Quantitative evaluation of the Gibbs–DiMarzio theory of the glass transition*

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The applicability of the Gibbs–DiMarzio (G–DM) theory of the glass transition (T_g) is quantitatively evaluated for PS, PVC, PαMS and PMMA. The analysis was conducted under the assumption that both the inter-/intramolecular energy ratio (r) and the effective chain segment density (n) remain constant while the fractional free volume at $T_g(V_0)$ varies as a function of the reciprocal degree of polymerization $(10^3/\bar{P})$. Based upon reduced parametric plots of $T_g/T_{g\infty}$ versus $10^3/\bar{P}$, the results showed that the G–DM equations were satisfactory for PS and PVC but unsuccessful in the cases of PαMS and PMMA. For the former cases the analysis indicated that when $0.015 \leqslant V_0 \leqslant 0.045$ optimum agreement occurred at $n=1.80$, $r=10.5$ and $n=1.36$, $r=0.95$, respectively. Although potential n, r values were obtained for PαMS when the allowable V_0 range was expanded to 0.010–0.050, none of these combinations satisfied all of the analytical requirements. No agreement for the PMMA data sets could be obtained even when this less stringent V_0 criterion was adopted. Attempts to improve this situation by incorporating 'beads' and 'flexes' into the statistical mechanical equations are also considered.

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

INTRODUCTION

Over the past 30 years a number of theories have been developed to account for the variation in the glass transition temperature (T_g) of polymeric materials as a function of molecular weight (MW). Three of the most notable of these approaches have included the straight line technique of Fox and Flory[1] and the statistical mechanical theories of Gibbs[2] and Gibbs–DiMarzio[3] (G–DM). Because of the universal applicability claimed for the latter approach, the G–DM theory applicability claimed for the latter approach, the G–DM theory has received considerable attention[4–7].

Recently Kusy and Greenberg[6] introduced a reduced variables technique which simplified the use of the rather unwieldy statistical mechanical equations. Subsequent expansion of this work in terms of the inter-/intramolecular energy ratio (r) and the fractional free volume at $T_g(V_0)$ explicitly characterized the functional dependence of each of these parameters on MW[8]. In addition, an index (n) which related the effective number average of chain atom segments $(\bar{x})$ per degree of polymerization $(\bar{P})$ was incorporated into the reduced variable equations in order to better account for structural differences among polymers. By assigning reasonable values to the parameters n, r, and V_0, the theoretical predictions of the statistical mechanical equations were compared with T_g data obtained from the literature for four well documented polymers. Qualitative assessment of these results suggested that the G–DM theory adequately described the PMMA, PS and PVC cases but was unsuccessful for PαMS.

Because of the complexities inherent in a theory which incorporates multifunctional dependencies, further examination has indicated that a qualitative evaluation is not sufficient to establish the validity of a particular approach. Recently a statistical analysis technique was utilized in a comparison of the Gibbs theory with experimental results obtained for PMMA, and the advantages of such a quantitative determination were clearly demonstrated[9]. The present effort applies these quantitative analytical techniques to the PMMA, PS, PVC and PαMS data sets in order to make an unbiased assessment of the G–DM theory.

THEORETICAL DEVELOPMENT

The system of equations which comprises the G–DM theory has been presented in detail elsewhere[3,6,8]. However, the approach can be summarized by consideration of the following two equations of state: the entropy equation (1) and the PVT equation at atmospheric pressure (2), i.e.,

$$\frac{2\beta \exp \beta}{1+2 \exp \beta} - \ln[1+2 \exp \beta]$$

$$= \frac{\bar{x}}{\bar{x}-3} \left(\frac{1}{1-V_0} \left(\ln V_0 + (1+V_0) \right. \right.$$

$$\left. \left. \times \ln \left(\frac{(\bar{x}-1)(1-V_0)}{2\bar{x}V_0} + 1 \right) \right) + \frac{\ln[3(\bar{x}+1)]}{\bar{x}} \right) \quad (1)$$

$$\beta = -\frac{1}{r} \frac{\ln V_0 - 2 \ln \left(\dfrac{2\bar{x}V_0}{2\bar{x}V_0 + (\bar{x}+1)(1-V_0)} \right)}{\left(\dfrac{(\bar{x}+1)(1-V_0)}{2\bar{x}V_0 + (\bar{x}+1)(1-V_0)} \right)^2} \quad (2)$$

Here β is a dimensionless parameter equal to $-\varepsilon/kT_g$ where ε is the flex energy and k is Boltzmann's constant. In accordance with the assumption that V_0 decreases monotonically with decreasing MW, equations (1) and (2) can be solved iteratively by maintaining $\bar{x}=n\bar{P}$ and r constant while simultaneously varying V_0 until a unique β derived from equation (2) satisfies equation (1). This procedure is repeated for different combinations of $\bar{x}=n\bar{P}$ and r.

