The Glass Transition Temperature of Monodispersed Polystyrenes and Their Binary Mixtures*

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Glass transition measurements on monodispersed polystyrenes of different molecular weight and their binary mixtures result in the following conclusions: (a) the effect of molecular weight on the glass transitions of monodispersed samples satisfies the Fox and Flory equation written as $T_g = T_{g\infty} - A/M_n$, with constant $A = 0.84 \times 10^{-5}$; (b) polymers of the same number average molecular weight with a broad distribution show lower glass transitions than the monodispersed; (c) the binary mixtures follow the Gordon-Taylor equation derived for copolymers, with constant k (experimental) 0.5.

Key words: Binary mixtures; glass transition temperature; monodispersed polystyrene.

1. Introduction

At the glass transition temperature, T_g, there is a discontinuity in both the thermal expansion coefficient and the heat capacity, which is characteristic of the given material [1]. Glass transition temperatures, therefore, can, in principle, be measured by dilatometry and differential thermal analysis. Extensive studies of the T_g of polystyrenes have been made [2, 3, 4]. The glass transition point is known to increase with molecular weight to a limiting value. For an extensive discussion of theoretical and experimental information on the glassy state, see the review article by Boyer [5].

The polystyrenes used in previous work [2, 3, 4][1] were whole polymers and fractionated samples prepared by free radical polymerization. In this study we have measured the glass transition temperature of anionically prepared monodispersed polystyrenes and their binary mixtures and compared our results with those obtained by the earlier workers [2, 3, 4]. The results of this investigation elucidate to a greater or lesser degree questions relating to the following points:

a. whether the more rapid DTA measurement procedures [6, 7] for T_g give results comparable to the dilatometric method;

b. whether the T_g of anionically prepared polymers differs from that of free radically prepared polymers;

c. whether the T_g of highly monodispersed polymers differs from that of fractions and whole polymers; and

d. the effect of molecular weight distribution.

2. Experimental Procedure

2.1. Glass Transition Temperature Measurement by DTA

The glass transition measurement of the samples was carried out with the Dupont 900 Differential Thermal Analyzer[2] using the standard cell. A 10 mg. sample was placed in the sample macrocell and glass beads were used as the reference. All samples were given the same thermal history, i.e., heating the sample at the rate of 20 °C/min from room temperature to

[2]Certain commercial meterials and instruments are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

about 30 °C beyond the glass transition; examining the sample at this temperature to determine whether it needed a little pressing to make it compact, and then cooling to 0 °C at the same rate. The cooling was carried out using a constant flow of cold nitrogen gas obtained by boiling liquid nitrogen. During the experiments, a nitrogen flow of one standard cubic foot per hour was used. The heating rate chosen for this experiment was 20 °C/min and each sample was run at least three times. The reported values are the average of those which were obtained by the extrapolation method, i.e., by taking the intersection of the two straight lines drawn through the initial base line and the sloping portion of the thermogram. The reproducibility of T_g using this method is within ±1 °C. Some samples were also run at the rate of 10 °C/min and the glass transition temperature was slightly lower than that obtained at the rate of 20 °C/min (the difference being less than 1 °C). Although the "onset" temperature method of taking the T_g values may be closer to the reported values determined by the dilatometric method, unfortunately, it is much less reproducible.

2.2 Monodispersed Polystyrene Samples

The monodispersed polystyrene samples of different molecular weight were available in the Polymer Chemistry Section of the National Bureau of Standards as a result of recent work on polystyrene degradation [8]. Table 1 shows the molecular weights of the monodispersed samples used in this experiment as determined by different methods and also the glass transition temperatures measured by DTA. Also in column four are the $\bar{M}_n$ values used in the calculations and plots that are presented in the subsequent sections of this article.

