Glass transition elevation by polymer entanglements

D. T. Turner

Dental Research Center, University of North Carolina, Chapel Hill, NC 27514, USA

(Received 14 November 1977; revised 16 December 1977)

For some polymers a plot of glass transition temperature, T_g, *versus* reciprocal molecular weight can be taken to define two lines which intersect at a molecular weight which is designated as M_g. The value of M_g agrees, within a factor of two, with critical values of molecular weight reported for other properties which are generally attributed to incipient formation of a network of entanglements. Therefore, it is suggested that an increased elevation of T_g at molecular weights greater than M_g is due to an increasing concentration of entanglements.

A more detailed analysis was made by extending the Fox–Flory theory of the glass transition to include negative contributions to the free volume from entanglements. This extension leads to revised estimates of the free volume per chain end which are much smaller (6–19 Å^3 near T_g) than previous estimates which took no account of entanglements. These smaller values are interpreted to mean that the jump units are correspondingly small at T_g, such as envisaged in the Gibbs–diMarzio theory of the glass transition.

INTRODUCTION

There are hints in the literature that entanglements may influence the glass transition temperature, T_g, of a polymer$^{1-6}$. These generally take the oblique form of a warning that data obtained above some critical molecular weight for entanglements should be treated with caution. In the present paper a direct attempt is made to analyse this matter on the working hypothesis that, by analogy with chemical crosslinks, entanglements may elevate T_g. This hypothesis is evaluated by examination of previously reported data on the dependence of T_g on molecular weight, M, in order to judge whether there is evidence for a critical molecular weight phenomenon which might be attributed to entanglements. In order to go into more depth, data are analysed by free volume theory$^{7-13}$, this being one of a number of theories which treat the dependence of T_g on M^{13-17}.

EXTENSION OF FREE VOLUME THEORY TO TAKE ACCOUNT OF ENTANGLEMENTS

Fox and Flory plotted experimental data^{8,18} for polystyrene fractions of the dependence of T_g on M according to equation (1), in which $T_{g\infty}$ is the value of T_g at infinite molecular weight and K is a constant:

$$T_g = T_{g\infty} - K/M \qquad (1)$$

On the assumption that the glass transition occurs at a constant value of the free volume fraction they derived a theoretical expression of the same form as equation (1). In the derivation they reasoned that a reduction of molecular weight increases the number of chain ends and, concomitantly, the free volume fraction. As a consequence, a depression of the temperature is necessary in order to attain the constant free volume fraction characteristic of the glass transition.

The above treatment has been restated with a more economical notation by Bueche (equation 2). The total increase in free volume due to the number of chain ends per cm^3 ($2\rho NM^{-1}$; ρ = density, N = Avogadro's number), each end contributing θ cm^3, is equated to a change in free volume due to a depression of the glass transition temperature of ($T_{g\infty} - T_g$). For reasons rationalized by Bueche an appropriate free volume expansion coefficient is $\alpha = \alpha_l - \alpha_g$ where α_l and α_g are, respectively, volume expansion coefficients in the liquid and glassy states, ile. just above (α_l) and just below (α_g) the glass transition temperature. Equation (2) was rearranged to the same form as equation (1) (equation 3)^{19}.

$$\theta(2\rho N/M) = \alpha(T_{g\infty} - T_g) \qquad (2)$$

$$T_g = T_{g\infty} - (2\rho N\theta/\alpha)(1/M) \qquad (3)$$

The free volume treatment can be extended to take account of contributions from other structural features in addition to chain ends. For example, this extension has been made to include a contribution from chemical crosslinks by Fox and Loshaek^9. To pursue the analogy with crosslinks an idealized 'cooked spaghetti' model for entanglements is considered (*Figure 1*). One molecule is shown in extended form in order to convey the idea of an average molecular weight between entanglements at the glass transition, M_e (*Figure 1a*). By analogy with a crosslink, an entanglement is supposed to reduce the free volume by an amount which is designated as θ_1. The effect of reducing the molecular weight is to increase free volume both by formation of chain ends and by 'release' of entanglements (*Figure 1b*).

An expression for the number of entanglements released as molecular weight is decreased can be obtained by analogy with analysis of the influence of chemical crosslinks on the modulus of rubber elasticity. For a tetrafunctionally crosslinked molecule of infinite molecular weight the number of

0032–3861/78/1907–0789$02.00

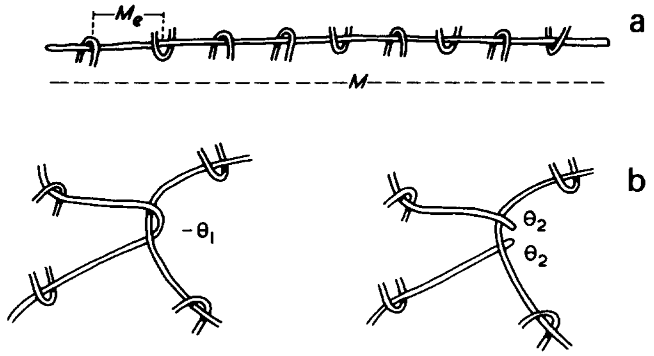

Figure 1 Schematics of polymer entanglements: (a) one extended molecule, of molecular weight *M*, with its complement of entanglements; (b) one fracture of an infinitely long randomly coiled molecular increases the free volume by $\theta_1 + 2\theta_2$ i.e. by release of one entanglement and formation of two chain ends

crosslinks per cm^3 is given by $\rho N(2M_x)^{-1}$, where M_x is the average molecular weight between adjacent crosslinks. However in the case of a network formed from primary molecules of finite molecular weight, *M*, crosslinks immediately adjacent to chain ends are not expected to contribute to the elastic modulus. Flory[20] made the approximation[21] that the number of elastically effective crosslinks should be estimated by introduction of the reduction factor $(1 - 2M_xM^{-1})$. By analogy, it is now assumed that the number of entanglements per cm^3 which can influence T_g is given by equation (4) in which M_e is assumed to remain constant while M varies:

$$\frac{1}{2}\frac{\rho N}{M_e}\left(1-\frac{2M_e}{M}\right)=\frac{\rho N}{2}\left(\frac{1}{M_e}-\frac{2}{M}\right) \qquad (4)$$

The number of entanglements released in decreasing the molecular weight from infinity ($T_{g\infty}$) to $M(T_g)$ is obtained by the difference of concentration terms given by equation (4) i.e.

$$\frac{\rho N}{2}\left(\frac{1}{M_e}-\frac{2}{\infty}\right)-\frac{\rho N}{2}\left(\frac{1}{M_e}-\frac{2}{M}\right)=\frac{\rho N}{M} \qquad (5)$$

Equation (5) is applicable in the range $\infty \leqslant M \leqslant 2M_e$. The limiting values for the number of entanglements released are as follows: zero at $M = \infty$ and $\rho N(2M_e)^{-1}$ at $M = 2M_e$.