Using the reduced variables method, a plot of $T_g/T_{g\infty}$ vs. $\bar{P}^{-1}$ generates a family of curves each corresponding to a specific value of n (c.f. *Figure 1*). Each value of n is in turn plotted for the cases where $r=0.8$, 1.0 and 1.2. These results suggest that large variations in r have relatively little effect on the family of curves; however, this latitude is not possible unless V_0 is allowed to float over rather wide limits as a function of $\bar{P}^{-1}$ (c.f. *Figure 2*). Close examination of *Figures 1* and 2 indicates that if V_0 is to be restricted to reasonable limits within the range $1 \leqslant 10^3/\bar{P} \leqslant 100$ then only certain combinations of n and r can be considered (c.f. *Figure 3*). For example, if $n=1.4$ and V_0 is to be kept within 0.015–0.045, then r must remain within 0.94–1.07. If these restrictions are somewhat relaxed such that $0.010 \leqslant V_0 \leqslant 0.050$, then under the same conditions (i.e., $n=1.4$) r may range from 0.89–1.23. Unless otherwise indicated, only n–r combinations corresponding to $0.015 \leqslant V_0 \leqslant 0.045$ will be utilized in the comparison which follow.
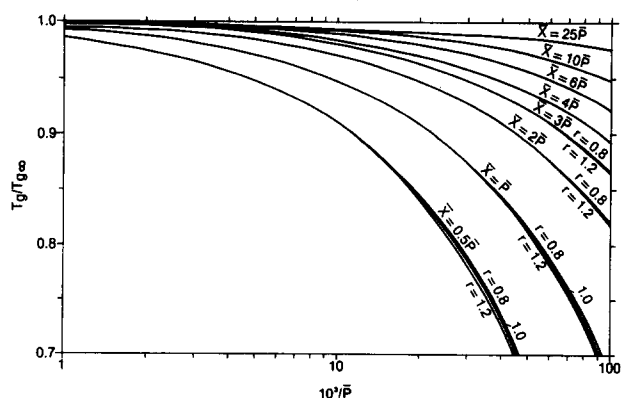

Figure 1 Reduced variables plot indicating the dependence of the glass transition (T_g) upon the logarithmic reciprocal degree of polymerization $(\bar{P})^{-1}$ as a function of constant values of the ratio of hole energy to flex energy ($r=0.8$, 1.0 and 1.2) and number average of chain atom segments per $\bar{P}$ ($n=0.5$, 1, 2, 3, 4, 6, 10 and 25). The relationships assume any constant value of ε and require the variation in V_0 indicated in *Figure 2* (cf. Ref. 8)
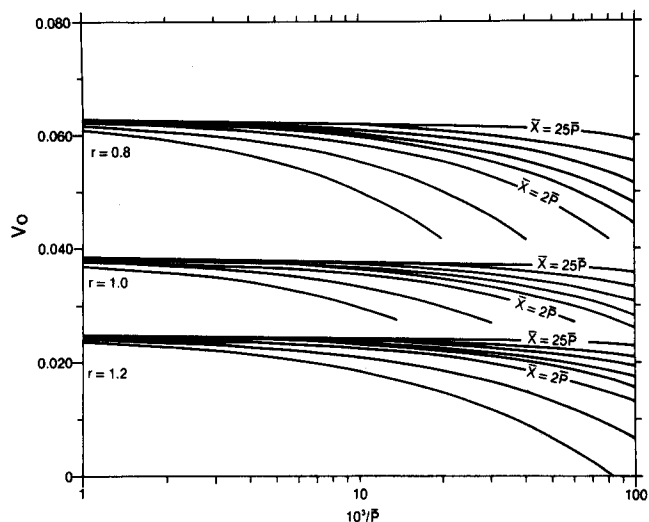

Figure 2 Relationship between the parameter V_0 and $(\bar{P})^{-1}$ as determined from equations 1 and 2. Values for r and $\bar{x}$ correspond to those indicated in *Figure 1* (cf. Ref. 8)
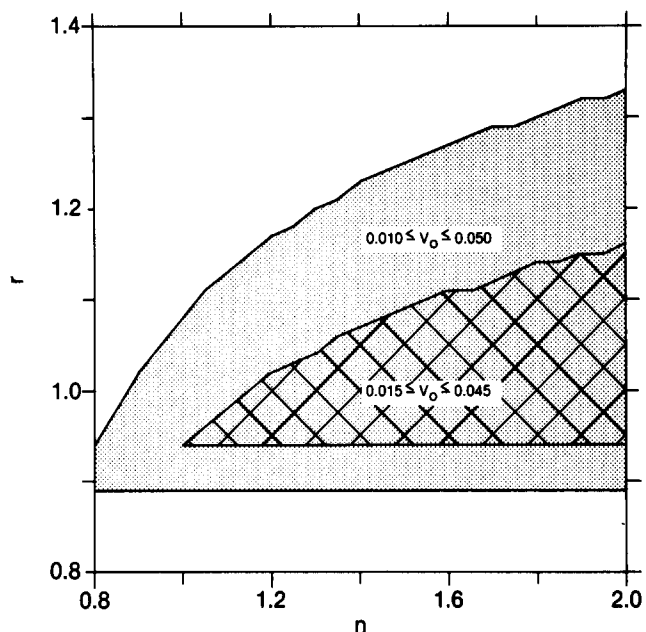

Figure 3 Interrelationship among n, r and V_0 as determined from equations 1 and 2. Cross-hatched region indicates n–r combinations for which $0.015 \leqslant V_0 \leqslant 0.045$. Stippled area designates the $0.010 \leqslant V_0 \leqslant 0.050$ region

RESULTS

The details of the statistical analysis technique have been discussed in Ref. 9. The method utilizes a transformation of variables and a linear regression of the differences between the predicted and experimental values (δ) as a function of $\bar{P}^{-1}$ [10]. If the theory perfectly described the data, then all of the δ values would be zero and both the slope and intercept of the resulting regression line would also equal zero (null hypothesis)[11]. Since in general this is not the case, the F statistic is utilized to test the null hypothesis (H_0) at the $p=0.05$ level. If H_0 cannot be rejected, the theory is regarded as having fit the data set for a particular combination of n and r.