2.3. Binary Mixtures of Monodispersed Polystyrene

Each binary mixture of monodispersed polystyrene was prepared by freeze-drying a dilute solution of the the binary mixture at the concentration of 0.1 g/100

cm³ using benzene as a solvent. After freeze-drying for 48 h with the use of an ordinary vacuum pump, the sample was then evacuated under high vacuum using an oil diffusion pump for 48 h at room temperature followed by 2 h heating at the temperature of boiling water. This procedure of taking the benzene out of the sample is sufficient for the purpose of this experiment, since several checks with the pure monodispersed samples show no change in the glass transition temperature measured before and after the freeze-drying.

3. Results

In figure 1, we present for comparison our experimentally measured glass transition temperatures and
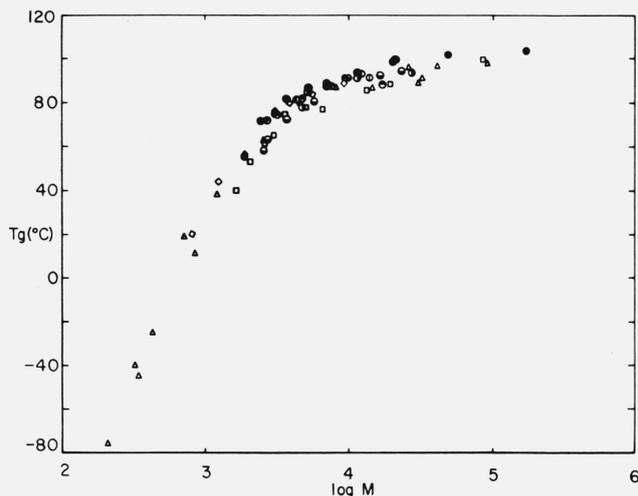

FIGURE 1. *The glass transition temperature of polystyrene as a function of number average molecular weight.*

The experimental results and the data from literature are represented by the following symbols: monodisperse polystyrene=●; binary mixtures of monodisperse (170,000)/(1,900)=◕, (170,000)/(2,450)=◒, (170,000)/(3,700)=◐, (20,000)/(2,450)=◑, (48,500)/(1,900)=⊕, (20,000)/(1,900)=⊖, (11,400)/(1,900)=○; Fox and Flory [2]=□; Ueberreiter and Kanig [3]=△; Schulz, Gunner, and Gerrens [4]=◇.

TABLE 1. *Molecular weight and the glass transition temperature of monodispersed polystyrenes*

$\bar{M}_n$				$\bar{M}_v$, Visc.	$\bar{M}_w$ G.P.C.	T_g(°C) by DTA at 20 °C/min
Chem. anionic	V.P.O.s	Mem.Os.	Value Used in Plots			
....	1,900	....	1,900	....	....	56.0
2,250	2,450	....	2,450	....	....	72.0
3,900	3,700	....	3,700	....	....	80.8
5,300	5,300	5,200	5,300	5,600	5,400	87.5
10,300	11,400	12,000	11,400	12,500	12,000	94.5
16,800	....	22,000	20,000	20,000	22,000	99.2
20,800	....	....	22,500	22,500	....	100.0
43,000	....	49,000	48,500	48,500	50,000	102.0
....	....	170,000	170,000	180,000	....	104.0

Note: V.P.O. = vapor phase osmometer; Mem.Os. = membrane osmometer; Visc. = viscometry; G.P.C. = gel permeation chromatography.

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those of earlier investigations, plotted as a function of the logarithm of number average molecular weight. This plot shows in general the way the value for T_g increases with increasing molecular weight to a constant saturation value after which the T_g is independent of molecular weight.

One easily detects small but well defined trends in the results. The monodispersed polystyrenes tend to give values a few degrees higher than those reported earlier [2, 3, 4], while our binary mixtures show values that agree closely with the earlier data [2, 3, 4].

