Second-Order Transition Temperatures and Related Properties of Polystyrene. I. Influence of Molecular Weight*

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Dilatometric and viscometric data on fractionated polystyrenes containing diethylbenzene end groups are presented over wide temperature ranges. The second-order transition temperature, viscosity-temperature coefficient, and specific volume all change rapidly with increasing molecular weight toward asymptotic limits which are practically reached at $M \cong 30{,}000$. Empirical expressions are presented relating these properties to molecular weight and temperature. In each case the dependence on molecular weight is expressed as a simple function of $\bar{M}_n^{-1}$. These observations are interpreted and correlated on the basis of the hypothesis that the local configurational order in a liquid polymer is disturbed by the introduction of end groups to a degree that is proportional to their number. The second-order transition does not represent an isoviscous state. The internal local configurational structure appears to be equivalent, and independent of temperature, in all polystyrenes below their second-order transition temperatures.

INTRODUCTION

A LIQUID which may be cooled without incidence of crystallization solidifies to a glass over a fairly narrow temperature range which is characteristic of the substance.[1,2] This is true not only of hydrocarbons, polar and hydrogen-bonding liquids, inorganic glasses, etc., but also of amorphous polymers (including semicrystalline, or semi-amorphous polymers) regardless of their composition or structural pattern (i.e., non-linear network polymers as well as linear ones). The temperature about which this transformation takes place is usually referred to as the "glass" temperature T_g, or the "second-order transition temperature"; for polymers it is often designated as the "brittle temperature," inasmuch as the polymer changes from a highly viscous liquid, or rubbery solid, to a brittle substance which will not tolerate appreciable deformation without fracture at all lower temperatures.

It is well established that this so-called "second-order transition" is not an equilibrium transition in the thermodynamic sense, but that it originates from kinetic limitations on the rates of the internal adjustments occasioned by changes in temperature (or by mechanical stress). At temperatures below T_g, the internal mobility is insufficient for maintenance of the equilibrium internal configuration and, hence, of the equilibrium volume. No discontinuity is observed in the first-order properties, volume and internal energy, but the second-order properties, thermal expansion coefficient and heat capacity, exhibit abrupt changes by means of which the "transition" is easily located.

The macroscopic viscosity often is employed as an inverse measure of internal mobility in monomeric substances, and it has been pointed out that the second-order transition generally occurs at a viscosity of about 10^{12} poises. The macroscopic viscosity of a polymer, however, depends not only on the mobility of each segment but also on an intersegment cooperation factor which increases rapidly with molecular weight.[3,4] If the second-order transition in polymers depends only on the local segment mobility and not on the interactions between all of the segments of a given molecule, then the magnitude of the macroscopic viscosity should not afford a universal measure of the approach to the second order transition; viscosities well above 10^{12} poises at T_g should be expected if the molecular weight is large. On the basis of the same postulate, the second-order transition might be expected to be independent of the molecular weight of the polymer except insofar as it affects the liquid configuration of the polymer.

Considerations such as these point to the desirability of securing reliable information on the dependence of the volume (as an index of liquid configuration) and of the viscosity of polymers on their molecular weights and temperatures, and on the dependence of T_g on molecular weight. Asymptotic increases of T_g's for polystyrenes,[5] polyisobutylenes,[6] and poly-(ethylacrylates)[7] with their "molecular weights" have been indicated by previous work on polymers of unknown degrees of heterogeneity. In a recent paper we have reported a qualitatively similar asymptotic increase in the viscosity-temperature coefficient with the molecular weights M of polystyrene fractions.[4] The rapid increase of both T_g and the viscosity-temperature coefficient toward their limiting values with increase in M contrasts sharply with the sustained increase in viscosity with increasing M even to the highest values investigated.[4]

[1] W. Kauzmann, Chem. Rev. **43**, 219 (1948).
[2] R. F. Boyer and R. S. Spencer, *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II, p. 1.
[3] P. J. Flory, J. Am. Chem. Soc. **62**, 1057 (1940).
[4] T. G. Fox, Jr. and P. J. Flory, J. Am. Chem. Soc. **70**, 2384 (1948).
[5] E. Jenckel and K. Ueberreiter, Zeits. f. physik. Chemie **A182**, 361 (1938).
[6] K. Ueberreiter, Zeits. f. physik. Chemie **B45**, 25 (1940).
[7] R. H. Wiley and G. M. Brauer, J. Polymer Sci. **3**, 647 (1948).

TABLE I. The polystyrenes used for fractionation.

Polymer	Molar ratio styrene/diethylbenzene	Reaction temperature	Reaction time, hours	Extent of reaction (percent)	$\bar{M}_v$	Initial conc. for fractionation g/100 ml
A	1	150°	2	27	120,000	2.0
B	0.093	150°	9	72	9560	2.0
C	0.051	150°	17	90	4870	1.5

In the present investigation the specific volumes of polystyrene fractions have been investigated as functions of temperature and molecular weight. Second-order transition temperatures have been secured in the customary fashion from the discontinuity in the thermal expansion coefficient. The results have been correlated with the viscosity-temperature coefficient and its observed dependence on M. Polystyrene has been chosen as a model non-polar polymer for this investigation on account of the convenient location of its second-order transition temperature, the simplicity of its structure, and the comparative abundance of information concerning its various properties.

EXPERIMENTAL

Preparation and Fractionation

Three polymers of styrene of varying molecular weights (Table I) were prepared by thermal polymerization in diethylbenzene *in the absence of added catalyst*. The concentrations of styrene employed and other details pertinent to these polymerizations are summarized in Table I. The polymers were separated by precipitation in an excess of vigorously stirred methanol and were dried in vacuum at 60°.

These polymers were fractionated by the single precipitation technique described in a previous paper.[4] The initial concentrations of the solutions employed are shown in the last column of Table I. Each of the two
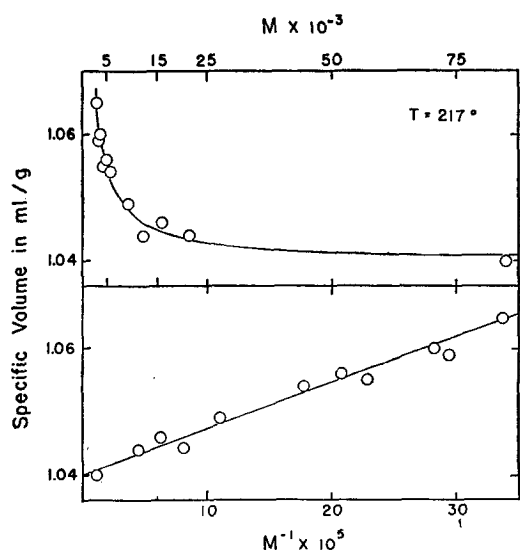
polymers of lower molecular weight was separated into nine fractions by fractionating from acetone solution at 30° using as the precipitant a mixture consisting of equal volumes of water and methanol. Each individual fraction employed here represented from 5 to 17 percent of the whole polymer (Table II). The polystyrene of higher molecular weight (120,000) was separated into three fractions employing methyl ethyl ketone-methyl alcohol as the solvent-precipitant combination. Only the middle fraction, $M = 85,000$, representing 38 percent of the whole polymer was retained for subsequent experiments.