The first step in the procedure is to obtain F vs. n curves for applicable values of r. A typical plot for the case of PS is shown in *Figure 4a*. Here the four parabolas correspond to $r=0.95$, 1.00, 1.05 and 1.10, respectively. If all
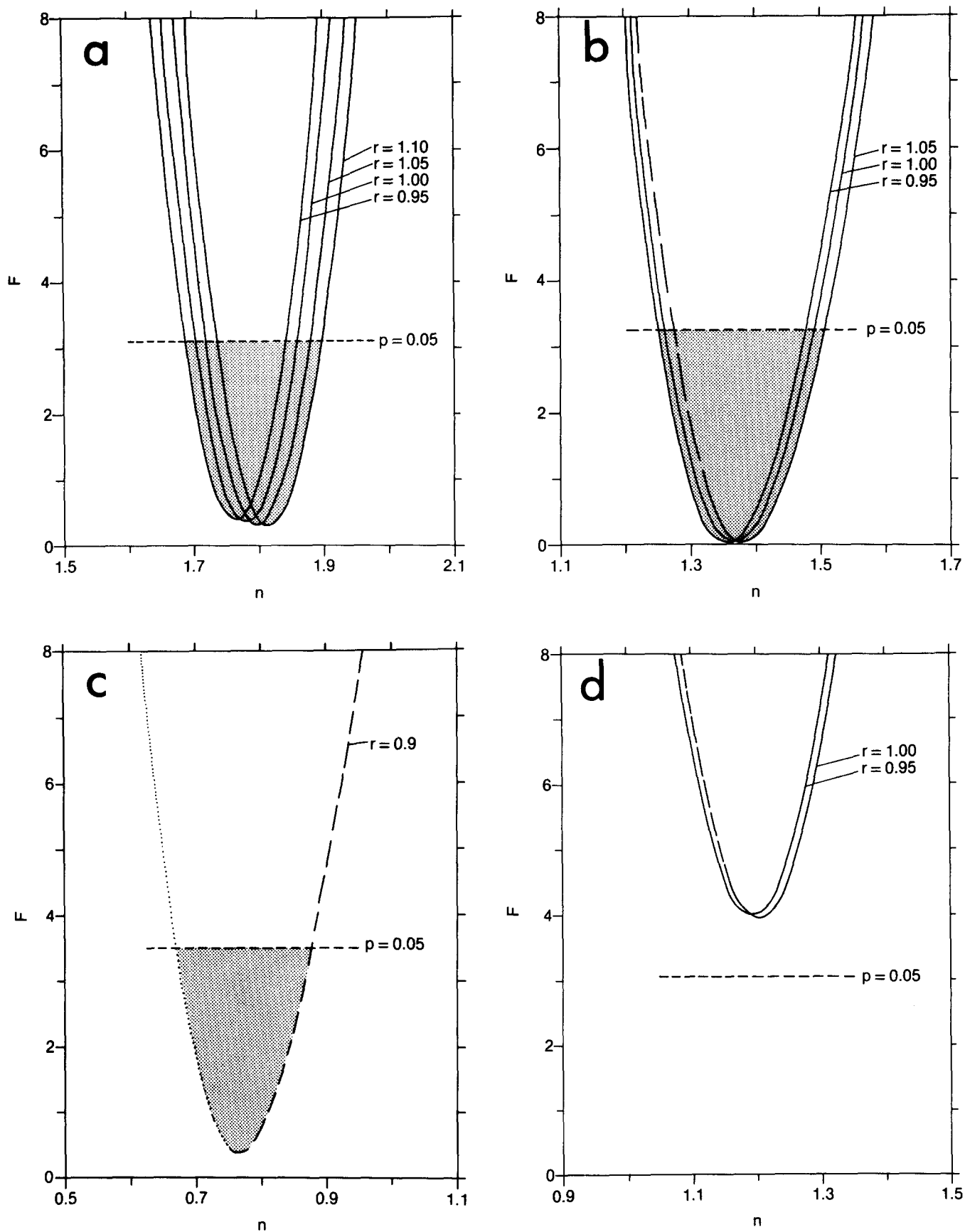
Figure 4 F-test results as a function of n and r using the G–DM theory: (a) for PS. (b) for PVC. The dashed line portion of the parabola denotes particular $n-r$ values which do not satisfy $0.015 \leqslant V_0 \leqslant 0.045$ but which lies within the range $0.010 \leqslant V_0 \leqslant 0.050$ (cf. *Figure 3*). (c) for PαMS. The dotted line represents values of $n-r$ for which $0.010 > V_0 > 0.050$. (d) for PMMA

intervening values of r were plotted, the resulting curve would take the form of a single band bounded by the values for $r = 0.95$ and $r = 1.10$. The dashed line at $F = 3.1$ indicates the critical level, $p = 0.05$, which depends upon the number of points in the data set. The best fit between the predicted and experimental values is assumed to occur at the minimum value of F, i.e., at the vertex of the parabola. Based on this criterion, the results indicate that for PS the best fit occurs at two points: $n = 1.80, r = 1.05$ and $n = 1.82, r = 1.10$.

Similar plots for PVC, PαMS and PMMA are presented in *Figures 4b, c* and *d*, respectively. Here a dashed line portion of the parabola corresponds to n–r combinations which lie outside of the $0.015 \leqslant V_0 \leqslant 0.045$ boundaries but are within the $0.010 \leqslant V_0 \leqslant 0.050$ region (*c.f. Figure 3*). For the case of PVC the results demonstrate that n–r combinations of 1.36–0.95, 1.37–1.00 and 1.38–1.05 would all provide equally acceptable fits to the data. For PαMS the best fit is taken at $n = 0.77, r = 0.9$ for which $0.010 \leqslant V_0 \leqslant 0.050$. For PMMA the vertices of the two parabolas do not fall below the $p = 0.05$ line; therefore, H_0 must be rejected because no combination of n and r will allow the G–DM theory to describe the data.

