Quantitative evaluation of the Gibbs–DiMarzio theory of the glass transition: Comment on the paper by Greenberg and Kusy

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The molecular parameters of the Gibbs–DiMarzio theory, the hole energy, flex energy and coordination number are computed by the simplified procedure for polystyrene, poly(vinyl chloride), poly(methyl methacrylate) and poly(α-methyl styrene). The theoretical dependency of the glass transition temperature T_g on the molecular weight is compared with the experimental data taken from the literature. By statistical analysis it is shown that, if the configurational entropy S_{cg} at T_g is to a first approximation taken as molecular weight independent and equal to S_{cg} of the high molecular weight polymer species, the agreement between theory and experiment is satisfactory for all the investigated polymers.

(Keywords: Gibbs–DiMarzio theory; poly(α-methylstyrene); poly(methyl methacrylate); polystyrene; poly(vinyl chloride); glass transition)

INTRODUCTION

In their recent paper Greenberg and Kusy[1] (GK) have used Gibbs–DiMarzio (GD) theory[2–4] for the comparison of the experimental dependence of the glass transition temperature, T_g, on the polymerization degree, P, of four polymers: poly(vinyl chloride) (PVC), polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(α-methyl styrene) (PαMS). They have carefully analysed a great amount of literature data by the statistical F-test in order to test the significance of the difference between theoretical and experimental values. In the application of GD theory, GK have assumed that the coordination number, z, is equal to 4 and the configurational entropy at T_g, S_{cg}, equal to zero. Moreover, instead of the hole (intermolecular) energy, E_h, and the flex (intramolecular) energy, ε, they have taken the ratio $r = E_h/\varepsilon$ ranging from 0.8 to 1.2. GK have then tried to find the best agreement when $0.015 \leqslant V_0 \leqslant 0.045$, where V_0 is the fractional free volume at T_g. They have concluded that the GD theory is satisfactory for PS and PVC but unsuccessful in the case of PαMS and PMMA.

In fact, it is possible to determine the molecular parameters z, E_h and ε.[5] The required experimental data for the computational procedure are ΔC_p, $\Delta\alpha$, T_g and T_2 where ΔC_p and $\Delta\alpha$ are respectively the changes in the isobaric heat capacity and in the thermal expansion coefficient at T_g. T_2 is the temperature at which the GD configurational entropy falls to zero and is taken to be equal to a limiting temperature for relaxation processes[6] and therefore can be estimated from viscoelastic measurements[7]. Using these data a complete set of molecular parameters has been obtained for 15 different polymers[5]. The results have shown that z varies between 3.76 and 13.5, E_h/k between 420 K and 965 K, ε/k between 321 K and 1172 K, and V_0 between 0.021 and 0.059 (k is the Boltzmann constant). The comparison with other methods[8,9] of estimation of E_h and ε has shown in both cases the same order and trend in dependence on T_g.

The GD model is not sophisticated enough to take into account all peculiarities of polymers; therefore the computed parameters do not need to have exactly the prescribed meaning. Nevertheless they reflect certain microscopic features of a particular polymer species. It is our opinion that an adequate application of the GD theory for an arbitrary polymer should start with a determination of relevant molecular parameters. For this reason, we suggest a simplified procedure for the computation of the molecular parameters and show that such characteristics, in the case of the dependence of T_g on P, lead to good agreement between theory and experiment. This result cannot be considered unsatisfactory in the frame of statistical analysis similar to that used by GK.

THEORY

In ref. 5, it has been suggested that the GD configurational entropy at T_g, S_{cg}, can be approximated by the relation[6]

$$S_{cg} = \Delta C_p \ln(T_{g\infty}/T_{2\infty}) \tag{1}$$

where index ∞ denotes properties of high molecular weight polymers. Let us assume that S_{cg} is molecular weight independent. The GD entropy equation reads[2–4]

$$\begin{aligned} S_{cg}/n_r R = & -(V_0/V_x)\ln S_0 + ((z-2)/2V_x)\ln(V_0/S_0) \\ & -\{\ln S_x - \ln[(z-2)X/2+1)(z-1)] \\ & -(X-3)[f\beta - \ln(1-f)]\}/X \end{aligned} \tag{2}$$