Using equation (5), equations (2) and (3) can be extended to include a contribution from entanglements:

$$\theta_1(\rho N/M) + \theta_2(2\rho N/M) = \alpha(T_{g\infty} - T_g), M \geqslant 2M_e \qquad (2a)$$

$$T_g = T_{g\infty} - (\rho N/\alpha)(\theta_1 + 2\theta_2)(1/M), M \geqslant 2M_e \qquad (3a)$$

In these extended equations the volume per chain end has been redesignated as θ_2 i.e. this value is the volume per chain end when account is taken of entanglements. Equation (3) is a special case of the more general equation (3a) when $\theta_1 = 0$.

OVERVIEW

In order to give an introductory overview of the way in which data analysis would be revised by taking account of entanglements comparison will be made with Bueche's schematic representation of data[8,9,18] for polystyrene (*Figure 2*). The full line is the representation based on the assumption that equation (3) is adequate. In contrast, taking into account entanglements (equation 3a) requires conformity of data to two straight lines, AB and BC, which intersect at $M = 2M_e$. Elsewhere in his book[22] Bueche gives for polystyrene $M_e = 20\,000$, a value deduced from low shear gradient viscosity measurements. On this basis the abscissa of B is taken as $M^{-1} = 0.25 \times 10^{-4}$. The slopes of the lines AB and BC taken in *Figure 2* are only conjectural values.

Bueche's representation follows the early analysis of such data by Fox and Flory but nowadays it is clearly recognized that experimental data do not conform to a single straight line when a wide range of molecular weights is considered. An empirical approach to this problem, by Boyer[23], is to retain the form of equation (1) by fitting data[24] to three intersecting straight-line sections (*Table 1*). The assignment of the first two lines, with an intersection at $M^{-1} = 10^{-4}$, is comparable to the lines AB and BC in *Figure 2* and, therefore, not inconsistent with the entanglement hypothesis. Boyer's third line relates to very low molecular weight data which are outside the scope of the present analysis.

Finally it is important to note in this overview that data on the dependence of T_g on M^{-1} have been analysed also by reference to an entirely different theory of the glass transition of polymers due to Gibbs and diMarzio[14]. This theory details a convincing case that, if the glass transition did not intervene at a higher temperature, then a second order transition would be expected at a lower temperature at which sterically hindered rotations about main chain bonds cease. This equilibrium theory has been applied to discussions of the glass transition on the grounds that these same conformational restraints would be expected to constitute a rate con-

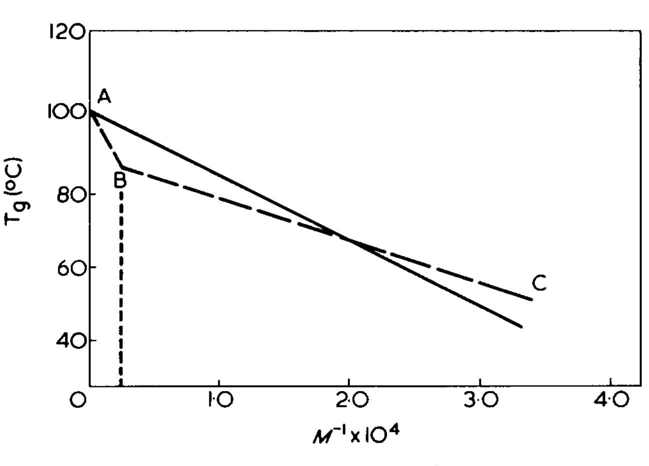

Figure 2 Interpretation of plots of T_g vs M^{-1}. The full line is Bueche's schematic representation which interprets data taking into account chain ends only (equation 3). The broken lines take into account an additional contribution from entanglements. The slopes of these lines are $\rho N\alpha^{-1}$ $(\theta_1 + 2\theta_2)$, for AB i.e. $M \geqslant 40\,000$; and $2\rho N\theta\alpha^{-1}$, for BC i.e. $40\,000 > M >$several thousand

Table 1 Boyer's analysis of plots of T_g vs. M^{-1} for polystyrenes

M	$K \times 10^4$
$> 10^4$	20
$10^4 > M > 10^3$	8
$10^3 > M$	2

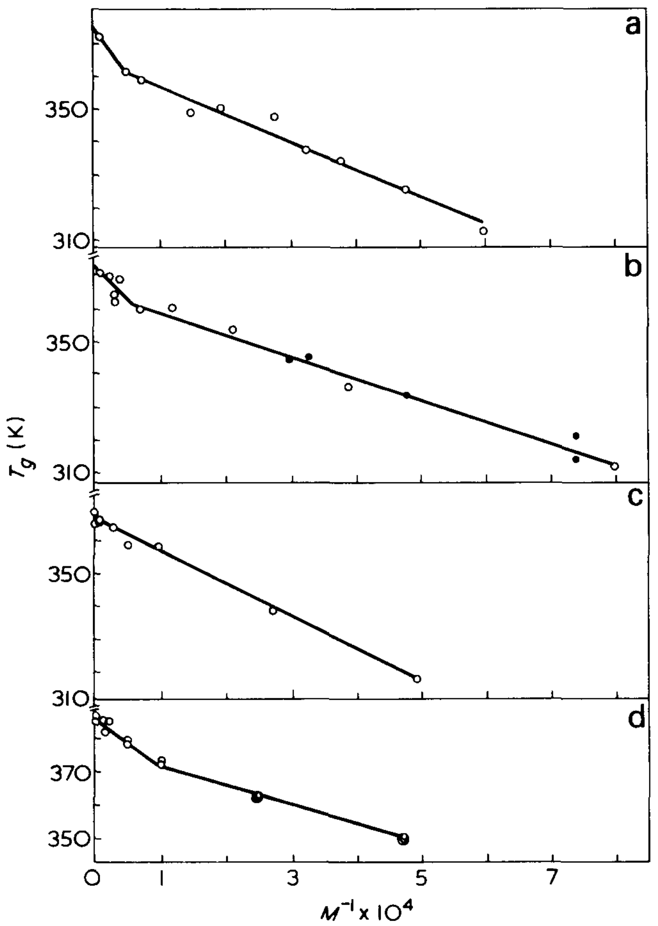

Figure 3 Plots of T_g vs. M^{-1}: polystyrene. (a) Fox and Flory[8,18]: fractions and made-up mixtures, dilatometry. (b) Ueberreiter and Kanig[24,29]: do., ○, fractions; ●, mixtures. (c) Richardson and Savill[30]: anionic polymers, dilatometry. (d) Rudin and Burgin[31]: anoinic polymers, d.t.a.