The differences between the T_g's of the monodispersed polystyrenes and those of the earlier workers are more discernible if one considers figure 2, in which the T_g is plotted as a function of the reciprocal number average molecular weight. A straight line can be drawn through the solid points for the monodispersed polystyrenes which differs somewhat from that drawn by previous workers [2]. These lines can be represented by the equation

$$T_g = T_{g\infty} - \frac{A}{\bar{M}_n}, \qquad (1)$$

where $T_{g\infty}$ is the saturation value of T_g at higher molecular weight and the slope is A. For the mono-
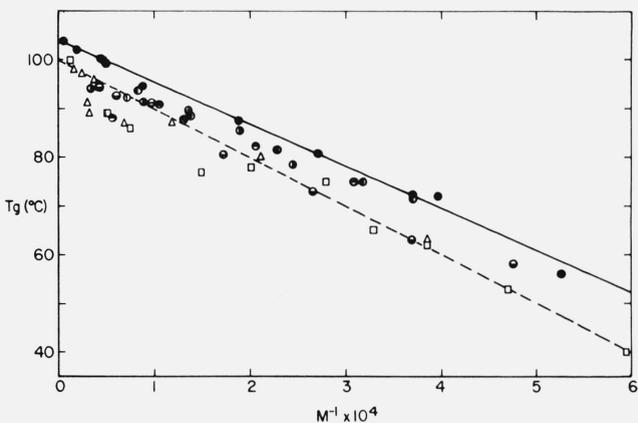

FIGURE 2. Glass transition temperature as a function of the reciprocal of number average molecular weight.

The solid line refers to the monodisperse polystyrene and the dashed line is the Fox-Flory line. Same symbols as in figure 1.

dispersed polystyrenes, $A = 0.84 \times 10^{-5}$ (see the full line in fig. 2) approximately the same as the value, 1×10^{-5}, found by Fox and Flory. The intercepts show a more definitive difference. Since the mixtures give values more in line with that for the dashed line, this difference is presumptively a result of differences in the molecular weight distributions.

Bueche [9] has derived eq 1 using the free volume concept, in which the constant A has the following meaning:

$$A = \frac{2\rho N_{av}\theta}{\Delta \alpha}, \qquad (2)$$

where ρ is the density of the polymer, N_{av} is the

Avogadro number, 2θ is the excess free volume at T_g contributed by the chain ends, and $\Delta \alpha$ is the difference in the thermal expansion coefficient in the liquid or glassy state and the glassy state ($\Delta \alpha = \alpha_1 - \alpha_g$).

The influence of the composition of the binary mixture on the glass transition temperature is shown in figure 3 in which the T_g is plotted as a function of weight percent of Polymer II.

The behavior of the binary mixtures was also examined using the Gordon-Taylor relation [10] derived for copolymers. This equation normally relates the glass transition temperature of homopolymers (T_{g_1} and T_{g_2}) and the weight fraction (w_1 and w_2). It can be expressed in two ways, as proposed by Wood [11]. By choosing $T_{g_1} > T_{g_2}$, the Gordon-Taylor equation may be written as
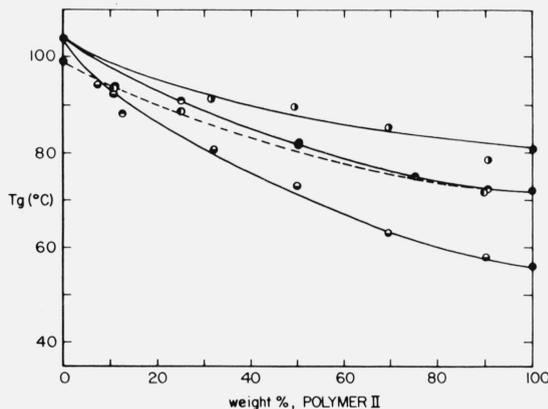

FIGURE 3. Glass transition temperature of binary mixtures of polystyrenes as a function of composition expressed as weight percent.

Same symbols as in figure 1.

$$T_g = T_{g_2} + k(T_{g_1} - T_g)\frac{w_1}{1 - w_1}, \qquad (3)$$

or as

$$T_g = T_{g_1} - \frac{1}{k}(T_g - T_{g_2})\frac{1 - w_1}{w_1}. \qquad (4)$$

It is seen that T_g varies nonlinearly with weight percent.

