

The Glass Temperature and Related Properties of Polystyrene. Influence of Molecular Weight

Experimental results on the molecular weight dependence of the glass temperature (T_g), bulk viscosity η , viscosity-temperature coefficient (E_T), and specific volume (v) for fractionated polystyrenes were presented in previous publications.¹ Subsequently, it was shown that the relationship used to calculate the molecular weights (M) of the fractions from their intrinsic viscosities in benzene at 30° was in error for values of $M < 30,000$.^{2,3} The data are therefore re-examined here and the previously reported empirical equations relating the above properties to molecular weight and temperature are re-expressed in terms of a revised molecular weight scale. The results of more recent investigations are also discussed.

Molecular weights of the polystyrene fractions were calculated previously¹ from their intrinsic viscosities, $[\eta]$, at 30° in freshly distilled benzene, using the relationship of Ewart:⁴

$$\log \bar{M}_v = (\log [\eta] + 4.013)/0.74 \quad (M > 3 \times 10^4) \quad (1)$$

which was established from measurements extending over the molecular weight range of 5×10^4 to 8×10^5 . Results in substantial conformity with this equation have been obtained more recently^{3,5} for molecular weights between 3×10^4 and 1×10^6 . Pepper² has also reported cryoscopic molecular weights and intrinsic viscosities in benzene at 25° for polystyrene fractions of molecular weight between 800 and 11,000. His results correspond to the equation:^{2,3}

$$\log \bar{M}_v = (\log [\eta] + 3.380)/0.60 \quad (M < 3 \times 10^4) \quad (2)$$

This equation has now been used to recalculate all molecular weights below 30,000.

In Table I we have listed for twelve polystyrene fractions the intrinsic

TABLE I
PHYSICAL DATA FOR POLYSTYRENE FRACTIONS

Polymer fractions	$[\eta]$	M	v at 140°C.*	t_g , °C.*	η at 217°C., poises*
A-2	0.430	85,000	0.990	100	2000
B-1	0.156	19,300	0.992	89	51.3
B-2	0.124	13,300	0.993	86	26.7
B-3	0.103	9,660	—	—	15.7
B-4	0.082	6,650	0.996	77	9.13
B-5	0.0689	4,980	0.998	78	5.29
B-6	0.0566	3,590	1.002	75	2.60
C-6	0.0513	3,041	1.003	65	1.36
B-7	0.0467	2,600	1.002	62	1.55
C-7	0.0409	2,085	1.005	53	0.59
B-8	0.0396	1,977	—	—	0.80
C-8	0.035	1,675	1.006	40	0.32

* The values tabulated here were taken from Tables II and III of reference (1b). In a few cases they represent the average of several determinations.

viscosities determined in the previous investigation^{1b} together with the revised molecular weight values calculated according to equation (1) for $M > 3 \times 10^4$ and equation (2) for $M < 3 \times 10^4$. The previously published values of v_{140}° , t_g , and η_{217}° are also listed. When these data and the viscosity-temperature data^{1b} are treated by methods outlined previously,^{1b} the empirical equations given in Table II are obtained.

TABLE II
TABLE OF REVISED EQUATIONS*

Equation no.	New empirical equations with revised mol. wt. scale	Ref. to previous equations
I	$v_{217} = 1.040 + 46/M$	Eq. (1), ref. (1b)
II	$v = 0.913 + 5.5 \times 10^{-4}t + 33/M \quad (160 \geq t \geq t_g)$	Eq. (3), ref. (1b)
III	$T_g = 373 - 1.0 \times 10^5/M$	Eq. (2), ref. (1b)
IV	$\log (\eta_T/\eta_{217}) = 2.68 \times 10^{16}(1/T^6 - 1/490^6)e^{-1330/M}$	Eq. (7), ref. (1b)
V	$E_T = (7.4 \times 10^{17}/T^5)e^{-1330/M}$	Eq. (8), ref. (1b)
VI†	$\log \eta_{217} = 3.4 \log \bar{M}_w - 13.40 \quad (\bar{M}_w \geq 38,000)$	Eq. (12), ref. (1c)†
VII	$\log \eta_{217} \cong 1.65 \log M - 5.38 \quad (38,000 \geq \bar{M}_n \geq 4000)$	Eq. (13), ref. (1c)

* In these equations and throughout this communication we use a small letter t and a large T to indicate the temperature in °C. and °K., respectively.