Molecular Weight Determination

Molecular weights of the polystyrene fractions have been calculated from their intrinsic viscosities, $[\eta]$, in freshly distilled benzene, using the relationship of Ewart[8]

$$\log \bar{M}_v = (\log[\eta] + 4.013)/0.74,$$

where $\bar{M}_v$ is the viscosity average molecular weight. The solution viscosities were measured at $30.00 \pm 0.01°$ using a Ubbelohde No. 1 viscometer the calibration of which included the kinetic energy term.[9] In each case the intrinsic viscosity has been calculated from the relative viscosity, η_r, of a single solution by means of the viscosity-concentration relationship reported by Tingey.[10]

$$\ln \eta_r / c = [\eta] - 0.125[\eta]^2 c,$$

where c is expressed in g/100 ml.

Molecular weights determined in this way are generally reproducible to ± 2 percent.

Determination of Specific Volumes

The pycnometers and the technique employed were similar to those described in a previous publication.[3] Densities were determined at 217° by filling a weighed pipette of known volume (from 1 to 2 ml) with the liquid polymer at this temperature, and subsequently weighing at room temperature. The reproducibility of the data was generally within ± 0.1 percent.

Dilatometric Measurements

The dilatometers and techniques employed resemble those described by Bekkedahl.[11] A weighed quantity (generally about two grams) of bubble-free polymer, previously dried under vacuum at 217°, was placed in the bulb of a glass dilatometer and the bulb was sealed, with precautions to avoid heating the polymer. Mercury was introduced under vacuum (0.005 mm Hg).

FIG. 1. Specific volume at 217° for polystyrene fractions *vs.* molecular weight (upper curve) and *vs.* M^{-1} (lower curve).

[8] R. H. Ewart, paper presented at the Atlantic City Meeting of the American Chemical Society (April 14, 1947).
[9] The calibration method outlined in ASTM Designation D445–39T was employed.
[10] H. C. Tingey, unpublished data referred to by R. H. Ewart, *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II, p. 210.
[11] N. Bekkedahl, J. Research Nat. Bur. Stand. **43**, 145 (1949).

TABLE II. Dilatometric data on polystyrene fractions.

Polymer fraction	Percent of un-fractionated polymer	M	T_g	v_{140} ml/g	v_g ml/g Obs.	v_g ml/g Calc. by Eq. (4)	$(dv/dT)_1$	(dv/dT), ml/g/° ×10⁴ $(dv/dT)_2$	$(dv/dT)_3$
$A2$	38	85000	100°	0.989	0.969	0.968	—	4.9	2.3
$A2$	38	85000	100	0.990	0.969	0.968	7.2	5.1	2.0
$A2$	38	85000	98	0.989	0.970	0.968	—	4.6	2.2
$A2$	38	85000	99	0.991	0.970	0.968	7.1	5.0	2.4
$B1$	10.0	22000	89	0.992	0.963	0.965	—	5.7	2.7
$B2$	15.0	16000	86	0.993	0.962	0.964	—	5.7	2.3
$B4$	16.7	9150	77	0.996	0.960	0.962	—	5.6	2.4
$B5$	12.5	7200	78	0.998	0.964	0.962	7.0	5.5	—
$B6$	10.0	5600	73	1.003	0.963	0.960	—	6.1	2.6
$B6$	10.0	5600	75	1.000	0.967	0.960	—	5.1	2.7
$B6$	10.0	5600	76	1.002	0.966	0.960	7.3	5.6	—
$C6$	16.7	4810	64	1.003	0.962	0.959	—	5.3	2.6
$C6$	16.7	4810	66	1.003	0.962	0.959	7.6	5.5	—
$B7$	5.4	4300	62	1.003	0.956	0.958	—	6.0	2.4
$B7$	5.4	4300	63	1.003	0.957	0.958	—	5.8	2.5
$B7$	5.4	4300	62	1.002	0.956	0.958	7.6	6.0	—
$B7$	5.4	4300	63	1.003	0.957	0.958	—	5.9	2.8
$C7$	12.3	3540	53	1.005	0.957	0.956	—	5.5	2.6
$C8$	10.5	2970	40	1.007	0.955	0.953	—	5.3	2.1
$C8$	10.5	2970	—	1.005	0.953	0.953	8.4	5.3	—
$C8$	10.5	2970	—	1.006	0.953	0.953	8.0	5.3	—
$C8$	10.5	2970	—	1.007	0.952	0.953	—	5.5	—

The amount of mercury in the dilatometer was determined by weighing. The volume of polymer plus mercury was calculated at the calibration temperature, 217°, where the density of the polymer was known from the absolute specific volume measurements. The position of the mercury in the capillary tube was noted at 217° and then at lower temperatures usually at intervals of 10°. The measurements were made in a constant temperature bath regulated within ±0.1° and the relative densities generally were accurate to ±0.03 percent. At all temperatures except those in the vicinity of T_g, volume equilibrium was quickly established and in trial experiments no further change could be observed over a period of 24 hr. Hence before recording the volume the sample was held for a period of 10 to 60 min. at each temperature 10° or more above T_g and from 6 to 12 hr. at all lower temperatures.

Melt Viscosities

Melt viscosities in the range of 10 to 10⁶ poises were determined by observing the rate of flow into uniform bore capillary viscometers under a measured pressure differential. The calibration and use of these viscometers have been described.[4] For measurement of viscosities from 0.1 to 10 poises, pipette type viscometers were employed. These consisted in each case of a Pyrex capillary tube of 1-mm bore with a small bulb (capacity 0.2 to 1.0 ml) about 12 to 15 cm from the lower end of the capillary. Absolute viscosities in poises were calculated in this case from $\eta = ktp$, where t is the measured time required to fill the viscometer bulb under a predetermined pressure differential p, and k is a constant determined from the tp product for an oil the viscosity of which was accurately determined with the capillary viscometers mentioned above. Temperature control was provided by means of vapor baths

(±0.3°) above 100° and by thermostated oil baths (±0.1°) at lower temperatures. The viscosity values usually were reproducible to ±3 percent.