A necessary condition for the use of this statistical methodology is that the data points not be preferentially distributed about the regression line[10]. In order to verify that this requirement is met, a scatter diagram must be plotted for each of the polymer data sets for which H_0 was accepted. Typical results for PS are shown in *Figure 5*[12–20]. Here the residuals (δ) are plotted as a function of $10^3/\bar{P}$ for the 'best fit' case of $n = 1.80$ and $r = 1.05$ as determined from *Figure 4a*. The two salient features of this

diagram are that the regression line does approximate the equation $\delta = 0$ and that the individual data points are indeed reasonably distributed around the regression line. Similar statements apply to the corresponding diagram for PVC in which $n = 1.36$ and $r = 0.95$ (*c.f. Figure 6*)[21].

The situation is much different for the case of PαMS in which $n = 0.77$ and $r = 0.9$[22,23]. Examination of *Figure 7* indicates that the distribution is extremely skewed such that for $1 \leqslant 10^3\bar{P} \leqslant 10$ the data lies almost entirely above the regression line whereas for $10^3/\bar{P} \geqslant 10$ the converse is
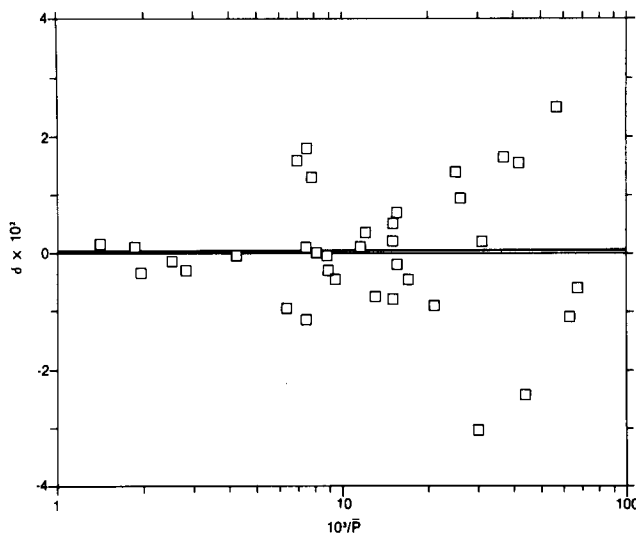
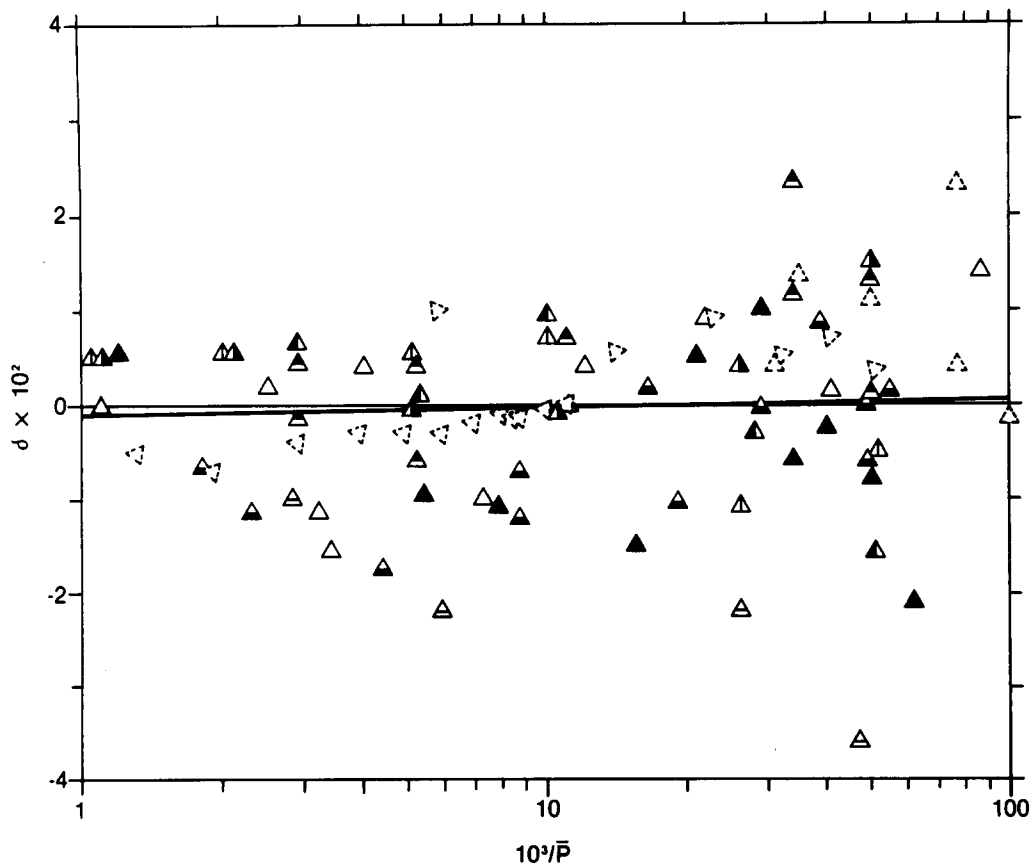**Figure 6** Scatter diagram for PVC using the G–DM theory with $n = 1.36$ and $r = 0.95$ with data from Pezzin *et al.*[21] ($\square$)

Figure 5 Scatter diagram for PS using the G–DM theory with $n = 1.80$ and $r = 1.05$: $\triangle$, Enns *et al.*[12]; $\blacktriangle$, Fox and Flory[13]; $\odot$ and $\ominus$, Glandt *et al.* on blends[14]; $\triangle$, Krause and Iskandar[15]; $\blacktriangle$, Richardson and Savill[16]; $\blacktriangle$, Rudin and Burgin[17]; $\triangle$ and $\triangle$, Stadnicki *et al.*[18]; $\triangle$, Ueberreiter and Kanig[19]; and $\triangle$, Ueberreiter and Kanig on blends[20]

true. Therefore, despite the nominal fit suggested by *Figure 4c*, the violation of the normal distribution requirement invalidates the acceptance of H_0 (*c.f.* Ref. 9).

