Influence of free volume fraction, inter-/intramolecular energy ratio, and chain segment density on the Gibbs–DiMarzio theory of the glass transition

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Based upon computer analysis, the Gibbs–DiMarzio (G–DM) theory is evaluated for the case of (a) constant V_0 and (b) constant r where V_0 is the fractional free volume at T_g and r is the ratio of the hole (E_0) to the flex (ε) energy. For each respective case, results are presented in a reduced variables format that indicate the extent to which r and V_0 vary at the transition temperature as a function of the reciprocal degree of polymerization (P^{-1}). To further account for chemical differences that exist among polymers, an index (n) is introduced that ultimately incorporates the effective number average of chain atom segments ($\bar{x}$) per P. Using these reduced variables plots, the effects of V_0, r, and n are compared with the T_g data for four well-documented polymers. Although the theory adequately describes the PMMA, PS, and PVC data, for PαMS the fit is doubtful. The analysis demonstrates that, in order to maintain V_0 within the range of 0.015–0.045, r must remain within approximately 1.0–1.1. Moreover, under conditions of either constant V_0 or r, other more flexible polymers require that $n \gtrsim 10$.

Keywords Free volume; glass transition; poly(methyl methacrylate); polystyrene; poly(vinyl chloride); poly-α-methyl styrene

INTRODUCTION

The statistical mechanical theory of the glass transition has received considerable attention since Gibbs and DiMarzio (G–DM) introduced it 25 years ago[1]. Over that period a number of workers have utilized the G–DM theory to predict the empirically determined dependence of the glass transition temperature (T_g) on polymer molecular weight (MW)[2–10]. This theoretical relationship between T_g and MW is embodied in two parametric equations which contain both intra- and intermolecular contributions to the configurational entropy. If the lattice coordination number, z, is assumed to equal 4, then these equations can be stated for polydisperse systems as follows:

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

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

$$\frac{2\alpha S_x{}^2}{kT_g} = \ln\left(\frac{V_0}{S_0{}^2}\right) \qquad (2)$$

Here β is a dimensionless parameter equal to $-\varepsilon/kT_g$, ε is the energy difference between *gauche* and *trans* conformations for the hydrocarbon chain (i.e., the intramolecular or flex energy), $\bar{x}$ is the number average of

chain atom segments, V_0 is the fractional free volume at T_g, k is Boltzmann's constant, α is the energy of interaction between a pair of chemically unbonded but nearest neighbouring segments (i.e., the intermolecular or hole energy), and S_x is the fraction of these unbonded but nearest neighbouring segments, where

$$S_x = 1 - S_0 = \frac{(\bar{x} + 1)(1 - V_0)}{2\bar{x}V_0 + (\bar{x} + 1)(1 - V_0)} \qquad (3)$$

Recently a method for greatly simplifying equation (1) was introduced[11]. This procedure was based upon a plot of the reduced T_g *versus* the reciprocal number average degree of polymerization, $\bar{P}^{-1}$. When $\bar{x}$ was equated to $2\bar{P}$ ($\bar{x}/\bar{P}$ constant over the range of $\bar{P}^{-1}$), a single curve was generated which was independent of ε and only slightly dependent upon V_0 over the range $\bar{P} = 10$ to ∞ for $0.015 \leqslant V_0 \leqslant 0.045$. Comparison of selected empirical results for five different polymers of varying degrees of stiffness with the theoretical predictions of equation (1) indicated that the G–DM relationship failed to adequately describe the T_g vs. MW behaviour for this representative collection of polymers. These preliminary results suggested that improvements in the accuracy of the theoretical predictions might require a re-examination of the Flory–Huggins lattice model[12] and the associated definition of $\bar{x}$ upon which the G–DM theory is based.

The present effort expands the previous reduced variables plot, which assumed a constant value of V_0 over the molecular weight range, to include the parallel development of a constant value for the ratio of the inter-/intramolecular energy (i.e., r). Moreover by setting $\bar{x} = n\bar{P}$ (n = any positive number), a simple modification is introduced which may relate not only the chemical structure but also the intrinsic mobility within a given