High Temperature Stability

It was reported previously[4] that phenyl β-naphthylamine greatly retards the degradation of polystyrene at high temperatures, and that 0.5 percent of this substance assures adequate stability to permit measurement of viscosities up to 217°. The experiments on which this conclusion was based were conducted on polymers of high molecular weight, the assumption being made that the lower polymers would be at least
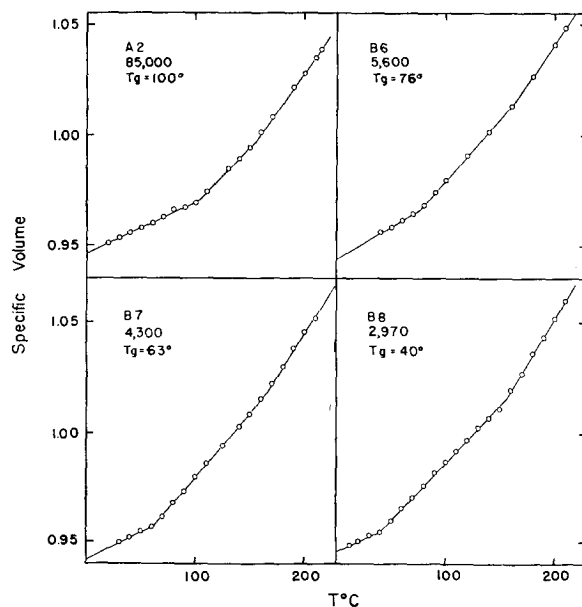

FIG. 2. Specific volume-temperature curves for polystyrene fractions.

TABLE III. Viscosity-temperature data for polystyrene fractions.

| Polymer fraction | M | η_{217}, poises | $\log(\eta_T/\eta_{217})$ at the indicated temperature (°C) | | | | | | | | | | | |
			190	160	140	130	120	110	100	95	90	85	80	75
A2	85000	2000		2.0										
B1	21500	51.3	0.70	1.94	3.36	4.10								
B2	16000	26.7	0.74	1.85	3.21	3.89								
B3	12300	15.7												
B4	9100	9.13	0.54	1.61	2.80[a]	3.45	4.31							
B5	7230	5.29												
B6	5600	2.60	0.50	1.44		2.99		4.58	5.72					
C6	4810	1.36	0.45	1.25	2.17			4.03	4.95	5.52				
B7	4300	1.55	0.38	1.26		2.53		4.06	4.96					
C7	3540	0.59	0.47	1.11	1.89			3.54	4.29		5.24	5.83		
B8	3400	0.80	0.42	1.01		2.16			4.19		5.25			
C8	2970	0.32	0.41	0.93	1.58			3.07	3.58		4.38		5.33	5.92

[a] Interpolated.

as stable. Subsequent experiments revealed, however, that phenyl β-naphthylamine fails to inhibit degradative reactions in the lower polystyrenes included in the previous investigation. These low polymers were prepared with the aid of benzoyl peroxide initiation, and a connection between the observed instability and the presence of benzoate end groups in the polystyrene molecules[12] was indicated by the sublimation of a quantity of pure benzoic acid when these polymers were heated at 217° under reduced pressure. The low molecular weight polystyrenes prepared as described above *without the use of catalyst* (Table I) were relatively stable. When heated for an hour at 217° in an inert atmosphere (pure nitrogen) they discolored only slightly and exhibited no change in intrinsic viscosity even in the absence of inhibitor.

RESULTS

Specific Volumes at 217° *vs.* Molecular Weight for Polystyrene Fractions

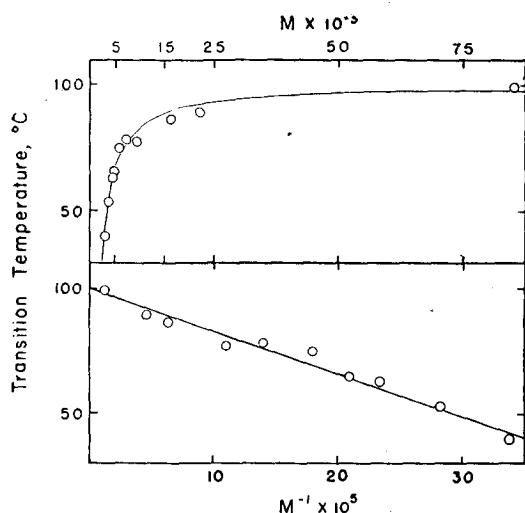The specific volumes of eleven polystyrene fractions ranging in molecular weight from 2970 to 85,000 were

FIG. 3. Transition temperatures of polystyrene fractions *vs.* molecular weight (upper curve) and *vs.* M^{-1} (lower curve).

[12] P. D. Bartlett and S. G. Cohen, J. Am. Chem. Soc. 65, 543 (1943).

determined at 217° by the constant volume pipette method. The specific volume at 217°, v_{217}, decreases with increasing molecular weight in the lower range and is relatively constant for molecular weights above 25,000 (upper curve of Fig. 1). When the specific volume is plotted against $1/M$ as in the lower portion of Fig. 1, the data are well represented by the straight line, the equation of which is

$$v_{217} = 1.040 + 72/M. \qquad (1)$$

The units employed for the specific volume throughout this paper are ml/g.

Dilatometric Data on Polystyrene Fractions

Specific volumes were measured by the dilatometric method as a function of temperature on ten polystyrene fractions ranging from 2970 to 85,000 in molecular weight. As illustrated in Fig. 2, the volume-temperature curve up to 160° for each polymer may be represented by two intersecting straight lines. The temperature at which these lines intersect is taken as the second-order transition temperature, T_g. In the vicinity of 160°, the volume-temperature coefficient (i.e., the slope) exhibits a further increase with increasing temperature. The results in this range may again be approximated, for simplicity, by two intersecting straight lines, the temperature at the intersection being about 160°. Hence, each polymer may be characterized by five quantities: T_g, the volume v_g at T_g, and three volume-temperature coefficients, $(dv/dT)_1$ above 160°, $(dv/dT)_2$ between 160° and T_g, and $(dv/dT)_3$ below T_g. The values of these parameters, as obtained from a series of experiments, details for which are not included here, are presented in Table II.

The transition temperature T_g becomes almost independent of molecular weight above 25,000 but decreases rapidly with decreasing molecular weight below this value (upper curve of Fig. 3). In analogy with the dependence of specific volume on M^{-1}, T_g is likewise a linear function of M^{-1}, as is shown in the lower curve of Fig. 3. The equation of the straight line is

$$T_g = 100 - 1.7 \times 10^5/M \qquad (2)$$

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from which the upper curve of Fig. 3 has been calculated.

Although at T_g the abrupt change in slope and the accompanying increase in the time needed for equilibration justify the use of a function with a discontinuity in its slope at this temperature, the use of two straight lines intersecting at 160° to represent the data above T_g is arbitrary. The change of slope at 160° is much smaller than that observed at T_g, and a line with curvature over a wide range about 160° would represent the data equally well.