DISCUSSION

Based upon the results of the statistical analysis the G–DM theory can be regarded as satisfactory for PS and PVC but unsuccessful for PαMS and PMMA. The necessity for such a quantitative evaluation becomes apparent when the information contained in the F–n curves (*c.f. Figure 4*) and the scatter diagrams (*c.f. Figures*
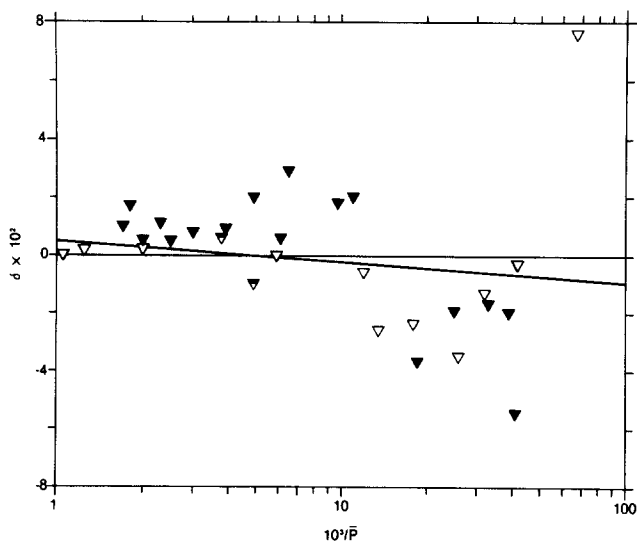

Figure 7 Scatter diagram for PαMS using the G–DM theory with n=0.77 and r=0.9 with data from Cowie and Toporowski[22] on atactic (△) and syndiotactic (△) polymers and Malhotra *et al.*[23] (▲)

5–7) is presented in a reduced variables format. These plots are shown in *Figures 8–11* where the individual data points are superposed by a theoretical curve derived for the 'best fit' situation for each of the four polymers. For the case of PMMA this is taken at n=1.2, r=1.0 (*c.f. Figure 4d*)[24–30]. (This does represent the best fit sutation though it does not meet the $p \geqslant 0.05$ criterion.)

Visual examination of *Figures 8* and *9* would indeed suggest that there is good agreement between the theory and the data. However, inspection of *Figures 10* and *11* would prompt a similar judgment even though a statistical analysis would not support this conclusion. While this strongly suggests that opinions concerning the applicability of any T_g vs. MW theory should be based upon an unbiased quantitative technique, some caution must be exercised in the use of such methodology inasmuch as the conclusions drawn are only as good as the information on which they are based. As previously described, the current data sets include all published results for both pure polymers and blends irrespective of tacticity, test methodology, physical form or thermal history[8]*. *Figures 8–11* indicate that each of the data sets contains a substantial amount of scatter. The relative contributions of each of the above mentioned factors to the overall variation cannot presently be determined. Indeed the relative importance of each of these factors may vary for different polymers. Nonetheless these contributions should be established since such information could prove critical with regard to the acceptance or rejection of a particular theoretical approach.

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* If glass transition temperature measurements were more accurate, then differences would likely be observed between several of these factors, including tacticity. At present, however, the precision of the measurements does not warrant further discrimination
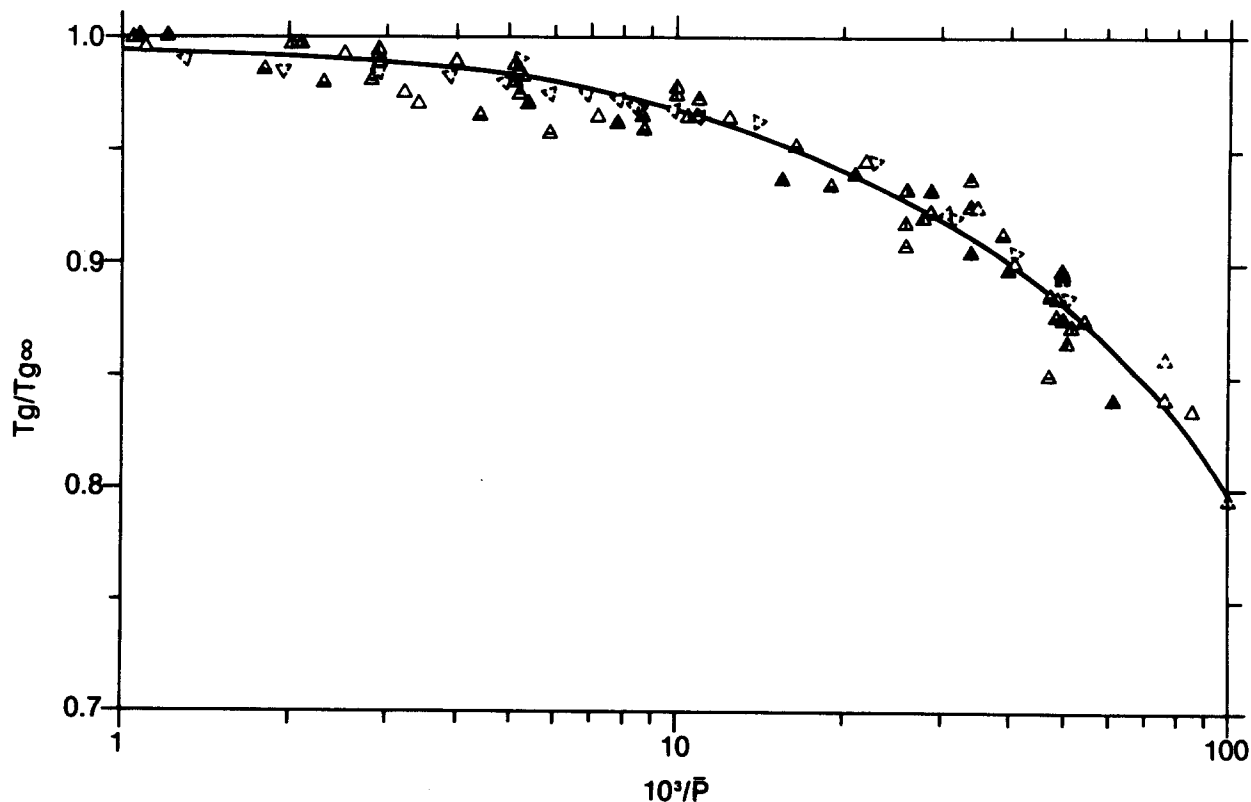

