

The glass temperature of polymer blends: comparison of both the free volume and the entropy predictions with data*

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Experimental glass temperatures for 30 compatible blends have been compared with an equation derived from the hypothesis that the glass temperature is determined by conformational entropy changes and with the well known glass transition temperature (T_g) versus composition equation of Fox based on volume additivity. Since these equations neglect interactions, it is not surprising that they fail in predicting at least half the experimental T_g data. Nevertheless the approximate equivalence of the predictions of these two equations suggests that the glass temperature of an infinite molecular weight polymer is proportional to the mass divided by the number of flexible bonds of the monomer unit. As the interactions are disregarded, the two equations are zero-order treatments and thus they can both be improved.

(Keywords: glass temperature; blends; free volume; entropy)

INTRODUCTION

The glass transition temperature (T_g) is an important characteristic property of a compatible polymer blend. It is also an important processing variable. It would thus be useful to be able to predict the T_g of a blend as a function of the glass temperatures T_{g1} and T_{g2} of the two components, and of the composition.

Of the proposed equations in the literature, the Gordon–Taylor equation¹, which is based on volume additivity, is one of the most commonly used to verify experimental T_g data. Di Marzio recently extended the Gibbs–Di Marzio theory of glass transition² for polymer blends by supposing additivity of the flexible bonds to be responsible for conformational changes³. The resulting equation is of the form:

$$T_g = B_1 T_{g1} + B_2 T_{g2} \quad (1)$$

where B_i is the fraction of flexible bonds of type i . For large molecular weights B_i is given by the expression:

$$B_1 = x_1 n_1 \gamma_1 / (x_1 n_1 \gamma_1 + x_2 n_2 \gamma_2) \quad B_1 + B_2 = 1 \quad (2)$$

where γ_i is the number of flexible bonds per monomer unit, x_i is the number of monomer units per molecule and n_i is the number of molecules of species i .

Relating the bond fraction to the weight fraction, W_i , via:

$$W_1 = w_1 B_1 \gamma_2 / (w_1 B_1 \gamma_2 + w_2 B_2 \gamma_1) \quad W_1 + W_2 = 1 \quad (3)$$

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with w_i the weight of the monomer unit, equation (1) finally leads to:

$$T_g = \frac{(\gamma_1/w_1)W_1 T_{g1} + (\gamma_2/w_2)W_2 T_{g2}}{[(\gamma_1/w_1)W_1 + (\gamma_2/w_2)W_2]} \quad (4)$$

This equation has the same form as the Gordon–Taylor equation¹

$$T_g = \frac{W_1 T_{g1} + K W_2 T_{g2}}{(W_1 + K W_2)} \quad (5)$$

but the parameter K is given by the ratio $\gamma_2 w_1 / \gamma_1 w_2$ rather than by $\rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1$ as in the original Gordon–Taylor equation based on volume and free volume additivity⁴. ρ_i are the densities and $\Delta\alpha_i$ the increments at T_g of the expansion coefficients of the blend components.

Neglecting the differences of the appropriate densities, as a first approximation the ratio $\rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1$ can be replaced by the corresponding ratio of the glass temperatures of the blend components T_{g1} / T_{g2} if one assumes the validity of the Simha–Boyer rule⁵, $\Delta\alpha T_g = 0.113$. The value of the constant is unimportant. The result of this substitution of the K parameter in the Gordon–Taylor equation [equation (5)] is the well known Fox expression⁷:

$$(1/T_g) = (W_1/T_{g1}) + (W_2/T_{g2}) \quad (6)$$

Equations (1) and (6), which are based on additivity rules, are easily generalized to calculate either the entropy equation of state (SVT) or the PVT equation of state for the blend. We must, however, be careful in this process

of generalization not to introduce any adjustable parameters.

To improve the fit of the experimental T_g data of polymer blends second power equations in concentration have been proposed in the literature to account for the effect of interactions. A second power equation in concentration has also been obtained by Di Marzio³ by taking into account the volume changes for the case of zero plasticizer content for the two components:

$$T_g = B_1 T_{g_1} + B_2 T_{g_2} + K_m B_1 B_2 (T_{g_1} - T_{g_2})(V_{g_1} - V_{g_2}) \quad (7)$$

This equation is of the form both of the empirical equations of Jenckel-Heusch⁸

$$T_g = W_1 T_{g_1} + W_2 T_{g_2} + b(T_{g_2} - T_{g_1})W_1 W_2 \quad (8)$$

and of Kwei⁹, the latter being an extension of the Gordon-Taylor expression:

$$T_g = \frac{W_1 T_{g_1} + K W_2 T_{g_2}}{(W_1 + K W_2)} + q W_1 W_2 \quad (9)$$

where b characterizes the 'solvent quality' and q the specific interactions between the blend components.

Because of b , q and K_m these equations are able to correlate much more experimental T_g data, but they do not have predictive power because the parameters b , q and K_m cannot be obtained from other considerations.

A second power equation has also been obtained by Kanig¹⁰ who related the changes in interaction energies to the respective Gibbs energies for generating one mole of holes in the equilibrium polymer melt. Again these Gibbs energies are not accessible by other considerations.

Using corrected weight fractions to account for the different expansivities of the blend components [$W_{1c} = W_1/(W_1 + K W_2)$ and $W_{2c} = K W_2/(W_1 + K W_2)$; $K = \rho_1 \Delta\alpha_2/\rho_2 \Delta\alpha_1$] equation (5) can be rewritten in reduced form:

$$(T_g - T_{g_1})/(T_{g_2} - T_{g_1}) = W_{2c} \quad (10)$$

This expression can be generalized by regarding the right-hand side as the first term of a 'virial'-like expansion of a power series in concentration¹¹. All second power equations in concentration can thus be regarded as virial extensions of equation (10).

