Glass transition temperature of poly(methyl methacrylate) blends

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The glass transition temperature (T_g) of atactic poly(methyl methacrylate) (PMMA) blends was measured over a wide range of molecular weights ($\bar{M}_n$) via differential thermal analysis. Comparison of these results critically questions the validity of the Fox–Flory relationship as anything other than a first order approximation of a more complex functional relationship.

In the last twenty-five years, several approaches have been advocated to explain the relationship between molecular size/shape and the second-order transition associated with amorphous polymers[1–6]. By far the two most popular theories have been the free-volume theory of Fox and Flory[3,4] and the statistical mechanical approaches of Gibbs and DiMarzio[5,6]. Various degrees of success have been reported using these theories. The Fox–Flory approach generally is used to approximate T_g vs M_n^{-1} either for $M_n > 10^4$ [7,8] or as a series of straight line segments[1,2,9], and the Gibbs–DiMarzio theories set either the fractional free-volume at T_g (V_0) or the energy barrier to segmental rotation (ε) to a constant (most commonly with $V_0 = 0.025$[10,11]) and floating the other parameter to obtain the best fit. The present study considers both theories, although the statistical methods yield more consistent results.

Three feedstocks were used to prepare some 24 blends by precipitation in a hexane solution after dissolution in acetone at 37°C (*Table 1*)[12]. These were designated high (H), medium (M), and low (L) molecular weights. Both H and M were obtained commercially; L was prepared in this laboratory by solution polymerization in toluene at 60°C[13,14]. Molecular weights were determined by g.p.c. in THF using polystyrene standards. Additionally, a PMMA secondary standard was evaluated using the same g.p.c. procedure and compared with the reported light scattering ($\bar{M}_w = 60.6 \times 10^3$) and membrane osmometry results ($\bar{M}_n = 33.2 \times 10^3$)[15]. Glass transition temperatures for each vacuum-dried blend were obtained using a Dupont 990 Differential Thermal Analyser (d.t.a.) at a heating rate of 20°C min^{-1} under nitrogen (0.2 l min^{-1}). Multiple run results for each blend combination (e.g. H/M) are shown in *Figure 1*. Here regression lines for *H*/*M*, *H*/*L*, and *M*/*L* are highly significant (0.001 level), the T_gs averaging 395, 382 and 347 K for H, M, and L, respectively.

Based on the previous observations of heterogeneous systems, that the mean number-average molecular weight is the primary consideration,[3,4,6,16,17] a reduction of the T_g *vs* composition plots to T_g *vs* $\bar{M}_n^{-1}$ via $\bar{M}_n^{-1} = (w/\bar{M}_n)_i + (w/\bar{M}_n)_j$ (where i and j refer to the feedstock components and w are their respective weight fractions) is shown in *Figure 2*. Once again the Fox–Flory expression yields lines that are significant at the 0.001 level, although the

Table 1 Characterization of PMMA Feedstocks

Designation	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
H[a]	364	122	2.99
M[b]	64.4	32.1	2.01
L	5.03	3.90	1.30
S[c]	61.5 (60.6)	29.6 (33.2)	2.07 (1.82)

[a] Aldrich Chemical Company, Milwaukee, Wis. (cat. no. 18, 226–5, $[\eta] = 1.3$ for $\bar{M}_w = 500 \times 10^3$)

[b] Polysciences, Warrington, Pa. (cat. no. 4554, lot no. 1888–125, $[\eta] = 0.2$ for $\bar{M}_w = 50.0 \times 10^3$)

[c] Aldrich Chemical Company, Milwaukee, Wis. (cat. no. 18, 225–7, lot no. 03)