† This equation is unchanged, *i.e.*, is exactly the same as equation (12) in reference (1c)

The equations in Table II are identical with the corresponding equations presented earlier, excepting that the numerical values of some of the constants have been changed. The main conclusions of the previous papers are therefore found to be unaltered. Thus the specific volume at a fixed temperature and the glass temperature change linearly with $1/M$, while the quantity $\log (\eta_T/\eta_{217})$ may be expressed as the product of a function dependent only on the absolute temperature (on T^{-6}) and a function which decreases exponentially with $1/M$. As before it can be concluded that the glass temperature represents a state of "iso-free volume" rather than an isoviscous state, and that the viscosity-temperature coefficient at the glass temperature is independent of molecular weight. On the basis of these two concepts it can be predicted from equations (II) and (V), respectively, by methods described previously^{1b} that:

$$T_g = T_{g, \infty} - 1.1 \times 10^5/M \quad (\text{iso-free volume concept}) \quad (\text{VIII})$$

$$\text{and:} \quad T_g = 373 - 1.0 \times 10^5/M \quad (\text{constant } E_T \text{ at } T_g) \quad (\text{IX})$$

These equations are in good agreement with equation (III).

It can also be shown that the use of revised molecular weight values does

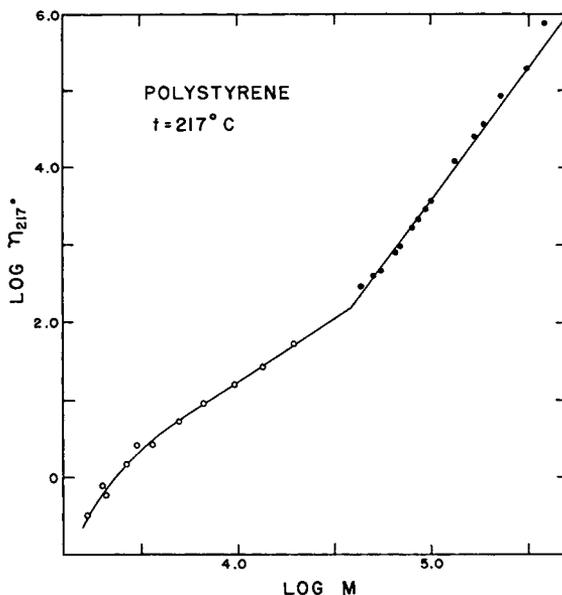


Fig. 1. $\log \eta_{217}$ vs. $\log M$ for polystyrene fractions. This plot is similar to Figure 10 in reference (1c), excepting that the molecular weight values below 30,000 (open circles) have been recalculated according to equation (2). The straight lines representing the data for $M > 4000$ correspond to equations VI and VII.

not alter the previous conclusion that for a heterogeneous polystyrene the specific volume, transition temperature, and the viscosity-temperature coefficient depend explicitly on the number-average molecular weight of the polymer, in accordance with equations (I), (II), (III), (IV), and (V).

The revised plot of $\log \eta_{217}$ vs. $\log M$ for polystyrene at 217° is shown in Figure 1. The results at high molecular weight ($M > 4000$) may be represented by two straight lines which intersect at $M \cong 38,000$. According to Bueche,⁶ this behavior is to be expected if in the flow process the effects of the coupling of the motions of long chain molecules by entanglements are considered. Thus he predicts an abrupt decrease in the slope of the log-log plot from a high value (whose magnitude depends on the value of a slippage factor) for long chains to a low value (1.0) for chains that are so short that entanglements do not lead to effective couplings between chains. The increase in slope of this plot with decreasing molecular weight for $M < 4000$ occurs in the region where the specific volume and viscosity-temperature coefficient begin to change appreciably with decreasing M , and no doubt represents the superposition of the additional effect of the variation in the liquid structure (or free volume) with decreasing M .^{1b,1c,6} In accordance with Bueche's suggestion,⁶ it is probable that this latter effect is not inconsequential even at somewhat higher molecular weights ($M > 4000$), which may be the reason that the observed slope (1.65) in this region is higher than the value of 1.0 predicted by theory.⁶

It is believed that, even if subsequent investigations should lead to a more precise intrinsic viscosity-molecular weight relationship supplanting equation (2), or even equation (1), the only result would be a relatively minor change in the values of the numerical coefficients in the equations in Table II. In that case, the new constants based on the altered molecular weight scale could be calculated from the intrinsic viscosities and other data given in Table I for twelve polystyrene fractions.

We shall now compare the results of the earlier study of the properties of polystyrene fractions with those obtained in more recent investigations.^{7,10,12}

Confirmation of the values of 5.5×10^{-4} and 2.5×10^{-4} reported^{1b} for the v - T coefficients for high molecular weight polystyrene above and below T_g , respectively, has been obtained in the precise measurements of Gordon and Macnab,⁷ who found the corresponding values of (5.60 ± 0.07) and $(2.27 \pm 0.01) \times 10^{-4}$, and by Ueberreiter and Kanig,⁸ who found 5.4×10^{-4} for the first coefficient. The latter authors report a low value of 1.8×10^{-4} for the second coefficient, however. From measurements extending over a wide molecular weight range ($M > 200$), they also report a linear increase of these coefficients with increasing $1/M$. Such a dependence can be justified on theoretical grounds,^{8,9} at least for the v - T coefficient above T_g . This molecular weight dependence was not detected in our earlier investigation^{1b} since for the high molecular weight polystyrenes studied ($M > 1600$) the expected variations are less than the precision ($\pm 10\%$) of the determination.