A third power series in concentration results directly from assuming that the 'free volume' distribution and the conformational mobility in polymer mixtures are dependent on the specific interaction between the blend components¹².

$$\frac{T_g - T_{g_1}}{T_{g_2} - T_{g_1}} = (1 + K_1)W_{2c} - (K_1 + K_2)W_{2c}^2 + K_2 W_{2c}^3 \quad (11)$$

The parameter K_1 depends mainly on the differences between the interaction energies of the binary hetero and homo contacts. Conformational redistributions in the neighbourhood of the binary contacts accompanied by entropy changes are considered supplementary. Positive values of K_1 suggest a predominant contribution of the energetic effects of the hetero interaction, whereas negative values indicate a prevailing effect of the conformational rearrangements accompanied by changes of the free volume. K_2 considers only effects related to redistributions in the contact neighbourhood. For the special case of additivity, $K_1 = K_2 = 0$.

Equation (11) is consistent with all experimental T_g data, but the parameters K_1 and K_2 could not previously be obtained by independent considerations.

It has also been shown that T_g data of compatible polymer blends exhibit both positive and negative deviations from supposed volume additivity⁵. In view of the above considerations the findings that the T_g data of some polymer blends obey the volume additivity rule, as is observed for instance in the polystyrene/poly(2,6-dimethyl-1,4-phenylene ether) blend, may be the result of the compensation of energetic and configurational entropic ('free volume') effects of the binary contact interaction.

The aim of this paper is to give a comparative analysis of the T_g data of compatible polymer blends in view of the equations of Di Marzio⁴ and Fox⁶, which are both based on additivity rules. Also, the third power expression (11) has been used to accommodate all experimental T_g data.

The composition dependence of the glass transition of the following compatible polymer blends was analysed using literature data. These blend systems are:

- 1 Polystyrene/poly(2,6-dimethyl-1,4-phenylene ether), PS/PPE¹³⁻²⁰
- 2 Poly(vinylmethyl ether)/polystyrene, PVME/PS²¹⁻²⁶
- 3 Polystyrene/poly(α -methylstyrene), PS/P α MS²⁷⁻³⁰
- 4 Poly(ethylene oxide)/poly(methyl methacrylate), PEO/PMMA³¹⁻³³
- 5 Poly(vinylidene fluoride)/poly(methyl methacrylate), PVF₂/PMMA^{34,35}
- 6 Polyacrylates and methacrylates of (β -hydroxyethyl-3,5-dinitrobenzoyl)/*N*(2-hydroxyethyl)carbazolyl, PDNBA/PHECA³⁶ and PDNBM/PHECM^{37,38}
- 7 ULTEM 1000, aromatic poly(ether imide)/poly(benzimidazole), ULT/PBIAz³⁹
- 8 Poly(vinyl pyridine)/poly(benzimidazole), PVPy/PBIAz⁴⁰
- 9 Poly(*p*-*N,N*-dimethylaminostyrene)/poly(2-isopropenylcholine), P2AS/PIPCh⁴¹
- 10 Aliphatic polyesters with poly(vinyl chloride)^{42,43}, poly(epichlorohydrin)⁴⁴, polyhydroxyether of bisphenol-A^{45,46} and tetramethyl bisphenol-A polycarbonate⁴⁷
- 11 Styrenic polymers/tetramethyl bisphenol-A polycarbonate^{48,49}

RESULTS AND DISCUSSION

Table 1 lists the values of the K_1 and K_2 coefficients of the concentration power equation (11). They were obtained by the least square fit method to the data displayed in Figures 1-9. The blends are listed in order of decreasing energetic contributions. It is interesting to notice that at one end of the list are blends with strong energetic interactions ($K_1 > 0$), such as the charge-transfer interaction of polymers containing electron-donor and electron-acceptor groups, respectively. At the other end of the list are the compatible blends PVME/PS and PS/P α MS ($K_1 < 0$).

Table 2 shows the values of the T_g s, molecular weights and number of flexible bonds, as well as the mass per flexible bond of the monomeric unit.

For values of the coefficients K_1 and $K_2 > -0.4$ and $< +0.4$ a more or less accurate fit of the T_g data of the

Table 1 Parameters of the concentration power equation (11)