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where $V_x = 1 - V_0$, $S_0 = zV_0/(z - 2V_x(1 - 1/X)$, $S_x = 1 - S_0$ and $\beta = \varepsilon/kT_g$. The number of rotatable groups per monomer unit is denoted by n_r and R is the ideal gas constant. X denotes the number of lattice sites occupied by one polymer molecule and is related to the polymerization degree by the relation $X = nP$, where n is a scaling factor. Physically, n denotes the average number of rotatable groups which are accommodated on one lattice site. The fraction of the bonds which are in the *gauche* conformation, f, is given by

$$f = (z-2)\exp(-\beta)[1 + (z-2)\exp(-\beta)] \qquad (3)$$

Following the GD theory[4], we have for ΔC_p the relation

$$\Delta C_p/n_r R = \Delta\alpha E_h S_x^2/kV_x + \beta^2 f(1-f)(X-3)/X \qquad (4)$$

where $\Delta\alpha$ is given by

$$\Delta\alpha k T_g^2 = V_0 E_h S_x^2/(zS_x/2 - 2E_h S_x^2 S_0/kT_g - (z-2)V_x/2] \qquad (5)$$

The hole energy is given implicitly by

$$2E_h S_x^2/kT_g = \ln[V_0^{(z-2)}/S_0^z] \qquad (6)$$

Now, in order to obtain molecular parameters of a given polymer, we use the following experimental values: $T_{g\infty}$, ΔC_p, $\Delta\alpha$ and $T_{2\infty}$. Then we have a system of three nonlinear equations, namely equations (2), (4) and (5) (in which X is limited to infinity) for unknowns z, β and V_0. If the system is solved numerically, for example by the Newton method, it converges very rapidly. The hole energy is estimated from equation (6).

By knowing z, E_g and ε the $T_g(X)$ dependence can be obtained using equation (2). At first, T_g is extracted from equation (6) and substituted into equation (2). Equation (2) is then solved by different values of X for the unknown V_0. Finally, T_g as a function of X is obtained from equation (6).

RESULTS AND DISCUSSION

Molecular parameters of the GD theory

The proposed method is illustrated for the same four polymers investigated by GK. The experimental data abstracted from literature are given in *Table 1*. The data are essentially the same as in ref. 5, only for T_g of PVC a value 2 K higher has been assumed according to the measurements by Pezzin *et al.*[10]. The resulting molecular parameters are given in *Table 2* together with the molecular parameters computed without approximation given by equation (1)[5]. The comparison of both methods shows very small differences; thus the present simplified method can be used to calculate the GD molecular parameters. The investigation of the influence of the scatter in experimental data on the computed molecular parameters has been done in ref. 5 and will not be repeated here.

Table 1 Experimental data used for the calculation of the molecular parameters according to the GD theory (references to experimental data are given in brackets)

Polymer	ΔC_p (J mol^{-1} K^{-1})	$\Delta\alpha \times 10^4$ (K^{-1})	$T_{g\infty}$ (K)	$T_{2\infty}$ (K)	n_r[a]
PVC	18.6 (11)	2.93 (14)	352	296 (7)	2
PS	33.5 (12)	3.12 (12)	373	325 (7)	3
PMMA	34.2 (11)	3.10 (15)	388	305 (7)	4
PαMS	37.5 (13)	3.98 (13)	445	395 (7)	3

[a] n_r is understood as the number of bonds (per monomer unit) about which rotation is possible with the exclusion of bonds of end atoms and of rotationally symmetrical groups

Table 2 Molecular parameters calculated according to the GD theory

Polymer	z	z[a]	E_h/k (K)	E_h/k[a] (K)	ε/k (K)	ε/k[a] (K)
PVC	4.98	4.97	870	867	755	751
PS	5.64	5.66	889	889	909	907
PMMA	4.78	4.82	904	904	758	753
PαMS	5.89	5.90	905	905	1172	1172

[a] Values taken from ref. 5, Table 2

In the GD theory two coordination numbers should be distinguished. The first one, z, i.e. the number of primary valences of each of the atoms constituting the chain backbone, is, in the case of carbon atoms, equal to 4, while the second one, z', i.e. the number of nearest neighbouring segments and holes can be greater than 4. For practical purposes $z = z'$ is assumed, which results in the value of the coordination number being also greater than 4. For this reason all values of z in *Table 2* range between 4 and 6. The interaction between chemically nonbonded segments is characterized by the hole energy E_h which, for all polymers under investigation, changes very little. On the other hand, the intramolecular energy ε representing the polymer chain rigidity grows with increasing T_g. The comparison of PS and PαMS can serve as an example for both energies. Similar chemical structure implies similar E_h, whereas substitution of hydrogen atom in PS by methyl group in PαMS causes considerably lower chain flexibility and results in higher ε.

