The Dependence of Viscoelastic Flow Functions on Polymer Structure for Linear and Branched Polystyrene and Polybutadiene

Experimentally determined viscosities, first and second normal stress differences, and compliances for concentrated solutions of linear and four-arm star-branched polystyrenes and polybutadienes depend on the shear rate and the molecular weight, in agreement with theory and previously reported experimental results. The ratios of the second to first normal stress difference are −0.29 and −0.214 for the linear and branched polymers, respectively, independent of molecular weight, molecular weight distribution, concentration, and shear rate.

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SCOPE

The viscosity, first and second normal stress differences, and related functions of the shear rate are important in the design and operation of systems for processing polymer solutions and melts and in the development of viscoelastic flow theory. Both steady- and transient-shearing functions are important. This study is limited to the steady-shearing case. The dependence of the viscosity function on molecular structure, i.e., molecular weight, M, molecular weight distribution, MWD, branching and similar factors in steady-state shearing, has been extensively investigated. The dependencies on M and MWD are fairly well understood for linear polymers, but the effects of branching are much less clear. While the effects of M and MWD on the first normal stress difference are fairly well known for linear polymers, information on the effect of branching is very limited.

The only information on the dependence of the second normal stress difference on polymer structure is that from our laboratory. (Gao et al., 1981; Ramachandran and Christiansen, 1983). The more reliable reported values of the ratio of the second to the first normal stress difference function, ψ, vary from near zero to about −0.4 for a variety of polymer solutions and polymer melts. Reported here are additional results from a continuing effort to more definitively establish the dependence of the steady-state shearing flow functions on polymer structures with emphasis on the normal stresses and particularly the second normal stress difference. The best established means of determining the normal stress differences is via cone-plate shearing with measurement of the total normal (axial) force on the plate and the plate pressure distribution generated during shearing. However, this method is limited to shear rates $\tilde{<}10\cdot$ In the present research, the plate-pressure distribution was determined by means of improved miniature variable-capacitance pressure transducers mounted with their pressure-sensing diaphragms flush with the plate surface. The simultaneous measurement of the total normal force on the plate, the plate pressure distribution, and the viscosity was enabled by use of a modified Weissenberg rheogoniometer for the cone-plate shearing.

CONCLUSIONS AND SIGNIFICANCE

In the presently reported experimental research, concentrated solutions (100 kg to 600 kg polymer per m^3) of linear and four-arm, star-branched polystyrene and polybutadiene were studied. Much of the data extends from the Newtonian (low) shear-rate range into the shear-thinning or decreasing-viscosity shear-rate region. The viscosity, first normal stress difference, and the derived steady-shear compliance functions are in good agreement with theoretical predictions and generally accepted experimental results. For example, in the Newtonian shear-rate range, the viscosity and first normal stress difference coefficients are proportional to the 3.5 and 7+ power of the molecular weight, respectively. The unique contribution is that the ratio of the second to first normal stress difference was found to be −0.29 ± 5% and −0.214 ± 5% for the linear and four-arm star-branched polymers, respectively, independent of M, MWD, concentration, and shear rate. The ratio, $\psi = -0.214$, is within about 1% of the average for solutions of four-arm star, random, and block styrene-butadiene copolymers reported earlier (Ramachandran and Christiansen, 1983). These unique and significant experimental results demonstrate a significant effect of branching and show that the dependence of the second normal stress difference on the variables considered is the same as for the first normal stress difference after accounting for the

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ratio ψ. These results should serve as guides in the development of viscoelastic flow theory and in polymer processing applications. Also, the foregoing effect of branching together with additional definitive results for other types of branching may be useful in identifying the nature of branches in cases where other methods fail.

INTRODUCTION

The viscosity and normal stress viscometric flow functions $\eta(\dot{\gamma})$, $N_1(\dot{\gamma})$, and $N_2(\dot{\gamma})$, and functions derived from these are of importance in the effective design and operation of systems for the processing of polymer solutions and melts. However, the kinematics of many practical polymer flows are so complex that viscometric flow functions may not apply. It is often difficult, even if possible, to identify the important material functions which control the flow. Fortunately, there are many industrially important flows for which the kinematics are relatively simple, and viscometric flow functions are valid or may be taken as approximately so for the entire flow field or portions thereof (Goddard, 1976). Furthermore, viscometric flow parameters serve as indices to some very complicated flow phenomena in polymer processing and otherwise (Petrie and Denn, 1976; Williams, 1975) and are important in the development of viscoelastic flow theory (Bird et al., 1977; Williams, 1975).