trolling factor even at the higher temperature, T_g. Beevers and White[25] first pointed out how the relationship between T_g and M^{-1} deduced from this theory gave a better fit to experimental data for poly(methyl methacrylate), PMMA, than did equation (1). Subsequently similar fits were noted on this same basis for poly(vinyl chloride), PVC[26], and polystyrene[27]. In the present context the pertinent question is whether such fits are better than could be achieved with a two line analysis such as is indicated in *Figure 2*. In fact it is difficult to make a distinction of this kind because of the inadequate precision of T_g data. In such circumstances it is appropriate to suspend a final judgement and to adopt a working hypothesis. The present working hypothesis is that entanglements do influence T_g and agreement of experimental data, obtained at $M > 10^4$, with predictions of the Gibbs–diMarzio theory is regarded as illusory.

PLOTS OF EXPERIMENTAL VALUES OF T_g vs. M^{-1}

Analysis of experimental data is facilitated by reference to Boyer's compilation[23] of values of K (equation 1) for polymers of molecular weight greater than about 10 000. On the present point of view such data are limited to the region in which entanglements influence T_g. However in order to see things in better perspective attention will be confined to those systems for which data are also available in the lower molecular weight region where the influence on T_g is attributed solely to chain ends. Use is made of tabulated values of T_g, where available, but in some cases it was necessary to make more subjective estimates from plots. The literature values of T_g were obtained using a variety of techniques such as dilatometry, refractometry, and differential thermal analysis (d.t.a.). In some experiments molecular weights were determined on approximately monodisperse samples prepared by anionic polymerization or by fractionation. Where polydisperse samples were studied, M refers to the number-average molecular weight, this being the appropriate measure on both theoretical and empirical grounds[8,24]. The above variables are not critical and generally they are specified only briefly in the captions to Figures.

Polystyrene was the first polymer studied, by Jenckel and Ueberreiter[28], to provide detailed information about the dependence of T_g on M and still remains the best documented system (*Figure 3*). In three out of four sets of data it is evident that a single straight line fit is inadequate. Instead a two-line fit has been made with an intersection at a value of the molecular weight, designated M_g, between 10 000 and 20 000. It is generally difficult to decide whether a straight line fit is justified for high molecular weight data ($M > M_g$) although the results of Rudin and Burgin are amenable to such an interpretation (*Figure 3d*). Evidence for a straight line fit for lower molecular weight data ($M_g > M$) appears more satisfactory, especially for the data of Ueberreiter and Kanig (*Figure 3b*). The set of data due to Richardson and Savill appears anomalous in that it can be fitted by a single straight line (*Figure 3c*) but it is difficult to evaluate in detail because primary experimental data were not reported. Instead values of T_g had been calculated from the intersections of empirical relationships for the dependence of specific volume on temperature. Richardson and Savill were primarily interested in 'equilibrium' data obtained at temperatures above T_g designed to investigate 'liquid–liquid' transitions[4]. They state that 'only superficial attention has been paid to the transition region ($T_g \pm 15°$C) itself since here rate effects are very important'.

The next best documented polymer is PMMA. Beevers and White reported an approximately linear plot down to $M = 10\,000$ but noted departures at still lower values of molecular weight (*Figure 4a*). As mentioned in the preceding section, they showed that a better fit to the whole of their data could be obtained by reference to the Gibbs–diMarzio theory[25].

Generally a range of molecular weights must be obtained by control of polymerization conditions or by fractionation but Thompson used the convenient technique of reducing molecular weight by high energy irradiation[32]. It has been shown previously by Shultz that, at least after low doses, this results in random fracture of main chain bonds of PMMA accompanied by negligible crosslinking[23]. Thompson's experiments were limited to molecular weights above 10 000 and gave results similar to those reported by Beevers and White (*Figure 4b*). Recently the irradiation technique has been extended to provide samples of much lower molecular weight giving the results shown in *Figure 4c*[27]. The initial slope is not defined by the rather scattered data but is selected taking into account the results of the earlier investigations. The second slope was selecting ignoring the lowest molecular weight data in the belief that additional phenomena may assume importance in such extreme conditions. The intersection of the two slopes occurs at $M_g = 8000$.

It should be noted that additional caution is required in the interpretation of T_g values for a polymer such as PMMA because tacticity is a possible variable[34]. For example, for

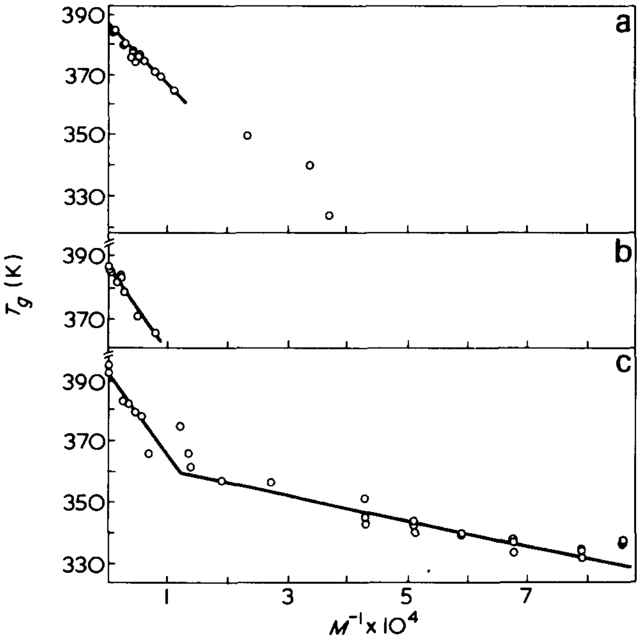

Figure 4 Plots of T_g vs. M^{-1}: PMMA. (a) Beevers and White[25]: whole polymer, refractometry. (b) Thompson[32]: irradiated polymer, d.t.a. (c) Kusy, Katz and Turner[27]: irradiated polymer, d.t.a.