Figure 8 Reduced variables plot for PS. Curve represents solution for equations 1 and 2 with n=1.80 and r=1.05 (*Figures 4* and *8*)
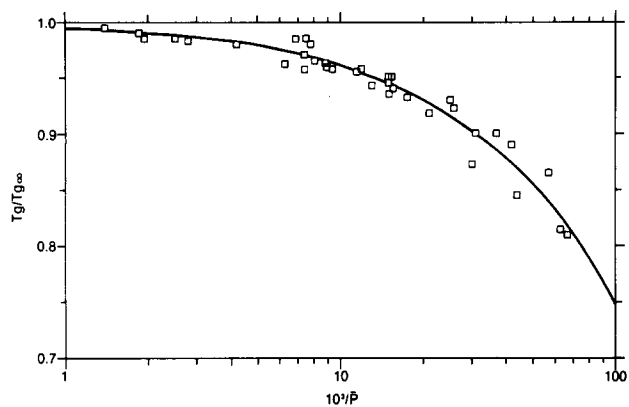
Figure 9 Reduced variables plot for PVC. Curve represents solution for equations 1 and 2 with $n=1.36$ and $r=0.95$ (*cf. Figures 4b* and *6*)
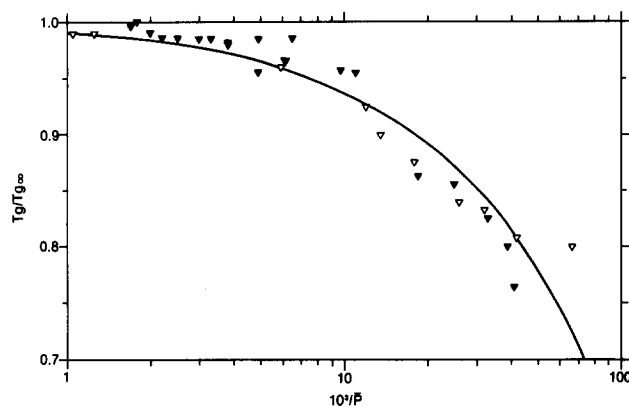

Figure 10 Reduced variables plot for PαMS. Curve represents solution for equations 1 and 2 with $n=0.77$ and $r=0.9$ (*Figures 4c* and *7*)

The present results have been evaluated under the assumption that r remains constant while V_0 varies as a function of MW. This situation is in agreement with an iso-viscosity viewpoint[31]. However from the standpoint of the iso-free volume theories one could argue for a constant V_0 and variable r[32]. While the same analytical techniques could be utilized to obtain solutions within the constraints of the latter assumption, there is a strong basis for taking the former approach[31,33,34]. Unfortunately relatively little information is available concerning the dependence of V_0 on MW. For PS measured values of V_0 over a wide range of MW have been reported by Williams[33]. Starting with this same data set, Miller[31] subsequently presented somewhat different V_0 values such that the two sets differ by a constant amount. This situation is shown in *Figure 12* in conjunction with the 'best fit' curves obtained from *Figure 4a* ($n=1.80$). Here the data points centre on the $r=1.10$, 1.14 and 1.05 curves for $(10^3/P)=1$–5, 5–20 and 20–100, respectively. Whether the measured dependence of V_0 on MW would have supported the statistical mechanical approach or would have substantiated a different functional relationship cannot be determined because of the inconsistency in the distribution of the data. Nonetheless the information suggests the validity of the iso-viscosity assumptions made at the outset.