The $N_1(\dot{\gamma})$ or $\psi_1(\dot{\gamma})$ and $N_2(\dot{\gamma})$ or $\psi_2(\dot{\gamma})$ and related functions are of particular interest owing to their important effects in polymer processing and to the theoretical and experimental evidence that they depend much more strongly on molecular weight than do the viscosity functions (Curtiss and Bird, 1981; Gao et al., 1981; Lodge and de Vargas, 1983).

The present study is unique in that the viscometric second normal stress difference, $\psi_2(\dot{\gamma})$, as well as the viscosity, $\eta(\dot{\gamma})$, and the first normal stress difference, $\psi_1(\dot{\gamma})$, and derived functions are presented for relatively concentrated solutions of well-characterized linear and branched polymers. Among its many practical roles, the second normal stress difference represents a force which promotes the centering of the wire in wire coating (Tadmor and Bird, 1974), the migration of particles away from a tube wall (Ho and Leal, 1976; Leal, 1979), and it plays an important role in viscoelastic flow stability (McIntire and Schowalter, 1970; Petrie and Denn, 1976). Furthermore, it is important in the development and evaluation of constitutive theory (Bird et al., 1977; Williams, 1975).

In this presentation, the sign convention of Bird et al. (1977) is used; i.e., N_1 is considered negative corresponding to a tension along stream lines and N_2 is positive. However, some systems, e.g., liquid crystal systems, reportedly yield positive or negative values for N_1 depending on conditions (Kiss and Porter, 1980; Wissbrun, 1981; Mason, 1982; Baird et al., 1983). At low shear rates, ($\dot{\gamma} \rightarrow 0$), $-N_1(\dot{\gamma})$ is quadratically dependent on $\dot{\gamma}$; and consequently, $\psi_1(\dot{\gamma})$ asymptotically approaches a limiting value ψ_1^0 as does $\eta(\dot{\gamma})$ (Ferry, 1980; Bird et al., 1977; Gao et al., 1981). However, in the shear thinning regime, $\psi_1(\dot{\gamma})$ declines more rapidly than $\eta(\dot{\gamma})$. At present it is not clear that $\psi_1(\dot{\gamma})$ approaches a high shear-rate limit analogous to η_∞. In the lower shear rate range, $N_2(\dot{\gamma})$ and $-\psi_2(\dot{\gamma})$ exhibit the same behavior as $-N_1(\dot{\gamma})$ and $\psi_1(\dot{\gamma})$ except that they are lower by the ratio $\psi = N_2/N_1$ (Gao et al. 1981). Reported experimental values of ψ vary from near zero (the Weissenberg hypothesis) to about -0.4 (Tanner, 1973; Keentok and Tanner, 1982). Such models as the continuum corrotational model predict values up to 0.5 (Bird et al., 1977). Also, there are empirical and theoretical grounds for 0.5 as a maximum though unrealistic value (Bird et al., 1974; Petrie and Denn, 1976).

Of the three material functions, viscosity has been the most thoroughly investigated (Berry and Fox, 1968; Peterlin, 1972; Berry and Cassasa, 1970; Graessley, 1974; Bywater, 1979; and Kumar, 1980). The effects of molecular weight and molecular-weight distribution on viscosity have been established rather well for linear polymers, but the effects of branching are less clearly understood (Graessley, 1977; Bywater, 1979; Yasuda et al., 1981; Small, 1975).

TABLE 1. MOLECULAR CHARACTERIZATION DATA FOR LINEAR POLYSTYRENE AND POLYBUTADIENE POLYMERS†

Sample(a)	M_w(b)	M_n(c)	M_z or M_v(d)	M_w/M_n
PS37	33	36	38	1.09
PS110	111	111	111	1.00
PS200	200	193	111	1.04
PS390	392	355	383	1.10
PS600	599	600	607	1.00
PS670	670	640	678	1.05
PS2000	2050	1990	2340	1.03
PS-DOW	272(e)	113(e)	586(f)	2.41
PBC-tr	—	—	—	—

† All molecular weights expressed as 1,000's.

(a) PS, polystyrene; PBC-tr, polybutadiene.

(b) Obtained from light scattering (±5%), Pressure Chemical Co.

(c) Obtained from membrane osmometry (±5%), Pressure Chemical Co.