The specific volume-temperature coefficients $(dv/dT)_2$ and $(dv/dT)_3$ (Table II) appear to be independent of molecular weight within the admittedly large experimental error involved in their evaluation over limited temperature ranges. Average values are 5.5 and 2.5 $\times 10^{-4}$, respectively. The value of $(dv/dT)_1$ is about 7×10^{-4} with an indication of an increase at very low molecular weight.

The portion of the volume-temperature curve between T_g and 160° may be represented by the equation

$$v = A + 5.5 \times 10^{-4} T + 53/M, \quad 160 \geq T \geq T_g, \quad (3)$$

where A is a constant equal to 0.913 and T is in degrees centigrade. Combining this with Eq. (2), we obtain

$$v_g = 0.943 + 2.4 \times 10^{-4} T_g. \quad (4)$$

Values of v_g calculated by this equation agree within experimental error with the observed values, as shown in Table II. In view of the non-dependence of $(dv/dT)_3$ on molecular weight, the specific volume below T_g is given by

$$v = v_g - 2.5 \times 10^{-4} (T_g - T), \quad T \leq T_g$$

and combining this with Eq. (4), ignoring the slight difference between the two temperature coefficients, we obtain

$$v = 0.943 + 2.5 \times 10^{-4} T, \quad T \leq T_g. \quad (5)$$

This equation illustrates the important observation that the specific volume below the transition temperature is substantially independent of the molecular weight.

Volume-Time Relationships

The effect of temperature on the rate of volume relaxation was determined for several polystyrene fractions exhibiting values of T_g from 60 to 100°. In each case a dilatometer containing the polymer (and mercury) was quickly transferred from a bath at temperature T_1, generally about 30° above T_g, to a second constant temperature bath at a lower temperature T_2. The volume was then observed as a function of time. Subsequently the polymer was again heated to T_1 and the procedure repeated at a different temperature T_2. At temperatures T_2 exceeding T_g by about 10°, temperature and volume equilibria appeared to be attained simultaneously. At lower temperatures the vol-

ume was observed to decrease approximately linearly with the logarithm of time, at least for periods up to 24 hr. The magnitude of the rate of volume relaxation, which was too high to measure about 10° above T_g, had a value of about 30 to 50×10^{-4} at T_g, as measured by the slope of the v vs. log$t$ curve (t in min.), and decreased rapidly with decreasing temperature, becoming practically constant at a temperature generally about 10° below T_g. This limiting value of $-dv/d\log t$ was about 8×10^{-4} for all polystyrenes studied.

These results emphasize the fact that although the value of T_g depends on the observation time employed, the marked temperature dependence of the rate of volume relaxation in the vicinity of T_g makes it impossible, using reasonable periods of time, to appreciably alter the value of T_g; it would, for example, be increased by only 5 or 10° on decreasing the time scale of the experiment from 24 hr. to 5 min.

It has been reported[13] that high molecular weight polystyrene previously kept at 20° for two years can be heated from 20 to 140° without undergoing a second-order transition and, further, that the annealing times for this polymer at 20 to 30° below the usual value of T_g are measured in hours or at most in a few days. This reported observation cannot be reconciled with the present results which indicate that the annealing time in this range would consist of many centuries at the least. It is therefore doubtful whether an equilibrium volume-temperature curve for polystyrene has been obtained in the indicated range.[14]
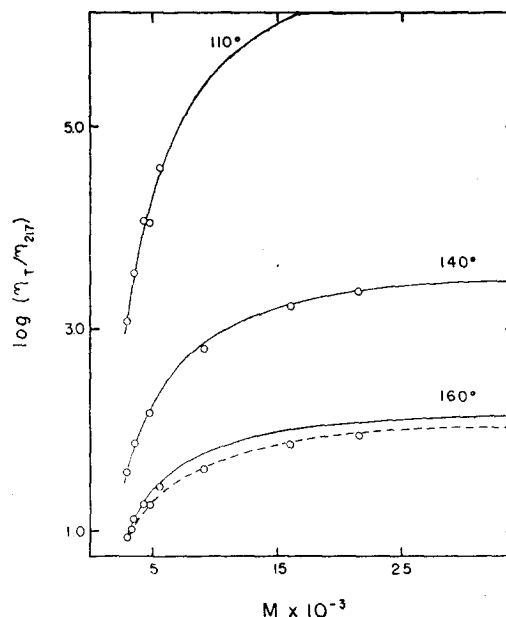

FIG. 4. Log(η_T/η_{217}) vs. M for polystyrene fractions at several temperatures. The solid curves are calculated by Eq. (7). The dotted line is calculated by Eq. (6) using the value of $F(T)$ at 160° obtained from Fig. 5.

[13] R. S. Spencer and R. F. Boyer, J. App. Phys. 17, 398 (1946).
[14] Close scrutiny indicates that the reproducibility of the data of reference 13 is poor. In at least one of the two experiments the

Viscosity-Temperature-Molecular Weight Relationships for Polystyrene Fractions

Viscosities were measured at 217° and at lower temperatures for twelve polystyrene fractions of molecular weight from 2970 to 85,000 (Table III). The viscosities at 217° (η_{217}) for the fractions of higher molecular weight are in good agreement with the viscosities previously reported,[4] while those for the fractions of lower molecular weight are generally about 10 percent higher. This discrepancy almost certainly arises from the susceptibility to decomposition of the lower polystyrenes previously used as pointed out in the Experimental section. The relation between $\log(\eta_T/\eta_{217})$ and $1/T$ (in °K) is non-linear and its dependence on molecular weight is qualitatively similar to that previously reported.[4,15]

The dependence of the viscosity-temperature coefficient on molecular weight is illustrated in Fig. 4 where values of $\log(\eta_T/\eta_{217})$ at 160, 140, and 110° are plotted vs. the molecular weight. At a given temperature T the quantity $\log(\eta_T/\eta_{217})$ increases with increasing molecular weight up to about 25,000 beyond which it is relatively constant. Its dependence on M is similar for different temperatures, which suggests that $\log (\eta_T/\eta_{217})$ may be expressed as the product of two factors, one of which depends only on T and the other only on M. In further support of this supposition, and in analogy with the dependence of the specific volume and the second-order transition temperature on
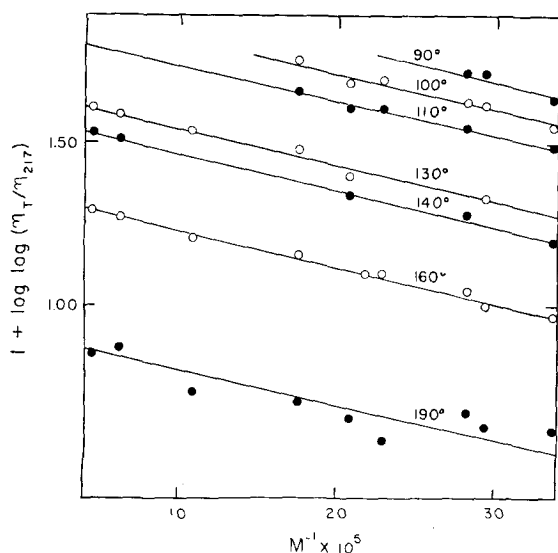

FIG. 5. Log $\log(\eta_T/\eta_{217})$ vs. $1/M$ for polystyrene fractions at various temperatures.