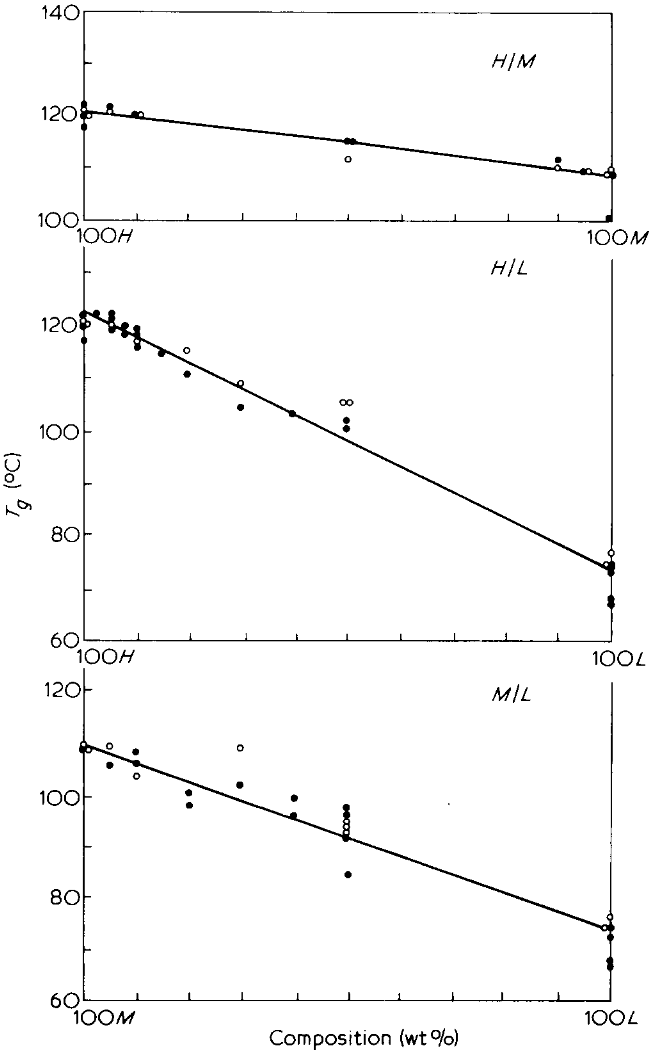

Figure 1 Dependence of T_g on blend composition: ●, ○, denote the first and second d.t.a. scans, respectively

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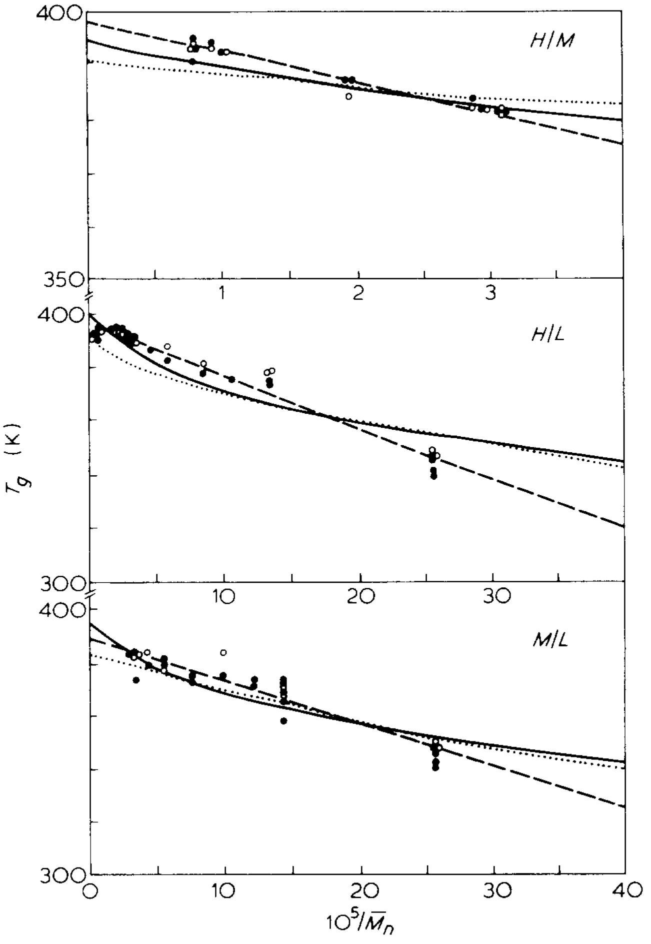

Figure 2 Influence of M_n^{-1} on T_g and the associated theoretical analyses: — — —, Fox–Flory; ——, Gibbs; and · · · ·, Gibbs–DiMarzio (*Table 2*)

three slopes differ by a factor of >3 (*Table 2*). In contrast for $V_0 = 0.025$, the Gibbs and Gibbs–DiMarzio relationships gives $\varepsilon = 0.99$–1.00 and $\varepsilon = 1.66$–1.69 kcal (mol segments)$^{-1}$, respectively. The extrapolated T_gs for the infinite molecular weight polymer, T_g^∞, are displayed in parentheses in *Table 2*.