Polymer blend ^a	$K = T_{g1}/T_{g2}$	K_1	K_2
PDNBM/PHECM ^{37,38}	0.90	2.42	1.90
High-PVPy/PBIAz ⁴⁰	0.61	1.90	1.53
Oligo-PVPy/PBIAz ⁴⁰	0.73	1.54	2.41
PVF ₂ /PMMA ^{34,35}	0.61	1.42	0.84
PDNBA/PHECA ³⁶	0.86	1.12	0.51
ULTEM/PBIAz ³⁹	0.70	0.95	-0.19
Poly(butylene adipate)/poly(epichlorohydrin) ⁴⁴	0.82	0.32	1.45
PS/PC ^{48,49}	0.79	0.22	1.89
PEO/PMMA ^{31,32}	0.56	0.18	0.26
Poly(ϵ -caprolactone)/PVC ⁴²	0.57	0.04	0.37
Poly(1,4-cyclohexanedimethanal succinate)/PVC ⁴²	0.75	0	0.04
Poly(butylene adipate)/PHEBA ⁴⁶	0.55	-0.04	0.04
PS/PPE ¹³⁻²⁰	0.77	-0.08	0.11
Poly(1,4-cyclohexanedimethanal succinate)/PHEBA ⁴⁶	0.74	-0.17	-0.63
Poly(ϵ -caprolactone)/PHEBA ⁴⁶	0.55	-0.21	-0.36
Poly(butylene adipate)/PVC ⁴²	0.57	-0.28	-0.02
Poly(2,2-dimethyl-1,3-propylene sebacate)/PHEBA ⁴²	0.60	-0.28	0.34
Poly(ethylene adipate)/poly(epichlorohydrin) ⁴⁴	0.90	-0.31	0.09
P2AS/PiPCh ⁴¹	0.88	-0.33	-0.41
Poly(ethylene adipate)/PHEBA ⁴⁶	0.61	-0.37	0.30
Poly(hexamethylene sebacate)/PVC ⁴²	0.59	-0.40	-0.22
Poly(hexamethylene sebacate)/PC ⁴⁷	0.46	-0.41	0
Oligo-P α MS/PC ⁴⁸	0.73	-0.42	-1.49
Poly(butylene sebacate)/PVC ⁴³	0.57	-0.50	-0.18
Poly(ϵ -caprolactone)/PC ⁴⁷	0.44	-0.84	-1.72
Poly(2,2-dimethyl-1,3-propylene succinate)/PVC ⁴²	0.71	-0.90	0.53
Poly(2,2-dimethyl-1,3-propylene succinate)/PHEBA ⁴⁶	0.69	-0.91	0.02
Poly(butylene sebacate)/PC ⁴⁷	0.45	-1.21	-2.24
PVME/PS ²¹⁻²⁶	0.65	-1.28	-0.99
PS/P α MS ²⁷⁻³⁰	0.83	-2.40	-2.05

^aPHEBA, poly(hydroxyethylene bisphenol-1); PC, tetramethyl bisphenol-A polycarbonate; for the other abbreviations used, see blend systems in text

blends is observed by using the equations based on additivity. Generally values of the K_2 coefficient outside this range are obtained by fitting more pronounced asymmetric or S-shaped curves of the T_g versus composition behaviour. Such curves cannot be fitted either by the Fox⁶ or by the Di Marzio equation⁴.

The composition dependence of the T_g data of the PS/PPE blend is shown in *Figure 1*. It is evident that for this blend equations (4) and (6) both reproduce the data nicely. This is valid for the blend PEO/PMMA (*Figure 2*) and for the majority of the blends of the aliphatic polyesters with PVC, poly(epichlorohydrin) (*Figure 3*) and polyhydroxyether of bisphenol-A (*Figure 4*). For the first blend, Assman and Schneider³³ suggested, however, two-phase behaviour of the blends with the higher molecular weight PMMA. Concerning the different blends with aliphatic polyesters, except for poly(ϵ -caprolactone) and poly(hexamethylene sebacate), the molecular weights of the polyesters were < 6000.

Both equations (4) and (6) predict reasonably accurately the T_g data displayed in *Figures 1-4* and, except for the blend PVF₂/PMMA, they lie close to each other.

Although the majority of the blends of the aliphatic polyesters are characterized by T_g data

approaching additivity behaviour some of them also show negative deviations [see the blends poly(butylene adipate)/poly(epichlorohydrin) (*Figure 3*) and poly(cyclohexanedimethylsuccinate)/polyhydroxyether of bisphenol-A (*Figure 4*)]. Blends of tetramethylbisphenol-A polycarbonate with styrenic polymers show even larger negative deviations (*Figure 5*).

It is remarkable that the T_g data of all blends studied with K_1 values < -0.4 or > +0.4 (*Figures 5-9*) are fitted neither by the Fox (F) nor by the Di Marzio (DM) equation.

The large scatter of the T_g data of the PS/P α MS blends is partly the result of the different methods used for the blend preparation³⁰. The solid symbols represent T_g data obtained for compression moulded samples, whereas the open symbols refer to T_g values of solution blended films. Any attempt at explaining the T_g data by changing the number of flexible bonds fails because the two monomers should have the same number of flexible bonds.

In *Figure 7* (PVME/PS), either three flexible bonds (curve DM 1) or two flexible bonds (curve DM 2) were used for PS. The latter curve approaches more nearly the experimental T_g data but it does not reproduce the results for blends with small PS content.

Positive deviations of the T_g data from supposed

Table 2 Glass temperatures, monomeric unit weights and number of flexible bonds of polymers for the analysed blends

No.	Polymer	T_g (K)	w	γ	w/γ	Ref.
1	PS ($M_w = 73\,500$)	317.3	108	3 (2)	36 (54)	23
1 ^a	PS ($M_w = 800$)	260.8	108	3 (2)	36 (54)	23
2	P α MS ($M_w = 22\,700$)	425–455.8 ^a	122	3	40.7	30
3	PPE ($M_w = 17\,000$)	490.2	120	2	60	19
4	PVME ($M_w = 97\,500$)	241.9	58	3	19.3	25
5	PEO	211	44	3	14.7	33
6	PMMA	378	100	4	25	33
7	PVC	358	65.3	2	32.7	43
8	PVF ₂	220	54	2	27	35
9	PC	473.2	294	5 (6)	59 (49)	49
10	Poly(epichlorohydrin)	251.7	93.5	4	23.4	44
11	PhebA ^b	370	284	8	35.5	47
12	PeCL ^b	202.2	114	7	16.3	43
13	PBlAz	698.2	308	3	102.6	39
14	PVPy	415	106	2	53	40
15	ULTEM	490.2	592	9	65.8	39
16	PiPCh	473	158	3	52.7	41
17	P2AS	400	147	4	36.8	41
18	Pdmps ^b	256.2	186	9	20.7	44
19	Pchdms ^b	272	234	11	21.3	44
20	PEA ^b	226.2	172	10	17.2	44
21	Pdmpa ^b	220	214	11	19.5	45, 46
22	PBA ^b	205.2	200	12	16.7	44
23	PBSeb ^b	203.2	256	14	18.3	43
24	PhmSeb ^b	213.2	284	16	13.3	47
25	PDNBA	336	310	8	38.8	36
26	PDNBM	367.2	324	8	40.5	37, 38
27	PHECA	380	265	7	37.8	36
28	PHECM	419.2	279	7	39.8	37, 38