Recent investigations on plasticized polystyrene¹⁰ show that a linear dependence of T_g on the volume fraction of diluent and a linear dependence of the viscosity-temperature coefficient on an exponential term in this volume fraction are approximations which hold only at low concentrations of diluent, the rate of decrease of the values of these properties with increasing diluent concentration being smaller at higher diluent concentrations. This suggests that the analogous dependence of these properties on $1/M$ for polystyrene fractions given in equations (III) and (IV) also represent approximations which will fail at low values of M . Ueberreiter and Kanig⁸ have reported such curvature in the $T_g - 1/M$ relationship for polystyrene fractions. According to their results, deviations from the linear $T_g - 1/M$ relation observed for high molecular weight polystyrenes became marked only for molecular weights below 1000. They represent their data on polystyrene fractions ranging in M from 200 to over 90,000 by an equation of the form:

$$1/T_g = 1/T_{g, \infty} + \text{constant}/M \quad (3)$$

It can be shown⁹ that at high M (>1000) equation (III) represents an approximation to equation (3), and that both equations for the dependence of T_g on M can be predicted simply from suitable $v - T$ data for the monomer (styrene) and for the infinite molecular weight linear polymer.

In an earlier paper we defined the free volume, v_f , as the difference between the specific volume, v , and the occupied volume, $v_0 = A_0 + (dv/dt)_s t$, where t is the temperature in $^{\circ}\text{C}$., $(dv/dt)_s$ is the $v - T$ coefficient below T_g ,

and A_0 is the *hypothetical* volume of the solid (glass) at 0°C. Unfortunately, the use of the term "hypothetical volume" for A_0 is ambiguous and misleading. Thus we meant A_0 to represent the "occupied volume" or "net volume" at 0°C. occupied by the vibrating polymer chains rather than the actual specific volume of the glass at this temperature. Recently Ueberreiter and Kanig,⁸ on the basis of the latter interpretation, concluded that our definition requires that v_f be zero at the glass temperature for all kinds of glasses. If we employ the definition of A_0 that was originally intended, albeit not clearly stated, it follows for temperatures at and below T_g that v_0 may be less than v , and v_f need not be zero.

On the other hand, it is difficult to visualize the physical significance of the "free torsion oscillation volume" as defined by Ueberreiter and Kanig,⁸ since their definition requires that its extrapolated value be negative for the equilibrium (liquid) polymer below T_g . Other recent attempts to define the free volume of a liquid polymer appear elsewhere.^{9,11} In one of these⁹ it is shown that the conclusion that the free volume is constant at T_g represents an approximation which is valid only for sufficiently high molecular weights, *i.e.*, for polystyrene fractions of $M > 1000$.

In confirmation of our previous prediction^{1b} that the viscosity-temperature coefficient, E_T , for a glass-forming polymer should go through a maximum at T_g and fall to a low value at lower temperatures, McLoughlin and Tobolsky¹² have found the temperature coefficient of stress relaxation for polymethyl methacrylate goes through a maximum at 111°C., which they state is "in the middle of the transition region."

References

1. T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **70**, 2384 (1948); (b) *J. Appl. Phys.*, **21**, 581 (1950); (c) *J. Phys. Chem.*, **55**, 221 (1951).
2. D. C. Pepper, *Sci. Proc. Roy. Dublin Soc.*, **25**, 239 (1951).
3. W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, **11**, 37 (1953).
4. R. H. Ewart, Abstracts of papers presented at the 111th Meeting of the American Chemical Society, Atlantic City, New Jersey, April 14-18, 1947.
5. C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 1107 (1950).
6. F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).
7. M. Gordon and I. A. Macnab, *Trans. Faraday Soc.*, **49**, 31 (1953).
8. K. Ueberreiter and G. Kanig, *J. Colloid. Sci.*, **7**, 569 (1952).
9. T. G. Fox and S. Loshaek, *J. Polymer Sci.*, in press.
10. T. G. Fox, A. R. Schultz, and W. B. Schultz, to be published. See *Phys. Rev.*, **86**, 652 (1952).
11. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
12. J. R. McLoughlin and A. V. Tobolsky, *J. Colloid. Sci.*, **7**, 555 (1952).

THOMAS G FOX

Rohm and Haas Company
Philadelphia, Pennsylvania

PAUL J. FLORY

Cornell University
Ithaca, New York

Received June 11, 1954