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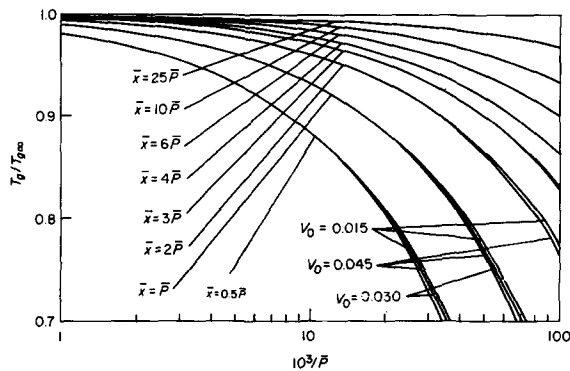
Figure 1 Reduced variables plot indicating the dependence of the glass transition (T_g) upon the logarithmic reciprocal degree of polymerization $(\bar{P})^{-1}$ as a function of free volume fraction $(V_0 = 0.015, 0.030, \text{ and } 0.045)$ and number average of chain atom segments per $\bar{P}$ $(n = 0.5, 1, 2, 3, 4, 6, 10, \text{ and } 25)$. The relationships assume any constant value of ϵ and require the variation in r indicated in *Figure 2*
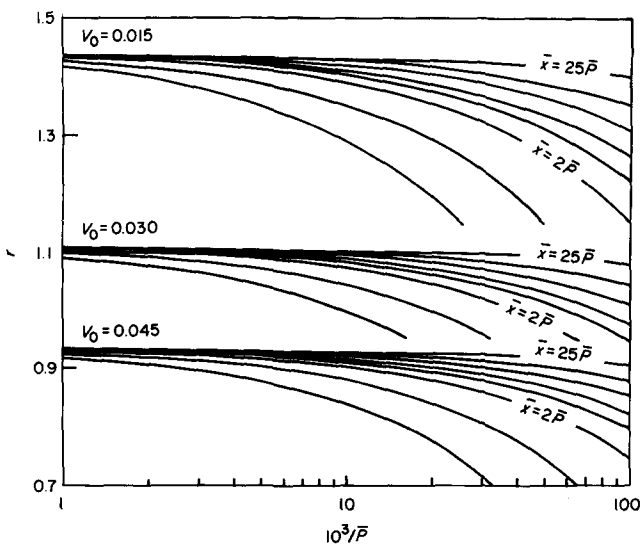

Figure 2 Relationship between the parameter r and $(\bar{P})^{-1}$ as determined from equations (1) and (5). Values for V_0 and $\bar{x}$ correspond to those indicated in *Figure 1*

Equations (1) and (5) can now be solved iteratively by maintaining $\bar{x}$ and V_0 (or $\bar{x}$ and r) constant while simultaneously varying r (or V_0) until a unique β, derived from equation (5), satisfies equation (1). Each situation will now be considered for several combinations of $\bar{x}$ and V_0 (or $\bar{x}$ and r).

Using the reduced variables method, a plot of $T_g/T_{g\infty}$ *versus* $\bar{P}^{-1}$ is presented in *Figure 1*. Here theoretical lines have been obtained as a function of V_0 and n, where V_0 has been set equal to 0.015, 0.030 and 0.045, respectively and n spans the range 0.5–25. The abscissa has been plotted on a logarithmic scale to better resolve the data between the values of $10^3/\bar{P} = 1$–10 and to best assess the statistical fit of the theory to the data[15,16]. The family of lines shown in the figure is quite dependent upon the value of n but relatively insensitive to V_0. However, as a consequence of the conditions imposed by the solution of equations (1) and (5), this slight dependence of the theory on V_0 requires that the value of r varies significantly. This is demonstrated in *Figure 2* where r is plotted as a function of $\bar{P}^{-1}$ for the parameters, V_0 and n. While the absolute value of r varies considerably with changes in $\bar{P}^{-1}$, V_0 and n, the relative change in r depends primarily upon the
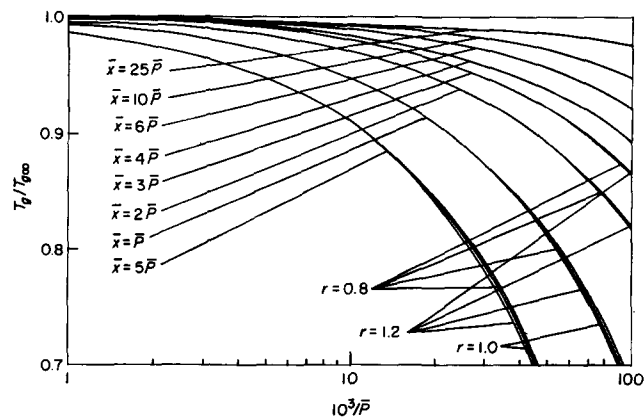

Figure 3 Reduced variables plot indicating the dependence of the glass transition (T_g) upon the logarithmic reciprocal degree of polymerization $(\bar{P})^{-1}$ as a function of constant values of the ratio of hole energy to flex energy $(r = 0.8, 1.0, \text{ and } 1.2)$ and number average of chain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

polymer. The resulting family of curves is compared with detailed data sets compiled for a number of polymers, and the adequacy of the G–DM theory is reconsidered.

