Flow Behavior of Polystyrene Systems in Steady Shearing Flow

William W. Graessley and Leon Segal

Chemical Engineering Department and Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received June 26, 1968*

ABSTRACT: Viscosity and normal stresses have been measured on concentrated solutions of polystyrene in steady shearing flow. The polymers were linear and represented a variety of molecular weight distributions. Master curves of viscosity *vs.* shear rate were calculated from the distribution with a recently proposed theory and were found to be in good agreement with the experimental curves. Time constants were deduced independently from the viscosity and normal stress behavior of each solution. Each time constant closely paralleled the Rouse relaxation time of the solution, but contained a simple dependence on entanglement density as well. Accordingly, the molecular weight and concentration shift factors for viscoelastic properties in the terminal region depend on entanglement density. At low entanglement densities the factor is $\eta_0 M/cT$, while at high entanglement densities it becomes η_0/c^2T.

A study of viscosity–shear rate behavior in concentrated polystyrene solutions has recently been reported.[1] The polymers all had narrow molecular weight distributions; concentrations in *n*-butylbenzene ranged from 20 to 55% by weight. The onset of shear rate dependence in the viscosity was characterized by an experimental time constant or relaxation time τ_0. The value τ_0 for each solution was observed to parallel closely the Rouse relaxation time τ_R of that solution[2–4] (eq 1). The viscosity at zero shear rate is

$$\tau_R = \frac{6}{\pi^2}\frac{\eta_0 M}{cRT} \tag{1}$$

η_0, M is the polymer molecular weight, c is the concentration of polymer in the solution (weight per volume), R is the gas constant and T is the absolute temperature. Equation 1 applies when the solution viscosity, η_0, is much larger than the viscosity of pure solvent, η_s, as was always the case in the reported study.

Residual variations in the ratio τ_0/τ_R were noted, the ratio changing systematically with both polymer concentration and molecular weight. These variations were found to be a unique and simple function of the product cM alone (eq 2), where α_1 and β_1 are constants.

$$\frac{\tau_0}{\tau_R} = \frac{\alpha_1}{1 + \beta_1 cM} \tag{2}$$

The entanglement density in polymer systems is proportional to the product cM[5,6] (eq 3), where E is the

$$E = 2\frac{\varphi M}{M_c} = 2\frac{cM}{\rho M_c} \tag{3}$$

average number of entanglement points per molecule, ρ is the density of the undiluted polymer, φ is the volume fraction of polymer and M_c is the critical molecular weight for entanglement network formation in the undiluted polymer. The cM term in eq 2 suggests therefore that the molecular process is influenced explicitly by chain entanglements, *i.e.*, beyond the effect on the magnitude of η_0 for the solution, although recent work has shown other interpretations of this term can also be made.[7]

This paper reports further studies on the same polymer–solvent system. Measurements of viscosity *vs.* shear rate have now been made for polystyrene samples with broad but known molecular weight distributions. These and the previous results have been compared with published viscosity data on undiluted polystyrene. In addition, normal stress coefficients have been measured for solutions of both the broad and narrow distribution polymers. One purpose of these studies was to examine the generality of eq 2 when applied to undiluted samples and to samples with broad molecular weight distributions. In particular we wanted to establish what average molecular weight for the polydisperse samples would replace M in eq 2. Another purpose was to determine whether the normal stress behavior contains a residual systematic dependence on the cM product of the solution, similar to eq 2 for the viscosity behavior.

Viscosity–Shear Rate Behavior. The non-Newtonian nature of polymer liquids is well known. The viscous behavior in steady shearing flow is similar for many types of polymers and concentrated (>10%) polymer solutions. The viscosity coefficient of the fluid approaches a constant value at sufficiently low shear rates, but within some intermediate region of shear rates it begins to decrease, and continues to decrease monotonically with increasing shear rate throughout the observable range. The behavior of any particular fluid can be partially characterized by giving the values of two parameters, the viscosity at zero shear rate η_0 and a time constant τ_0 which locates in some systematic way the onset of non-Newtonian behavior in the viscosity.

In the earlier study of narrow distribution polystyrene plots of log η *vs.* log $\dot{\gamma}$ could be superimposed to form a single curve by shifts parallel to the coordinate

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axes. Because such a master curve fitted all the data, any consistent method of assigning numerical values of τ_0 to the individual curves would lead necessarily to the same form of correlation with the variables of the system. One could, for example, choose τ_0 as the reciprocal of the shear rate at which η had dropped to some fixed fraction of η_0. Alternatively, one could extend the lines defining the low shear and high shear regions of the viscosity curve and take τ_0 as the reciprocal of the shear rate at the intersection. Another method, and the one used in the earlier paper, assigns τ_0 by superposition of the experimental data on a theoretical master curve of η/η_0 *vs.* $\dot{\gamma}\tau_0$, where τ_0 has some meaning according to the particular theory used.

All these methods have been used at various times, and any would yield the same relative values of τ_0 for the data on narrow distribution polystyrene. Thus the form of eq 2 represents a purely experimental observation, and only the numerical value of α_1 depends on the particular method of choosing τ_0. In particular, the result does not demand a commitment to any particular theory of viscosity. Such a clear separation between experiment and interpretation is not possible in comparing the values of τ_0 from samples of different molecular weight distributions. The form of the viscosity master curve depends on the distribution,[8–11] so different methods of assigning τ_0 will lead to different relative values.

