adjustable parameter in GD theory and is not accessible by independent methods[5]. In the theory based on the principle of corresponding states of polymer liquids, the same difficulty exists as with GD theory[3].

In addition to theoretical approaches, numerous empirical equations have been proposed to summarize the relationships between T_g and cohesive energy[6], T_g and chain stiffness factor (σ^2)[7] etc. However, since T_g has multi-functional dependences and the empirical equations were obtained only by examining the change of T_g with another parameter over a limited range of experimental data, one can expect that it is always not correct to predict T_g according to these empirical relationships, and it is sometimes possible to reach an erroneous conclusion by using them.

The purpose of this paper is to discuss a general relationship between the molecular parameters and T_g which arises from polymers themselves, rather than from external influences. A modified model will be proposed for glass transition based on the lattice representation of Flory and Huggins[8]. A theoretical equation is derived to predict T_g from molecular parameters measurable by independent experiments.

THEORY

It has been recognized by a large number of experimenters that T_g is the critical temperature of motion of polymeric segments. Below T_g the segments are frozen in and the configurational entropy S_c does not change with temperature, but above T_g the polymeric segments are able to move about and S_c varies with temperature. Moreover, it has been shown that the chain conformations in bulk amorphous polymers (above T_g) are essentially unperturbed[8,9]. Then the polymer chain can be described as a random-flight chain composed of N_a segments of length L_a, just as in the Kuhn model for polymer chain in solution.

To evaluate the S_c above T_g, it is more desirable to consider a bond as the statistical unit. However, this

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requires introducing some parameters which are not measurable by experiment as we do not know the real space distribution function of the bonds in the main chain and side groups. On the other hand, it is well known that glass transition is only relative to the dynamic segments. As a result, it is appropriate to scale the dynamic segment as the basic statistical unit and assume that the segments are dynamically independent for the present aim. Because the lattice representation of Flory and Huggins is adequate for the description of polymer liquids where the polymer chains disperse homogeneously in space and no similar simplification exists for polymer–solvent systems, we apply the lattice model to the calculation of ΔS_c.

Consider a polymer chain with N_a segments distributed over a lattice which can accommodate one segment on each site. If the number of polymer chains in unit volume is N_p, the configurational entropy of unit volume is[8]

$$\Delta S_c = kN_p\{\ln(N_a) + (N_a - 1)\ln[(Z-1)/e]\} \quad (1)$$

where Z is the coordination number of the lattice. In this model, the length of the segment is allowed to vary with molecular species of polymer, i.e. the intramolecular interaction and geometry of chain only affect the length of the segment. Therefore, Z is a constant and independent of the chain structure of the polymer. According to Voeks[10], it would be appropriate to take $Z = 8$.

On the other hand, the mean-square end-to-end distance for an unperturbed chain is

$$h_0^2 = N_a L_a^2 = (nL)^2/N_a \quad (2)$$

in which n and L are the number and length of the bonds in the main backbone of the chain, respectively. For a freely rotating chain with fixed bond angle (θ), the mean-square end-to-end distance is

$$\overline{h^2} = nL^2 b(\theta) = \frac{(nL)^2}{2DP}\, b(\theta) \quad (3)$$

where $b(\theta)$ is the backbone factor of polymer chain[8], and for vinyl polymer $b(\theta) = (1-\cos\theta)/(1+\cos\theta)$. DP is the degree of polymerization of polymer chain. With equations (2) and (3), the stiffness factor σ^2 and characteristic ratio C_∞ for isolated chains are defined as

$$\sigma^2 = h_0^2/h^2 = (R_g^2)_0/(R_g^2)_f = 2DP/[b(\theta)N_a] \quad (4a)$$

$$C_\infty = h_0^2/(nL^2) = 2DP/N_a = b(\theta)\sigma^2 \quad (4b)$$

Substitution of equation (4) into equation (1) leads to

$$S_c = kN_p\left\{\ln\left[\frac{2DP}{b(\theta)\sigma^2}\right] + \left[\frac{2DP}{b(\theta)\sigma^2} - 1\right]\ln[(Z-1)/e]\right\} \quad (5)$$

and

$$\frac{\mathrm{d}(S_c)}{\mathrm{d}T} = kN_p\left\{\frac{\mathrm{d}[\ln(1/\sigma^2)]}{\mathrm{d}T} + \frac{\mathrm{d}[\ln(1/\sigma^2)]}{\mathrm{d}T} \times \frac{DP\cdot C}{\sigma^2}\right\}$$
$$= kN_p\beta DP(1/DP + C/\sigma^2) \quad (6)$$

where

$$C = 2\ln[(Z-1)/e]/b(\theta) \quad (7)$$

$$\beta = \frac{\mathrm{d}\ln(1/\sigma^2)}{\mathrm{d}T} = -\frac{\mathrm{d}\ln(\overline{h_0^2})}{\mathrm{d}T} \quad (8)$$

Obviously, β is the parameter which characterizes the dynamic flexibility of the polymer chain. The value of C only depends on the structure factor $b(\theta)$ of the main chain and approaches unity for vinyl polymers with $\theta = 109°$.