Dependence of T_g *on molecular weight*

In order to test the applicability of the GD theory for the prediction of the molecular weight dependence of T_g, GK have adopted a large number of literature experimental data and they have emphasized the statistical analysis. Sources of the experimental data used in our paper are not so extensive and the present statistical analysis differs in some respects from GK's method. At first the difference δ between the theoretical and experimental $T_g(X)$ is evaluated for each $X = nP$. The minimum of standard deviation of the set of $\delta(X)$ is taken as a criterion for the 'best' scaling factor n for a given polymer. Only when the theoretical dependence fits the experimental data in this way is the statistical F-test[16] applied. When a straight line can be drawn through points $\delta(X)$, the F-test is used to answer if the slope of this straight line significantly differs from zero or not.

Results of the statistical analysis are collected in *Table 3*. N is the number of experimental points taken into account, $\bar{\delta}$ and σ are the mean and the standard deviations of differences δ respectively; s and i are the slope and the intercept of the straight line obtained as linear regression on the plot δ against $\log X$. The calculated variance ratio is denoted by p whereas F is the tabulated value of the F-distribution for the corresponding number of degrees of freedom at the significance level 0.05. If $p < F$, the null hypothesis holds, i.e. the dependence of δ on $\log X$ for tested data does not significantly differ from $\delta = 0$.

Table 3 shows good agreement between theory and experiment for PVC. In the case of PS we omit the data of Ueberreiter and Kanig[19] for which P is lower than 5 due to computational difficulties in solving equation (2). Greater value of σ is caused by different preparations of samples and different methods of determination of T_g by various authors. This is true also for PMMA. For analysis of this polymer we adopt from the paper by Thompson[25] only data of series 4 and 5 for which content of isotactic triads in polymer was not greater than 10%. For example Biroš *et al.*[28] have shown that with increasing content of isotactic triads in PMMA T_g decreases from 396.6 to 315.9 K and ΔC_p increases from 0.25 to 0.39 J kg^{-1}. It follows that the molecular parameters also will depend on the tacticity of PMMA. The same problem arises with PαMS. From *Table 3* it is evident that the null hypothesis should not be rejected for this polymer, but we prefer a separate investigation of atactic PαMS (data by Cowie and Toporowski[26]) and syndiotactic PαMS from the paper by Malhotra *et al.*[27]. For the latter we have used both $T_{g\infty}$ and $T_{2\infty}$ about 15 K higher and have obtained $E_h/k = 924$ K, $\varepsilon/k = 1217$ K and $z = 5.85$. $T_g(X)$ dependence for PMMA and PαMS has been treated in the literature as incompatible with the GD theory[1,24,25]. The fact that in our case the agreement between the theory and experiment is obtained, demonstrates the importance of application of the proper molecular parameters.

Table 3 Results of the statistical analysis

Polymer	Refs.	N	n	$\bar{\delta}$ (K)	σ (K)	s (K)	i (K)	p	F
PVC	10	37	1.09	3.0	4.0	−0.21	0.35	0.02	4.13
PS	17–20	40	1.37	4.1	5.6	0.41	0.93	0.18	4.10
PMMA	21–25	83	1.32	6.1	8.1	0.78	0.73	0.65	3.97
PαMS	26,27	28	0.59	10.2	12.4	−5.4	9.9	2.6	4.23
PαMS(a)[a]	26	11	0.63	9.5	13.0	−2.0	8.5	0.23	5.12
PαMS(s)[a]	27	17	0.42	4.2	5.7	1.5	−3.2	0.26	4.54