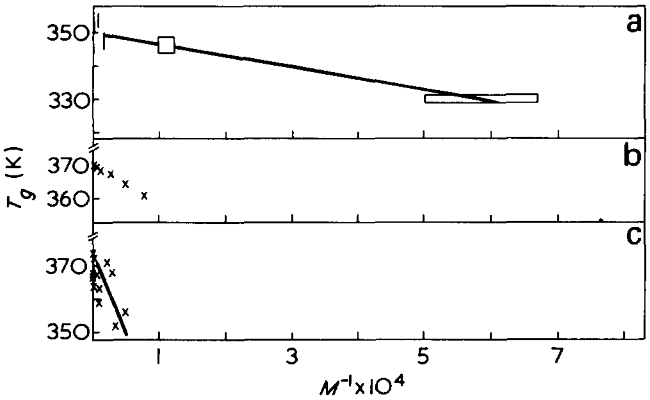

Figure 5 Plots of T_g vs. M^{-1}: polyacrylonitrile. (a) Keavney and Eberlin[36]: whole polymers, d.t.a. (b) Beevers and White[37]: fractions, refractometry. (c) Beevers[38]: fractions, refractometry

an isotactic sample of high molecular weight T_g is only 45°–50°C whereas a highly syndiotactic sample can have a value of at least 115°C[35]. The data shown in *Figure 4* were obtained using atactic polymers which generally include about 60% syndiotactic triads. The irradiation technique was found to have little influence on the tacticity of such samples[27].

Only a limited amount of data, obtained in a pioneering application of d.t.a. to estimate T_g for polymers by Keavney and Eberlin, is on record for polyacrylonitrile of low molecular weight. Nevertheless this has been used to define a slope as shown in *Figure 5a*. Subsequently much effort was made by Beevers and White (*Figure 5b*) and then by Beevers (*Figure 5c*) to define trends for polymers of high molecular weight by refractometric measurements. It was shown that a source of variation is the occurrence of conjugated ring structures which stiffen the chain and raise T_g. The data shown in *Figure 5c* were selected by Beevers using only colourless specimens for which conjugation is not an obvious problem. Despite this selection, the data remain scattered and the slope shown is that chosen by Beevers himself.

For some polymers, such as polystyrene, the analysis of plots of T_g vs. M^{-1} into two slopes may appear dubious because of the limited data which define the initial slope. In contrast the data of Cowie and Toporowski on poly(α-methylstyrene) are more decisive in definition of an initial slope (*Figure 6*). This is because the initial rate of decrease of T_g is large and also because M_g has a relatively low value, in the range 5000 to 7000. Cowie and Toporowski also studied syndiotactic samples but such data are too limited for present purposes of analysis.

Numerous data of Pezzin, Zilio-Grandi, and Sanmartin for PVC samples prepared by a variety of synthetic methods are shown in *Figure 7*. It is difficult to define an initial slope from these data but a choice has been made which is limited to the similarly prepared samples indicated by open circles. As mentioned at the beginning of this section it has been helpful to have on record Boyer's estimate of initial slopes for purposes of comparison. Generally, there is reasonable agreement but his estimate for the data shown in *Figure 7* is $K = 17 \times 10^4$ which differs considerably from the present slope of $K = 9 \times 10^4$. The difference serves to illustrate the subjective factor in an analysis of the data in *Figure 7*. Data at lower molecular weights are so scattered that limits have been chosen as shown. Apparently M_g lies, uncertainly, between 5000 and 7000.

Ke's data on polypropylene are used to assign the initial slope shown in *Figure 8a*. The second slope, at lower molecular weights, has been defined using Cowie's data which include measurements on isotactic samples. Inclusion of such data is justified according to the rule of Karasz and MacKnight[34] that stereoregularity has little influence on T_g for polymers which have the repeat unit $-CH_2-CHR-$.

A number of polymers, with low glass transition temperatures, are insensitive to changes in molecular weight e.g.

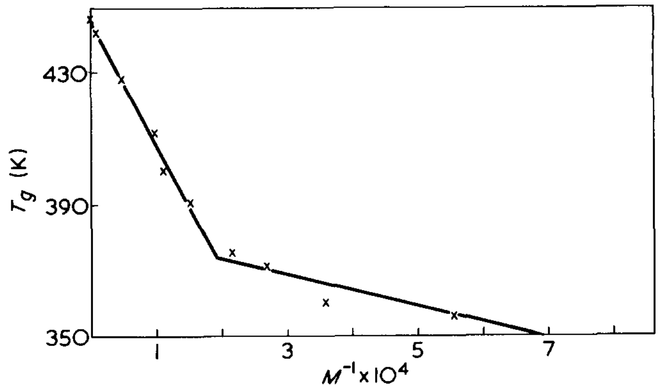

Figure 6 Plot of T_g vs. M^{-1}: poly(α-methylstyrene). Cowie and Toporowski[39]: d.t.a.

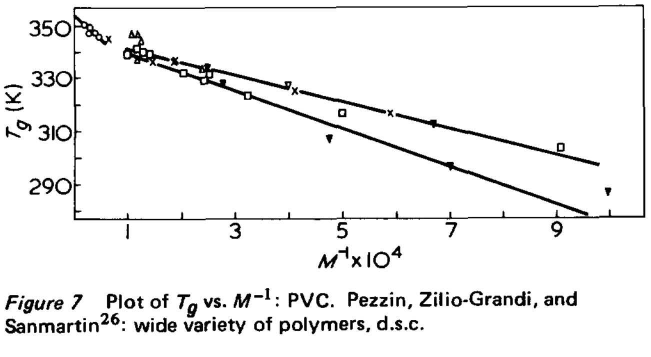

Figure 7 Plot of T_g vs. M^{-1}: PVC. Pezzin, Zilio-Grandi, and Sanmartin[26]: wide variety of polymers, d.s.c.