THEORETICAL CONSIDERATIONS

By setting 2α equal to the hole energy[13], E_0, and letting $r = E_0/\varepsilon$[14], equation (2) can be rewritten as:

$$\beta r = -\frac{\ln(V_0/S_0{}^2)}{S_x{}^2} \tag{4}$$

Substitution for S_0 and S_x and rearrangement of equation (4) yields:

$$\beta = -\frac{1}{r}\left[\frac{\ln V_0 - 2\ln\left[\dfrac{2\bar{x}V_0}{2\bar{x}V_0 + (\bar{x}+1)(1-V_0)}\right]}{\left[\dfrac{(\bar{x}+1)(1-V_0)}{2\bar{x}V_0 + (\bar{x}+1)(1-V_0)}\right]^2} \right] \tag{5}$$
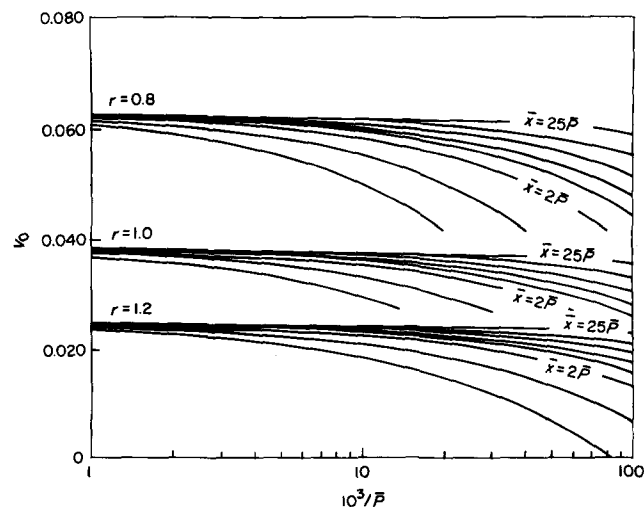

Figure 4 Relationship between the parameter V_0 and $(\bar{P})^{-1}$ as determined from equations (1) and (5). Values for r and $\bar{x}$ correspond to those indicated in *Figure 3*
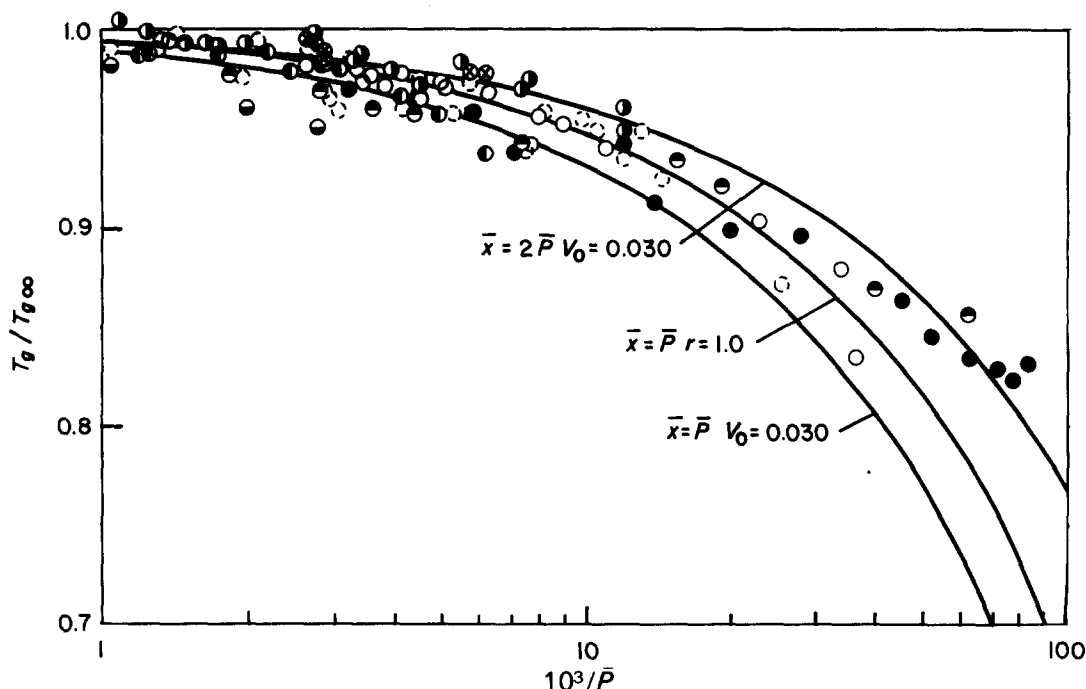
Figure 5 Reduced variables plot for poly(methyl methacrylate): $\bigcirc$, Beevers and White[2]; $\ominus$, Kim *et al.*[17]; $\ominus$, Kusy and Greenberg[3]; $\bullet$, Kusy *et al.*[4]; $\bigcirc$, Kusy *et al.* on blends[5]; $\otimes$, Pratt[18]; $\mathbb{O}$, Thompson on isotactic PMMA[19]; and $\mathbb{O}$, Thompson on dyndiotactic PMMA[19]. Curves represent solution of the G–DM equations for combinations of $n = 1$, 2 and either $V_0 = 0.030$ or $r = 1.0$ as indicated

