Extension of the chain-end free volume theory for predicting the T_g–M_n^{-1} relationship for homopolymer bimodal blends

J. M. Pochan and D. F. Pochan
S. C. Johnson and Son, Inc., Racine, WI 53406, USA

and J. F. Elman
Eastman Kodak Company, Rochester, NY 14650, USA

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The chain-end theory of free volume has been extended to describe the T_g–M_n^{-1} behaviour of bimodal blends of homopolymers. The theory provides an equation of the form:

$$T_g = T_{g\infty} - \frac{K}{M_A}\left(\frac{1}{X+(1-X)P}\right)\left(X+(1-X)Q\left(\frac{M_A}{M_B}\right)\right)$$

where $P = \alpha_B/\alpha_A$ is the ratio of free volume expansion for the individual chain-ends and $Q = (\rho_B/\rho_A)(\theta_B/\theta_A)$ where ρ is the density and θ is the chain-end free volume of each component. X is the weight fraction of component A. The equation fits experimental data for the T_g–M_n^{-1} relationship in two polycarbonate and two polystyrene blends.

(Keywords: glass transition; molecular weight; free volume theory)

INTRODUCTION

Recently we have been involved in studying the dielectric relaxation of blends of chemically similar low and high molecular weight materials[1–3]. In these studies, it has been shown that, even though the mixed materials form apparently compatible blends, the T_g–M_n^{-1} relationship is nonlinear over the entire composition range. This is shown for a polycarbonate blend in *Figure 1*. For most polymers, plots such as *Figure 1* are extrapolated to $1/M_n = 0$ to obtain the T_g of an infinitely high molecular weight polymer. For the case shown and those of refs. 2 and 3, this extrapolation cannot be made due to the nonlinearity of the data. This has been taken to indicate that the high molecular weight component of the blends attains different chain conformations depending on whether it is the major or minor component of the blend. Such behaviour could not be explained theoretically. We wish now to extend the chain-end theory[4] to bimodal homopolymer blends to explain the observed data.

THEORY

Consider two identical homopolymers with end-groups A and B, whose free volumes are θ_A and θ_B, respectively. If the polymer has a density, ρ, and a number-average molecular weight M_n, then the number of chains per unit volume will be $(\rho/M_n)N$, and the number of chain-ends will be $(2\rho/M_n)N$. N is Avogadro's number. The total free volume per unit volume (f_c) is then $2\rho N\theta_A/M_{n_A}$ for component A.

therefore:

$$f_c = \frac{2\rho N\theta_A}{M_{n_A}} \tag{1}$$

In the original theory, it is reasoned that if a polymer with this value of f_c has a glass transition T_g, then f_c is the equivalent to the increase in free volume on expanding the polymer thermally between T_g and $T_{g\infty}$; i.e. ref. 2,

$$f_c = \alpha_f(T_{g\infty} - T_g) \tag{2}$$

where α_f is the coefficient of expansion of the free volume, and $T_{g\infty}$ is the glass transition of an infinite molecular weight polymer A.

Equating equations (1) and (2) provides:

$$T_g = T_{g\infty} - \frac{2\rho N\theta_A}{\alpha_f M_{n_A}} = T_{g\infty} - \frac{K}{M_{n_A}} \tag{3}$$

Now, let X be the weight fraction of component A in a blend of homopolymers A and B. The total free volume of a unit volume of material is now:

$$\begin{aligned} f_c &= \frac{2\rho_A N\theta_A}{M_{n_A}}X + \frac{2\rho_B N\theta_B}{M_{n_B}}(1-X) \\ &= 2N\left(\frac{\theta_A X\rho_A}{M_{n_A}} + \frac{\theta_B(1-X)\rho_B}{M_{n_B}}\right) \end{aligned} \tag{4}$$

Two approaches can be made in considering the calculation of free volume with the free volume coefficient of expansion. The first would be to equate equation (4) to equation (2) assuming the blend was homogeneous and that α_f is an average coefficient of expansion. This provides:

$$2N\left(\frac{\theta_A X\rho_A}{M_{n_A}} + \frac{\theta_B(1-X)\rho_B}{M_{n_B}}\right) = \alpha_f(T_{g\infty} - T_g) \tag{5}$$