[a] (a) and (s) denote atactic and syndiotactic PαMS respectively

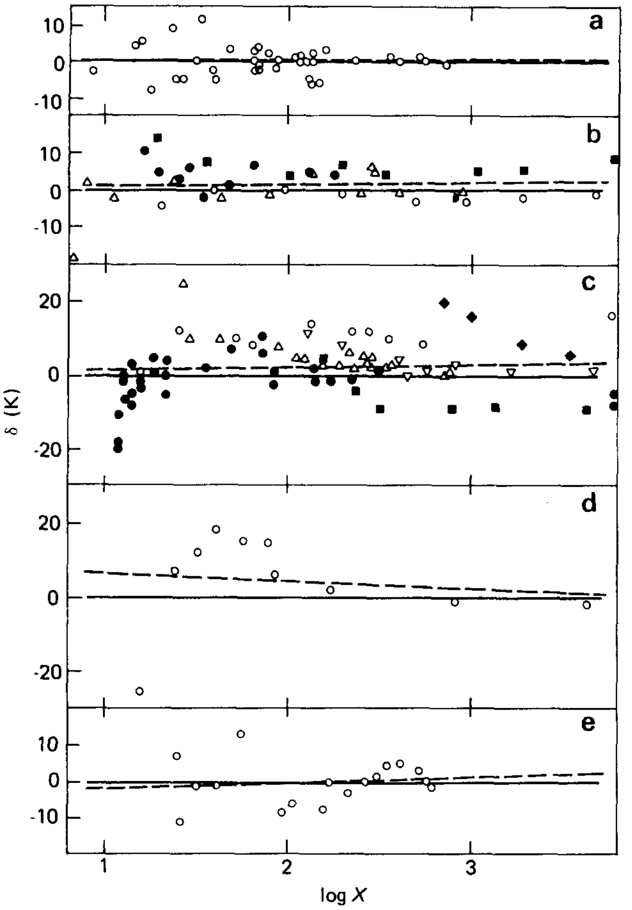

Figure 1 Molecular weight dependences of differences between theoretical and experimental values of T_g. Full line is zero level, dashed line represents linear regression. (a) Poly(vinyl chloride) data: Pezzin *et al.*[10]; (b) polystyrene data: (■) Richardson and Savill[17], (●) Fox and Flory[18], (▲) Ueberreiter and Kanig[19], (○) Rudin and Burgin[20]; (c) poly(methyl methacrylate) data: (○) Kusy and Greenberg[21], (■) Kim *et al.*[22], (●) Kusy *et al.*[23], (▲) Beevers and White[24], (▼) Thompson (series 4)[25], (◆) Thompson (series 5)[25]; (d) atactic poly-α-methyl styrene—data of Cowie and Toporowski[26]; (e) syndiotactic poly-α-methyl styrene—data of Malhotra *et al.*[27]

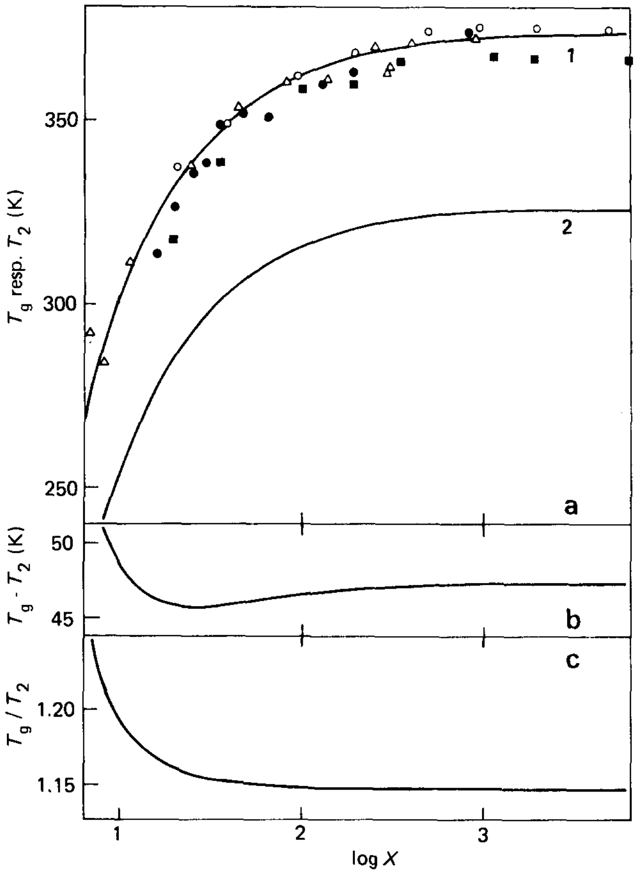

Figure 2 Molecular weight dependence of temperatures T_g and T_2 for polystyrene. (a) curve 1: theoretical dependence of T_g compared with experimental data (cf *Figure 1*); curve 2: theoretical dependence of T_2; (b) dependence of $T_g - T_2$ on molecular weight; (c) dependence of T_g/T_2 on molecular weight