According to the thermodynamic relation,

$$\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_p = \frac{C_p}{T} \quad (9)$$

As mentioned above, the first temperature derivative of configurational entropy ($\mathrm{d}(\Delta S_c/\mathrm{d}T)$) is discontinuous at T_g, i.e.

$$\left.\frac{\mathrm{d}(\Delta S_c)}{\mathrm{d}T}\right|_{T=T_g} = \frac{\Delta C_p}{T_g} \quad (10)$$

Combination of equations (6) and (10) leads to

$$\frac{1}{T_g} = \frac{RV(T_g)\beta(T_g)}{V_s\Delta C_p}\left[\frac{1}{DP} + \frac{C}{\sigma^2(T_g)}\right] \quad (11)$$

where R is the gas constant, ΔC_p is the change in the isobaric heat capacity, $V(T_g)$ and $\sigma^2(T_g)$ are, respectively, the molar volume of polymer monomers, and the dynamic stiffness and static stiffness factor at T_g. V_s is the scalar parameter, because the site volume is much larger than the real volume of a segment in this model. For a real system, the number of segments in the space of a site is approximately

$$N_0 = L_a^3/(L_a L^2) = C_\infty^2 \quad (12)$$

which shows that the site volume is about C_∞^2 times the real volume. It can be estimated that the value of N_0 is close to the value of $V(T_g)$ ($\mathrm{cm^3\,mol^{-1}}$) for some polymers, e.g. polypropylene, polystyrene and poly(methyl styrene), and so we will choose $V_s = 1$ and $Z = 8$ in later calculations, though this choice may be considered as arbitrary.

RESULTS AND DISCUSSION

Effect of the chain flexibility on T_g

Theoretical prediction. As demonstrated in equation (11), T_g has multifunctional dependences on the molecular parameters of a polymer. From equation (11), the theoretical dependency of T_g on the other measurable molecular parameters can be deduced. For high molecular weight polymers, equation (11) reduces to

$$T_g = \frac{\Delta C_p}{RV(T_g)\beta(T_g)C}\,\sigma^2(T_g)$$
$$= A\sigma^2(T_g) \quad (13)$$

Equation (13) indicates the important fact that the value of T_g is essentially governed by the molecular properties of polymer at T_g, which is in line with the prediction by the principle of corresponding states. Although many empirical relations of T_g to other molecular parameters (such as T_g *versus* σ, T_g *versus* E_c etc.) have been proposed in the literature, most were obtained by summarizing the experimental data at temperatures other than T_g. Thus one can expect these relations to be quite crude because the molecular parameters, σ^2 or E_c, are dependent on temperature. Strictly, before correlating T_g with a molecular parameter, the parameter should be reduced to the state at T_g.

Table 1 Values of A calculated by equation (13)

Polymer	ΔC_p (J mol^{-1} K^{-1})	$10^4\,\beta\,(T_g)$ (K^{-1})	V	A	$\bar{A}$
PS	26.8[a]	4.5[b] (4.7[c])	100.4	71.5 (68.5)	70.0
PMMA	34.1[d]	6.7[b]	86.4	70.7	70.7
PP	20.1[d]	6.0[b] (8.8[e])	49.5	81.3 (61.4)	71.4
PMA	42.1[a]	11.1[f]	70.0	65.2	65.2

[a] Reference 11
[b] Reference 12
[c] Reference 13
[d] Reference 14
[e] Reference 15
[f] Reference 16

Table 2 Values of A calculated by equation (15)

Polymers	ΔC_p (J g^{-1})^{14}	$V(T_g)$	$10^4\,\alpha_1$	A
PE	0.60	32.9	8.2[a]	74.8
PP	0.48	49.4	6.8[b]	72.2
PIB	0.40	66.7	5.8[a]	69.7
PVC	0.30	45.6	7.2[a]	68.7
PEA	0.35	89.3	6.8[a]	69.0
PMMA(c)	0.30	85.5	6.3[a]	66.8
PS	0.27	100.0	5.1[b]	66.4
PMS	0.32	110.8	5.5[b]	74.2
PIP	0.47	74.9	7.0[b]	73.3
PVAc	0.41	72.4	7.2[a]	81.4
PDMS	0.42	67.3	9.1[a]	61.1
PET	0.33[c]	143.8	8.0[a]	66.2
PBA	0.35[a]	128.2	6.0[a]	70.2
PB	0.49[a]	65.1	7.5[a]	67.0

[a] Reference 11
[b] Reference 14
[c] Reference 17

Since the parameters in equation (13) are all measurable by independent experiment and theoretical calculation, the equation provides a convenient means of predicting T_g from other parameters and vice versa. If the value of A is known, it is easy to predict T_g from the stiffness factor $\sigma^2(T_g)$ or $C_\infty(T_g)$, which can be measured from polymer solution or bulk by standard methods. It is easy to see that $\beta(T_g)$ has a closer relationship with T_g in nature and is certainly very helpful in interpreting the change of properties of polymers near T_g. However, there is less data available about $\beta(T_g)$ for estimating the value of A. We have only estimated the values of A for some well known vinyl polymers. Fortunately, it is found that A is essentially a constant for polymers with similar chain backbones such as vinyl polymers. *Table 1* collects data abstracted from the literature and estimated values of A for polystyrene (PS), poly(methyl methacrylate) (PMMA), polypropylene (PP) and poly(methyl acrylate) (PMA). The comparison shows that A is essentially constant with an average value of 69.3 for vinyl polymers.