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which can be rearranged to provide:

$$T_g = T_{g\infty} - \frac{2N\theta_A\rho_A}{\alpha_f M_{n_A}}\left[X + (1-X)\left(\frac{M_{n_A}}{M_{n_B}}\right)\left(\frac{\theta_B}{\theta_A}\right)\left(\frac{\rho_B}{\rho_A}\right)\right] \quad (6)$$

$$= T_{g\infty} - \frac{K_A}{M_{n_A}}\left[X + (1-X)\left(\frac{M_{n_A}}{M_{n_B}}\right)\left(\frac{\theta_B}{\theta_A}\right)\left(\frac{\rho_B}{\rho_A}\right)\right]$$

where $K_A = \left(\frac{2N\theta_A\rho_A}{\alpha_f}\right)$

Equation (6) provides an equation relating T_g to M_n for a bimodal mixture of homopolymers. If M_{n_A} and M_{n_B} are known, it also provides for a method of determining the product $(\theta_B\rho_B/\theta_A\rho_A)$ for given mixtures of homopolymers with different end-groups. A series of theoretical plots of equation (6) are shown in *Figure 2* for various values of the theta ratios. Note, that equation (6) only provides for a change in slope of the T_g–M_n^{-1} relationship, and cannot be used to generate curves as shown in *Figure 1*. This same result would apply for various ratios of density. An obvious assumption related to equation (5) is that $T_{g\infty}$ is identical for the homopolymers A and B.

A second approach to calculating the free volume coefficient of expansion in equation (5) is simply a weight average of the pure components, i.e.,

$$\alpha = (X_A\alpha_A + (1-X)\alpha_B) \quad (7)$$

If this is done, equation (6) now becomes:

$$T_g = T_{g\infty} - \frac{2N\theta_A\rho_A}{\alpha_A M_{n_A}}\left(\frac{1}{X + (1-X)\frac{(\alpha_B)}{(\alpha_A)}}\right)\left(X + (1-X)\left(\frac{\rho_B}{\rho_A}\right)\left(\frac{\theta_B}{\theta_A}\right)\left(\frac{M_A}{M_B}\right)\right)$$

$$= T_{g\infty} - \frac{K_A}{M_{n_A}}\left(\frac{1}{X + (1-X)\frac{(\alpha_B)}{(\alpha_A)}}\right)\left(X + (1-X)\left(\frac{\rho_B}{\rho_A}\right)\left(\frac{\theta_B}{\theta_A}\right)\left(\frac{M_A}{M_B}\right)\right) \quad (8)$$

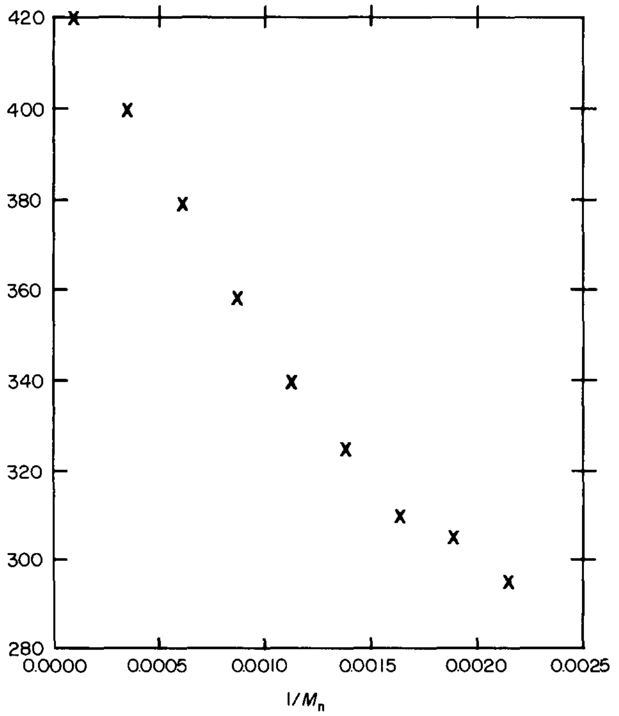

Figure 1 T_g *versus* M_n^{-1} for blends of bis(phenol-A) diphenylcarbonate with polycarbonate

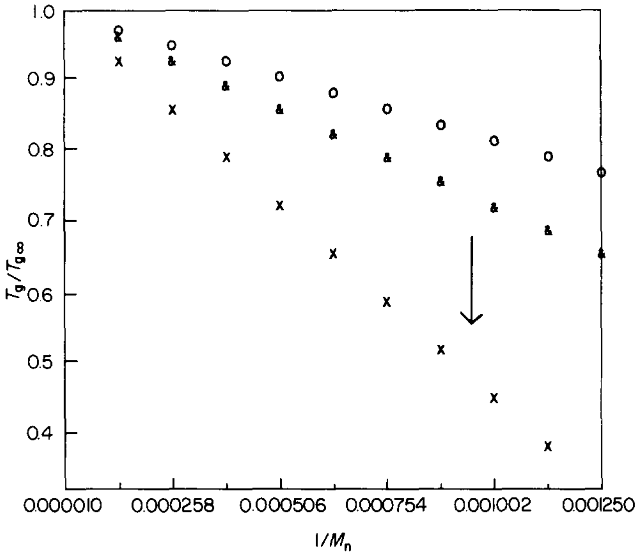

Figure 2 $T_g/T_{g\infty}$ *versus* M_n^{-1} for various θ ratios from equation (6). All other ratios held constant at 1. ○ $=\theta_R = 1.5$; & $=\theta_R = 1.0$; × $=\theta_R = 0.5$