(d) M_v from intrinsic viscosity for monodisperse polymers (±5%), Pressure Chemical Co.

(e) Obtained from gel permeation chromatography, Eastman Kodak Research Lab.

(f) M_z obtained from gel permeation chromatography, Eastman Kodak Research Lab.

The effects of molecular weight and molecular weight distribution (MWD) on the first normal stress difference have also been investigated extensively (Graessley, 1974). However, published research on the effects of long-chain branching on the first normal stress difference in concentrated solutions and melts is very limited (Graessley, 1974, 1982; Bywater, 1979; Yasuda et al., 1981).

To our knowledge, the only reports on the effect of molecular parameters on N_2 are our previous publication (Gao et al., 1981) concerned with the effect of M and MWD on the η, N_1, and N_2 steady-state, transient and oscillatory shearing functions for concentrated solutions of linear polystyrenes and a report concerned with four-arm, star-branched copolymers of styrene and butadiene (Ramachandran and Christiansen, 1983). The present study extends the results to the effect of branching on the η, N_1, and N_2 functions for concentrated solutions of additional four-arm, star-branched polymers and includes more recent information on the effect of M and MWD on the functions for linear polymers. The instrumentation used in previous studies (Gao et al., 1981; Christiansen and Leppard, 1974; Miller and Christiansen, 1972) was modified to increase the accuracy of the results (Ramachandran, 1985).

EXPERIMENTAL

Materials

The polymers of concern in this report are a series of seven monodisperse and one polydisperse linear polystyrenes, a series of five monodisperse four-arm, star-branched polystyrenes, and one linear and two four-arm, star-branched, polydisperse polybutadienes. Molecular characterization data are presented in Tables 1 and 2. The polydisperse linear polybutadiene was not characterized. With the exception of PS37, the monodisperse polystyrenes were fractionated by dissolution and fractional precipitation.

TABLE 2. MOLECULAR CHARACTERIZATION DATA FOR FOUR-STAR BRANCHED MONODISPERSE POLYSTYRENES AND FOUR STAR BRANCHED POLYBUTADIENES[†]

Sample	M_{arm}[(a)]	M_w, Total[(b)]	M_w/M_n
*PS110	27.5	110	<1.06[(c)]
*PS200	50	200	<1.06[(c)]
*PS404	101	404	<1.06[(c)]
*PS640	160	640	<1.06[(c)]
*PS2400	600	2,400	<1.06[(c)]
Sol233[(d)]	75[(e)]	300	1.77
Sol250[(d)]	83[(e)]	330	1.74

[†] All molecular weights expressed as 1,000's.

* Four-arm branched polystyrene polymers.

(a) Arm molecular weights from gel permeation chromatography, Inst. of Polymer Sci., Univ. of Akron.

(b) Estimated as four times M_{arm}. Also confirmed by gel permeation chromatography in our laboratory.

(c) Estimated from chromatograms.

(d) 40% Cis, 50% trans, 10% vinyl (100% polybutadiene).

(e) Estimated as $M_w/4$.

Also, some of the four-arm, star-branched polystyrenes were fractionated to remove small amounts of precursor arms.

Gel permeation chromatograms (GPC) determined by us for the solprenes 233 and 250 indicate that these are bimodal. Periodic checks by GPC for the linear mono- and polydisperse polystyrenes before and after shearing indicated no noticeable change in molecular properties.

The solvent used was normal butylbenzene, which has a low viscosity (0.001 Pa·s at 30°C) and a relatively low vapor pressure (boiling point: 183°C). Also, with a Hildebrand solubility parameter of 8.2, it is a good solvent for both polystyrene (solubility parameter 9.1) and polybutadiene (solubility parameter 8.4). In general, polymer concentrations varied from about 100 to 600 kg/m^3.

Procedure

The reported viscometric flow functions were determined in cone-plate shearing with a stiffened model R17 Weissenberg rheogoniometer (Ramachandran and Christiansen, 1980) in which the cone, which is rotated, is below the plate. The cones and plates were 7.4 cm in diameter, and the cone angles were 0.5, 2, and 4°. All shearing measurements were made with the cone and plate enclosed in a constant-temperature environmental chamber with the temperature controlled at 25 ± 0.1°C. Of particular interest, the normal stress differences were determined from the total normal or axial force on the plate and the normal force distribution on the plate or from combinations of these.