One way to avoid purely arbitrary comparisons among samples of different distribution is to settle upon some theory which predicts the viscosity master curve of a polymer from its molecular weight distribution. In the present study we have used a recent theory of polymer viscosity.[12] The relationship of this theory to others has been examined, and good agreement has been found between calculated and experimental master curves.[13]

According to the theory τ_0 is a characteristic time constant for the fluid, reduced to zero shear rate. Its magnitude controls the time for formation of molecular chain entanglements between any molecule in the system and other molecules passing through its sphere of influence. Its value is of the order of the Rouse relaxation time of the system (eq 1), with M replaced by the weight-average molecular weight $\bar{M}_w$. The entanglement time for a molecule with molecular weight M in a polydisperse system is

$$\tau(M) = \left(\frac{M}{\bar{M}_w}\right)^2 \tau_0 \tag{4}$$

at sufficiently low rates of shear. Hence the entanglement time is determined both by the size of the chain and by the parameters of the medium that control τ_0. This is not to say that one relaxation time describes the motions of the chain in detail. Indeed it is presumed that each chain possesses a discrete set of relaxation times, but that, like the relaxation times of an isolated Rouse chain, all are fixed fractions of some largest relaxation time. The entanglement time in eq 4 is expected to represent the sum of contributions from all modes, dominated by those of the longest relaxation times.

The calculation of viscosity is based on the assumption that the net entanglement density in a steady flowing system depends on the rate of deformation. The arguments in favor of this point of view and the detailed relationships between the entanglement time, the entanglement density, the molecular weight distribution, the viscosity, and the shear rate are developed elsewhere.[12] The detailed procedure for calculating η/η_0 *vs.* $\gamma\tau_0/2$ for a known distribution function $P(n)$ is also described elsewhere.[12,13] The utility of the theory in this study is that it provides a way to make comparisons between τ_0 values for polymers of different dispersity.

Normal Stress Behavior. Flow generates stresses in polymer liquids in addition to the shear stresses, these extra stresses being associated with the storage of elastic energy. The difference between the normal stresses parallel to the lines of flow and perpendicular to the planes of flow, $p_{11} - p_{22}$, is the first normal stress difference. At sufficiently low shear rates

$$p_{11} - p_{22} = K\dot{\gamma}^2 \tag{5}$$

where K is the normal stress coefficient. The theoretical coefficient for a polydisperse collection of Rouse chains is[14]

$$K_R = \frac{2\pi^2}{15}\eta_0\tau_R\frac{\bar{M}_z\bar{M}_{z+1}}{\bar{M}_w^2} \tag{6}$$

where τ_R is given by eq 1 with M replaced by $\bar{M}_w$. Experimental values of K may be obtained from

$$K = \lim_{\dot{\gamma}\to 0}\left[\frac{p_{11} - p_{22}}{\dot{\gamma}^2}\right] \tag{7a}$$

or

$$K = \eta_0^2 \lim_{\dot{\gamma}\to 0}\left[\frac{p_{11} - p_{22}}{p_{12}^2}\right] \tag{7b}$$

or

$$K = \eta_0^2 \lim_{\dot{\gamma}\to 0}\left[\frac{d[(p_{11} - p_{22})/\eta^2]}{d[\dot{\gamma}^2]}\right] \tag{7c}$$

and an experimental time constant associated with the normal stress can be evaluated as

$$\tau_N = \frac{15K}{2\eta_0\pi^2}\frac{\bar{M}_w^2}{\bar{M}_z\bar{M}_{z+1}} \tag{8}$$

The ratio τ_N/τ_R measures the deviation of any solution from the Rouse theory, and plays a role for normal stresses similar to that of τ_0/τ_R for the viscosity behavior. If the Rouse model is obeyed exactly, then $\tau_N/\tau_R = 1$. If deeply interpenetrating and interacting collections of polymer molecules behave only

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TABLE I

MOLECULAR CHARACTERISTICS OF POLYSTYRENE SAMPLES

Sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$		Source and preparation
P1	97,000	1.06	(reptd)	Pressure Chem. Co., anionic polymerzn
P2	160,000	1.06	(reptd)	Pressure Chem. Co., anionic polymerzn
P3	411,000	1.01	(reptd)	Pressure Chem. Co., anionic polymerzn
P4	860,000	1.15	(reptd)	Pressure Chem. Co., anionic polymerzn
F1	2,400,000	1.1	(estd)	Fraction; free radical polymerzn
G1	48,500	1.08	(measd)	Stratton data[a]
S103	117,000	1.07	(measd)	Stratton data[a]
S109	179,000	1.07	(measd)	Stratton data[a]
S111	217,000	1.08	(measd)	Stratton data[a]
S108	242,000	1.03	(measd)	Stratton data[a]
Shell	371,000	2.74	(measd)	Arnold data[b]
B1	209,000	2.0	(estd)	Solution free radical polymrzn, 100°
B2	241,000	2.0	(estd)	Solution free radical polymrzn, 100°
B3	677,000	1.8	(estd)	Bulk free radical polymerzn, 100°
B4	1,600,000	1.8	(estd)	Bulk free radical polymerzn, 60°
B5	1,900,000	1.8	(estd)	Bulk free radical polymerzn, 60°
B6	3,370,000	1.8	(estd)	Bulk free radical polymerzn, 40°
Blend	418,000	3.1	(calcd)	Mixture 87% by weight B2 and 13% B4

[a] See ref 18. [b] This paper and ref 13.

approximately as collections of isolated Rouse molecules, then τ_N/τ_R might be a constant, but not necessarily equal to unity. If finally the elastic and viscous components of behavior depend on the molecular structure of the solutions in similar ways, then τ_N/τ_R will obey a relation of the form of eq 2 and show a residual dependence on cM.