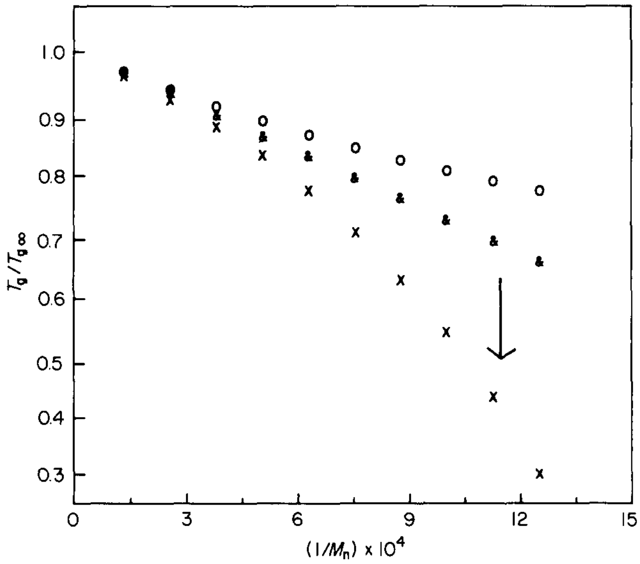

Figure 3 $T_g/T_{g\infty}$ *versus* M_n^{-1} for various α ratios from equation (8). All other ratios held constant at 1. ○ $=\alpha_R = 1.5$; & $=\alpha_R = 1.0$; × $=\alpha_R = 0.5$

Equation (8) is a more complicated function than equation (6); however, both can be considered as showing the end-group effect on T_g of bimodal homopolymer blends. It would be naturally easy to extend the equation to a system of more than two components. The effect of the coefficient of expansion ratio on equation (8) is shown in *Figure 3* where T_g is plotted as a function of M_n^{-1} for various ratios of α. In this case, curvature is added to the relationship. Equation (8) is thus applicable to analysis of data such as that in *Figure 1*.

DATA ANALYSIS

Nonlinear regression analysis has been used to obtain ratios of the various constants in equation (8). The ratio M_A/M_B is a known quantity; however, ρ_B/ρ_A, θ_B/θ_A and α_B/α_A are generally not known for a given system. ρ_B/ρ_A and θ_B/θ_A can be lumped into one constant and equation (8) becomes:

$$T_g = T_{g\infty} - \frac{K_A}{M_A}\left(\frac{1}{X + (1-X)P}\right)\left(X + (1-X)Q\left(\frac{M_A}{M_B}\right)\right) \quad (9)$$

where $p=\alpha_B/\alpha_A$ and $Q=(\rho_B/\rho_A)(\theta_B/\theta_A)$. If the value for K_A is not known, it can also be considered as a mathematical fit parameter. A nonlinear regression analysis of equation (9) was done for four blended systems: bisphenol-A diphenylcarbonate/Lexan® polycarbonate, bisphenol-A bis(cumylphenyl) carbonate/Lexan® polycarbonate, and two blends of narrow molecular weight distribution polystyrenes. Component A was always the high molecular weight material. In the case of the PS blends, a value of $K_A=10^5$ was used for the fit. For the polycarbonate blends, the value of K_A was determined via the nonlinear analysis of the bisphenol-A/diphenyl carbonate data. In fitting polycarbonate results it was noted that three standard deviations for K_A and Q are almost as large as K_A and Q; however, the value determined for P always had an error of 10% or less. The value for K_A for polycarbonate was, therefore 'fixed' by choosing the best value from the regressions, and P and Q determined. In this way, the smaller errors were obtained. Results of these fits are shown in *Table 1*. The fits are shown in *Figures 4* and *5* for two of the systems. None of the fit parameters are unreasonable. The results indicate large differences in Q for the polycarbonate systems when compared to polystyrenes. Since the densities could not be different by more than a factor of 1.5, the chain-end free volumes must be the dominant effect in the PC case.

In the case of the PS blends, it is known that both systems are terminated identically, with a butyl group on one end and a hydrogen atom on the other. Equation (9) should in fact be modified to include the different groups, but this would only provide for expansion of the α, θ and ρ terms, and since the experimental data can be fit almost perfectly with equation (9), would provide no new information. It is noted that the fit provides $Q\sim 1$, as expected.