value of n. For example if $\bar{x} = 2\bar{P}$, r varies by $\sim 20\%$ for $V_0 = 0.015$, 0.030 and 0.045 over the range of $\bar{P}^{-1}$. The magnitude of this change decreases for increasing n.

The situation in which r is assumed constant at 0.8, 1.0 and 1.2, respectively, is shown in *Figure 3*. Here the reduced plot is relatively independent of r but once again rather sensitive to n. While a family of lines similar to those of *Figure 1* is produced when $n = 0.5–25$, comparison of these two figures indicates that when r is held constant the curves corresponding to the same values of n are shifted upward. Analogous to the first case, a constant value for r requires variation in V_0 (cf *Figure 4*). If $\bar{x} = 2\bar{P}$, then V_0 will vary between ~ 39 and 46% over the range of $\bar{P}^{-1}$ for $r = 0.8–1.2$.

RESULTS

From the available literature the T_g *versus* molecular weight data of four different polymers[2–7,17–29] were compared with the theoretical curves derived from equations (1) and (5). This collection included three vinyl polymers, poly(methyl methacrylate) (PMMA)[2–5,17–19], polystyrene (PS)[20–28], and poly(vinyl chloride) (PVC)[6], and one divinyl polymer, poly-α-methyl styrene (PαMS)[7,29]. These data sets represented an expansion of previous preliminary results[11] to include all available published information for both pure polymers and blends regardless of tacticity, test methodology, physical form, or thermal history. These particular polymers were included in this study because their data sets contained at least 25 data points reasonably distributed over the range $\bar{P}^{-1} = 1$ to 100. Such restrictions were based on a knowledge of the prerequisites necessary for a meaningful statistical analysis[15].

The 122 point data set for PMMA is shown in the reduced plot of *Figure 5*. Superposed are the theoretical curves for $n = 1, 2$, $V_0 = 0.030$, and $n = 1, r = 1.0$. While each of these lines best describes only a particular portion of the data, to a first approximation the first two curves

provide an upper and lower bound, whereas the third curve best represents the entire range of $\bar{P}^{-1}$. A somewhat different situation exists for PS which contains 110 data points (cf *Figure 6*). Here the parametric lines $n = 3$, $V_0 = 0.030$, and $n = 2$, $r = 1.0$ delineate an upper bound while the curves for $n = 2$, $V_0 = 0.030$, and $n = 1$, $r = 1.0$ represent the lower limit. To adequately describe the entire data set parametric values intermediate to those shown in the figure are apparently required. For the case of PVC (37 data points) the match between the curve $n = 2$, $V_0 = 0.030$ appears quite good with $n = 2,1$, $r = 1.0$ identifying the upper and lower limits, respectively (cf *Figure 7*). In contrast, the PαMS results (25 data points) shown in *Figure 8* seem to be rather distinctly divided among particular curves depending upon the region of $\bar{P}^{-1}$ under consideration. Over the first decade the results are best represented between $n = 2$, $V_0 = 0.030$, and $n = 1$, $r = 1.0$ while in the second decade they fall between $n = 1$, $V_0 = 0.030$, and $n = 0.5$, $r = 1.0$. Within the present context, no one curve can adequately describe this data set.