As *Figure 2* shows, each set of results appear to fit the Fox–Flory relationship best. However, these seemingly good fits do not yield consistent values for the constants, T_g^∞ and K_g. Since any theoretical argument should uniquely describe a relationship that is independent of molecular weight (at least for molecular weights greater than the entanglement molecular weight, i.e. $\bar{M}_n \simeq 10^4$ (*Table 2* of ref 9)), the only recourse is to suggest that these apparent straight line relationships really represent approximations of some curvilinear function. This hypothesis is borne out by the observation that both K_g and T_g^∞ decrease as the $\bar{M}_n$s of the respective blend combinations extend into the lower molecular weight regions. Earliest results by Fox and Loshaek[18] predict $K_g = 0.6$–1.5×10^5K, while Pratt[19] reported 1.55×10^5K for γ-irradiated PMMA, Beevers and White[20] found 2.1 $\times 10^5$K for a molecular weight range of 2.7–77×10^3, and Thompson[21] observed 3.0 and 3.4×10^5K for 0.75 and 0.82 s-PMMA, respectively. Interestingly our three basic blends fall within the scatter envelope formed by the compilation of data presented by Boyer (*Figure 1*, ref 2). Moreover, the present results indicate that, in the highest temperature region, K_g may increase at a greater rate than Boyer's plot indicates. The implication, that T_g^∞ is asymptotically approaching a maximum, can be rationalized on the grounds that there must be a maximum permissible segmental chain stiffness above which coordinated chain motion does not occur.

Table 2 Theoretical comparison of dependence of T_g on $\bar{M}_n$ for PMMA Blends

	Fox–Flory	Gibbs[a]	Gibbs–DiMarzio[a]
H/M	$K_g{}^b = 5.402$ (398.0)[d]	$\epsilon^c = 0.99$ (395.1)	$\epsilon = 1.69$ (391.2)
H/L	$K_g = 1.952$ (397.1)	$\epsilon = 1.00$ (399.1)	$\epsilon = 1.68$ (388.9)
M/L	$K_g = 1.588$ (388.1)	$\epsilon = 0.99$ (395.1)	$\epsilon = 1.66$ (384.2)

[a] Evaluated for $V_0 = 0.025$
[b] K_g in K x 10^{-5}
[c] ϵ in kcal (mol segment)$^{-1}$
[d] Values for T_g^∞ (K)

With the foregoing arguments in mind, the Gibbs and Gibbs–DiMarzio functions were fitted (*Figure 2*) assuming an iso-free-volume state[1] (i.e. $V_0 = 0.025$). Although the data point to the theoretical line correspondence is not as good as the Fox–Flory relationship, a uniform value for ε prevailed, $\Delta\varepsilon$ varying by only 0.01 kcal (mol segment)$^{-1}$ between H/M, H/L, M/L (*Table 2*). Using d.t.a., several authors[17,21] have shown that $\varepsilon = 0.98$–1.00 kcal (mol segments)$^{-1}$, further confirming the solidarity of the observations. Similar agreement between past and present work is noted for the Gibbs–DiMarzio relationships, wherein $\varepsilon = 1.66$ kcal (mol segment)$^{-1}$ is typical[20]. Further support is found in the observation that both these functions are sensitive to changes in ε, V_0, or the degree of polymerization.

These experiments question the validity of the free-volume theory of Fox–Flory as the explanation for the T_g vs $\bar{M}_n{}^{-1}$ of PMMA. Although both within the present context and with respect to the general acrylic literature the Gibbs theory yields the most consistent results (cf overview in ref 22*), that fit is not totally satisfactory either. One approach which this latter observation has fostered is a systematic reexamination of the statistical mechanical relations. While a common interrelationship is sought between ε, V_0, and the reported T_g vs $\bar{M}_n{}^{-1}$ data, nevertheless, reservations persist that either the variability in the literature (either because of different observers, instrumentation, or sample preparation[9,20,22]) or the assumptions inherent in theory (e.g. the failure to account for nearest neighbour interactions[1,23]) may preclude a conclusive interpretation of results such as those addressed in this report.

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* Note error on p 123 of ref 22, ε on line 37 should read 0.99 and not 1.02.