On the other hand, if we assume that the site volume V_0 does not change with temperature and the number of lattice sites is allowed to increase as temperature increases, then

$$\beta = \frac{\mathrm{d}\ln N_a}{\mathrm{d}T} = \frac{\mathrm{d}\ln[V(T_g)]}{\mathrm{d}T} = \alpha_1 \tag{14}$$

where α_1 is the heat expansivity of polymer in liquid state above T_g. Then A is approximately expressed as

$$A = \frac{\Delta C_p}{RV(T_g)\alpha_1} \tag{15}$$

In *Table 2* we tabulate values of A calculated from equation (15) for 14 polymers. These values can be compared with those tabulated in *Table 1*. The average values, 70.0 and 69.3, are similar. In reality, it can be shown that A is a constant by noting the Boyer empirical relation[11]:

$$T_g\Delta C_p = \text{const.} \tag{16a}$$

and

$$T_gE_1 = \text{const.} \tag{16b}$$

From equations (15) it is obtained that

$$A = R\frac{T_g\Delta C_p}{T_gE_1} = \text{const.}$$

Comparison with experimental data. Experimental research on T_g and σ^2 is very advanced and provides much reliable data[1,16]. Values of T_g and $\sigma^2(T_g)$ for a number of vinyl polymers with different chemical composition are listed in *Table 3*. Since values of σ^2 for many polymers were not measured at T_g, we only use values of σ^2 which were measured near their T_g or whose temperature coefficients $\beta(T)$ are known so as to estimate $\sigma^2(T_g)$. Moreover, since σ^2 values for some polymers reported by different authors are quite scattered, preference was usually given to newer and presumably more reliable results.

A plot of the values of T_g *versus* $\sigma^2(T_g)$ in *Table 3* is shown in *Figure 1*. The data points show good agreement with the prediction according to equation (13) with $A = 70.0$ (straight line). Application of linear least squares treatment to the data in *Table 3* leads to $A = 69.5$, which is almost the same as that calculated directly from the molecular parameters in *Table 1* or *2*.

Table 3 has not listed data for PE, because the location of T_g of PE has long been disputed, even though PE has the simplest molecular structure. Most experimental evidence has shown that it is preferable to place T_g below 223 K (Reference 21), but the exact location is still a matter of controversy. Hence it is pertinent to predict T_g for PE by using equation (13) because the value of $\sigma^2(T_g)$ for PE can be derived from the solution properties and the crystalline problem does not exist. If $\sigma(\approx 370\text{ K}) = 1.6$ (Reference 16) and $\beta = (1.0 \pm 0.1) \times 10^{-3}$ (Reference 16), equation (13) gives

$$T_g = 69.5 \times 1.6^2 \exp[-1.0 \times 10^{-3} \times (T_g - 370)] \tag{17}$$

Table 3 T_g and σ^2 data (Reference 16)

	Chain repeating unit	T_g	$\sigma(T)$	$10^3 \frac{d \ln \sigma^2}{dT}$	$\sigma(T_g)$
1	Isobutylene	203	1.70 (359)	−0.28	1.74
2	Octene-1	226	1.96 (298)	2.00	1.82
3	Pentene-1	223	1.97 (305)	0.53	1.93
4	Butene-1	249	1.86 (296)	−0.66	1.92
5	Octyl methacrylate	253	2.10 (293)	2.20	2.01
6	Propylene	260	1.85 (347)	−0.60	1.90
7	Isopropyl acrylate (atactic)	267	1.88 (298)	−0.30	1.89
8	Isopropyl acrylate (syndio-)	270	1.90 (333)	−0.30	1.92
9	Methyl acrylate	283	2.00 (293)	−0.20	2.00
10	Butyl methacrylate	286	2.06 (296)	2.50	2.04
11	Vinyl acetate	305	2.12 (298)		2.12
12	Chlorotrifluoroethylene	318	2.03 (403)		2.03
13	Iso-methyl methacrylate	322	2.18 (313)	−2.50[a]	2.15
14	Cyclohexyl methacrylate	324	2.15 (296)	1.00	2.18
15	Ethyl methacrylate	338	2.21 (338)[b]		2.21
16	Vinyl alcohol	343	2.24 (303)		2.24
17	Vinyl chloride	351	2.32[c]		2.32
18	*N*,*N*′-dimethylacrylamide	362	2.17 (298)	1.00	2.24
19	4-Methylstyrene	366	2.18 (303)	1.40	2.28
20	Acrylonitrile	369	2.30[c]		2.30
21	Styrene	373	2.28 (303)	0.44	2.31
22	2-Vinylpyridine	377	2.24 (293)	1.20	2.34
23	2,5-Dichlorostyrene	379	2.18 (303)	1.40	2.30
24	2-Chlorostyrene	392	2.36		2.36
25	4-Chlorostyrene	399	2.41		2.41
26	Syndio-methyl methacrylate	390	1.92 (303)	4.00[a]	2.33
27	3,4-Dichlorostyrene	401	2.20 (321)	1.60	2.38
28	2-Vinyl-2-methylpyridine	403	2.36 (321)	0.80	2.43
29	2-Methyl styrene	409	2.26 (303)	1.60	2.39
30	4-Vinyl pyridine	415	2.37 (298)	0.80	2.48
31	Morpholinocarbonylethylene	420	2.42 (303)	0.80	2.50
32	2-Vinylnaphthalene	423	2.40 (338)		2.40
33	Vinyl priolidone	443	2.48 (298)	0.80	2.60
34	α-Methyl styrene	446	2.37 (303)	1.20[a]	2.58
35	(Biphenyl-4-al)ethylene	453	2.63 (303)	0.20	2.65
36	Vinyl carbazole	481	2.82		2.82
37	Methacrylic acid	501	2.65 (303)	0.40	2.75