Experimental Section

Materials. The narrow distribution polystyrenes were obtained from the Pressure Chemical Co., Pittsburgh, Pa. They ranged in reported $\bar{M}_w/\bar{M}_n$ from 1.01 to 1.15. A number of broad distribution polystyrenes were prepared by thermal polymerization (without added catalyst) at various temperatures. Polymerizations were conducted with distilled monomer in the absence of air. Some samples were prepared in undiluted (bulk) polymerizations and some in solution polymerizations with a 1:1 mole ratio of ethyl benzene. An analysis of molecular weight distribution as a function of conversion has been recently made for these systems.[15,16] Characterizations were made by light scattering to obtain $\bar{M}_w$ and by osmotic pressure to obtain $\bar{M}_n$. Polymerization conditions and distribution information are given in Table I.

One system was a blend of two most-probable distribution samples with $\bar{M}_w$ values of 241,000 and 1,600,000, respectively. The composition, 13% by weight of the high molecular weight component, was chosen to render the ratio $\bar{M}_z/\bar{M}_w$ as large as possible and thereby accentuate the broadness of the high molecular weight end of the distribution. Complete viscosity and distribution data for one undiluted polystyrene sample with a broad molecular weight distribution were generously provided to the authors by Dr. Kenneth Arnold of the Shell Development Co.

Measurements. Solutions in *n*-butyl benzene (99+% purity, Phillips Chemical Co.) were prepared, ranging from 0.20 to 0.55 g/ml of polymer. Weighed amounts of polymer were combined with measured volumes of solvent, and concentrations were calculated by assuming additivity of volumes. Shear stress and normal stress data were measured in the plate–cone geometry with a Weissenberg rheogoniometer (Model R-16). Cone angles were 0.5 and 4.0° for the shear stress data and 4.0° for the normal stress data. The development of a flow instability at high shear rates with exudation of solution from the gap limited the experimental range. The shear rates for all solutions lay within the range 0.05–500 sec^{-1}. The torque T and total thrust F at each angular velocity of the plate Ω_0 were converted into viscosity and normal stress difference with the equations for plate–cone geometry[17]

$$\dot{\gamma} = \frac{\Omega_0}{\Delta} \tag{9}$$

$$\eta = \frac{3T}{\pi R^3 \dot{\gamma}} \tag{10}$$

$$p_{11} - p_{22} = \frac{2E}{\pi R^2} \tag{11}$$

in which R is the plate radius and Δ is the gap angle. Details of the procedure and verifying experiments in different geometries are reported elsewhere.[1,14]

The viscosity data on the undiluted Shell polystyrene were furnished to the authors, having been obtained at 200° on a Wiessenberg rheogoniometer at low shear rates and an Instron capillary rheometer at high shear rates.

Data Analysis. Examples of the experimental viscosity data are given in Figures 1, 2, and 3. The solid lines were calculated from the molecular weight distributions and shifted parallel to the viscosity and shear rate axes to match the experimental viscosities. The Zimm–Schulz distribution (a modified γ distribution) was used in some of these calculations. The distribution function $P(n)\,\mathrm{d}n$ is the fraction

$$P(n) = \frac{(Z+2)^{Z+1}}{Z!\bar{n}_w}\left(\frac{n}{\bar{n}_w}\right)^Z \exp\left[-\frac{n}{\bar{n}_w}(Z+2)\right] \tag{12}$$

of chains in the system with n repeating units, and the parameter Z is related to distribution breadth by

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{Z+2}{Z+1} \tag{13}$$

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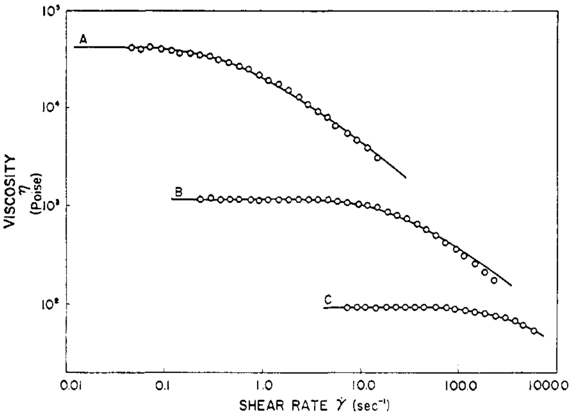

Figure 1. Examples of viscosity–shear rate results on solutions of polystyrene with narrow molecular weight distribution: curve A, M = 2,400,000 and c = 0.255 g/ml; curve B, M = 860,000 and c = 0.255 g/ml; curve C, M = 411,000 and c = 0.255 g/ml. The solid lines were calculated from the distribution.

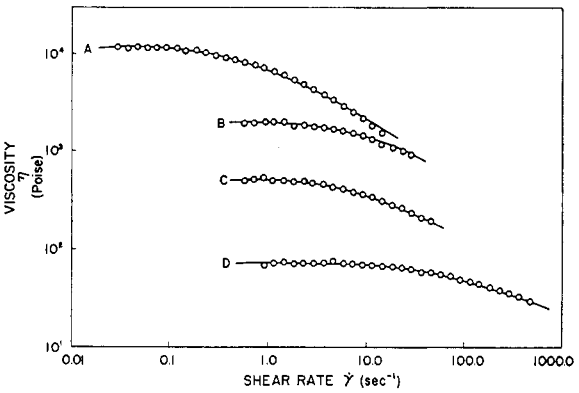

Figure 2. Examples of viscosity–shear rate results on solutions of polystyrene with broad molecular weight distributions: curve A, M = 1,900,000 and c = 0.255 g/ml; curve B, $\bar{M}_w$ = 677,000 and c = 0.40 g/ml; curve C, $\bar{M}_w$ = 418,000 and c = 0.30 g/ml; curve D, the blend sample, c = 0.30 g/ml. The solid lines were calculated from the distribution.