M, plots (Fig. 5) of $\log \log(\eta_T/\eta_{217})$ vs. $1/M$ from 90 to 190° are represented by a set of parallel straight lines. The indicated relationship may be written

$$\log(\eta_T/\eta_{217}) = F(T)e^{-2530/M} \tag{6}$$

where $F(T)$ is a function of the absolute temperature only. This equation offers a satisfactory limiting form at both very low and very high molecular weights.[16]

In the quest for a suitable empirical expression for $F(T)$, the viscosity-temperature function at $M = \infty$, it has been found (Fig. 6) that the values of $F(T)$ obtained from the intercepts at $1/M = 0$ in Fig. 5 are linear functions of $1/T^6$, where T is in °K.[17] Hence the empirical relationship

$$\log(\eta_T/\eta_{217}) = 2.92 \times 10^{16}(1/T^6 - 1/\langle 490 \rangle^6)e^{-2530/M} \tag{7}$$

expresses the dependence of the temperature coefficient of viscosity on both temperature and molecular weight. Differentiating we obtain the expression for E_T, a quantity which we have called the "apparent energy of activation for viscous flow."[4]

$$Rd \ln(\eta_T/\eta_{217})/d(1/T) = E_T = (8.1 \times 10^{17}/T^5)e^{-2530/M} \tag{8}$$

where the units for E_T are cal./mole.

The extent to which the data of Table III conform to Eq. (7) is illustrated in Fig. 4. The solid curves are calculated by Eq. (7) and the circles represent the experimental points. At 110 and 140° the agreement is good, while at 160° the calculated ratio (solid line) is too high. This failure is due to the inadequacy of the form of the temperature dependence rather than to the exponential dependence on the molecular weight, as is indicated by the agreement between the dotted line of Fig. 6 and the experimental points at 160°. The latter line was calculated using the value of $F(T)$ obtained from the extrapolation of the data at 160° to $M = \infty$ (Fig. 5) rather than from Eq. (7). [The values of $F(T)$ at 140 and 100° obtained from the intercepts of Fig. 5 are in agreement with the respective values calculated for $M = \infty$ by Eq. (7).]

In general the discrepancy between viscosities calculated by Eq. (7) and the observed values is less than 20 percent. It is possible that the higher discrepancies which occur are due to a slight degradation of the polymer during the viscosity determinations. On the other hand, Eqs. (7) and (8) are presented merely as approximate empirical representations of the data, which may not necessarily be significant theoretically. They are included primarily for their value in interpolating and extrapolating the experimental measurements.

data could be represented as having a second-order transition at 90°. It may be significant that the values of the "equilibrium" expansion coefficients were about 25 to 30 percent lower than that corresponding to the value of $(dv/dT)_2$ reported here.

[15] The viscosity-temperature coefficients for the high molecular weight polystyrene fractions are identical with those reported in reference 4, but they decrease less rapidly with decreasing molecular weight. These differences probably are due to the occurrence of decomposition in the previous unstable fractions.

[16] Over the molecular weight range investigated, $\log(\eta_T/\eta_{217})$ may alternately be represented as decreasing linearly with $1/M$. However, this relationship must fail at low molecular weights when the quantity $(1 - \text{const.}/M)$ becomes small or negative (const. $\cong 1600$).

[17] The use of the sixth power of the temperature affords a better approximation to the data than either the fifth or the seventh powers. No attempt was made to employ a fractional power of T.

The use of these equations is illustrated in Table IV where values of $\log\eta$ and E_T have been calculated for polystyrenes of various molecular weights at their transition temperatures. Here T_g has been calculated in each case from the molecular weight by Eq. (2); $\log\eta_T$ at T_g has been calculated from Eq. (7) together with the viscosity-molecular weight relationship at $217°,$[4] and E_T has been calculated by Eq. (8). The viscosities of polystyrene fractions at their transition temperatures are not identical but on the contrary vary considerably with molecular weight. The calculated values of E_T at T_g for the various polystyrene fractions, however, are all within 2 kcal. of 110 kcal. per mole. The second-order transition temperatures for a series of polystyrenes do *not* occur at an isoviscous state but *the viscosity-temperature coefficient at the transition temperature is independent of molecular weight.*

The approximate constancy of E_T at T_g may be deduced alternately from Eq. (8). If we require the temperature T at which a polystyrene of molecular weight M has the same value of E_T as that for polystyrene of $M=\infty$ at the transition temperature of the latter $(T_{g,\infty})$, then from Eq. (8)

$$\frac{8.1\times10^{17}}{T^5_{g,\infty}} = \frac{8.1\times10^{17}}{T^5}e^{-2530/M}$$

or solving for T and using the first two terms of the series expansion of the exponential term

$$T = T_{g,\infty}(1-506/M). \qquad (9)$$

Inserting the value of 373°K for $T_{g,\infty}$, and converting to °C
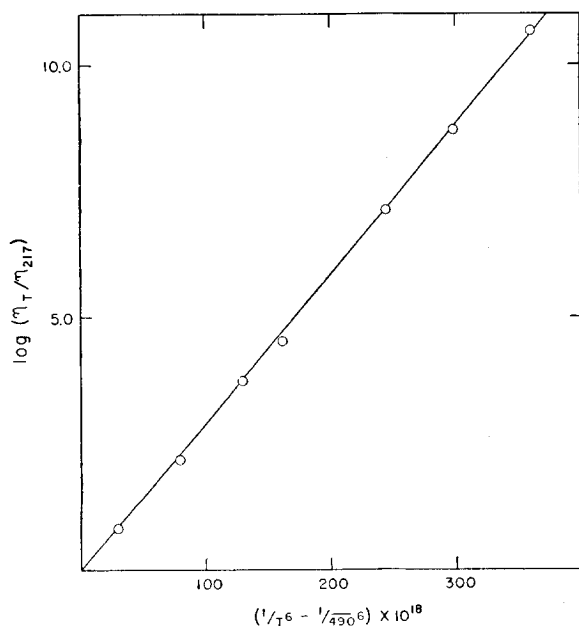
$$T = 100 - 1.9\times10^5/M \qquad (10)$$

FIG. 6. Log (η_T/η_{217}) for polystyrene of infinite molecular weight *vs.* $(1/T^6-1/\langle490\rangle^6)$.

TABLE IV. Viscosities and viscosity-temperature coefficients of polystyrene fractions at their transition temperatures.