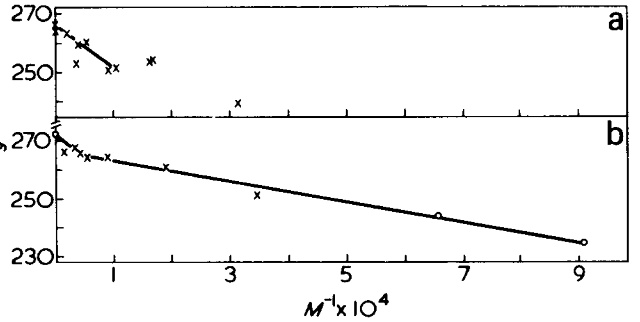

Figure 8 Plot of T_g vs. M^{-1}: polypropylene. (a) Ke[40]: atactic whole polymers, d.t.a. (b) Cowie[41]: atactic fractions (x) and isotactic whole polymers (O)

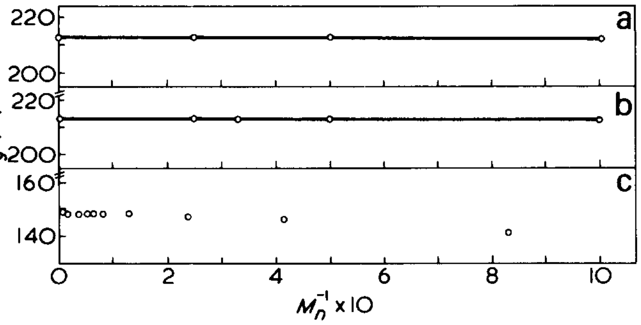

Figure 9 Plot of T_g vs. M^{-1}: various polymers. (a) Faucher: poly(butylene oxide), whole polymers, torsion pendulum using cellulose support. (b) Faucher: poly(propylene oxide) whole polymers, d.o. (c) McCowie and Ewen: poly(dimethyl siloxanes) with methyl end-groups. d.s.c.

poly(butylene oxide)[42], poly(propylene oxide)[42] and poly(dimethyl siloxane)[43] (*Figure 9*). Poly(ethylene oxide) has also been reported to have a low T_g = 213K which, in the range from 3000 to 22 000 is independent of molecular weight[44]. On the other hand, there is also a conflicting report[45] of a complex dependence of T_g on M. Fauche and Koleske have presented evidence that such complexity may be attributed to crystallization and, for quenched amorphous samples, reported an increase in T_g with increase in M[46].

ROLE OF ENTANGLEMENTS

Figures 3 to *8* provide evidence that there is a critical molecular weight, M_g, above which there is an increasing elevation of T_g with increasing molecular weight. This elevation is attributed to polymer entanglements on two grounds. First, entanglements are known to influence a number of physical properties in a way analogous to chemical crosslinks[47,48]. Chemical crosslinks are known to elevate T_g[49] and therefore it is reasonable to expect a similar effect from entanglements. Second, that values of M_g are similar in magnitude to other critical values of molecular weight which are accepted as being due to entanglements. One property chosen for comparison is the plateau elastic modulus which increases markedly when the molecular weight between entanglements rises above a value of M_e. The other value chosen for comparison is the critical weight average molecular weight above which values of viscosity, extrapolated to zero shear gradient, are found to increase abruptly, M_c. Values of M_e and M_c are obtained from experiments above T_g but, nevertheless, are sufficiently insensitive to temperature to make comparison with M_g appropriate: It will be seen that there is agreement, within a factor about two, of values of M_g and M_e for the first three polymers listed in *Table 2*. There is similar agreement for PVC, referring to the accepted rough correlation that $2M_e = M_c$. In the case of polypropylene the correlation is not so good but it is to be noted that the definition of M_g is inadequate (see *Figure 8*). Values of M_e and M_c for polyacrylonitrile are not available for comparison. The correlation fails for poly(dimethyl siloxane), which gives a T_g independent of molecular weight (*Figure 9*), even though this polymer exhibits clearly defined phenomena due to entanglements[47,48] including an influence on spin–spin n.m.r. relaxation times[50]. A similar failure is suspected for poly(propylene oxide) and poly(butylene oxide) although values of M_e and M_c are not known for these polymers. It is to be stressed that such discrepancies are not peculiar to the entanglement region but are an aspect of a more general problem which extends down to molecular weights $<M_g$. This unresolved problem was pointed out previously and discussed by Boyer in a more general context[23].

Opinions about the nature of entanglements vary and in the present work a definite model has been considered mainly for clarity of exposition (*Figure 1*). In order to put this choice in perspective it should be emphasized that a similar influence on T_g might be rationalized using other models. To take an extreme view, Privalko and Lipatov have suggested that entanglements in amorphous polymers may be regarded as loosely folded chains, analogous to the tightly folded chains more widely accepted to occur in crystalline polymers[51]. Suppose that all the molecules in an amorphous polymer are envisaged as regularly folded with a molecular weight between folds designated as M_F. Then for a polymer of molecular weight $M > M_F$, the number of folds per molecule is $(MM_F^{-1} - 1)$ and the number per cm^3 is $\rho NM^{-1}(MM_F^{-1} - 1) = \rho N(M_F^{-1} - M^{-1})$. The number of folds 'released' per cm^3 as the molecular weight is decreased from ∞ to M is given by equation (6):

$$\rho N\left(\frac{1}{M_F}-\frac{1}{\infty}\right)-\rho N\left(\frac{1}{M_F}-\frac{1}{M}\right)=\frac{\rho N}{M}, M \geqslant M_F \qquad (6)$$

Equation (6) is equivalent to equation (5) and, more generally, this same result is obtained from any model which prescribes division of a macromolecule into segments.