REFERENCES

1 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
2 Boyer, R. F. *Macromolecules* 1974, **7**, 142
3 Fox, T. G. Jr. and Flory, P. J. *J. Am. Chem. Soc.* 1948, **70**, 2384
4 Fox, T. G. Jr. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
5 Gibbs, J. H. *J. Chem. Phys.* 1956, **25**, 185
6 Gibbs, J. H. and DiMarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
7 Rudin, A. and Burgin, D. *Polymer* 1975, **16**, 291
8 Richardson , M. J. and Savill, N. G. *Polymer* 1977, **18**, 3
9 Turner, D. T. *Polymer*, 1978, **19**, 789
10 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am Chem. Soc.* 1955, **77**, 3701
11 Williams, M. L. *J. Appl. Phys.* 1958, **29**, 1395
12 Fox, T. G. Jr., Kingsinger, J. B., Mason, H. F. and Schuele, E. M. *Polymer* 1962, **3**, 71
13 'Use of acrylic monomers in the preparation of low number average molecular weight polymers', Rohm and Haas Technical Report TMM-23, March, 1965
14 Sandler, S. R. and Karo, W. 'Polymer Synthesis--Vol. 1', Academic Press, New York, 1974, p. 297
15 Characterization Data Sheet of PMMA Cat. No. 18,225-7, Lot No. 03 from Aldrich Chemical Company, Milwaukee, Wisconsin
16 Ueberreiter, K. and Kanig, G. *J. Colloid Sci.* 1952, **7**, 569
17 Kusy, R. P., Katz, M. J. and Turner, D. T. *Thermochim. Acta* 1978, **26**, 415
18 Fox, T. G. Jr. and Loshaek, S. *J. Polym. Sci.* 1955, **15**, 371
19 Pratt, G. J. *J. Mater. Sci.* 1975, **10**, 809
20 Beevers, R. B. and White, E. F. T. *Trans. Faraday Soc.* 1960, **56**, 744
21 Thompson, E. V. *J. Polym. Sci.* 1966, **4**, 199
22 Kusy, R. P. and Greenberg, A. R. *J. Thermal Anal.* 1980, **18**, 117
23 Cowie, J. M. G. and Toporowski, P. M. *Eur. Polym. J.* 1968, **4**, 621

Poly(β-ketothioethers) by polycondensation of bis-β-dialkylaminoketones with bis-thiols

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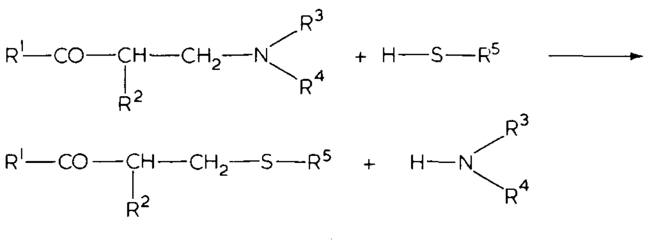
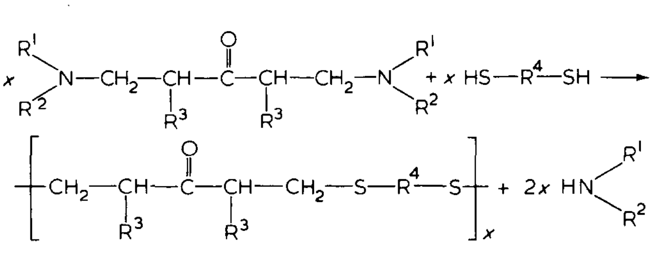
β-Dialkylaminoketones (Mannich bases) may react with thiols to give β-ketothioethers. Substitution of an -SR group for a dialkylamino group takes place[1-3]:



We have found that by using bifunctional compounds this reaction can open a synthetic route to a novel class of sulphur-containing polymers, the poly(β-ketothioethers):



The aim of this Report is to relate some results obtained using 2,6-bis(dimethylaminomethyl)cyclohexanone (I), and 1,2-ethanedithiol (II), oxydiethanedithiol (III) or 1,3-dimercaptobenzene (IV).

EXPERIMENTAL

^{1}H-n.m.r. spectra were run in $CDCl_3$ on a C-60 Jeol Spectrometer, with TMS as internal reference.

Bis-Mannich base I was prepared according to Barrett[4]. It was distilled just prior use, b.p. 90–92/0.4 mm.

Dithiols II and III were commercial products (Merck). They were purified by vacuum distillation just before use.

Dithiol IV (Fluka) was used without further purification.

Poly(β-ketothioether) V (*Table 1*) was prepared by dissolving I (10.0056 g, 47.13 mmol) and II (4.4395 g, 47.13 mmol) in a 3:1 dioxane/ethanol mixture (43 ml) and maintaining the reaction temperature at 60°C by means of a thermostatic alloy-controlled bath. A slow stream of nitrogen was passed through the reaction mixture, in order to prevent oxidation of the dithiol, and to carry out all dimethylamine which was formed during the reaction. The effluent gases were bubbled into aqueous 0.1 N H_2SO_4 (700 ml), and the progress of the reaction was followed by measuring the amount of dimethylamine absorbed by the acid titrimetrically.

After 40 h, 93.7% of the theoretical amount of dimethylamine had been evolved. The reaction was then brought to completion by raising the temperature to 90°C for 3 h. After this time, the solvents were eliminated by distillation under nitrogen, and the product was purified by dissolving the gummy residue in dichloromethane, and reprecipitating with an excess of light petroleum. The polymer was then recovered by filtration, and dried at room

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