The constant k is defined by Gordon and Taylor as $k = (\Delta\alpha)_1/(\Delta\alpha)_2 = (\alpha_l - \alpha_g)_1/(\alpha_i - \alpha_g)_2$, where α_l, α_g are the coefficients of thermal expansion of the homopolymer in the liquid and glassy state. On the other hand, Wood [11] regarded k as a characteristic parameter for the particular system and not necessarily related to the individual properties of the particular homopolymers. Furthermore, Wood [11], on the basis of contrary experimental evidence, questioned the two chief assumptions of Gordon and Taylor, that the partial specific volumes were additive and that the thermal expansivities of the homopolymers remained the same in the copolymers as in the homopolymers themselves. In the equation then a formulation of k as a function of the ratio of $\Delta\alpha_1$ to $\Delta\alpha_2$ implies that the mixture behaves as an ideal solution, that is, partial volumes are additive [10] and that the co-

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$\bar{M}_n(1)/\bar{M}_n(2)$	k (eq 3)	k (eq 4)	k (average)	k (calculated)	
				(eq 5)	(eqs 6 and 7)
(170,000)/(1,900)	0.51	0.57	0.53	0.87	0.94
(170,000)/(2,450)	.53	.57	.55	.91	.96
(20,000)/(2,450)	.58	.49	.53	.92	.96

efficients of expansion for the two components are also assumed to be the same in the mixture as in the homopolymers and are not functions of temperature.

Our experimental T_g's for mixtures (see legend fig. 1) gave quite linear fits to plots suggested by eqs (3) and (4), in which T_g is plotted against $(T_{g1}-T_g)w/(1-w_1)$ or against $(T_g - T_{g_2})(1 - w_2)/w_2$, respectively. However, the values of T_g for the monodispersed samples, determined from the intercepts, were several degrees lower than the values determined experimentally. A similar observation was reported [14] in a study of a system composed of compatible mixtures of poly-ϵ-caprolactone and polyvinyl chloride.

The values obtained for k from the above-mentioned plots are shown in table 2, together with the values calculated using eq (5), a general equation, derived by Simha and Boyer [12] and from eqs (6) and (7). [13]

$$\Delta\alpha \cdot T_g = \text{constant} = 0.113 \qquad (5)$$

$$\alpha_g = 1.84 \times 10^{-4} + 224 \times 10^{-4}/\bar{M}_n \qquad (6)$$

$$\alpha_l = 5.5 \times 10^{-4} + 643 \times 10^{-4}/\bar{M}_n. \qquad (7)$$

Equations (6) and (7), experimentally determined equations, give the thermal expansion coefficients of the glassy and liquid polystyrenes as a function of number average molecular weight. The numerical constants are from references 5 (eq (6)) and 13 (eq (7)).

As can be seen in table 2, the predicted values of k are always greater than the experimental values. This indicates a failure of Gordon-Taylor additivity assumptions. For copolymers, Wood has pointed out similar results which indicate a deviation from the assumptions in the derivations.

4. Discussion

By assuming only that both mono- and polydisperse polystyrenes obey exactly eq (1), we can derive the Gordon-Taylor (GT) equation with $k = 1$ in the form:

$$T_g = T_{g_1} + w_2 (T_{g_2} - T_{g_1}). \qquad (8)$$

Since the data on the binary mixtures shown in figure 2 and in figure 3 deviate from eq (1) in figure 2 and from eq (8) in figure 3, it is evident that while eq (1) may apply to the monodispersed samples, it fails or is only approximate for polydispersed mixtures. The values of the constants, $T_{g\infty}$ and A, in eq (1) are, of course, different for the polydispersed system and with the different values of the constants it follows that a somewhat different eq (1) applies to the polydispersed polymers.