A more detailed interpretation of the way in which entanglements cause an elevation of T_g is only speculative. One possibility, raised by the fact that entanglements are so noticeable

Table 2 Comparison of values of M_g with other values which are known to depend on entanglements

Polymer	M_g	M_e	M_c
Poly(α-methylstyrene)	5000–7000	13 500	31 200
PMMA*	7000–13 000	5900 (10 000)	27 500
Polystyrene*	10 000–20 000	18 100	31 200
PVC†	5000–7000	–	5800
Polypropylene†	10 000–20 000	3400	–
Polyacrylonitrile	–	–	–
Poly(dimethyl siloxane)*	–	8100	24 400

* Values of M_e and M_c quoted Graessly (Table 52, ref 48)

† Average values of M_e and M_c calculated from Johnson and Porter (Table III, ref 47)

Table 3 Estimate of free volumes, per chain end (θ_2) and per entanglement (θ_1)

Polymer	Slope, $K \times 10^{-4}$		ρ (g/cm^3)	$\alpha \times 10^{-4}$ (cm^3/T)	θ_2(Å^3)	θ_1(Å^3)
	$M < M_g$	$M > M_g$				
Polystyrene:						
Figure 3a	8	25	1.04[8]	3.00[57]	19	82
Figure 3b	7	21			17	67
Figure 3c	–	–			–	–
Figure 3d	6	15			14	44
Boyer's values*		20,11				
PMMA:						
Figure 4a	–	25	1.18[25]	2.72[25]		
Figure 4b	–	29				
Figure 4c	4	33			8	124
Boyer's value		21				
Polyacrylonitrile:						
Figure 5a	3	–	1.19[38]	1.2[38]	6	–
Figure 5b	–	–			–	–
Figure 5c	–	46			Assume 6	65
Boyer's value		28				
Poly(α-methylstyrene)						
Figure 6	5	37	1.035[39]	3.00[57]	12	155
Boyer's value		36				
Poly(vinyl chloride)						
Figure 7	5–6	18	1.37[26]	3.4[26]	10–12	50–54
Boyer's value		8,17				
Polypropylene						
Figure 8a	–	14	1.18[41]	3.70[41]	Assume 10	53
Figure 8b	4	–			10	–
Boyer's values		3,5				
Poly(butylene oxide)	<1					
Poly(propylene oxide)	<1					
Poly(dimethyl siloxane)	<1					
Figure 9	<1					
Boyer's values	<1					

* Boyer's values are taken from ref 23. He obtained the underlined value from a more extensive set of data.

$\theta_2 = \frac{\alpha K}{2N\rho}$ (K for $M < M_g$); $\theta_1 = \frac{\alpha K}{N\rho} - 2\theta_2$($K$ for $M > M_g$)

in influencing rheological properties, is that they cause decrease in the rate of shrinkage towards an equilibrium volume when the temperature of testing is dropped[52–54]. This possibility assumes added significance with reference to the absence of any marked break at M_g in the experiments of Richardson and Savill in view of their claim to have taken unusual precautions to approach equilibrium conditions of measurement (*Figure 3c*). This situation is reminiscent of earlier studies of polystyrene in which it was claimed that the change in slope of specific volume *versus* temperature, defining T_g, was not detectable in experiments which allowed very long periods of time for relaxation to occur[55] Further analysis of the matter[8] led to a consensus of opinion that complete relaxation could not be achieved within any time scale practicable within the laboratory. Nevertheless, this experimentally tedious question must be raised once again in respect of T_g data obtained at molecular weights in the entanglement region. Another interpretation would consider the influence of entanglements on the motion of segments of the main chain of the polymer molecule. This interpretation is too complex to pursue dynamically[56] but a static aspect may be isolated for analysis by recourse to free volume concepts.

RESULTS FROM FREE VOLUME ANALYSIS

An important assertion of the present work is that, properly, estimates of the free volume associated with chain ends should be derived only from data obtained at molecular weights $\leqslant M_g$. This leads to estimates which differ significantly from those made by previous procedures which did not make this distinction. For example, Beuche[19] estimated a value of θ = 80 Å^3 for chain ends in polystyrene whereas the revised basis gives a smaller value of θ_2 = 14–19 Å^3 (*Table 3*).

A broader view of this difference is obtained by reference to the compilation by Pezzin, Zilio-Grandi, and Sanmartin[26] for ten polymers which gave θ-values ranging from 11 to 110 Å^3. They commented that the broadness of this range is difficult to explain, and, in contrast it is interesting to note that the extremes of the θ_2-values are only 6 and 19 Å^3 (*Table 3*). Of course more refined comparisons of this kind would need to take account of the actual structure of the chain ends relative to that of the main chain, since it is possible to make macromolecules with disproportionately large end-groups which serve to actually raise[58] T_g and which, therefore, must be presumed to decrease free volume.

Table 4 Values of θ_1 and θ_x

	Polystyrene	PMMA	Natural rubber
θ_1 (Å^3)	44–82	124	Not known
θ_x (Å^3)	30–40	40–50	26

Previously it has been suggested that a value of θ = 80 Å^3 is reasonable for polystyrene on the grounds that is about half the size of a repeat unit[19] (165 Å^3 at T_g). Presumably the basis of this suggestion is the need for a hole sufficiently large to accommodate a jump unit comprising one main atom with its average complement of side groups. On this view it might be objected that the θ_2-values appear too low. However, this objection loses cogency if an alternative view is accepted that at T_g the hole need only be large enough to allow a main chain atom to jump from a potential well to one of its neighbours on the base of its cone of revolution. This is the view of the jump process envisaged in the Gibbs–diMarzio theory of the glass transition which has been interpreted in terms of free volume theory by Eisenberg and Saito[59].

Values of θ_1, in the range 50 to 155 Å^3, for the decrease in free volume per entanglement, seem large in comparison with values for chemical crosslinks θ_x. A reliable value of θ_x is available only for natural rubber, because this polymer can be crosslinked quantitatively using the Moore–Watson calibration[60]. From a study of the dependence of specific volume on crosslink density Mason[61] deduced a value of θ_x = 34 Å^3. For the present purposes of comparison, Mason's T_g data[62] have been analysed, using an analogue of equation (3), and found to give a similar value of θ_x = 26 Å^3. Other attempts to prepare networks with known concentrations of crosslinks have been made by copolymerization of mixtures of bifunctional and tetrafunctional monomers. Work by Loshaek on methyl methacrylate showed that inclusion of a tetrafunctional monomer may actually depress T_g because of a 'copolymer effect'[63]. Ethylene glycol dimethacrylate was the only tetrafunctional monomer found to elevate T_g and the influence of crosslinks was estimated by making a correction for the copolymer effect. These data allow an estimate of θ_x = 45–50 Å^3. Finally, a value of θ_x = 30–40 Å^3 was calculated for polystyrene crosslinked via divinyl benzene using data of Ueberreiter and Kanig[64], along with a correction factor for crosslinking efficiency subsequently reported by Dušek[65]. Values of θ_1 and θ_x are summarized in *Table 4*.