DISCUSSION

When the reduced variables method was first introduced, the G–DM theory (equation (1)) was shown to be reasonably independent of V_0 over the range $0 \leq 10^3/\bar{P} \leq 100$[11]. Moreover when the mean number of chain segments were restricted to a value of $2\bar{P}$, the theory was not applicable to many polymers. This major shortcoming was attributed to the inability of the theory to take into account differences in chemical structure among polymers. The current analysis places these results in better perspective by the inclusion of equation (5) and by the addition of the index n. The first considers the energy ratio (r) as the intermolecular energy per unit of intramolecular energy, while the second defines n as the number of chain segments per repeat unit, $\bar{x}/\bar{P}$. Since each segment is assumed to occupy one lattice site, n represents a chain segment density, i.e., the number of lattice sites
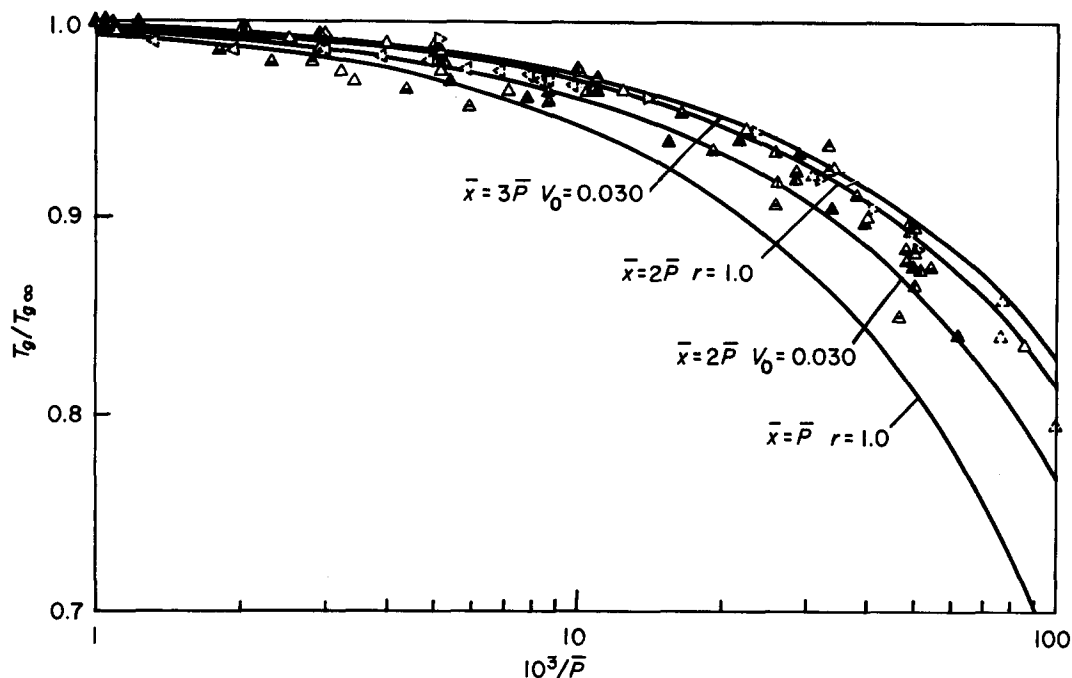
Figure 6 Reduced variables plot for polystyrene: △, Enns *et al.*[20]; ▲, Fox and Flory[21]; ◁ and ▽, Glandt *et al.* on blends[22]; △, Krause and Iskandar[23]; ▲, Richardson and Savill[24]; ▲, Rudin and Burgin[25]; ▲ and ▲, Stadnicki *et al.*[26]; △, Ueberreiter and Kanig[27]; and △, Ueberreiter and Kanig on blends[28]. Curves represent solution of the G–DM equations for combinations of *n*=1, 2 and 3 and either V_0=0.030 or *r*=1.0 as indicated
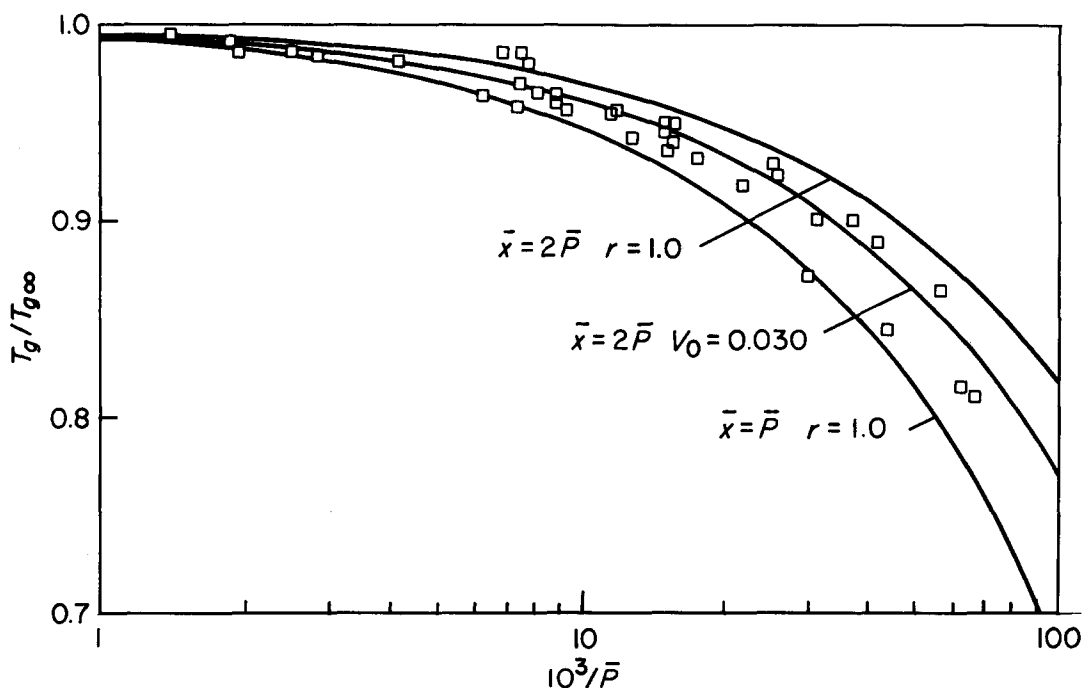