[a] Reference 19
[b] Reference 20
[c] Reference 7

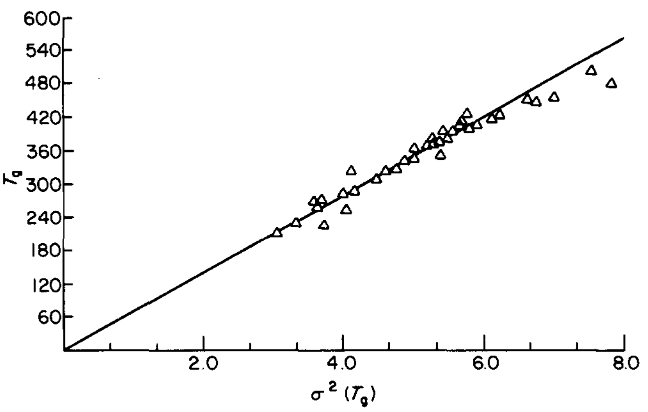

Figure 1 Dependence of glass transition temperature on stiffness factor $\sigma^2(T_g)$ for vinyl polymers. ———, Prediction from equation (13) with $A = 70.0$

Equation (17) was solved numerically and gave $T_g = 209$ K, which is very close to the newer experimental results $T_g = 200 \pm 10$ K (References 11 and 21).

Although the foregoing discussion was limited to vinyl polymers for simplicity, equation (13) can be applied to other kinds of polymer. As shown above, the quantity $\Delta C_p[RV\beta(T_g)]$ is independent of the structure of polymer backbones. In other words, if $b(\theta)$ or C can be deduced from the structure of the polymer backbone, A will be given by the following equation:

$$\begin{aligned} A &= 69.5/C \\ C &= 2.0/b(\theta) \end{aligned} \qquad (18)$$

For example, the chain of polydimethylsiloxane (PDMS) is composed of two different atoms (–Si–O–) with two bond angles ($\theta_1 = 110°$, $\theta_2 = 143°$)[8], and $b(\theta)$ can be

Table 4 Comparison of T_g predicted by equation (21) with observed values[16]

Repeat unit	$C_\infty(T)$	$-10^4\beta$	T_g(calc.) (K)	T_g(obs) (K)
100% *cis*, butadiene	5.15 (293)	4.0	170.4	171
100% *trans*, butadiene	5.80 (323)	−6.0	215	215
100% *cis*, isoprene	5.50 (295)	4.0	184	200
100% *trans*, isoprene	6.35 (320)		227	215
Ethylene oxide	6.15	2.3	209	206
Butene oxide	5.85		203	203
Propylene oxide	5.75		200	200
Tetrahydrofuran	4.8 (303)	−13.3	193	189

calculated from

$$b(\theta)=\frac{(1-\cos\theta_1)(1-\cos\theta_2)}{1-\cos\theta_1\times\cos\theta_2}=3.32 \qquad (19)$$

From equations (18) and (19), $A=115.4$ was obtained. The data of σ and β are, respectively, 1.27 (270–363 K)[16] and -0.78×10^{-3} (Reference 16) for PDMS. Thus equation (13) predicted T_g of PDMS to be 153 K, which is in good agreement with the experimental value 150 K.

In fact, the above relationship can be conveniently applied to other kinds of polymer except for those with bulky aromatic groups in the main chain, which are known to differ from polymers with a simple backbone structure both in the scale of the chain flexibility factor and in the mechanism of segmental mobility at T_g (Reference 8). For a chain with simple backbone structure, it is preferable to replace $\sigma(T_g)$ with the characteristic ratio, $C_\infty(T_g)$,

$$C_\infty(T_g)=b(\theta)\sigma^2(T_g) \qquad (20)$$

and

$$T_g=AC_\infty(T_g)/2=34.75C_\infty(T_g) \qquad (21)$$

The values of T_g calculated according to equation (21) are given in *Table 4*. Due to the errors inherent in the method used to obtain $C_\infty(T_g)$, the values are believed to be accurate to 10%. The agreement between the predicted and observed T_g in *Table 4* is, therefore, considered to be satisfactory.

Comparison with experimental relationship. Privalko and Liptov[7] proposed the following empirical equation relating T_g to chain stiffness factor

$$T_g=a(\sigma-b) \qquad (22)$$

in which a and b are constants. By analysis of the experimental data for some polymers, it was shown that the polymers may be divided into four groups. The values of a and b for the four groups are listed in *Table 5*.

Table 5 Values of a and b in equation (22)

Polymer series	a	a_1	b	b_1
1	630		1.35	
2	360	348	1.15	1.25
3	270	270	1.0	0.97
4	225	228	0.87	0.82

It is well known that σ varies with temperature and that the coefficient of temperature, $d(\ln\sigma^2)/dT$, may be either positive or negative, but equation (22) did not take this dependency into account and it was obtained by summarizing the data of T_g and σ at different temperatures (most of them at room temperature). If we intend to predict T_g by using equation (22), we will first meet the problem of which of the values of σ at several temperatures should be chosen. It can be shown that equation (22) may lead to an erroneous conclusion if the dependence of temperature, $d[\ln(\sigma^2)]/dT$, is not considered. For example, numerous experimental results (including the measurements in solutions[19] and bulk[22]) have shown that σ^2 of isotactic PMMA (i-PMMA) is about 40% larger than that of syndiotactic PMMA (s-PMMA) at room temperature. According to equation (22), the T_g predicted for i-PMMA would be higher than for s-PMMA. This is not the case because T_g of i-PMMA is actually much lower than that of s-PMMA, as can be seen from *Table 3*. On the other hand, if $\sigma(T_g)$ is considered according to equation (13), the correct prediction will be obtained by taking note of a negative value of $d(\ln\sigma^2)/dT$ for i-PMMA and a large positive value for s-PMMA[19].