The validity of such large estimates of θ_1 needs to be checked on several counts. First, these estimates were made using the values of $\alpha = \alpha_l - \alpha_g$ given in *Table 3*. These are mean values and it should be noted that there is probably a slight dependence on molecular weight[4]. In particular, it is possible that α_l might decrease more markedly as the concentration of entanglements increases. Should this be so, then use of the values given in *Table 3* would result in overestimates of θ_1. A second factor which would sensitively influence estimates of θ_1 is the concentration of entanglements and it is admitted that such an estimate merits a more subtle analysis than has been attempted in the present work. Nevertheless, despite the above reservations, it does seem justifiable to discuss the physical significance of high θ_1 values. One possibility, by analogy with crosslinking[66,67], is that an entanglement hinders the free rotation of atoms in the main chain of the polymer and thereby eliminates their contribution to the free volume[68]. On such a view it would appear reasonable that the largest θ_1 values are obtained with the most sterically hindered molecules i.e. poly(α-methylstyrene) and PMMA. In order to estimate the number of atoms involved it is necessary to assume a value for the free volume fraction at T_g. This remains a controversial matter[4] but Mason, in making an analysis of the effect of chemical crosslinks in natural rubber[61], adopted Williams[7] value of 0.025[69]. In an analysis of data for polystyrene Miller[70] has given reasons for supposing that the free volume fraction at T_g depends on molecular weight, varying from 0.025 to 0.032, but this variation is unimportant for present purposes. A value of 0.025 for polystyrene corresponds to an average free volume per main chain atom of about 2 Å^3. On this basis, and by reference to θ_1 values in *Table 3*, an entanglement would immobilize from 10 to 20 atoms on one polystyrene molecule.

Specific volume

The basic hypothesis on which the present analysis rests is that plots of T_g *versus* reciprocal molecular weight are to be defined by two lines which can be extrapolated to intersect at a critical molecular weight, M_g. An attempt has been made above to evaluate this hypothesis in detail by reference to free volume theory but it is equally important to inquire, more broadly, whether other physical properties related to volume change analogously. The most immediately pertinent analysis of this kind has been made by Eisenberg[71] who plotted values of specific volume (at 375K) *versus* molecular weight for PMMA. He noted a discontinuity at a molecular weight of ~15 000 which is similar to the value obtained in *Table 2* i.e. 7000 to 13 000.

The most extensive and precise data concerning the relationship between specific volume and molecular weight have been reported for polystyrenes. Francois, Candau and Benoit[72], plotted values[8,24] of specific volume ($T_g < T <$ 510K) *versus* reciprocal molecular weight and noted a critical value near 10 000 which, again, is in agreement with the value of M_g obtained in the present work i.e. 10 000 to 20 000 (*Table 2*). They showed that for molecular weights less than 10 000 data could be fitted to a straight line and this relationship rationalized in a satisfying way in terms of the concentration and volume of end-groups. At the same time they emphasized that data for molecular weights above 10 000 could not be rationalized in this way. This distinction was also made in respect of similar, but more definitive, data on partial specific volumes determined in a variety of solvents. It was suggested that the high molecular weight anomalies are due to intramolecular segment–segment contacts within the polymer coil. This description may be considered as equivalent to invoking intramolecular 'entanglements', at least in the broadest sense in which this term has been used in the present paper.

Rudin *et al.*[73] pursued the above line of inquiry in detailed studies of bulk samples of 'anionic' polystyrenes with butyl end-groups and agreed with the conclusions of François *et al.* Their plots of specific volume (383 < T < 459K) are strikingly similar, in defining two lines with an intersection at a molecular weight of 10 000, to the data in *Figure 3d*. From data obtained at 383K, closest to T_g, values can be computed of total volumes associated with end-groups (30 Å^3) and entanglements (330 Å^3). In the case of natural rubber estimates of free volume have been made[61] from changes in specific volume using an empirical reduction factor of one-quarter to one-third which was established by Martin and Mandelkern[74]. Application of this reduction factor to polystyrene would give estimates of θ_1 and θ_2 similar to those obtained from T_g data (*Table 3*).