The distribution with $Z = 10(\bar{M}_w/\bar{M}_n = 1.09)$ was used for all narrow distribution samples. No attempt was made to refine the analysis further, for example by using different values of Z for different samples based on their reported $\bar{M}_w/\bar{M}_n$ ratios. The calculated viscosity behavior is most sensitive to higher molecular weight ratios such as $\bar{M}_z/\bar{M}_w$ and $\bar{M}_{z+1}/\bar{M}_z$, and this information was not available.

The value $Z = 0$, corresponding to a most-probable distribution ($\bar{M}_w/\bar{M}_n = 2.0$), was used for the unfractionated samples prepared by free radical polymerization. This is perhaps an oversimplification since it is known thatfree radical polystyrene at low conversions can be somewhat narrower than the most probable distribution, while high conversion polymers made by solution polymerization tend to be somewhat broader.[15] Nevertheless, further refinement without additional information on the high molecular weight end of the distribution was not considered warranted.

The master curve for the blend was calculated from the composite distribution with the assumption of complete mixing. The master curve for the Shell polystyrene was calculated directly from the experimental molecular weight distribution.

In all samples η_0 and τ_0 were obtained by superposition of experimental and theoretical curves. The values are listed in Table II. Table II also contains η_0 and τ_0 values calculated from the viscosity measurements of Stratton.[18] Those data were obtained with a capillary viscometer on undiluted polystyrenes of narrow molecular weight distribution. The master curve for $Z = 10$ was used.

In general the agreement between calculated and experimental viscosity curves was excellent in the transitional region between Newtonian and high shear rate behavior. At high shear rates the experimental viscosities tended to decrease more rapidly than the calculated curves, especially for the samples with narrow distributions. This trend can be seen in Figure 1, and is particularly evident in the Stratton data (Figure 3) which extends more deeply into the non-Newtonian region than the solution data. Nevertheless, the generally good agreement at intermediate shear rates made the fit unique, and there was no difficulty in selecting the η_0 and τ_0 values.

The normal stress coefficient K was obtained for each solution by plotting $(p_{11} - p_{22})/\eta^2$ as a function of γ^2 (Figures 4 and 5) and measuring the slope at low shear rates (equation 7c). Such plots consistently gave good straight lines at low shear rates (Figure 5), in some cases extending well into the non-Newtonian viscosity region. By comparison, ordinary plots of $p_{11} - p_{22}$ *vs.* $\dot{\gamma}^2$ were more curved at low shear rates, expecially for the broad distribution samples, and establishing the limiting slope from these curves would have been difficult. Linearity in $p_{11} - p_{22}/\eta^2$ *vs.* $\dot{\gamma}^2$ is a consequence of the so-called Hooke's law in shear,[19,20] which appears to hold for these solutions over a limited range of shear rates. The behavior over an extended range is more complex however, with positive curvature in general for narrow distributions and negative curvature for broad distributions as illustrated in Figure 4. It was noted that several sets of normal stress data showed small but clearly nonzero intercepts at $\dot{\gamma} = 0$ (curve A in Figure 5, for example). No particular trends were noted, and they were assumed to be artifacts resulting from slight misalignments in the instrument.

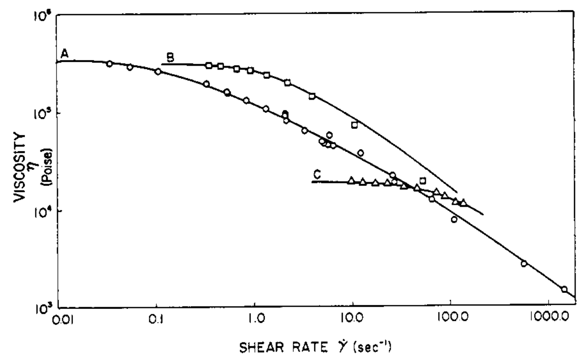

Figure 3. Examples of viscosity–shear rate results on undiluted polystyrenes: curve A, Shell sample $\bar{M}_w$ = 371,000 and T = 200°; curve B, sample S108 with $\bar{M}_w$ = 242,000 at T = 183°, and curve C, sample G1 with $\bar{M}_w$ 48,500 at T = 159°. The solid lines were calculated from the distribution.

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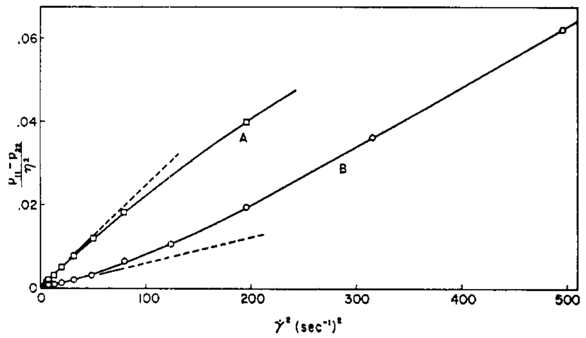

Figure 4. First normal stress difference *vs.* shear rate: curve A, broad distribution sample B6 with $\bar{M}_w$ = 3,370,000 and c = 0.20 g/ml; curve B, narrow distribution sample P4 with $\bar{M}_w$ = 860,000 and c = 0.20 g/ml.

Values of τ_N were calculated for each solution from the limiting slope, and are compiled in Table II. The polydispersity correction $\bar{M}_z\bar{M}_{z+1}/\bar{M}_w^2$ was calculated to be 3.0 for most probable distributions (Z = 0), 1.26 for narrow distribution (Z = 10), and 22.4 for the blend.