^aThe higher T_g is valid for the compression moulded samples

^bPhebA, polyhydroxyether of bisphenol-A; Pdmps, poly(2,2-dimethyl-1,3-propylene succinate); Pchdms, poly(1,4-cyclohexane dimethanol succinate); PEA, poly(ethylene adipate); Pdmpa, poly(2,2-dimethyl-1,3-propylene adipate); PBA, poly(butylene adipate); PBSeb, poly(butylene sebacate); PhmSeb, poly(hexamethylene sebacate)

volume additivity appear in blends with strong interactions, such as the charge-transfer complexation due to the electron donor/electron acceptor interaction. This is evidenced in *Figure 8*. The corresponding power equations are characterized by large positive values of K_1 . Using the number of flexible bonds listed in *Table 2* for the polymers, the Di Marzio equation leads to the same result as the Fox equation. Neither equation fits the experimental T_g data.

The T_g values can be fitted, however, either by using an arbitrary value of the fitting parameter ($K = 5$) in the Gordon–Taylor equation or by reducing unjustifiably the number of flexible bonds in PDNBM ($\gamma_1 = 2$ instead of 8; curve DM 2). A similar result is obtained by using the ‘normal’ number of flexible bonds for both polymers and the value $K_m = 0.50$ in the extended Di Marzio equation (7) (curve DM 3).

Positive deviations of T_g data are also observed in the blends PVF₂/PMMA (*Figure 2*) and of poly(benzimidazole) with ULTEM 1000 and PVPy, respectively (*Figure 9*). It is, however, remarkable that the blend PVF₂/PMMA is the only analysed polymer blend for which the discrepancy observed between the Fox and the Di Marzio equation is larger than the spread in the data.

One of the most unexpected results is the observation that the Di Marzio equation (4) and the Fox equation (6) predict much the same curves for the T_g versus composition behaviour, independent of whether they fit the experimental T_g data. In fact, both equations are of the form of the Gordon–Taylor expression (5) but with different significance assigned to the K parameter. In the Fox equation, derived by the assumptions of volume additivity and validity of the Simha–Boyer rule, the K parameter is given by the ratio of the glass transition temperatures ($K = T_{g1}/T_{g2}$). In the Di Marzio equation, based on additivity of the flexible bonds, the parameter K is given by the ratio of the number of flexible bonds per molecular weight of the monomeric units $K = (\gamma_2/w_2)/(\gamma_1/w_1)$.

We can thus equate the two values of K :

$$T_{g1}/T_{g2} = (w_1/\gamma_1)/(w_2/\gamma_2) \quad (12)$$

and if we suppose equation (13) to be universal then:

$$T_g = Cw/\gamma \quad (13)$$

where C is a universal constant and T_g is for infinite molecular weight. *Figure 10* is a test of this relation. The solid symbols refer to the polymers listed in *Table 2*. There are also data analysed from other polymers taken

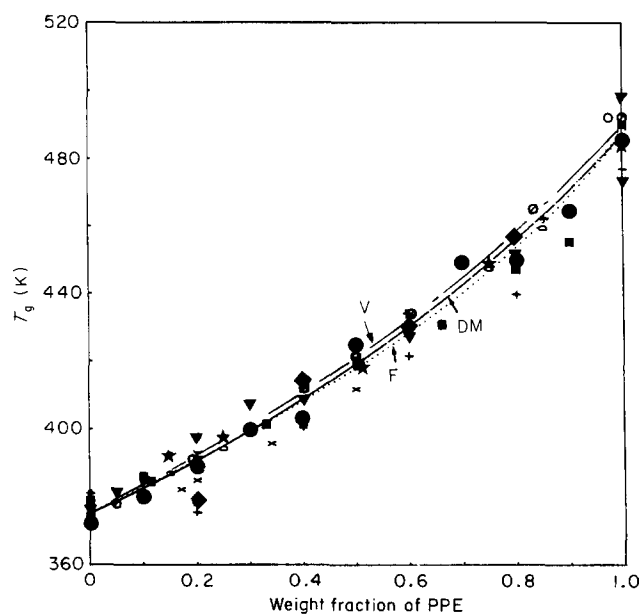


Figure 1 Glass transition temperature versus PS/PPE blend composition. The curves are drawn in accordance with the relations of Di Marzio (DM), Fox (F) and the concentration power equation (virial, V):

Symbol	M_w		Ref.
	PS	PPE	
○	40 000	17 000	19
★	600 000	17 000	19
⊙	97 200	69 000	13
x	37 000	45 000	15
◆	40 000	36 000	17
+	97 200	37 200	14
●	300 000	350 000	16
■	144 000	44 000	20
▼	144 000	5900	20