In a simplified case σ does not depend on temperature, and a Taylor series expansion of equation (13) about $\sigma=2b_1$ results in an approximate relation:

$$\begin{aligned}T_g&=4Ab_1(\sigma-b_1)\\&=a_1(\sigma-b_1)\end{aligned} \qquad (23)$$

It has already been shown that A is a constant with the value 69.5 for vinyl polymers, which corresponds to groups 2, 3 and 4 in *Table 5*. When the values of b_1 are chosen to be 1.25, 0.97 and 0.82, respectively, for the groups 2, 3 and 4, the values of a_1 are as given in *Table 5*. It can be seen that these values are little different from those reported by Privalko and Lipatov[7]. Therefore, it is no longer necessary for our treatment to divide vinyl polymers into different groups.

Effect of molecular weight on T$_g$

Theoretical prediction. When $DP\to\infty$, equation (11) reads

$$T_g^\infty=\frac{\Delta C_p}{RV\beta(T_g)C}\sigma^2(T_g)=\frac{\Delta C_p}{RV\beta(T_g)}\times\frac{C_\infty(T_g)}{2} \qquad (24)$$

The combination of equations (11) and (24) gives the dependence of T_g on the degree of polymerization (DP) or number average molecular weight (M_n) as:

$$\frac{T_g}{T_g^\infty}=\frac{DP}{DP+K'}=\frac{M_n}{M_n+K'M_u} \qquad (25)$$

$$K' = \frac{RV\beta(T_g)}{\Delta C_p} T_g^\infty = \frac{\sigma^2(T_g)}{C} = \frac{C_\infty(T_g)}{2} \qquad (26)$$

where M_u is the molecular weight of polymeric monomer unit. Since all the molecular parameters in equations (25) and (26) are measurable by independent experiments, it is very convenient to use these equations to predict the variation of T_g with molecular weight of polymers.

On the other hand, if the molecular weight of polymers is not very low, e.g. $M_n > 10^4$, equation (25) can be simplified to a linear equation, which is in the same form as the Fox and Flory empirical relation[23]:

$$T_g = T_g^\infty - K_g/M_n = T_g^\infty - K'_g/DP \qquad (27)$$

$$K_g = T_g^\infty C_\infty(T_g) M_u/2 = K_g M_u \qquad (28)$$

Equation (28) presents an unambiguous relationship between K_g and the other molecular parameters and provides a useful and convenient method of evaluating K_g from the other molecular parameters, which are much easier to obtain by experiment than K_g.

Prediction of the parameter K_g. As pointed out above, when $M_n > 10^4$, K_g approaches a constant for most polymers. In this case, the value of the ratio $C_\infty(T_g)/DP$ is vanishingly small and equations (27) and (28) are accurate enough to predict the variation of T_g with M_n as well as K_g. *Table 6* gives both the experimental values from the literature and the predicted values according to equation (28) for a number of common polymers. It is obvious that the fit between theory and experiment is remarkably satisfactory in view of the fact that there is no adjustable parameter involved in the prediction and there are errors in measurements of the experimental data, especially of K_g.

It has been found by analysis of the experimental data that there exists an empirical scalar relation between K_g and T_g^∞ (Reference 25):

$$K_g \propto (T_g^\infty)^{2+v} \qquad 0 \leqslant v \leqslant 2 \qquad (29)$$

On the other hand, equation (28) can also be expressed by

$$K_g = (T_g^\infty)^2 M_u/A \qquad A = \frac{\Delta C_p}{RV\beta(T_g)C} \qquad (30)$$

Table 6 Theoretical and experimental values of K_g[24,25]

Polymer	T_g	$\frac{C_\infty(T_g)}{2}$	$10^{-4} K_g$	
			Exp.	Calc.
a-PMS	446	6.66	36.0	35.1
s-PMMA	405	6.00	25.6[b]	24.3
PS	373	5.34	20.0	20.7
PVC	351	4.84	8.0, 16.5	10.6
PVAc	305	4.41	1.4, 16.4	11.6
PIB	243	3.35	6.4	5.1
PDMS	150	2.20	0.6	2.4
s-PMS	453	6.66	31.0[a]	35.6
a-PMMA	388	5.29	21.0	20.7
PAN	369	5.29	12.8[c]	10.5
i-PMMA	318	4.62	11.0	14.6
PP	266	3.84	5.0, 2.8	4.2
PPO	198	2.80	2.5	3.2
PDMT	225	2.50[d]	4.4[e]	5.1

[a] Reference 26

[b] Calculated from the data ($M_n > 2 \times 10^4$) in Reference 27

[c] Reference 28; other values reported are 4.0×10^4 (Reference 29), 20×10^4 (Reference 29) and 28×10^4 (Reference 30)

[d] Value at 25°C (Reference 31)

[e] Reference 32

Table 7 Values of C_∞ and $M_u^{1/2}$ for some vinyl polymers[16]

Polymer	$M_u^{1/2}$	C_∞
PE	5.3	5.2
PB	7.5	7.4
PS	10.2	10.4
PMMA	10.0	9.5
PEA	10.0	9.9/11.9
PVAc	9.2	9.0
PP	6.5	6.9
PVC	7.9	6.6/8.6
PαMS	10.8	11.2
PMA	9.3	8.4/9.4
PEMA	10.7	9.8/11.0