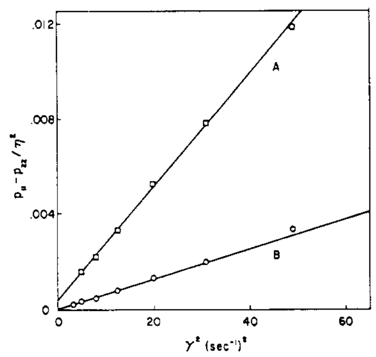

Figure 5. Normal stress in the range of low shear rates; same solutions as in Figure 4.

Results

Viscosity Relaxation Time. It was found that eq 2 could be extended to polydisperse systems by replacing M by $\bar{M}_w$. Values of τ_R/τ_0 are plotted in Figure 6 as a function of $\varphi\bar{M}_w$. The volume fraction φ was cal-

TABLE II
RHEOLOGICAL PARAMETERS OF POLYSTYRENE SYSTEMS

Samples	$\bar{M}_w$	c, g/ml	T, °C	η_0, P	τ_0, msec	τ_N, msec	τ_R, msec
			Narrow Distribution Polymers				
P1	97,000	0.55	30	364	2.15		1.55
P2	160,000	0.45	30	360		3.60	3.06
		0.50	30	1,120		5.99	8.19
		0.55	30	2,870	20.0		20.1
P3	411,000	0.255	30	92.5	3.5	2.92	3.59
		0.30	30	284	8.6	6.75	9.37
		0.35	30	763	19.0	13.3	21.5
		0.40	30	1,940	39.0	24.5	48.0
		0.45	30	6,080	102	101	134
		0.50	30	17,500	226		346
		0.55	30	48,500	550		872
P4	860,000	0.20	30	255	21	10.1	26.4
		0.255	30	1,150	64	36.0	93.3
		0.30	30	3,600	150	80	248
		0.35	30	9,600	290	216	568
		0.45	30	71,000	1,240		3,260
		0.55	30	470,000	6,400		17,700
F1	2,400,000	0.255	30	40,900	2,700		9,260
G1	48,500	Undiluted	159	19,000	16		15.2
S103	117,000	Undiluted	183	25,700	47.3		42
S109	179,000	Undiluted	183	109,000	230		304
S111	217,000	Undiluted	183	190,000	374		658
S108	242,000	Undiluted	183	295,000	700		1,110
			Broad Distribution Polymers				
B1	209,000	0.40	30	155	3.70	3.88	1.95
B2	241,000	0.20	30	4.5	0.10		0.13
Blend	418,000	0.30	30	72	0.52	0.645	2.42
B3	677,000	0.255	30	88	4.0	4.29	5.64
		0.40	30	2,000	56.0	47.2	81.5
B5	1,900,000	0.255	30	11,700	790		2,100
		0.255	50	7,500	580		1,270
		0.35	50	76,000	2,800		9,320
B6	3,370,000	0.20	30	520	53.0	31.2	212.0
Shell	371,000	Undiluted	200	330,000	1,080		1,910

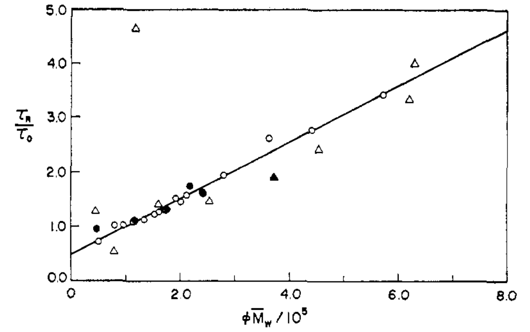

Figure 6. Viscosity time constant ratio *vs.* the product of volume fraction of polymer and polymer molecular weight: ●, undiluted, narrow distribution polystyrene; ○, solutions of narrow distribution polystyrene in *n*-butylbenzene; ▲, undiluted, broad distribution polystyrene Shell sample; △, solutions of broad distribution polystyrene in *n*-butylbenzene. The point △ well removed from the line is the blend.

culated by dividing c by 1.07 g/ml, the density of pure polystyrene. With the exception of the blend the data from solutions, undiluted polymers, and samples with different distributions appear to follow the same straight line. As this result would imply, correlations with significantly different average molecular weights, such as $\bar{M}_n$, yield different lines for different distribution breadths. The line drawn in Figure 6 was calculated by a least-squares analysis of the narrow distribution data. We conclude that $\varphi\bar{M}_w$ is the correct correlating variable for τ_0/τ_R when the viscosity data on polymers of different distributions are compared through master curves from the entanglement theory. The anomalous behavior of the blend also is evident in the normal stress results, and will be examined more thoroughly in a future study.

Normal Stress Properties. Values of τ_R/τ_N for the narrow distribution polymers are shown in Figure 7 as a function of the φM product (actually $\varphi\bar{M}_w$ is plotted). Although there is more experimental scatter than with the viscosity time constants, the data seem to indicate the same type of residual dependence on cM. The calculated least-squares line is shown. Figure 8 contains the data for polymers of all distributions plotted as a function of $\varphi\bar{M}_w$. As in the viscosity correlation the blend is considerably removed from the other points, but the other broad distribution samples seem to follow the trend established by polymers with narrow distribution. The necessity of using $\varphi\bar{M}_w$ rather than $\varphi\bar{M}_n$ is not as clear cut as with the viscosity data however. Fewer solutions with normal stress data are available, and the scatter is severe enough to leave some doubt about the proper average molecular weight to use. In fact, if $\varphi\bar{M}_n$ were used as the correlating variable, the three lower points from broad distribution would be brought into rather better accord with the narrow distribution samples, while the agreement with the one point at high φM would be disturbed. Clearly, more measurements on polydisperse samples are needed to resolve this important question.