Figure 7 Reduced variables plot for poly(vinyl chloride) with data from Pezzin *et al.* (□)[6]. The curves represent the solution of the G–DM equations for combinations of *n* = 1 and 2 and either V_0 = 0.030 or *r* = 1.0 as indicated

occupied per mer. With these modifications either the constant parameter V_0 or *r*, but not both, could be plotted against *n* to generate the complete solution set shown in *Figures 1–4*. While the first pair is most consistent with the iso-free volume theories which require that the glass transition occur at a constant value of the free volume fraction (cf *Figure 1*)[30–33], the second set requires that V_0 decrease monotonically with decreasing molecular weight (cf *Figure 4*). In their review of the literature, Eisenberg and Saito[34] have indicated that free volume at T_g is not absolutely constant and independent of molecular weight. Moreover Williams[35] has reported a general decrease in

the relative free volume fraction of polystyrene as the molecular weight was reduced from 134 000 to 1675. Similar observations were made by Miller[36] for both polystyrene and polyisobutylene fractions. This net decrease in free volume as a function of molecular weight occurs because the increased free volume associated with the greater number of chain ends is more than offset by the reduced free volume associated with a lower T_g.

To further amplify the interrelationship between V_0 and *r* the solution of the G–DM equation is presented in *Figure 9* on an absolute rather than a relative basis. In fact this β vs. $\bar{P}^{-1}$ plot represents a more detailed version of
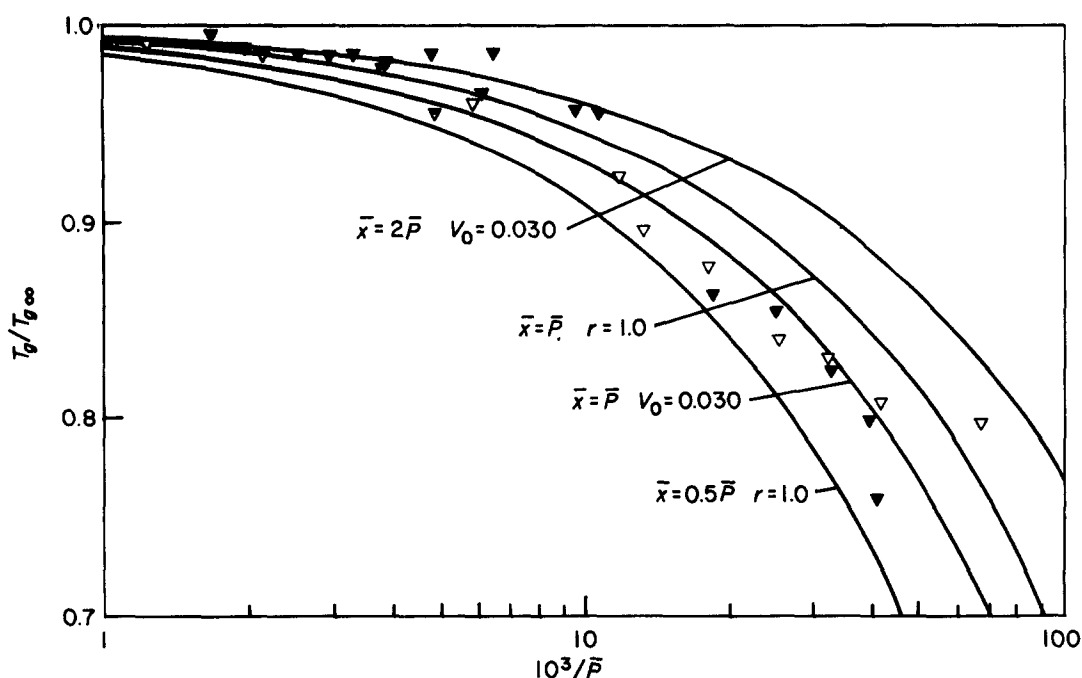
Figure 8 Reduced variables plot for poly-α-methyl styrene with data from Cowie and Toporowski[7] on atactic ($\triangledown$) and syndiotactic ($\blacktriangledown$) PαMS and from Malhotra *et al.*[29] ($\blacktriangledown$). The curves represent the solution of the G–DM equations for combinations of *n*=0.5, 1 and 2 and either V_0=0.030 or *r*=1.0 as indicated