In figure 4 we present again the experimental points for the binary mixture $\bar{M}_{n_1}$ (170,000)/$\bar{M}_{n_2}$ (1,900). It is seen that the points agree with minor scatter to the Gordon-Taylor relation with $k = 0.45$ and not when $k = 1.0$ or 0.9. Here the value of $k = 0.45$ was chosen on the best fit to the points in the mid composition range and is not based on plots suggested by eqs (3) and (4) that produced the values shown in table 2 and that failed to extrapolate to the exact value of the T_g for the monodispersed polymers.
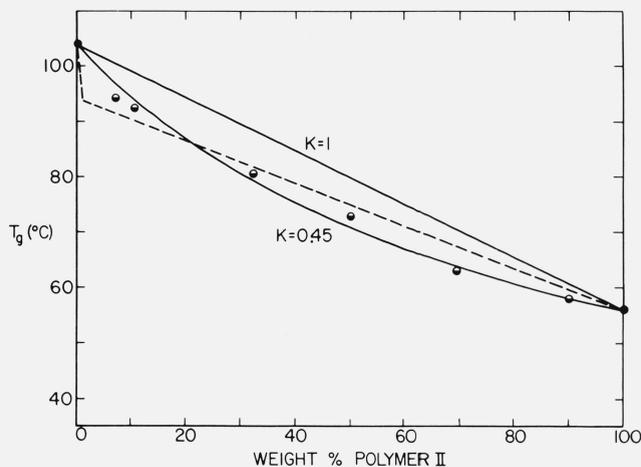

FIGURE 4. *Glass transition temperature of a binary mixture of monodisperse polystyrenes as a function of composition expressed as weight percent.*

The number average molecular weights of the two polymers are 170,000 and 1,900. Full lines Gordon-Taylor relation with $k = 1$ and 0.45. Dashed line entropy of mixing theoretical form.

One possible explanation of the observed data is on the basis of the entropy of mixing and the Gibbs-DiMarzio theory [15]. The entropy of mixing would operate to lower the glass transition and a maximum effect would occur at the composition of 0.5 mol or number fraction, which would correspond for the experimental system in figure 4 of 0.0111 weight fraction of polymer II (w_2). The dashed line then is the entropy of mixing effect normalized to the experimental points. It is seen that, while there may be some tendency towards the behavior of the dashed curve, the experi-

mental points are better fitted by the GT equation ($k = 0.45$). Theoretical calculation of the effect of the entropy of mixing involves knowledge of the exact number and distribution of the components in both substances mixed. A simple two-component mixing gives an entropy increase of $2 \ln 0.5 = 1.4$ cal/mol degree, in this case, mole of monomer units. This gives an estimated depression of the glass temperature of 0.32 °C at $w_2 = 0.0111$. Other entropic mixing effects may produce one or so degrees depression but it appears that the observed data are not readily accounted for in this way.

The relatively good fit to the GT eq ($k = 0.45$) suggests that an effect characteristic of the binary system is operating. At the moment several possible explanations of the observed results remain unexplored: a kinetic one, the observed T_g may approach more closely the Gibbs-DiMarzio T_2 [15] for a mixture than for a monodispersed material, or a thermodynamic one where a somewhat greater degree of order exists in the monodispersed polymers so that mixing produces a much greater increase in entropy. It should be added that Boyer's recent alternative treatment [16] likewise gives a satisfactory fit to the data.

5. Summary

Monodispersed polystyrene prepared anionically gives measurably higher glass transitions than fractionated or whole polymers prepared by free radical techniques. These monodispersed polystyrene data give an excellent correlation to the equation

$$T_g = T_{g\infty} - (8.4 \times 10^{-6})/\bar{M}_n.$$

Since mixtures of the monodispersed polymers also show lower values, the above difference is evidently an effect of distribution, that is, in binary mixtures low moleculas weight has a small plasticizing action on high molecular polymers of the same basic structure. Binary mixtures of low and high molecular weight monodispersed polystyrenes follow a Gordon-Taylor type relation having $k \cong 0.5$ which is lower than the value 0.9 estimated from either the Simha-Boyer equation or the Fox-Loshaek equation.

High and low molecular weight binary mixtures show T_g values which are smooth but nonlinear functions of the weight fraction. Their T_g's do not have the same proportionality with $1/\bar{M}_n$ as the monodispersed polystyrenes. Entropy of mixing does not appear to account for the lower T_g's of the binary mixtures.

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6. References

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