M	T_g	$\log\eta$ at T_g	E_T at T_g kcal./mole
300,000	99°	14.19	112
100,000	98	12.40	112
50,000	97	11.40	111
25,000	93	10.93	111
15,000	89	10.57	110
10,000	83	10.58	110
5000	66	10.66	109
4000	58	10.69	108
3000	43	11.31	111

which is identical with Eq. (2) within the limits of experimental accuracy and the approximations involved.

Mixtures of Polystyrene Fractions

Equations (1), (3), (2), and (7) relating the specific volume, the transition temperature, and the viscosity-temperature coefficient to the molecular weight M have been established from measurements on polystyrene fractions which, for the purpose of the experiments described, may be considered to be essentially homogeneous in molecular weight. In order to establish the particular average (if any) on which these properties depend, three mixtures of polystyrene fractions were prepared having the compositions given in Table V. The values of $\bar{M}_n$ and $\bar{M}_w$ calculated by the usual equations

$$\bar{M}_n = \sum_i w_i/\sum_i(w_i/M_i) \qquad (11)$$

$$\bar{M}_w = \sum_i w_i M_i/\sum_i w_i \qquad (12)$$

where w_i is the weight fraction of the species of molecular weight M_i are also listed in Table V. In each case a benzene solution containing the indicated proportions of the two fractions of widely separated molecular weights was evaporated to dryness in order to assure intimate mixing of the constituents. Measured specific volumes, transition temperatures, and viscosity-temperature coefficients are compared in Table V with the values computed from Eqs. (1), (2) and (7), using the number and the weight average molecular weights of each mixture. In every case the observed value of the given property agrees more nearly with that calculated for a fraction possessing a molecular weight which matches the number rather than the weight average molecular weight of the mixture. Agreement with the calculations based on the number average molecular weight is in all cases within the experimental error. Hence, for a heterogeneous polystyrene the specific volume, transition temperature, and the viscosity-temperature coefficient[18] depend explicitly on the number average molecular weight of the polymer, in accordance with Eqs. (1), (2), (3), (7), and (8).

The volume-temperature coefficients observed for the

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[18] The dependence of the viscosity-temperature coefficient for a heterogeneous polystyrene on $\bar{M}_n$ was reported in reference 4.

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TABLE V. Mixtures of polystyrene fractions.

A. Molecular weights and specific volumes

Designation	Components	$\bar{M}_v$, calc.	$\bar{M}_n$, calc.	v_{217} ml per g For fraction of same $\bar{M}_w$	For fraction of same $\bar{M}_n$	Obs.
1	85,000(0.5) 4810(0.5)	45,000	9110	1.042	1.048	1.046
2	85,000(0.5) 3540(0.5)	44,300	6800	1.042	1.051	1.048
3	85,000(0.25) 3540(0.75)	23,900	4650	1.043	1.055	—

B. Second-order transition temperature and volume temperature coefficients

Designation	T_g For fraction of same $\bar{M}_w$	For fraction of same $\bar{M}_n$	Obs.	(dv/dT) in ml/g/° ×10⁴ $(dv/dT)_1$	$(dv/dT)_2$	$(dv/dT)_3$
1	96	81	80	6.8	5.3	2.4
2	96	75	70	6.8	5.5	2.3
3	93	63	60	6.8	5.5	2.6

C. Viscosity-temperature coefficients

Designation	η_{217}, poises	$\log(\eta_{160}/\eta_{217})$ For fraction of same $\bar{M}_w$	For fraction of same $\bar{M}_n$	Obs.	$\log(\eta_{140}/\eta_{217})$ For fraction of same M_w	For fraction of same M_n	Obs.
1	128	2.19	1.76	1.64	3.57	2.85	2.83
2	88	2.19	1.60	1.54	3.57	2.60	2.63

mixtures (Table V) are similar to those found for the fractions.

DISCUSSION

According to current concepts,[19] the equilibrium configuration of a liquid changes continuously with temperature in a manner such that the density of packing of the molecules, or of the chain segments in the case of a polymer, increases with decreasing temperature. The degree of order also increases as the temperature is lowered, and the character of the spatial arrangement, as expressed for spherical molecules by the average coordination number, may change as well.

The linear increases in the specific volume v of polystyrene with $1/\bar{M}_n$ may be interpreted as an influence of the end groups which is proportional to their concentra-

$$CH_3$$
$$|$$

tion. Since the end groups, i.e., the C_2H_5—C_6H_4—CH— groups, occurring in the polystyrenes used here and the styrene structural unit should possess similar net densities, we are led to suggest that the observed dependence of specific volume on molecular weight reflects changes in average density of packing with the concentration of end groups. Thus, the end groups act like a foreign substance in disrupting the local configurational order of the styrene units, and this is manifested by an increase in the specific volume v which is proportional to the concentration of end groups, or to $1/\bar{M}_n$. It follows also that the specific volume affords a convenient index of the average internal configuration or of the average density of packing irrespective of M.

The specific volume-temperature relationships for polystyrene are summarized in Fig. 7. Three parallel straight lines represent the equilibrium v-T relationships for polystyrenes of different molecular weights. The broken line intersecting these v-T lines represents

the barrier imposed by the second-order transition. The dotted extensions of the v-T lines into the region below the second-order transition are essentially unrealizable experimentally. All polystyrenes whose *equilibrium v-T lines* would place them in this forbidden region exhibit the *same specific volume-temperature relationship,* as given by the broken line, *independent of molecular weight.* The position of the broken line representing the glassy state depends somewhat on the rate at which observations are made, but, as has been pointed out above, this rate must be altered by several orders of magnitude before it is shifted appreciably.

The internal changes in liquid configuration which must occur on lowering of the temperature obviously involve the motion of segments relative to their nearest neighbors from one configurational arrangement to another. When the temperature is altered well above T_g this motion of the segments relative to their neighbors in the relatively "loose" or "open" structure is rapid and volume equilibration is practically instantaneous. As the temperature approaches T_g however, the configurational structure becomes more and more compact and hence the rate of volume equilibration diminishes rapidly. Finally, at T_g the segments are so densely packed that the internal mobility is negligibly small and consequently, the liquid structure is "frozen-in," and therefore *remains the same for all temperatures below T_g.* The identity of the specific volumes for polystyrenes of different molecular weight at all temperatures below this second-order transition leads at once to the conclusion that *below T_g the local configurational arrangement of the polymer segments is independent of both M and T.* Furthermore, it is clear that since the presence of end groups in the liquid polymer at a given temperature decreases the density of the configurational structure in proportion to $1/\bar{M}_n$ and since lowering the temperature increases this density of packing in proportion to T, the temperature at which this critical

[19] J. D. Bernal, Trans. Faraday Soc. **33**, 27 (1937).

structure of low mobility is reached (T_g) must decrease in a linear fashion with $1/\bar{M}_n$.