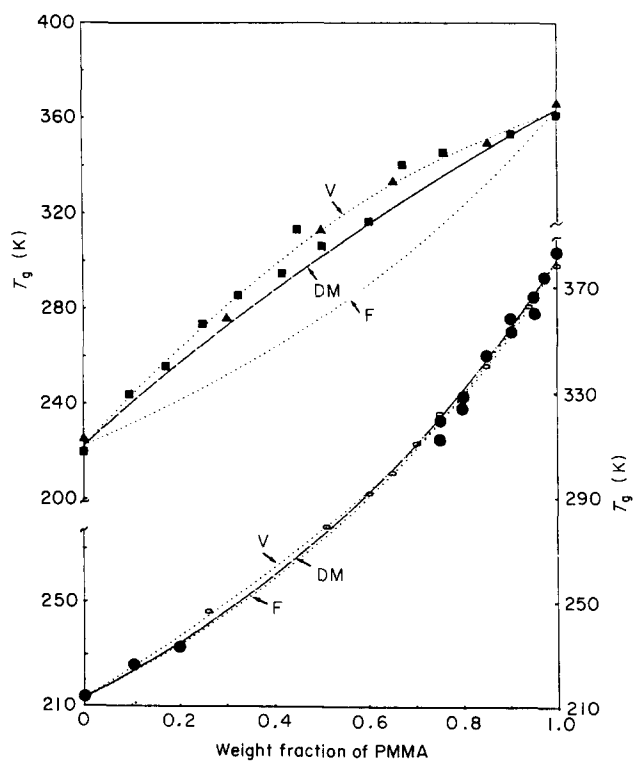


Figure 2 Glass transition temperature versus composition of blends of PMMA with PVF₂ and PEO, respectively. PVF₂: (▲) ref. 34, (■) ref. 35. PEO: (○) ref. 31; (●) ref. 32

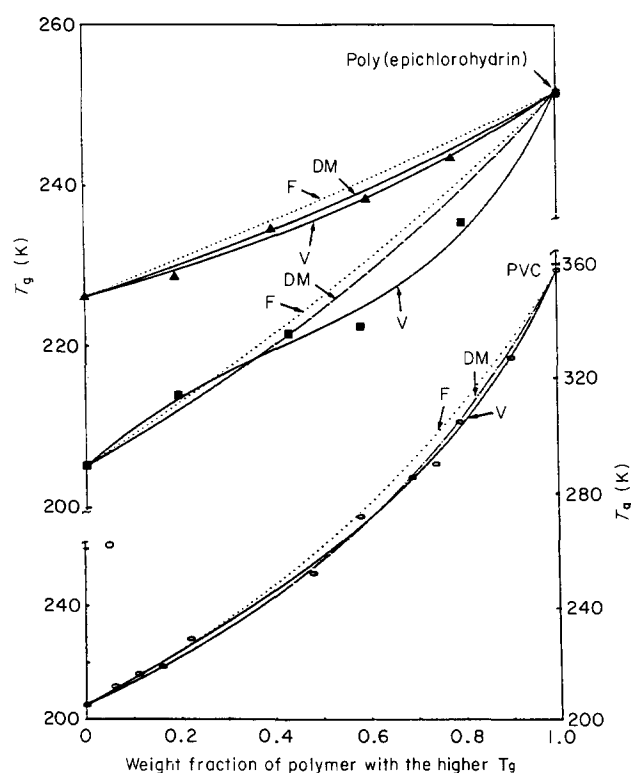


Figure 3 Glass transition temperature versus composition of blends of PVC and poly(epichlorohydrin) with aliphatic polyesters: (▲) poly(ethylene adipate)⁴⁴; (■) poly(butylene adipate)⁴⁴; (○) poly(ϵ -caprolactone)⁴⁴

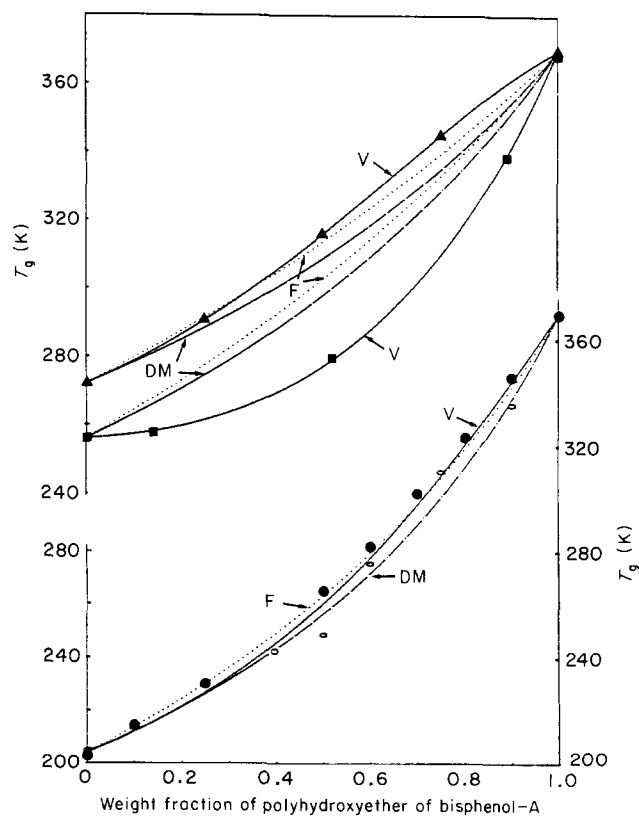


Figure 4 Glass transition temperature versus composition of blends of polyhydroxyether of bisphenol-A with aliphatic polyesters: (■) poly(dimethylpropylene succinate)⁴⁶; (▲) poly(cyclohexane dimethyl succinate)⁴⁶. Poly(ϵ -caprolactone): (○) ref. 45; (●) ref. 46