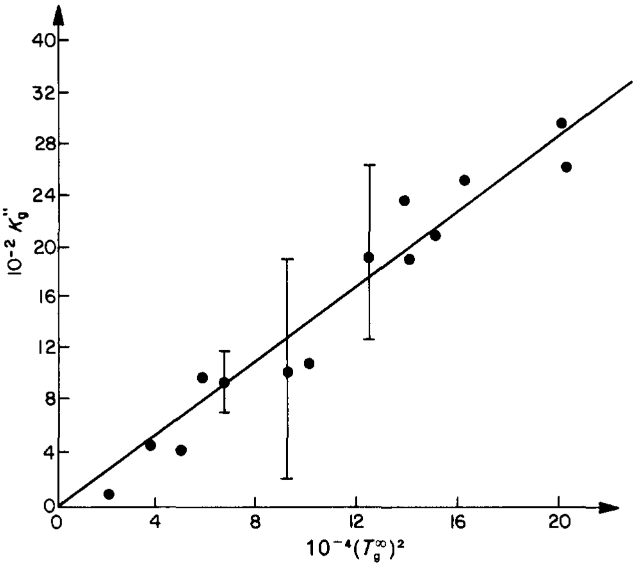

Figure 2 Variation of K'_g with $(T_g^\infty)^2$. ———, Prediction from equation (28) with $A = 69.5$

It was shown above that A is a constant with a value of 69.5 for vinyl polymers. However, it seems difficult to derive an exact scalar relation between K_g and T_g^∞ from equation (30) since the relation between M_u and T_g^∞ is not yet known, and it requires the consideration of many other factors such as symmetry and tacticity of polymeric chain. In general there is a strong tendency for C_∞ to increase with $M_u^{1/2}$, except for long alkyl side chains and strong polar side groups, as shown by *Table 7*, so equation (30) could lead to the correlation $K_g \propto (T_g^\infty)^4$; but in the other case of stereoregular polymers, T_g varies only with tacticity of the chain with same M_u, from which equation (30) results in $K_g \propto (T_g^\infty)^2$. It is evident that the empirical relation (equation (29)) is in the range predicted by equation (30).

To simplify the relation between K_g and T_g, it is preferable to consider

$$K'_g = K_g/M_u = A^{-1}(T_g^\infty)^2 \qquad (31)$$

Equation (31) indicates that a plot of K'_g *versus* $(T_g^\infty)^2$ will be a straight line through the origin. *Figure 2* presents data on K'_g and $(T_g^\infty)^2$ for the polymers in *Table 6*. By application of linear least squares treatment to the data. A was found to be 68.5. It was shown above that values of A for the vinyl polymers are 69.5 from the plot of data on T_g and $\sigma^2(T_g)$ and 70.0 from calculation from the molecular parameters based on the theoretical relationship. Three different methods based on the theory lead to almost the same value for A, which strongly suggests that the treatment of the glass transition put forward in this paper is successful. We emphasize that equation (28) is very useful for estimating K_g as well as for checking old and new literature data on K_g because the measurement of K_g is a time-wasting task and requires values of T_g with very high accuracy for polymer fractions of high molecular weight.

Variation of T$_g$ *over a wide range of molecular weight.* When the molecular weight of polymer is over a wide range, it is preferable to apply equation (25) to the dependence of T_g on M_n. It is well known that σ^2 or C_∞ varies with the length of the polymeric chain. Hence it is necessary to take this variation into account, to predict T_g over a wide range of M_n. With C_n denoting the characteristic ratio for a chain with n bonds, equation (25) can be written as

$$\frac{T_g}{T_g^\infty}=\frac{2DP}{2DP+C_n(T_g)} \tag{25a}$$

It is generally recognized that $C_n(T_g)$ changes very little with length of chain and approaches $C_\infty(T_g)$ if $DP > 50$ (Reference 8). In other words, equation (25) can be applied to the prediction of T_g without correcting $C_n(T_g)$ for the effect of chain length when $DP > 50$ or $M_n >$ 2–5 × 10^3. The theoretical dependences of T_g on DP have been calculated according to equation (25) for polydimethylsiloxane (PDMS), poly(vinyl chloride) (PVC), polystyrene (PS) and poly(α-methyl styrene) (PαMS). The theoretical curves and experimental data are shown in *Figure 3*. Good agreement between theory and experiment was obtained for these polymers when $DP > 40$. As predicted above, when $DP < 40$, the theoretical values of T_g obtained without consideration of the effect of chain length are lower than real values. Therefore, it is imperative to take this effect into account.