The deviations, δ, as function of log$X$ are plotted in *Figure 1*. Full lines represent always the null level, dashed lines are the linear regression lines. It can be seen that in cases (a), (b) and (e) the assumption that $\delta(X)$ corresponds to a straight line is completely justified. For PMMA (c) and atactic PαMS (d) the data form for lower X a curve which, in the case of PMMA, is only slightly different from a straight line. More serious deviation for atactic PαMS is caused by only one point, so that no conclusion can be made. In this context it should be noted that there is a necessity to investigate in greater depth the assumption of the molecular weight independent configurational entropy. If another assumption for the dependence of T_g in the GD theory is adopted, the curvature of the $\delta(X)$ can be changed.

The dependence of T_g on X is graphically illustrated only for PS. In the upper frame of *Figure 2* the theoretical

Table 4 Comparison of present calculation with the values estimated by Greenberg and Kusy[1]

Polymer	n^a	r	r^a	V_0	$V_0{}^a$	$S_{cg}{}^b$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
PVC	1.36	1.15	0.95–1.05	0.0316	0.015–0.045	1.56
PS	1.8	0.98	0.95–1.1	0.0393	0.015–0.045	1.54
PMMA	1.2	1.19	1.0	0.0378	0.015–0.045	2.06
PαMS(a)	0.77	0.77	0.9	0.0590	0.010–0.050	1.49
PαMS(s)	—	0.76	—	0.0598	—	1.44

[a] Values used by Greenberg and Kusy[1]
[b] Values of the configurational entropy related to one rotatable group

dependence of $T_g(X)$ (curve 1) together with the experimental data indicate good agreement between theory and experiment. In contrast curve 2 represents T_2 as a function of X computed once more according to equation (2) with the same set of molecular parameters but in this case with $S_{cg}=0$. However, since curves 1 and 2 are very similar in shape, an appropriate vertical shift will bring curve 2 close to the experimental data. This is what GK have done using their reduced variables technique. The vertical shift has been represented by the calculation of $T_2/T_{2\infty}$ instead of $T_g/T_{g\infty}$; these two ratios differ only slightly, mainly for higher X. A limited validity of the substitution T_2 instead of T_g as a function of X can be seen in *Figures 2(b)* and *2(c)*. They demonstrate that neither T_g-T_2 nor T_g/T_2 remain constant when X is changed.

Table 4 contains some quantities which can provide further comparison of both treatments. For PVC and PS GK have found satisfactory agreement of experimental data with GD theory and their ranges for r and V_0, which were optimal, roughly cover our corresponding values. The disagreement between theory and experiment for PMMA found by GK involves probably the tacticity as mentioned above and also the fact that the value of the configurational entropy for this polymer is high and the approximation $S_{cg}=0$ is not necessarily valid. In the case of PαMS the value of V_0 is higher than the interval used by GK. Further, for PαMS (and also for other polymers) the minimum of p does not correspond to minimum of σ and thus to the best fit of the curve to data. For this reason the minimization of σ is necessary before testing for significance. If this is done, agreement between the GD theory and data is obtained for PαMS also.

CONCLUSION

The present investigation of the GD theory is based on the assumption that the configurational entropy at T_g can be to a first approximation assumed to be molecular weight independent. From the point of view of the above described statistical analysis this method provides that the theoretical values of $T_g(X)$ do not significantly differ from the experimental values of PVC, PS, PMMA and PαMS if the tacticity of the latter two is taken into account. It can be concluded that the Gibbs–DiMarzio theory represents a good tool for prediction of the dependence of the glass transition temperature on the degree of polymerization if ΔC_p, $\Delta\alpha$, $T_{g\infty}$ and $T_{2\infty}$ of high molecular weight polymer are known. The treatment by Greenberg and Kusy reflects general features of the theory; however, for a detailed description, computation of molecular parameters is necessary.

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