To place the present results in their proper context the nature of certain terms in the G–DM equations needs to be more fully elaborated. Originally the G–DM equations were expressed in terms of '$\bar{x}$', the number of monomer segments[3]. The term 'monomer' was defined as a unit which occupied one lattice site such that it normally included one carbon backbone atom plus the attendant side groups. Hence the chain length could be given in
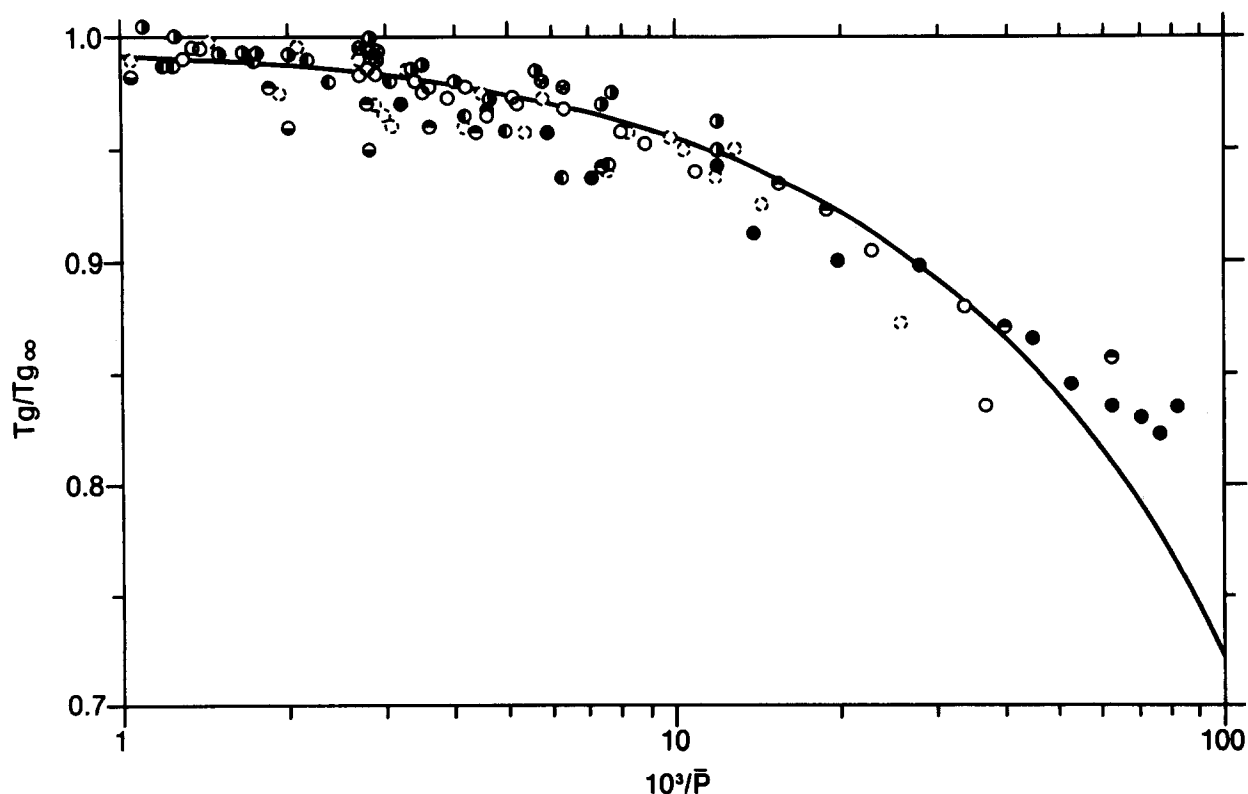

Figure 11 Reduced variables plot for PMMA. Curve represents solution for equations 1 and 2 with $n=1.2$ and $r=1.0$ (*cf. Figure 4d*). Data points from: ○, Beevers and White[24]; ◖, Kim *et al.*[25]; ◕, Kusy and Greenberg[26]; ●, Kusy *et al.*[27]; ◔, Kusy *et al.* on blends[28]; ⊗, Pratt[29]; ◑, Thompson on isotactic PMMA[30]; and ◐, Thompson on syndiotactic PMMA[30]

terms of $\bar{x}$, the number of carbon atoms in the main chain. Within the current terminology the chain length can be expressed via $\bar{x} = n\bar{P}$ where $n = 2$ for vinyl monomers having two carbon atoms backbone atoms per repeat unit. The qualitative results of a previous study have demonstrated that if 'n' were restricted to a value of 2.0, the G–DM theory could possibly apply to only a relatively small number of materials[8]. For this reason the index 'n' was utilized as a variable, dependent upon the chemical nature of the polymer[35]. Relatively large values of the index, $n \gtrsim 10$, were associated with flexible molecules such as PDMS while low values, $n \approx 1$, were

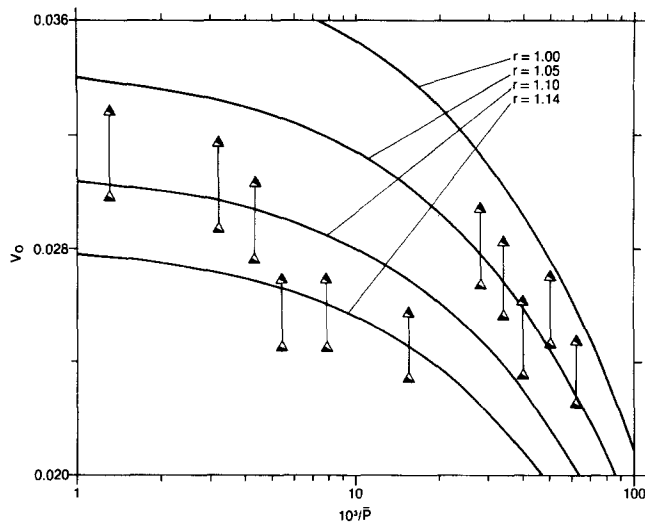representative of much stiffer materials such as PαMS[8]. The quantitative techniques utilized in the present study have demonstrated that the G–DM relationships satisfy only the PS and PVC cases when $n = 1.80$ and 1.36, respectively. If a fit were to be obtained for PαMS and PMMA, much lower values of n would be required.