It appears when comparing the data, that as the end-group becomes a significant part of the entire molecule, the ratio of α_A/α_B becomes large (Systems A and B in *Table 1*). This could be taken to mean that the effect of chain-ends becomes more significant as they become a large part of the molecule—an expected result.

CONCLUSION

The chain-end theory of free volume has been extended to describe the T_g–M_n^{-1} behaviour of bimodal blends of homopolymers. The theory provides an equation of the form:

$$T_g=T_{g\infty}-\frac{K}{M_A}\left(\frac{1}{X+(1-X)P}\right)\left(X+(1-X)Q\left(\frac{M_A}{M_B}\right)\right)$$

where $P=\alpha_B/\alpha_A$ is the ratio of free volume expansion for the individual chain ends and $Q=(\rho_B/\rho_A)(\theta_B/\theta_A)$ where ρ is the density and θ is the chain-end free volume of each component. X is the weight fraction of component A.

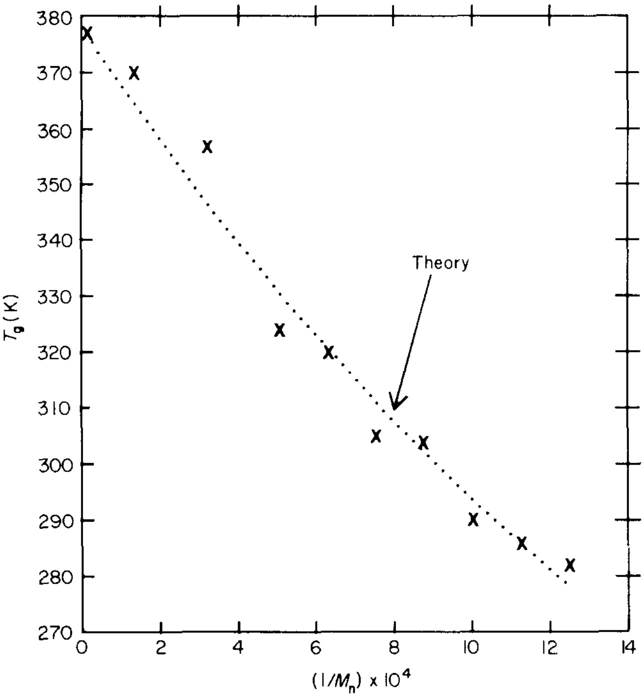

Figure 4 T_g *versus* M_n^{-1} for a blend of 800 and 100K molecular weight polystyrene. × = experimental data, (·····) = theoretical fit

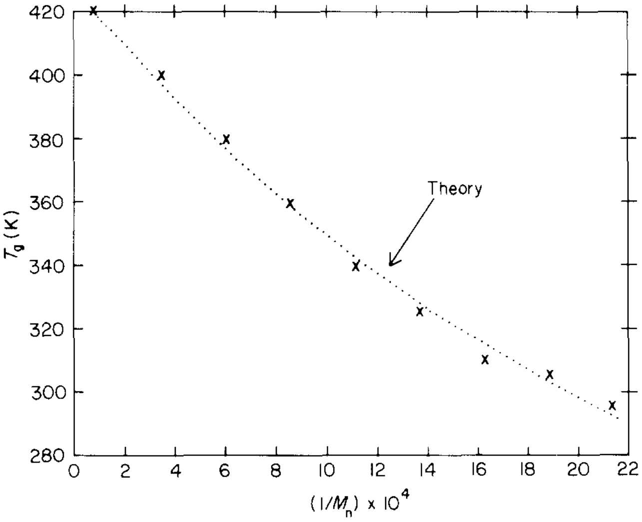

Figure 5 T_g *versus* M_n^{-1} for a blend of bisphenol-A diphenylcarbonate with Lexan® polycarbonate. × = experimental data, (·····) = theoretical fit

Table 1 Fit determination from equation (8)

	System	K_A	α_B/α_A	$\left(\frac{\rho_B}{\rho_A}\right)\left(\frac{\theta_B}{\theta_A}\right)$
A	PS blend (800/100K)	10^5	1.32 ± 0.22	1.042 ± 0.14
B	Mlex[a]/Lexan®	21500	1.51 ± 0.12	4.20 ± 0.27
C	Monolex[b]/Lexan®	21500	1.09 ± 0.04	3.52 ± 0.12
D	PS blend (2200/670K)	10^5	1.03 ± 0.13	1.05 ± 0.11

[a] Mlex = bis phenol-A diphenylcarbonate
[b] Monolex = bis phenol-A (biscumylphenyl) carbonate
Note: error limits are ±3 standard deviations

The equation fits experimental data for the T_g–M_n^{-1} relationship in two polycarbonate and two polystyrene blends.

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