Although the configurational structure remains unchanged as T is lowered below T_g, there remains a small linear decrease in volume with temperature associated with the crystal-like "contraction of the lattice" due to decreased amplitudes of oscillation of the segments about mean fixed positions. Obviously the equilibration rate for this process should be very rapid and should be essentially independent of the structural details mentioned above.

If a model for the liquid is chosen in which the chain segments are represented as hard, inelastic bodies, in accordance with certain approximate theories of the liquid state,[20,21] the above conclusions translate to the statement that the "free volume" (or volume of "holes" between the segments) in polystyrene below its transition temperature is a constant independent of both molecular weight and temperature. This follows from the separation of the specific volume into the sum of the free volume v_f and the occupied volume v_0, the latter being given by

$$v_0 = A_0 + (dv/dT)_3 T, \qquad (13)$$

where A_0 is the hypothetical volume of the solid (glass) at $T = 0°C$. Subtracting this expression from Eq. (3) for the temperature range from T_g to 160° we obtain

$$v_f = A_f + [(dv/dT)_2 - (dv/dT)_3]T + 53/M, \qquad (14)$$

where $A_f = A - A_0$. Imposing the requirement that the equilibrium free volume of a polystyrene of molecular weight M at its transition temperature T_g be equal to that of one for which $M = \infty$ at its transition temperature $T_{g,\infty}$, then

$$T_g = T_{g,\infty} - 53/[(dv/dT)_2 - (dv/dT)_3]M. \qquad (15)$$

Substituting the values of the parameters given above,

$$T_g = 100 - 1.8 \times 10^5/M, \qquad (16)$$

which is identical within the limits of experimental accuracy with Eq. (2). Hence, the second-order transition for polystyrene represents a state of "iso-free volume," and this same free volume is retained at all temperatures below T_g.

The above considerations suggest that the internal relaxation rate (mobility) is determined almost entirely by the configurational arrangement of the segments (or by the free volume associated with the given configuration) and that it is otherwise very nearly independent of both temperature and molecular weight. A corresponding dominant role of the volume in determining the internal mobility of simple non-polar liquids is illustrated by the fact that their fluidities depend primarily on the specific volume, i.e., the viscosity-temperature coefficient at constant volume is

nearly zero.[22] As the temperature is lowered (for any liquid substance) toward T_g, the free volume shrinks to a small value and below T_g remains constant for all lower temperatures. Inasmuch as the volume decreases about linearly with temperature, the *percentage* change in free volume per degree increases rapidly as the temperature is lowered near T_g. Both the observed precipitous decrease of $-dv/d\log t$ for polystyrene near T_g and the approximate constancy of this coefficient below T_g follow as consequences of these considerations.

These concepts may be re-stated in mathematical form. The observations cited[22] on the fluidities of simple liquids suggest that the viscosity of such a substance may be expressed as the product of two functions as follows:

$$\eta = f(v_f)g(T) \qquad (17)$$

where $f(v_f)$ is a function only of the free volume (and hence implicitly of the specific volume), or of the liquid configuration, and $g(T)$ is a function of temperature only. For non-polar liquids at least, the value of the latter function changes relatively slowly with T, hence the viscosity is determined primarily by the free volume. Since the internal mobility is also determined by the free volume, the manifestation of the second-order transition as an isoviscous state in *substances of low molecular weight* is consistent with Eq. (17).

The macroscopic viscosity of a polymer depends not only on the free volume and temperature but also on the length of the polymer chain, Z.[3,4] Equation (17) must be replaced therefore by a relationship of the form
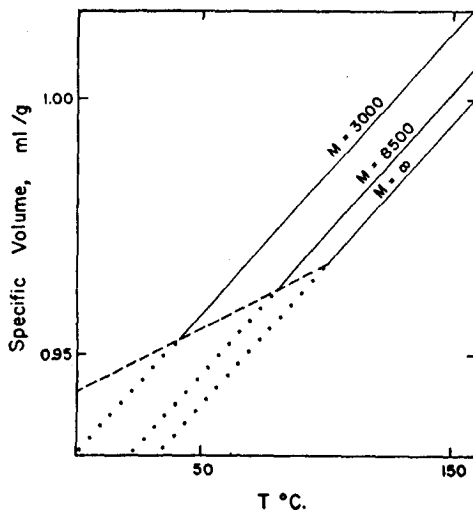
$$\eta = f(v_f)g(T)h(Z), \qquad (18)$$

FIG. 7. Specific volume-temperature relations for polystyrene. The parallel lines represent the equilibrium curves, the dotted portions being non-realizable. The dashed line is the v-T curve for polystyrenes in the glassy state.

[20] H. Eyring, J. Chem. Phys. 4, 283 (1936).
[21] Alfrey, Goldfinger, and Mark, J. App. Phys. 14, 700 (1943).

[22] A. J. Batschinsky, Zeits. f. physik. Chemie 84, 643 (1913). D. B. MacLeod, Trans. Faraday Soc. 19, 6 (1923); 21, 151 (1925). W. R. Van Wijk and W. A. Seeder, Physica 4, 1073 (1937); 6, 129 (1939).

where $h(Z)$ is the statistical factor expressing the required coordination of the motions of *all* segments of the polymer molecule. Since the internal mobility depends only on the first two factors (i.e., the rearrangement of local configurational structure does not require long range cooperation of the segments of a given molecule), it is clear that the macroscopic viscosity for a polymer at its second-order transition will vary with M. This is not true of the viscosity-temperature coefficient. If Eq. (18) is rewritten in the form

$$\ln\eta = F(v_f) + G(T) + H(Z) \qquad (19)$$

and differentiated with respect to $1/T$, there is obtained

$$E_T = Rd\ln\eta/d(1/T)$$
$$= R[(dF(v_f)/dv_f)(dv_f/d(1/T)) + dG(T)/d(1/T)$$
$$+ (dH(Z)/dZ)(dZ/d(1/T))]. \qquad (20)$$

For non-polar polymers the last two terms on the right should be very small, and presumably may be neglected for the purpose of the present discussion. The quantity $dv_f/d(1/T)$ is independent of M and is not sensitive to temperature [see Eq. (14)]. Hence, E_T depends predominantly on $dF(v_f)/dv_f$, which is a function of the free volume only, and the dependence of E_T on M must be related primarily to the dependence of v_f on M. The constancy of v_f below T_g requires that the first term on the right of Eq. (20) shall be zero below T_g. Hence, the viscosity of polystyrene below T_g will vary only as a result of the contributions of the second and third terms of Eq. (20). To the approximation that these terms may be neglected, the viscosity of a given polystyrene should remain constant at all temperatures below T_g.