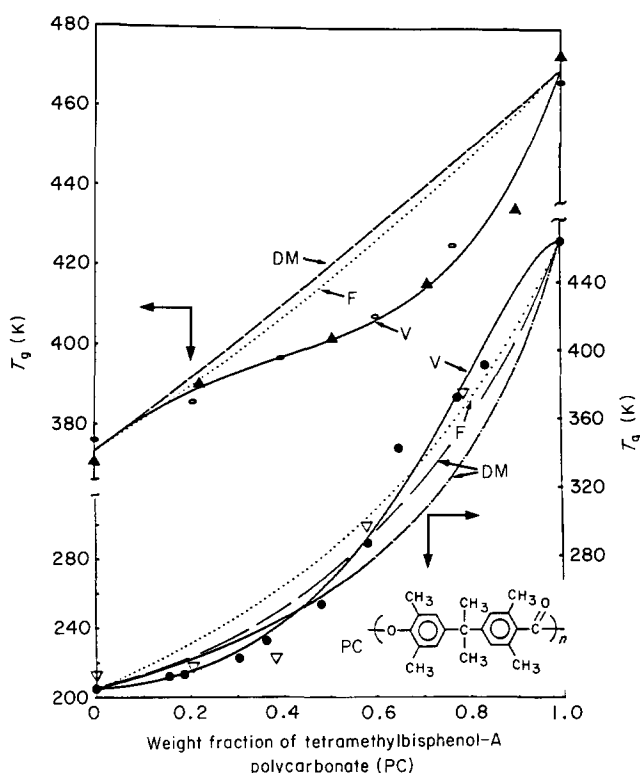


Figure 5 Glass transition temperature versus composition of blends of tetramethylbisphenol-A polycarbonate with polystyrene and aliphatic polyesters, respectively. Polystyrene: (○) ref. 48; (▲) ref. 49. Poly(ε-caprolactone): (●) ref. 47. Poly(butylene sebacate): (▽) ref. 47

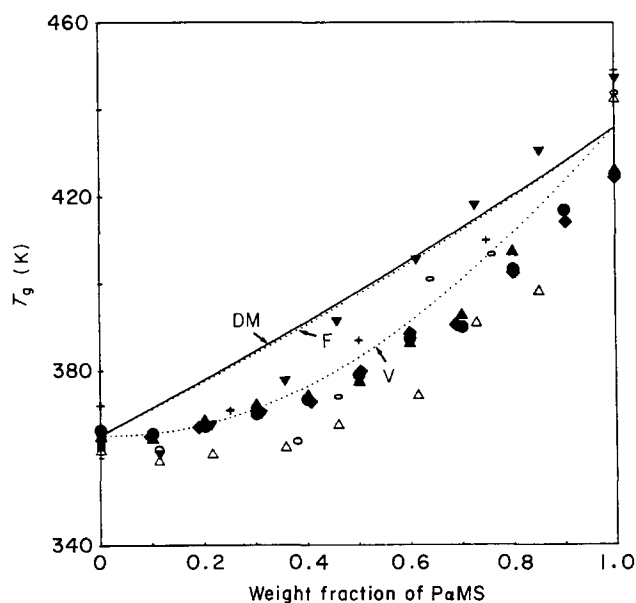


Figure 6 Glass transition temperature versus PS/PαMS blend composition. The solid symbols refer to T_g data of compression moulded samples; the open symbols refer to T_g data of solution cast films:

Symbol	M_w		Ref.
	PS	PαMS	
○	100 000	84 000	28
◆	35 000	41 500	29
●	46 000	52 500	29
▲	55 100	55 000	29
△	11 900	25 000	30
▽	11 900	25 000	30
+	17 000	80 000	27

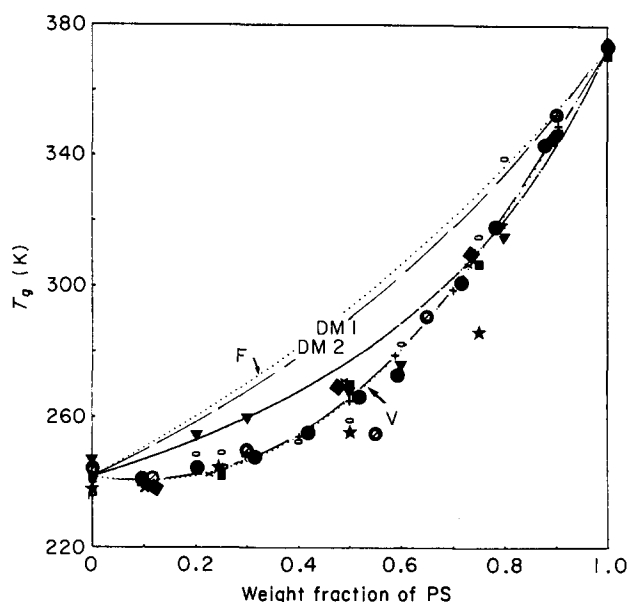


Figure 7 Glass transition temperature versus PVME/PS blend composition. The Di Marzio (DM) curves were drawn assuming different numbers of flexible bonds for PS: three flexible bonds for curve DM 1 and two for curve DM 2:

Symbol	M_w		Ref.
	PVME	PS	
○	524 000	15 000	21
★	73 000	75 000	23
∅	50 000	100 000	22
×	97 500	73 500	25
◆	10 500	73 500	25
■	97 500	73 500	25
+	99 000	35 000	26
●	99 000	233 000	26
▽	99 000	119 000	24

from the literature. The characteristics of these polymers are listed in Table 3. This is a remarkable correlation, and was completely unexpected.

Scatter in the data is related to a large extent to the different T_g evaluation procedures used by different authors and to uncertainties concerning γ , the number of flexible bonds per monomeric unit. This is illustrated in Figure 10. For instance for PS (labelled 1) we have plotted two points corresponding to $\gamma = 2$ and $\gamma = 3$. For PC (labelled 9) the two points represent five and six and for polybisphenol-A terephthalate (labelled x) five and seven flexible bonds.

As equation (13) refers only to T_g for infinite molecular weight, the molecular weight dependence is not considered (illustrated for PS, $M_w = 73\,500$, labelled 1 and PS, $M_w = 800$, labelled 1a). The same remark is valid for the influence on T_g of *cis-trans* isomerism (see data for *cis*-polybutadiene, labelled f, and *trans*-polybutadiene, labelled g).