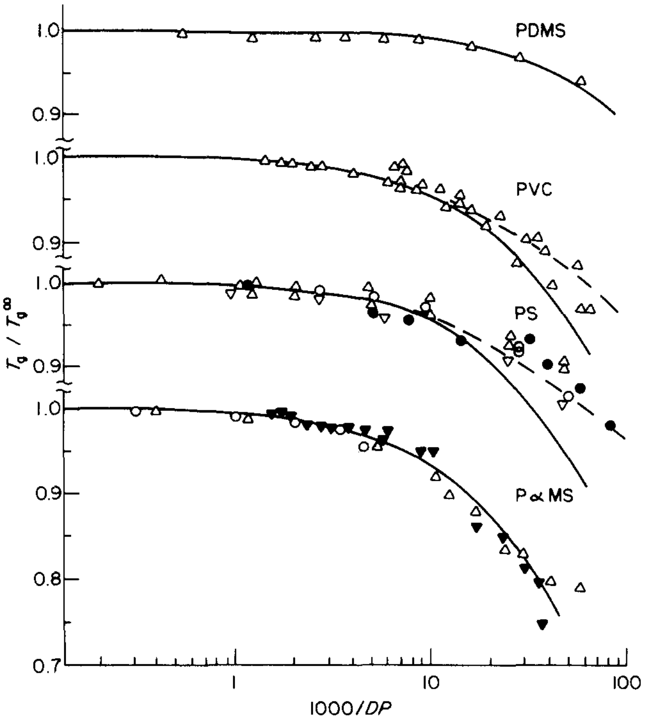

Figure 3 Reduced variable plots. ———, – – –, Predictions from equations (25) and (34), respectively. Data points from: △, Reference 33 for PDMS; △, Reference 34 for PVC; △, Reference 35, ▿, Reference 36, ●, Reference 37 and ○, Reference 1 for PS; ▼, Reference 24, △, Reference 38 and ○, Reference 38 for PαMS

Although it has been shown by numerical calculations[8] that C_n decreases with decreasing length of chain, the exact expression for C_n *versus* n cannot be obtained for a real polymeric chain. For convenience, here we apply the wormlike chain model[8] to the problem. Let us consider R_g, the mean square root of radius of gyration, which is directly measurable in experiment. According to the wormlike chain model, R_g corresponding to a polymeric chain with n bonds is given by

$$\left(\frac{R_g^2}{nL^2}\right)_n=\left(\frac{R_g^2}{nL^2}\right)_\infty\{1-3y+6y^2-6y^3[1-\exp(-1/y)]\} \tag{32}$$

Here $y = L_c/L_t$, where L_c and L_t are the total length and persistence length of polymeric chain, respectively, and L is the length of the bond. From equation (32), we have

$$\begin{aligned}\frac{C_n(T_g)}{C_\infty(T_g)}&=\frac{(R_g^2/nL^2)}{(R_g^2/nL^2)_\infty}\\&=1-3y+6y^2-6y^3[1-\exp(-1/y)]\\&=f(y)\end{aligned} \tag{33}$$

Substituting equation (33) into equation (25a) gives

$$\frac{T_g}{T_g^\infty}=\frac{2DP}{2DP+C_\infty(T_g)f(y)} \tag{34}$$

For a real polymeric chain, the value of y is known. Thus equation (34) can be used to predict T_g for lower DP, i.e. for a vinyl polymeric chain

$$y=\frac{C_\infty(T_g)}{4DP[\sin(\theta/2)]^2} \tag{35}$$

in which θ is the angle of C–C in the backbone. The dashed lines in *Figure 3* represent the predicted T_g according to equation (34) for PVC and PS. As has been seen, agreement between theory and experiment is satisfactory even when the DP decreases to ≈20. Comparison of equation (25) with equation (34) shows little difference if $DP > 40$.

Moreover, equation (25) has also been applied to the stereoregular polymers. It is well known that tacticity has a significant effect on the molecular parameters for polymeric chains with asymmetric side groups, so it can be expected that the dependence of T_g on DP will vary with the tacticity. We prefer a separate investigation of the different stereoregular PMMAs by adopting different molecular parameters. It has been demonstrated that

$$C_\infty(T_g)=2T_g^\infty/A=2T_g^\infty/69.5 \tag{36}$$

The values of T_g^∞ for different stereoregular PMMAs are known, and $C_\infty(T_g)$ can be estimated from equation (36). *Figure 4* shows T_g predicted by equation (25) and observed T_g for a series of PMMA with different tacticities. It has been seen that the theoretical predictions are also successful for this case.

CONCLUSIONS

The model proposed in the present paper leads directly to a relationship to predict T_g from molecular parameters measurable by independent experiments. The relationship has been successfully applied to predict the effects

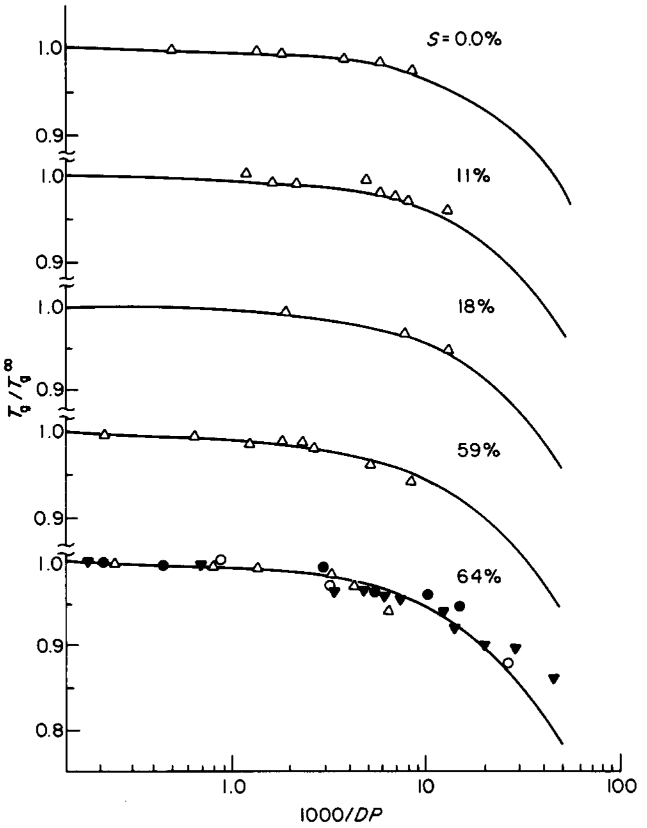

Figure 4 Variation of T_g with DP for PMMA with different tacticities; S denotes syndiotactic triads. Data points from: ○, Reference 40; △, Reference 27; ▼, Reference 39; ●, Reference 41

of chain flexibility and molecular weight of polymers on T_g. The theoretical predictions, which are in good agreement with experimental data for many polymers, indicate that T_g of polymers is governed by the chain flexibility factor at T_g.