REFERENCES

1 Shibayama, K. *High Mol. Chem. Jpn* 1961, **3**, 183
2 Zong-neng, Qi *Huaxue Tongbao* 1965, **5**, 1, English transl., Royal Aircraft Establishement Library transl. No. 1206, Farnborough, Hants, England, 1967
3 Bueche, F. 'Physical Properties of High Polymers', Interscience, New York, 1962, p 108
4 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303 1329
5 Meares, P. 'Polymers: Structure and Bulk Properties', Van Nostrand, London, 1965, p 268
6 Beatty, C. L. *Coat. Plast. Prepr.* 1977, **37**(2), 344
7 Alfrey, T. A. Goldfinger, G. and Mark, H. *J. Appl. Phys.* 1943, **14**, 700
8 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
9 Fox, T. G. and Loshaek, S. *J. Polym. Sci.* 1955, **40**, 371
10 Kanig, G. *Kolloid Z.* 1963, **190**, 1
11 Frenkel, J. 'Kinetic Theory of Liquids', Oxford Univ. Press. London, 1946, pp 174–182
12 Turnbull, D. and Cohen, M. H. *J. Chem. Phys.* 1961, **34**, 120
13 Kaeble, D. H. in 'Rheology', (Ed. F. R. Eirich), Academic Press, New York, 1969, Vol 5, ch 5, p 223
14 Gibbs, J. H. and DiMarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
15 Somcynsky, T. and Patterson, D. *J. Polym. Sci.* 1962, **62**, 5151
16 Ellerstein, S. M. *J. Polym. Sci. (Polym. Lett. Edn)* 1964, **2**, 379
17 Litt, M. H. *Polym. Prepr.* 1977, **18** (2), 338
18 Fox, T. G. and Flory, P. J. *J. Polym. Sci.* 1954, **14**, 315
19 Bueche, F. 'Physical Properties of High Polymers', Interscience, York, 1962, pp 113–116
20 Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, New York, 1953, pp 458–464
21 Scanlan, J. *J. Polym. Sci.* 1960, **43**, 501
22 Bueche, F. 'Physical Properties of High Polymers', New York, 1962, p. 76
23 Boyer, R. F. *Macromolecules* 1973, **7**, 142
24 Ueberreiter, K. and Kanig, G. *Z. Naturforsch (A)* 1951, **6**, 551
25 Beevers, R. B. and White, E. F. T. *Trans. Faraday Soc.* 1960, **56**, 774
26 Pezzin, G., Zilio-Grandi, F. and Sanmartin, P. *Eur. Polym. J.* 1970, **6**, 1053
27 Kusy, R. P., Katz, M. J. and Turner, D. T. *Thermochim. Acta* in press
28 Jenckel, E. and Ueberreiter, K. *Z. Phys. Chem. (A)* 1938, **182**, 361
29 Ueberreiter, K. and Kanig, G. *J. Colloid. Sci.* 1952, **7**, 569
30 Richardson, M. J. and Savill, N. G. *Polymer* 1977, **18**, 3
31 Rudin, A. and Burgin, D. *Polymer* 1975, **16**, 291
32 Thompson, E. V. *J. Polym. Sci. (A-2)* 1966, **4**, 199
33 Shultz, A. R., Roth, P. I. and Rathmann, G. B. *J. Polym. Sci.* 1956, **22**, 495
34 Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1968, **1**, 537
35 Goode, W. E., Owens, F. H. Rellmann, R. P., Snyder, W. H. and Moore, J. E. *J. Polym. Sci.* 1960, **46**, 317
36 Keavney, J. J. and Eberlin, E. C. *J. Appl. Polym. Sci.* 1960, **3**, 47
37 Beevers, R. B. and White, E. F. T. *Trans. Faraday Soc.* 1960, **56**, 1529
38 Beevers, R. B. *J. Polym. Sci. (A)* 1964, **2**, 5257
39 Cowie, J. M. G. and Toporowski, P. M. *Eur. Polym. J.* 1968, **4**, 621
40 Ke, B. *J. Polym. Sci. (Polym. Lett. Edn)* 1963, **1**, 167
41 Cowie, J. M. G. *Eur. Polym. J.* 1973, **9**, 1041
42 Faucher, J. A. *J. Polym. Sci. (Polym. Lett. Edn)* 1965, **3**, 143
43 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1973, **14**, 423
44 Törmälä, P. *Eur. Polym. J.* 1974, **10**, 519
45 Faucher, J. A., Koleske, J. V., Santee, E. R., Stratta, J. J. and Wilson, C. W. *J. Appl. Phys.* 1966, **37**, 3962
46 Bailey, F. E. Jr and Koleske, J. V. 'Poly(ethylene oxide)', Academic Press, New York, 1976, pp 136–138
47 Porter, R. S. and Johnson, J. F. *Chem. Rev.* 1966, **66**, 1
48 Graessly, W. W. *Fortschr. Hochpolym. Forsch.* 1974, **16**, 3
49 Boyer, R. F. and Spencer R. S. 'Advances in Colloid Science', (Eds H. Mark and G. S. Whitby), Interscience, New York, 1946, vol 2, p1
50 Charlesby, A., Folland, R. and Steven, J. H. *Proc. R. Soc. (A)* 1977, **355**, 189
51 Privalko, V. P. and Lipatov, Yu. S. *Makromol. Chem.* 1974, **175**, 641
52 Richards, W. T. *J. Chem. Phys.* 1936, **4**, 449
53 Jenckel, E. *Z. Elektrochem.* 1937, **43**, 796
54 Kovacs, J. *Fortschr. Hochpolym. Forsch.* 1963, **3**, 394
55 Spencer, R. S. and Boyer, R. F. *J. Appl. Phys.* 1946, **17**, 398
56 Bueche, F. *J. Chem. Phys.* 1953, **21**, 1850
57 Sharma, S. C., Mandelkern, L. and Stehling, F. C. *J. Polym. Sci. (Polym. Lett. Edn)* 1972, **10**, 345
58 Ueberreiter, K. and Rohde-Liebenau, U. *Makromol. Chem.* 1961, **49**, 164
59 Eisenberg, A. and Saito, S. *J. Chem. Phys.* 1966, **45**, 1673
60 Moore, C. G. and Watson, W. F. *J. Polym. Sci.* 1956, **19** 237
61 Mason, P. *J. Chem. Phys.* 1964, **35**, 625
62 Mason, P. *Polymer* 1964, **4**, 625
63 Loshaek, S. *J. Polym. Sci.* 1955, **40**, 391
64 Ueberreiter, K. and Kanig, G. *J. Chem. Phys.* 1950, **18**, 399
65 Dušek, K. *Collect. Czech. Chem. Commun.* 1962, **27**, 2841
66 Tuckett, R. F. *Trans. Faraday Soc.* 1942, **38**, 310
67 Ueberreiter, K. *Kolloid Z.* 1943, **102**, 272
68 Haward, R. N. *J. Macromol. Sci. (C)* 1970, **4**, 191
69 Williams, M. L. *J. Appl. Phys.* 1958, **29**, 1395
70 Miller, A. A. *J. Polym. Sci. (A)* 1964, **2**, 1095
71 Eisenberg, A. *J. Phys. Chem.* 1963, **67**, 1333
72 François, J., Candau, F. and Benoit, H. *Polymer* 1974, **15**, 618
73 Rudin, A., Wagner, R. A., Chee, K. K., Lau, W. W. Y. and Burns, C. M. *Polymer* 1977, **18**, 124
74 Martin, G. M. and Mandelkern, L. *J. Res. NBS* 1959, **62**, 141
75 Wall, L. A., Roestamsjah and Aldridge, M. H. *J. Res. NBS(A)* 1974, **78**, 447
76 Griffiths, C. H. and Van Laeken, A. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 1433

APPENDIX

A referee pointed out further pertinent data on monodispersed polystyrenes by Wall, Roestamsjah and Adridge[75]. The authors concluded that their data (*Table 1*) satisfy the Fox–Flory equation. However a closer scrutiny shows better conformity to a two-line plot, with M_g = 20 000, in agreement with *Figures 3a, 3b* and *3d*.

In a second pertinent paper Griffiths and Van Laeken concluded that data on poly(*N*-vinylcarbazole) are consistent with the Fox–Flory equation[76]. In this case there is no indication of a departure from linearity of the kind predicted in the present work. The interesting observation was made that no changes in density were detected with variations in molecular weight, such as would be expected from free volume theory.

ACKNOWLEDGEMENT

This investigation was supported by NIH research Grant No. DE02668 from the National Institute of Dental Research.