Finally, we wish to emphasize that the main conclusion of equation (13), that the glass temperature of polymers depends on the mass per flexible bond of the monomeric unit, is entirely consistent with the torsion angle theory of Hopfinger *et al.*⁵⁸. According to this theory the mass moments of the torsion angle units increase the T_g of the polymer, whereas the conformational flexibility of the torsion angle units decrease the T_g .

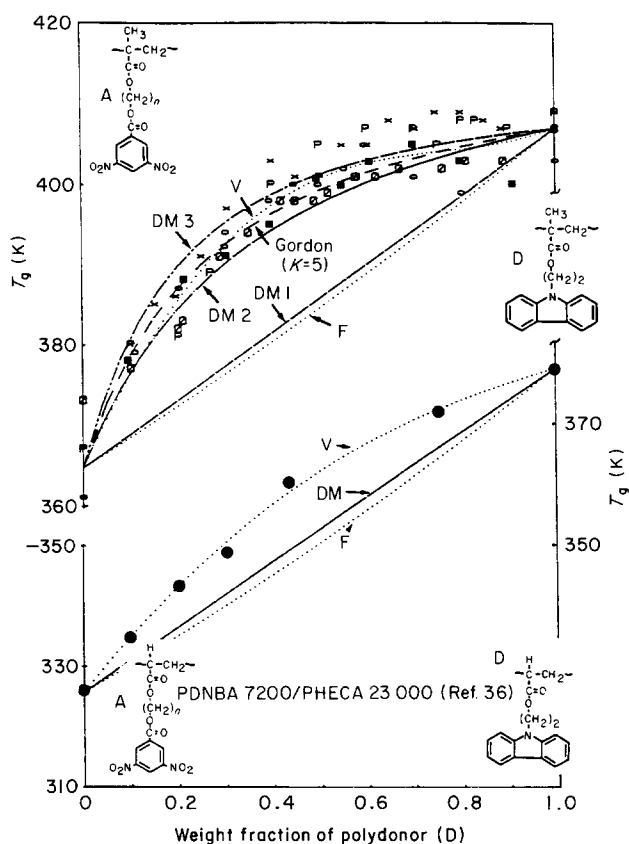


Figure 8 Glass transition temperature versus composition of blends of electron donor (D) and electron acceptor (A) polymers. For the significance of the various curves for the PDNBM/PHECM blends, see text:

Symbol	M_w^a	
	PDNBM	PHECM
○	19 200	3500
■	19 200	6800
◊	34 400	9500
×	19 200	16 900
P	24 200	35 800

^aRefs 37 and 38

CONCLUSIONS

The observation that only for a few of the analysed compatible polymer blends is the glass temperature versus composition behaviour fitted by equations based on either additivity of the volume (the Fox version of the Gordon-Taylor equation) or additivity of the flexible bonds (Di Marzio equation), indicates that effects of interactions have to be considered. Thus, there is a need for a more accurate prediction of blend glass temperature and to be credible this must be done with no adjustable parameters. This is the weakness of the 'virial' concentration power equation (proposed by Schneider) which considers the effect of interactions and related free volume redistributions, but offers no independent way for calculating the inherent coefficients.

The consideration of interactions includes the use of the entropy equation of state (SVT) in the configurational entropy theory of Di Marzio, and, respectively, the PVT equation of state in the free volume theory.

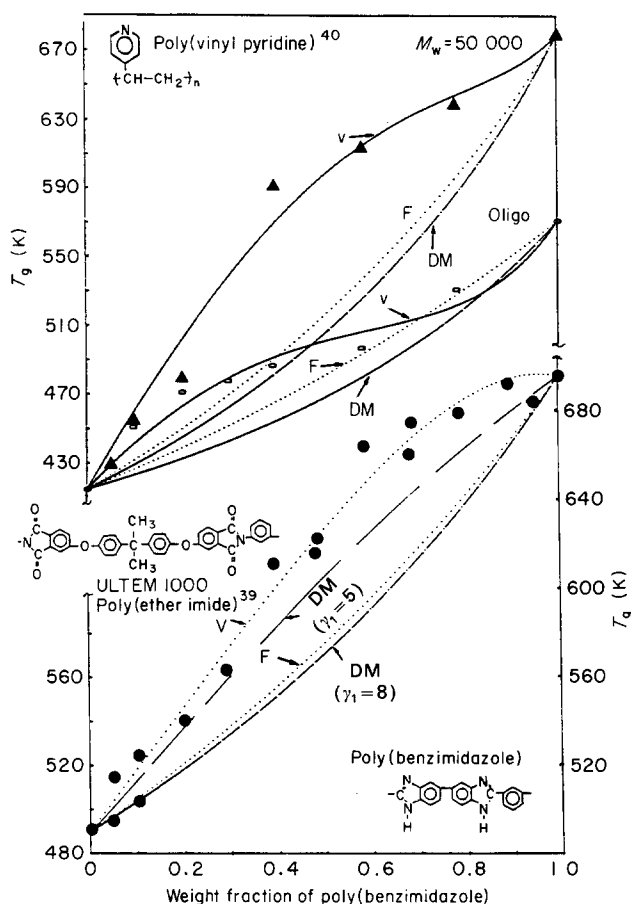


Figure 9 Glass transition temperature versus poly(benzimidazole) blend composition