No experimental data are available with which to test this latter prediction with regard to polystyrene. Viscosity measurements of silicate glasses, however, have been extended below their second-order transition temperatures. While the temperature coefficient does not fall to zero, it passes through a pronounced maximum at T_g.[23] This behavior is indeed to be expected, when, as in glass, the intermolecular forces between elementary units are large. The second term in Eq. (20) is then appreciable—perhaps comparable in magnitude with the first. The third term must be small or zero.[24] In other words, viscous flow involves a considerable activation, and the resulting temperature dependence persists below T_g notwithstanding the disappearance of the first term in Eq. (20).

Unpublished measurements that we have made of the specific volumes of polyisobutylene fractions at $217°$ and at lower temperatures indicate that the "free volume" of this polymer is given by

$$v_f = A_f + BT + 32/M \qquad (21)$$

which is the analog of Eq. (14) for polystyrene. Here B,

the change in the volume-temperature coefficient at T_g, is estimated as $4.5(\pm 1) \times 10^{-4}$ from the data of Ferry and Parks.[25] If we assume that the second-order transition occurs at a characteristic free volume, then

$$T_g = T_{g,\infty} - 6.9 \times 10^4/M. \qquad (22)$$

Values of T_g calculated from this equation are approximately equal to the corresponding literature values[6,25] provided $T_{g,\infty}$ is taken as $-63°$. This suggests that the correlations observed here for polystyrene may have general validity.

The second-order transition temperature ($100°$) that we have observed for high molecular weight polystyrene is somewhat higher than values reported elsewhere (Table VI). It is possible that those previously reported may have been vitiated by the presence in the polymer samples of low molecular weight impurities such as unpolymerized monomer, residual solvent, or degradation products formed from the polymer itself.

The volume-temperature coefficients reported here just above and below T_g correspond to values of the expansion coefficient (α) of 6.0 and 2.7×10^{-4}, respectively. These are in good agreement with most of the previously reported values of these coefficients (Table VI). The slightly lower values obtained by some workers for α below T_g may be due to their use of shorter observation times. The lower values obtained in a few cases for α above T_g are unexplained unless, as has been suggested elsewhere,[26] they are due to the presence of impurities. It should be emphasized that the present values were reproducible (within ± 10 percent) over wide ranges in temperature for polymers differing widely in molecular weight.

Since the configuration of complex liquids and their volume-temperature dependence are imperfectly understood, we prefer not to hazard an explanation for the non-linearity of the v-T curves above T_g at this time.

SUMMARY

1. The specific volumes of polystyrene fractions ranging in molecular weight from 2970 to 85,000, and of various mixtures of these fractions, have been measured at $217°$. The specific volume at a fixed temperature increases linearly with $1/\bar{M}_n$.

2. Measured values of the specific volume-temperature coefficients for these polystyrenes are 7.0, 5.5, and 2.5×10^{-4} above $160°$, between the second-order transition temperature (T_g) and $160°$, and below T_g, respectively. The last two coefficients appear to be independent of M; the first increases with decreasing M at low molecular weights. Alternately, the results above T_g may be represented by a line with curvature over a wide range in the neighborhood of $160°$.

3. The second-order transition temperature is 100 $\pm 2°$ for high molecular weight polystyrene, and it decreases linearly with $1/\bar{M}_n$.

[23] H. R. Lillie, J. Am. Ceram. Soc. 16, 619 (1933).
[24] R. W. Douglas, J. Soc. Glass Tech. 31, 74 (1947).

[25] J. D. Ferry and G. S. Parks, J. Chem. Phys. 4, 70 (1936).
[26] F. E. Wiley, Ind. Eng. Chem. 34, 1052 (1942).

4. At temperatures 10° or more above T_g volume equilibrium appears to coincide with the attainment of temperature equilibrium. In the vicinity of T_g the specific volume decreases approximately linearly with the logarithm of time. In this range the rate of volume relaxation (as measured by $-dv/d \log t$) decreases rapidly with decreasing volume, attaining a low limiting value about 10° below T_g. This limiting value is independent of molecular weight. The rate of internal relaxation (mobility) appears to depend primarily on the internal configurational structure (and on the associated free volume) and to be otherwise independent of T and M.

5. It has been observed that *the specific volumes of polystyrenes below their transition temperatures are independent of the molecular weight.* Hence, it appears that the same "frozen-in" internal configuration prevails in the glassy state independent of molecular weight as well as temperature. The observed dependence of T_g on M can be deduced as a consequence of this conclusion.

6. Bulk viscosities (η) of the same polystyrene samples have been measured from 217 to 75°. The quantity $\log(\eta_T/\eta_{217})$ may be expressed as the product of two factors, one of which depends only on the absolute temperature (as T^{-6}) and the other on $\bar{M}_n$. This ratio at a fixed temperature decreases exponentially with $1/\bar{M}_n$.

7. Generalized relationships for the viscosity of liquids are suggested which indicate that the second-order transition for simple liquids may represent an isoviscous state but that this concept should fail (as it did here) for polymers differing in M. The molecular weight dependence of the viscosity-temperature coefficient for polystyrene above T_g is related logically to

its specific volume-molecular weight relationship; the observed non-dependence of this coefficient on M for polystyrenes at their second-order transition temperatures is shown to be a consequence of the non-dependence on M of the specific volumes of these polymers at (or below) their second-order transition temperatures.

8. It is predicted that the viscosity of polystyrene should become relatively independent of T below T_g. The maximum observed in the viscosity-temperature coefficient for a soda-lime-silica glass is explained on the basis of the above relationships.

9. A relationship between T_g and M for polyisobutylene has been suggested.

TABLE VI. Second-order transition temperature and thermal expansion coefficients for polystyrene.

T_g	$\alpha \times 10^4$		Reference
	Above T_g	Below T_g	
$\geq 100°$	≥ 6	0.4 to 2.5	a
100°	6.0	2.7	b
88°	6.47	2.18	c
87°	6.22	2.33	d
82°	6.0	2.6	e
82°	4.63	2.15	f
82°	4.6	2.5	g
82°	—	—	h
—	4.25	2.7	i
—	4.25	2.4	j
78°	5.89	2.11	k

a See reference 5.
b Present work.
c H. J. Kolb and E. F. Izard, J. App. Phys. **20**, 564 (1949).
d See reference 2.
e W. Patnode and W. J. Scheiber, J. Am. Chem. Soc. **61**, 3449 (1939).
f F. E. Wiley, Ind. Eng. Chem. **34**, 1052 (1942).
g See reference 21.
h R. F. Boyer and R. S. Spencer, J. App. Phys. **15**, 398 (1944).
i See reference 13.
j R. S. Spencer and G. D. Gilmore, J. App. Phys. **20**, 502 (1949).
k R. J. Clash and L. M. Rynkiewicz, Ind. Eng. Chem. **36**, 279 (1944).