Figure 3, ref. 14, in which the upper and lower boundaries of the shaded area represent the iso-free volume fraction lines, $V_0 = 0.045$ and $V_0 = 0.015$. Of the several *r* curves delineated within these boundaries, only the parametric lines *r* = 1.0 and 1.1 offer solutions to the equations over the entire molecular weight range. Thus the *r* and V_0 combinations which can be utilized in the equations (1) and (5) are restricted. If *r* is kept within the limits of 1.0–1.1, the magnitude of the intra- and intermolecular energies will be approximately equal. Values of *r* can be increased within these limits either by increasing E_0 or by decreasing ε. *Table 1* summarizes the consequences of such variations assuming a reference energy of 1.5 kcal mol^{-1}. The results indicate that a change in ε has a significantly greater and opposite effect on T_g than does a corresponding variation in E_0. While this finding is supported by the observations of Moacanin and Simha[37], Eisenberg and Saito[34] have suggested that under certain situations the reverse may be true.

Recognizing the constraints imposed by the parameters *r* and V_0 on the G–DM theory, the experimental results presented in *Figures 5–8* can be reconsidered as a function of *n*. If for PMMA, PS and PVC, V_0 is assumed to equal 0.030 (cf *Figure 2* for corresponding variations in *r*), then the mean number of lattice sites occupied per mer equals ~ 1.5, 2.5 and 2, respectively. This implication, that PS is more flexible than either PMMA or PVC, is contrary to the results reported in the literature[38,39]. In contrast for PαMS, no single combination of *n* and constant V_0 or *r* will adequately represent the empirical results, although the low value of *n* observed for high $\bar{P}^{-1}$ is consistent with the recognized stiffness of the molecule[38,39]. Additional data sets for a number of polymers having various stiffnesses[8–10,40–48] (cf *Figure 10*) suggest that large values of *n* ($n \gtrsim 10$) would be required to describe the most flexible polymers such as polydimethyl siloxane. To attribute any physical significance to such large values of *n* is difficult, unless *n* is regarded as being representative of the 'effective' mean number of lattice sites occupied per mer. If a dynamic connotation is more correct, then the

Table 1 Comparison of the effects of changes in E_0 and ε on T_g

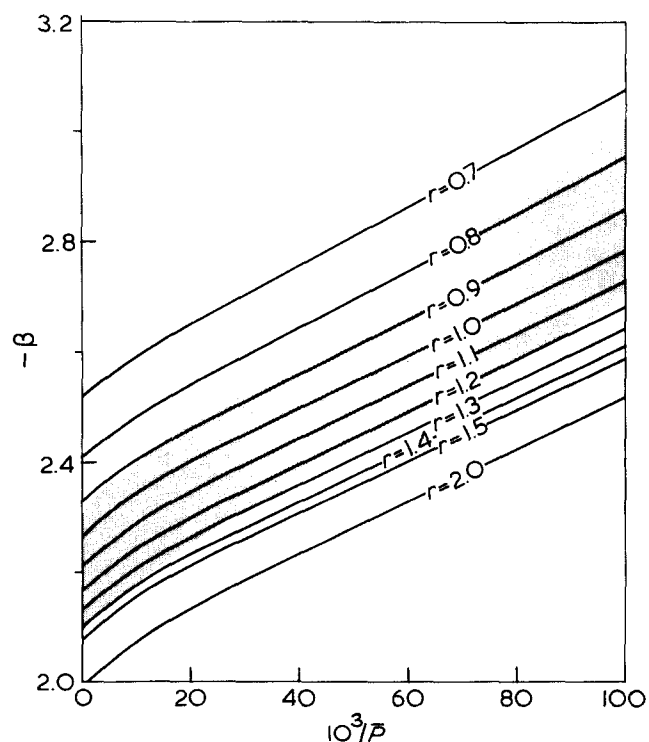| *r*	E_0 (kcal mol^{-1})	ε (kcal mol^{-1})	$-\beta^*$	T_g (K)	T_g (%)
1	1.50	1.50	2.4963	302.3	–
1.1	1.65	1.50	2.4412	309.1	+2.25
1.1	1.50	1.35	2.4412	278.0	−8.04