Another approach to the G–DM equations has been discussed by DiMarzio and Dowell[36] whereby the chain length could be related to 'beads' (b) and 'flexes' (f). Using the present notation, the 'n' within the denominator of the first term on the right hand side of equation (1) can be expressed as the number of flexes per repeat unit while all other 'n's' refer to the number of the beads per repeat unit[37]. Values for b and f for the four polymers of interest are presented in *Table 1*. With the exception of PMMA, $f = 2$ for these polymers; however, b increases with increasing stiffness ranging from 3.0 for PVC to 7.4 for PαMS. The effect of incorporating b–f values into a reduced variables plot is shown in *Figure 13*. The curves demonstrate the influence of both flex and bead variation whereby $f = 1$–3 with b held constant at 1.0 and $b = 1$–8 with f held constant at 2.0. For any value of $(10^3/\bar{P})$ the results demonstrate that either an increase in f (b held constant) or an increase in b (f held constant) produces an increase in $(T_g/T_{g\infty})$. Preliminary analysis indicates that

Figure 12 Dependence of V_0 on the logarithmic reciprocal degree of polymerization for PS. Data from Williams[33] (△) and as reinterpreted by Miller[31] (▲). Curves demonstrate the influence of the parameter r with $n = 1.80$ (*cf. Figures 4a, 5* and *8*)

Table 1 Material characterization in terms of beads and flexes*

Polymer	Beads(b)	Flexes(f)
Poly-α-methyl styrene	7.4	2
Polystyrene	6.1	2
Poly(methyl methacrylate)	5.9	3, 4
Poly(vinyl chloride)	3.0	2

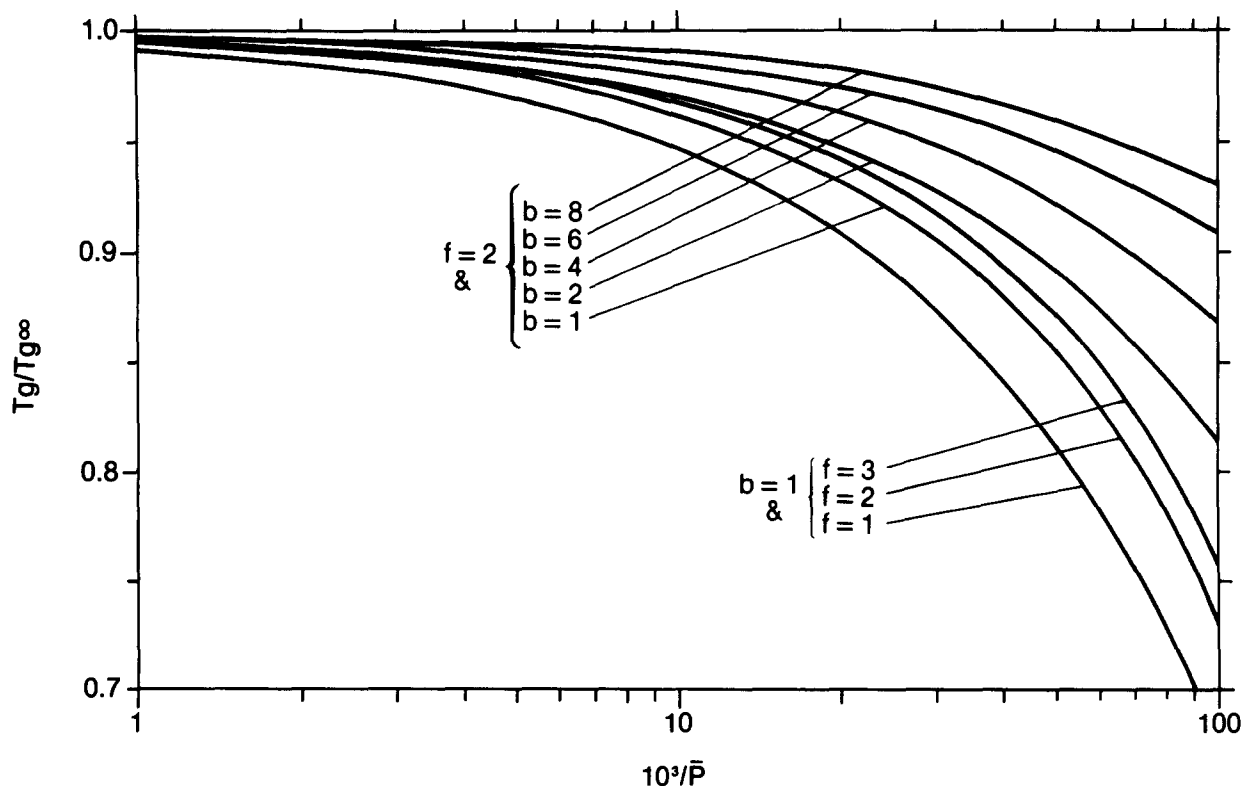* Abstracted from *Table 2* of Ref 36

Figure 13 Reduced variables plot in which beads (b) and flexes (f) are utilized as parameters ($r = 1.0$ for all curves). Compare with *Figure 1* and *Tables 1* and *2*

Table 2 Influence of beads and flexes on fractional free volume at T_g

b	f	V_0*
8	2	0.375–0.310[†]
6	2	0.269–0.211
4	2	0.143–0.102
2	2	0.039–0.022
1	3	0.007–0.002
1	2	0.012–0.004
1	1	0.039–0.012

* All values determined at $r = 1.0$

[†] Values at $10^3/\bar{P} = 0$ and 100, respectively

when the values for beads and flexes for the respective polymers (*c.f. Table 1*) are substituted into equations 1 and 2 and the previously described statistical methodology is employed, no improvement in the representation of the data sets (*c.f. Figures 8–11*) is obtained. Moreover calculations show that as b increases, V_0 attains values which by far exceed the acceptable limits of 0.015–0.045 (*c.f. Table 2*). For example, when b = 8 and f = 2, V_0 varies from 0.375 to 0.310 over the range $0 \leqslant 10^3/P \leqslant 100$. These facts do not necessarily invalidate the bead-flex approach but may indicate that the specific values for these parameters are in error. Nonetheless, the successful use of these concepts requires the resolution of the apparent contradiction that the stiffer molecules (i.e., those with more beads, *Table 1* and *Figure 13*) behave as though they were the more flexible molecules (*Figure 10* of Ref. 8).

ACKNOWLEDGEMENT

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