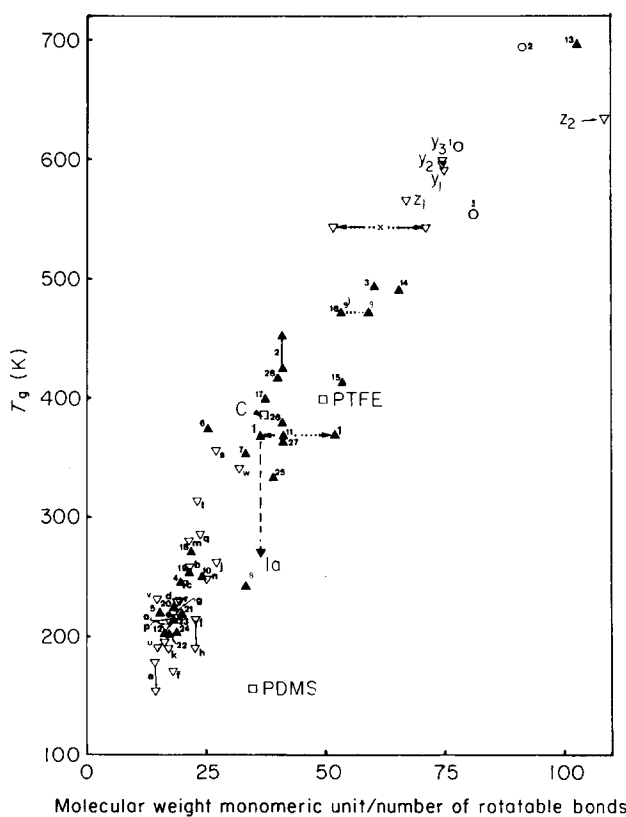
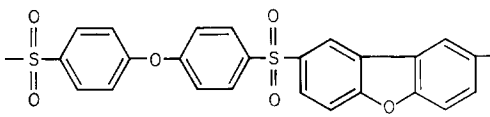
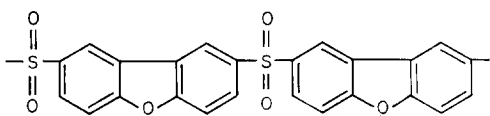
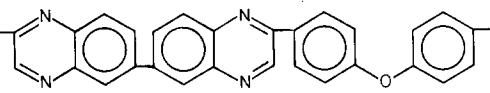
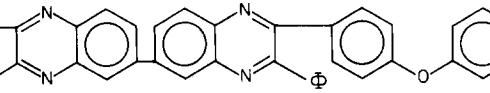
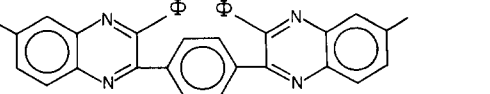


Figure 10 Glass transition temperature versus molecular weight per flexible bond of the monomeric unit. Numbers and letters correspond to polymers in Tables 2 and 3, respectively

Table 3 Glass temperatures, monomeric unit weights and number of flexible bonds for some polymers

	Polymer	T_g (K)	w	γ	w/ γ	Ref.
a	Polyethylene	148 (180 ^a)	28	2	14	50
b	Polypropylene	260	42	2	21	50
c	Poly (but-1-ene) poly (ethylethylene)	249	56	3	18.7	50
d	Poly (propylethylene)	233	70	4	17.5	50
e	Poly (butylethylene)	223	84	5	16.8	50
f	cis-Polybutadiene	171	54	3	18	50
g	trans-Polybutadiene	215	54	3	18	50
h	cis-Polyisoprene	190	68	3	22.7	50
i	trans-Polyisoprene	215	68	3	22.7	50
j	Poly (1,2-dimethyl-1-butylene)	262	82	3	27.3	50
k	Poly (ethyl-1-butylene)	191	68	4	17	50
l	Poly (propyl-1-butylene)	196	82	5	16.4	50
m	Poly (methyl acrylate)	283	86	4	21	50
n	Poly (ethyl acrylate)	249	100	5	20	50
o	Poly (n-butyl acrylate)	219	128	7	18.3	50
p	Poly (octyl acrylate)	208	184	11	16.7	50
q	Poly (n-butyl methacrylate)	293	124	7	20.3	50
r	Poly (vinyl ethyl ether)	230	72	4	18	50
s	Poly (vinyl alcohol)	358	44	2	22	50
t	PVF ₂	314	46	2	23	50
u	Poly (oxymethylene)	191	30	2	15	50
v	Poly (oxyethylene)	232	44	3	14.7	50
w	Poly (ethylene terephthalate)	342	192	6	32	50
x	Poly (bisphenol-A terephthalate)	543	358	5 (7)	72 (51)	50
y ₁	Poly (phenolphthaleinoyl isoterephthalate)	591	448	7	64	51
y ₂	Poly (phenolphthalimidinoyl isoterephthalate)	598	447	7	64	51
y ₃	Poly (phenolphthalimidinoyl terephthalate)	600	447	7	64	51
	Polyarylsulphone					
z ₁		563	460	6	76.7	52
z ₂		633	460	4	115	52
	Polyquinoxalines ^b					
o ₁		611	396	5	79.2	53
o ₂		693	550	7	78.6	53
o ₃		563	500	6	83.3	54
PDMS	Poly (dimethylsiloxane)	150	74	2	37	55
PTFE	Poly (tetrafluoroethylene)	400	100	2	50	56
C	Cellulose triacetate	380	308	8	38	55

^aCalculated by Di Marzio and Gibbs⁵⁷^bΦ represents the phenyl group

The fact that both the additivity based equations predict the same glass temperature *versus* composition behaviour, independent of whether the experimental T_g data are verified or not, led us to postulate the proportionality of glass temperature to molecular weight per flexible bond. This was verified as an approximate experimental relation in *Figure 10*. At this stage our understanding of *Figure 10* seems fortuitous. However, this fortuitous aspect is exactly what allows sensible glass temperature predictions to be made from either the entropy or the free volume views of glass formation.

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