* Calculated for $(10^3/\bar{P}) = 40$

Figure 9 Relationship between the dimensionless variable, $-\beta = \varepsilon/kT_g$, and the reciprocal degree of polymerization $\bar{P}^{-1}$ as a function of *r*. The upper and lower portions of the shaded regions represent the iso-free volume fraction lines $V_0 = 0.045$ and $V_0 = 0.015$, respectively. Only the curves *r* = 1.0 and 1.1 lie within this region over the entire range of $\bar{P}^{-1}$
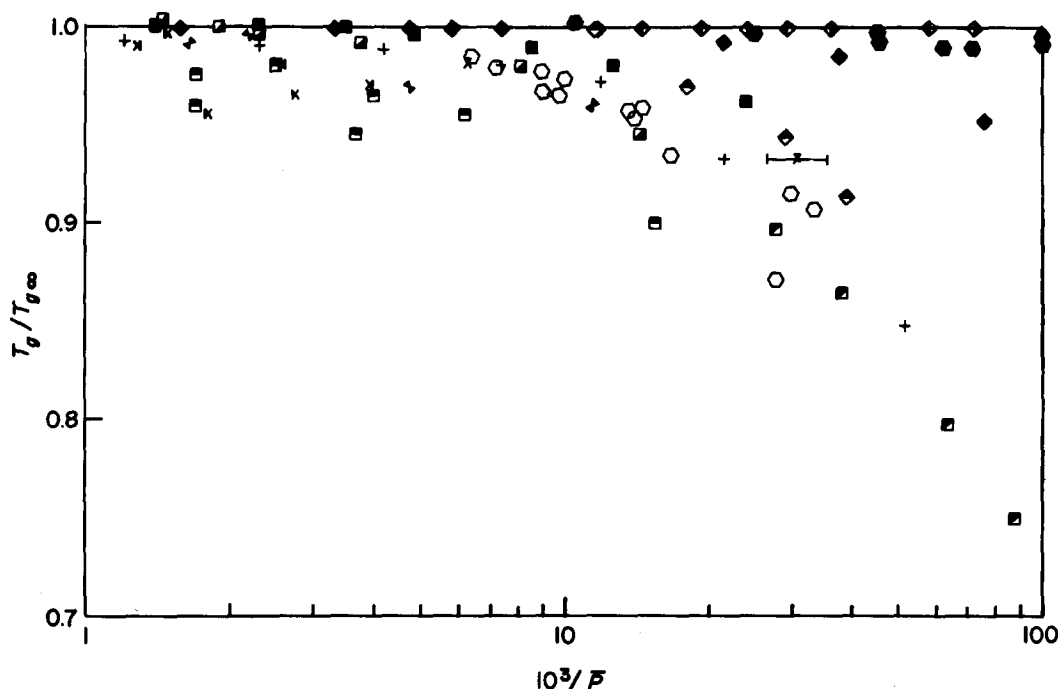
Figure 10 Reduced variables plot for polymers with varying degrees of chain stiffness including, Beevers (·κ·)[40], Beevers and White (**x**)[41], and Keavney and Eberlin (O)[42] on polyacrylonitrile; Faucher (◇) on polybutylene oxide[43]; Cowie and McEwen (◆) on polydimethyl siloxane[9]; Griffiths and Van Laeken (+) on poly-N-vinylcarbazole[44]; Eisenberg (O and ●) on sodium phosphate polymers[10]; Ke (▣)[45] and Cowie[8] on atactic (▨), isotactic (▰), and syndiotactic (■) polypropylene; Allen (◇)[46] and Faucher (◆)[43] on polypropylene oxide; and Enns and Boyer (✦)[47] and Wiley and Brauer (✦)[48] on polyvinylacetate. Comparison of the data with the curves of *Figure 1* and *3* indicates that very flexible polymers would best be described by an $n \gtrsim 10$ in combination with constant V_0 or r

introduction of n into the theory not only evaluates the segment size on the basis of a specified lattice space size (e.g., a methyl group)[49], but also indicates the inherent flexibility of the molecule within its lattice site, i.e., its jump frequency. In this regard the theory might be further tested if n were partitioned to represent values of 'beads' and 'flexes'[39] in the appropriate terms of equations (1) and (5).

ACKNOWLEDGEMENT

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