The normal stress data offers a point of connection with linear viscoelastic properties and an alternative interpretation of the results in Figures 7 and 8. According to the theory of second-order fluids[21] normal stress coefficients in the limit of zero shear rate can be converted into steady state shear compliances. Identification of the φM correlating product as the entanglement density can be justified to some extent by the following comparisons between these solution compliances and the compliances of cross-linked networks.

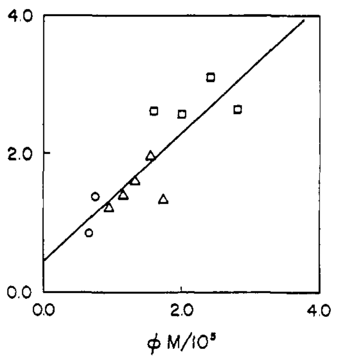

Figure 7. Normal stress time constant ratio *vs.* the product of polymer volume fraction and molecular weight; data are given for three narrow distribution polymers: ○, M = 160,000; △, M = 411,000, and □, M = 860,000.

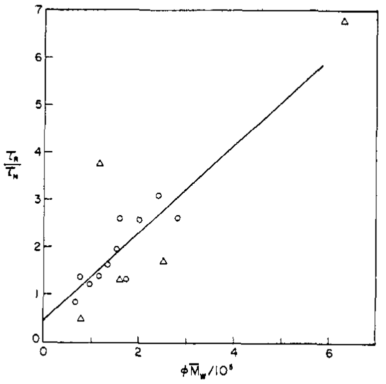

Figure 8. Normal stress ratio *vs.* the product of polymer volume fraction and weight-average molecular weight: ○, narrow distribution polymers; △, broad distribution polymers.

The steady state shear compliance of a monodisperse collection of Rouse chains is[22] given by eq 14,

$$J_R = \frac{2}{5\nu kT} \tag{14}$$

in which ν is the number of chains per unit volume, k is Boltzmann's constant, and T the absolute temperature. Consider now the properties of the same system as cross-links are introduced randomly and successively between the chains. The compliance first increases as the system approaches the gel point. Steady flow is impossible at higher cross-link densities, and imposition of a shear stress instead produces an equilibrium deformation. The equilibrium compliance of a cross-linked network of Rouse chains is given in the recent

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(21) B. D. Coleman, H. Markovitz, *J. Appl. Phys.* 35, 1 (1964).

(22) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961.

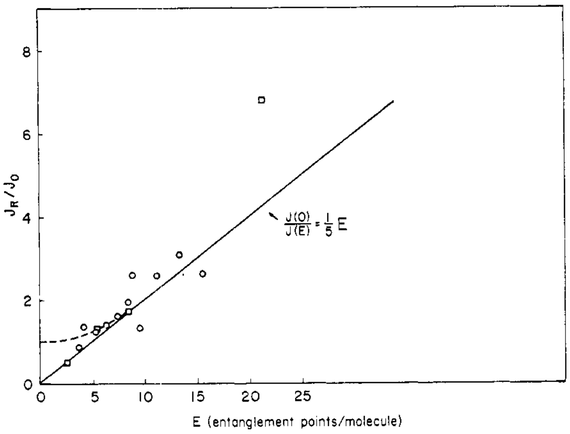

Figure 9. Compliance ratio *vs.* entanglement density. The ratio J_R/J_0 is the time constant ratio τ_R/τ_N. The average number of entanglement points per molecule was calculated from $\varphi \bar{M}_n$ with eq 3 and $M_c = 33{,}000$: ○, narrow distribution data; □, broad distribution data.

analysis by Chompff and Duiser[23] (eq 15), in which

$$J_e = \frac{1}{G_e} = \frac{2}{\nu_a kT} \qquad (15)$$

G_e is the equilibrium modulus of the network and ν_a is the number of active network elements per unit volume. If C is the average number of cross-linked units per chain, then $\nu_a = \nu(C - 1) \approx \nu C$ at high cross-linking densities. The compliance of the system, J, referred to its value at $C = 0$, thus obeys eq 16 and 17.

$$\frac{J_R}{J} = 1 \qquad (C \ll 1) \qquad (16)$$

$$\frac{J_R}{J} = {}^1/_5 C \qquad (C \gg 1) \qquad (17)$$

Steady flow is in principle always obtainable in an entangled polymer system. If we assume however that the elasticity of these systems, *i.e.*, their ability to store elastic energy when a shear stress is imposed, is related to entanglement density in the same way elasticity is related to cross-linking density in permanent networks, then eq 16 and 17 carry over to entanglement networks with C simply replaced by E from eq 3 (eq 18 and 19), in which J_R is the steady-state compliance

$$\frac{J_R}{J_0} = 1 \qquad (E \ll 1) \qquad (18)$$

$$\frac{J_R}{J_0} = {}^1/_5 E \qquad (E \gg 1) \qquad (19)$$

for a polydisperse collection of Rouse molecules[22] (eq 20) and J_0 is the steady state compliance obtained

$$J_R = {}^2/_5 \left(\frac{\bar{M}_z \bar{M}_{z+1}}{\bar{M}_w^{\,2}} \right) \frac{\bar{M}_w}{cRT} \qquad (20)$$

from the experimental normal stress coefficient.