In the present paper, a very useful equation was deduced which provides a convenient method of predicting quantitatively the variation of T_g with DP if only T_g^∞ or $C_\infty(T_g)$ is known. In fact, the values of T_g for polymer with high M_n (i.e. $M_n > 10^5$) are very little different from T_g^∞ and we can take the value as T_g^∞ for estimating $C_\infty(T_g)$. An inherent correlation for K_g, T_g^∞ and $C_\infty(T_g)$ was obtained from the theory. It has been shown that chain flexibility plays a vital role in the relationship between T_g and molecular parameter from both theoretical and experimental results.

REFERENCES

1 Richardson, M. J. and Savill, N. G. *Polymer* 1977, **18**, 3
2 Simha, R. and Wilson, P. S. *Macromolecules* 1973, **6**, 908
3 Prigogine, I. 'The Molecular Theory of Solutions', Interscience, New York, 1957
4 Gibbs, J. H. and DiMarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
5 Berry, G. C. *Macromolecules* 1980, **13**, 550
6 Kreibich, U. T. and Batzer, H. *Ang. Makromol. Chem.* 1979, **83**, 57
7 Privalko, V. P. and Lipatov, Yu. *J. Macromol. Sci. Phys.* 1974, **B9**, 551
8 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
9 Cotton, J. P., Decker, D., Benoit, H., Farnoux, B., Higgins, J. *et al. Macromolecules* 1974, **7**, 863
10 Voeks, J. F. *J. Polym. Sci. A2* 1964, **2**, 5314
11 Van Krevelen, X. 'Properties of Polymer, Their Estimation and Correlation with Chemical Structures', Elsevier, Amsterdam, 1976, Ch. 5 and 6
12 Bianchi, U. *J. Phys. Chem.* 1965, **69**, 1497
13 Yoon, D. Y., Sundarajan, P. R. and Flory, P. J. *Macromolecules* 1975, **8**, 776
14 O'Reilly, J. M. *J. Appl. Phys.* 1977, **48**, 4043
15 Suter, U. W. and Flory, P. J. *Macromolecules* 1975, **8**, 765
16 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', Interscience, New York, 1972
17 Dimarzio, E. A. *J. Appl. Phys.* 1979, **50**, 6061
18 Vacatello, M. and Flory, P. J. *Macromolecules* 1986, **19**, 405
19 Jenkins, R. and Porter, R. S. *Adv. Polym. Sci.* 1980, **36**, 1
20 Vasudevan, P. and Sanappa, M. *J. Polym. Sci. A2* 1971, **9**, 183
21 Boyer, R. F. *Polymer* 1976, **17**, 997
22 O'Reilly, J. M. *Macromolecules* 1985, **18**, 2747
23 Fox, T. C. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
24 Cowie, J. M. G. *Eur. Polym. J.* 1973, **9**,1041
25 Boyer, R. *Macromolecules* 1974, **7**, 142
26 Malhotra, S. L., Minh, L. and Blanchard, L. P. *J. Macromol. Sci. Chem.* 1978, **A12**, 167
27 Thompson, E. V. *J. Polym. Sci. A2* 1966, **4**, 199
28 Beevers, R. B. and White, E. F. T. *Trans. Faraday Soc.* 1960, **56**, 1529
29 Keavey, J. T. and Eberlin, E. C. *J. Appl. Polym. Sci.* 1960, **3**, 47
30 Beevers, R. B. *J. Polym. Sci. A2* 1962, **2**, 5257
31 Lazcano, S. and Marco, C. *Eur. Polym. J.* 1988, **24**, 991
32 Lazcano, S. and Marco, C. *Macromolecules* 1981, **14**, 608
33 Cowie, T. M. G. and McEwen, X. *Polymer* 1973, **14**, 423
34 Pezzin, G., Zolio, F. and Sanmartin, P. *Eur. Polym. J.* 1970, **6**, 1053
35 Rudin, A. and Burgin, D. *Polymer* 1975, **16**, 291
36 Glant, C. A., Toh, H. K., Gillman, J. K. and Boyer, R. F. *Polym. Prepr.* 1975, **16**, 126
37 Fox, T. G. and Flory, P. J. *J. Polym. Sci.* 1954, **14**, 315
38 Cowie, J. M. G. and Toporowski, P. M. *Eur. Polym. J.* 1968, **4**, 631
39 Kusy, R. P., Katz, M. J. and Turner, D. T. *Thermochim. Acta* 1978, **26**, 415
40 Kim, S. L., Skibo, M., Manson, J. A. and Hertzberg, R. W. *Polym. Eng. Sci.* 1977, 17
41 Kusy, R. P., Simmons, W. F. and Greenberg, A. R. *Polymer* 1981, **22**, 268