TABLE III

	$E \ll 1$	$E \gg 1$
$K \propto$	$\eta_0^2 M/cT$	η_0^2/c^2T
$\tau_0 \propto$	$\eta_0 M/cT$	η_0/c^2T
$J_0 \propto$	M/cT	$1/c^2T$

One should not expect this parallel to hold exactly, especially at intermediate entanglement densities. The total compliance in steady shearing flow is the sum of contributions from the various "load-bearing" members of the system—unentangled molecules, sections of molecules between entanglement points, and ends of molecules. Thus, unlike the imperfections in permanent networks, chain ends and other network flaws would contribute to the response of an entangled network to a steady shearing stress,[24] and the contributions of the various species would be weighted according to their concentration and their coupling with and deformation in the flow field. The quantity we have designated τ_R/τ_N is equal to J_R/J_N.[21] One would expect therefore a smooth transition in this ratio from eq 18 at low entanglement densities to eq 19 at high entanglement densities as the elastic elements of the system change from individual molecules to chain segments between entanglement points.

The φM product can be converted into entanglement density E with eq 3 and $M_c = 33{,}000$ for polystyrene. Figure 9 depicts J_R/J_0 (equal to τ_R/τ_N) for all samples except the blend. Values of E were calculated with the $\bar{M}_n$ values. The solid line in the figure is eq 26. The dotted extension to the ordinate value of unity (eq 18) was drawn only to suggest the type of behavior that might be expected in the intermediate entanglement regime. The experimental agreement with the permanent network equation (eq 19) is remarkably good, supporting the interpretation of the correlating variable φM as the entanglement density of the system.

Least-squares calculations with the viscosity and normal stress time constants yield eq 21 and 22 for the

$$\tau_0 = \frac{2.00\tau_R}{1 + 0.17E} \qquad (21)$$

$$\tau_N = \frac{2.2\tau_R}{1 + 0.34E} \qquad (22)$$

narrow distribution samples, in which $E = \varphi \bar{M}_w/16{,}500$. According to these forms the normal stress coefficient, the viscosity time constant and presumably also the steady state compliance depend on viscosity, polymer concentration, molecular weight, and temperature in a manner related to the entanglement density (Table III). These results also follow from William's theory of viscoelasticity in the limits of weak and strong intermolecular interaction.[7] Many data in the literature agree with these results. The loss of explicit molecular weight dependence in the normal stress coefficient[25] and in the terminal relaxation time and partial modulus[26]

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[23] A. J. Chompff and J. A. Duiser, *J. Chem. Phys.*, **45**, 1505 (1966).

[24] F. Bueche, *J. Appl. Phys.*, **26**, 738 (1955).

[25] H. J. M. Mieras and C. F. Van Rijn, *Nature*, **218**, 865 (1968).

[26] A. V. Tobolsky and K. Murakami, *J. Polym. Sci.*, **47**, 54 (1960).

is observed in bulk polystyrenes. A transition in the normal stresses from first to second power dependence on concentration, accompanied by a weakened molecular weight dependence, occurs in polystyrene–toluene solutions.[20] Master curve reduction of viscosity and shear modulus has been accomplished by shift factors proportional to c^2 in polyisobutylene–decalin solutions,[3] and similarly for normal stresses in polyisobutylene–cetane systems.[27] Explicit dependence on molecular weight is absent in the viscosity time constants of bulk polybutadiene[28] and silicones,[29] and c^2 shift factors were necessary to produce superposition of viscosity data in polybutadiene solutions.[30] The agreement is not unanimous, since creep compliance data on polyvinyl acetate fractions and blends[31] obey the Rouse equation even at high entanglement densities. Nevertheless, it does appear that a large number of polymer systems show effects similar to the polystyrenes in this study.

Master Curve Modifications. In the calculation of viscosity master curves the entanglement time was taken to be proportional to the Rouse time constant. This was combined with the assumption that the viscosity appearing in the time constant was the macroscopic viscosity at the imposed shear rate. The result for a monodisperse system was eq 23, in which $\tau(\dot{\gamma})$

$$\tau(\dot{\gamma}) = \frac{\eta}{\eta_0}\tau_0 \tag{23}$$

is the entanglement time at shear rate $\dot{\gamma}$. The equation for viscosity then was expressed in the form

$$\frac{\eta}{\eta_0} = f\left(\frac{\dot{\gamma}\tau(\dot{\gamma})}{2}\right) = f\left(\frac{\eta}{\eta_0}\cdot\frac{\dot{\gamma}\tau_0}{2}\right) \tag{24}$$

whose solution provided the desired master curve η/η_0 *vs.* $\dot{\gamma}\tau_0/2$.

According to eq 21 the time constant is more complex then the Rouse time. If we assume that the E which appears is the communal entanglement density of the medium, then it is not difficult to allow for changes in E at finite shear rates just as we allow for changes in viscosity. Thus

$$\tau_0 = \frac{k_1\tau_R}{1 + k_2E_0} \tag{25}$$

so at finite shear rates one might expect

$$\tau(\dot{\gamma}) = \left(\frac{\eta}{\eta_0}\right)\tau_0\left(\frac{1 + k_2E_0}{1 + k_2E_0\left(\frac{E}{E_0}\right)}\right) \tag{26}$$

in which E_0 is the entanglement density at $\dot{\gamma} = 0$, and E is the value at finite shear rates. The ratio E/E_0 is already given by the theory, being equal to the function g in ref 12. The generalization of the result to polydisperse systems can be made immediately by noting that, according to Figure 6, the weight-average entanglement density of the medium is needed. The ratio E/E_0 in eq 26 becomes

$$\bar{g}(\dot{\gamma}) = \frac{\int_0^\infty n^2 g(\dot{\gamma},n)P(n)\,\mathrm{d}n}{\int_0^\infty n^2 P(n)\,\mathrm{d}n} \tag{27}$$

The procedure for calculating master curves is only slightly affected by this modification. The integral in eq 27 is evaluated along with the other integrals required by the theory.[12] The reduced shear rate is given by eq 28, where $(\dot{\gamma}\tau_0/2)_0$ is the value obtained by

$$\frac{\dot{\gamma}\tau_0}{2} = \left(\frac{\dot{\gamma}\tau_0}{2}\right)_0\frac{1 + k_2E_0\bar{g}}{1 + kE_0} \tag{28}$$

the original calculation procedure.[12] When kE_0 is large compared to unity a limiting behavior is reached

$$\left(\frac{\dot{\gamma}\tau_0}{2}\right)_\infty = \left(\frac{\gamma\tau_0}{2}\right)_0 g \tag{29}$$

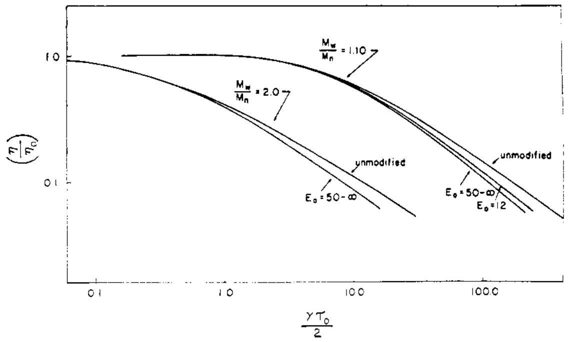

Figure 10. Theoretical master curves for viscosity, modified by the explicit presence of entanglement density in the time constant. Calculated effects for most probable distributions ($Z = 0$) and narrow distribution ($Z = 10$) are shown. The term E_0 is the entanglement density at zero shear rate. The curves for $Z = 10$ have been shifted parallel to the shear rate axis to avoid overlap.

Some results of this calculation, indicating the limits of behavior, are given in Figure 10. Table IV contains the values of used. The principle effect of the modification is to cause the master curves to decrease more rapidly at high shear rates, leaving the shape of the curves largely unchanged at low and intermediate shear rates. As the distribution broadens the difference between the modified and unmodified curves becomes smaller, at least in the experimentally important range $0.01 < \eta/\eta_0 < 1.0$. The function $\bar{g}$ depends on lower moments of the molecular weight distribution than the viscosity, so the net loss of entanglement points by the largest molecules in polydisperse systems decreases the viscosity more rapidly than $\bar{g}$.

The entanglement densities of most samples in this study are large enough to justify using the modified curves. The experimental agreement is somewhat improved in the region of high shear rates if this is done.

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(27) H. Markovitz and D. R. Brown, *Trans. Soc. Rheol.*, 7, 137 (1963).

(28) J. T. Gruver and G. Kraus, *J. Polym., Sci., Part A*, 2, 797 (1964).

(29) J. M. O'Reilly and W. M. Prest, presented at 37th Annual Meeting of the Society of Rheology, Atlantic City, N. J., 1966; *Rheol. Bull.*, 35 (3), 7 (1966).

(30) G. Kraus and J. T. Gruver, *Trans. Soc. Rheol.*, 9 (2), 17 (1965).

(31) K. Ninomiya, J. D. Ferry, and Y. Oyanagi, *J. Phys. Chem.*, 67, 2297 (1963).

TABLE IV

CALCULATED MASTER CURVES FOR ZIMM–SCHULZ DISTRIBUTION FUNCTION

$Z = 0$				$Z = 10$			
$\left(\frac{\gamma\tau_0}{2}\right)_0$	$\bar{g}$	η/η_0	$\left(\frac{\gamma\tau_0}{2}\right)_\infty$	$\left(\frac{\gamma\tau_0}{2}\right)_0$	g	η/η_0	$\left(\frac{\gamma\tau_0}{2}\right)_\infty$
0.0272	0.999	0.982	0.0272	0.0538	1.000	0.998	0.0538
0.0550	0.994	0.939	0.0547	0.106	0.998	0.987	1.106
0.115	0.982	0.843	0.133	0.213	0.991	0.938	0.211
0.253	0.956	0.692	0.242	0.444	0.966	0.808	0.430
0.583	0.911	0.512	0.531	0.975	0.914	0.600	0.891
1.40	0.850	3.43	1.19	2.24	0.837	0.385	1.87
3.45	0.775	0.210	2.68	5.32	0.746	0.222	3.98
8.66	0.693	0.120	6.01	12.9	0.653	0.119	8.42
21.9	0.610	0.0653	13.4	31.6	0.565	0.0607	17.9
55.8	0.531	0.0340	29.6	78.2	0.486	0.0302	38.0
142	0.458	0.0172	65.0	195	0.415	0.0148	80.9

However, the experimental values of τ_0 are essentially the same whether the modified or unmodified curves are used. Figure 6 is thus unaffected by the modification.

Summary

The rheological properties of polystyrene systems have been investigated in steady shearing flow. Viscosity master curves depend upon the molecular weight distribution of the polymer, and agree with calculations based on an entanglement theory of viscosity. Characteristic time constants τ_0 and τ_N were deduced for each system from the dependences of viscosity and normal stress on shear rate. Both are closely related to τ_R, the calculated Rouse relaxation time of the system, and both show a residual, linear dependence as the product $\varphi\bar{M}_w$ of the system. Viscosity data on polydisperse polymers show the same dependence on $\varphi\bar{M}_w$ as the narrow distribution samples. Considerably more scatter is evident in the normal stress data, and it is not possible to make a clear and unambiguous case in favor of $\varphi\bar{M}_w$ as the correlating variable for polydisperse systems. An alternative interpretation of the normal stress data, based on the analogy between permanent networks and an entanglement network at low shear rates, predicts τ_N/τ_R ratios which agree well with the experimental ratios.

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