The normal stress distributions on the plate were determined with miniature capacitive pressure transducers located, in the case of one plate, at radial positions of 1.366, 2.190, 2.563, and 2.991 cm; and, in a second plate, at radial positions of 1.316, 1.721, 2.268, and 3.003 cm. The 2.4 mm diameter pressure-sensing diaphragms of the transducers were located flush with the plate surface to avoid the well-known "hole pressure" effect. The transducers, made in-house, were continually improved, especially with respect to sensitivity. The transducers used in the present research had sensitivities of approximately 3×10^{-5} pF/Pa, and, with the associated electronic circuitry, had resolutions as small as about 0.1 Pa to 0.5 Pa in some cases. The use of the more sensitive transducers and improved computer data acquisitions reduced data scatter and increased accuracy as compared with our previous results.

DATA ANALYSIS

The relations expressed in Eqs. 1–6, together with definitions given in the Nomenclature section, were used in the data analysis. The derivations of Eqs. 1 through 5 are readily available (Walters, 1975; Bird et al., 1977] as is the derivation of Eq. 6 from Eq. 5 (Ramachandran and Christiansen, 1983). If in spherical coordinates the azimuthal angle, ϕ, direction is designated as the 1-direction, the polar angle, θ, the 2-direction, and r, the 3-direction, then

$$\dot{\gamma} = -\frac{\Omega}{\alpha} \tag{1}$$

$$\eta(\dot{\gamma}) = -\tau/\dot{\gamma} = \frac{3T\alpha}{2\pi R^3\Omega} \tag{2}$$

$$N_1(\dot{\gamma}) = \Pi_{11} - \Pi_{22} = \frac{-2F}{\pi R^2} \tag{3}$$

$$N_2(\dot{\gamma}) = \Pi_{22} - \Pi_{33} = \Pi_{22}(R) \tag{4}$$

$$\frac{\partial \Pi_{22}(r)}{\partial ln r} = (\Pi_{11} - \Pi_{22}) + 2(\Pi_{22} - \Pi_{33}) \tag{5}$$

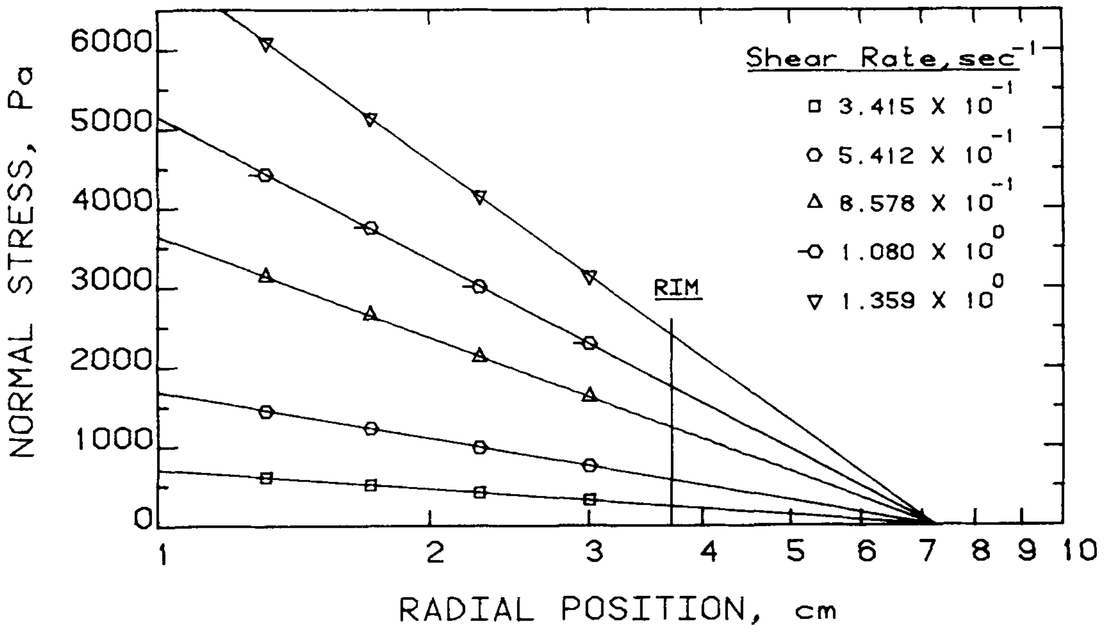

Figure 1. Total normal stress on plate relative to atmospheric pressure vs. radial position. 465.8 kg·m^{-3} solution of PS600 in n-butylbenzene; 2° cone angle, heavy spring.

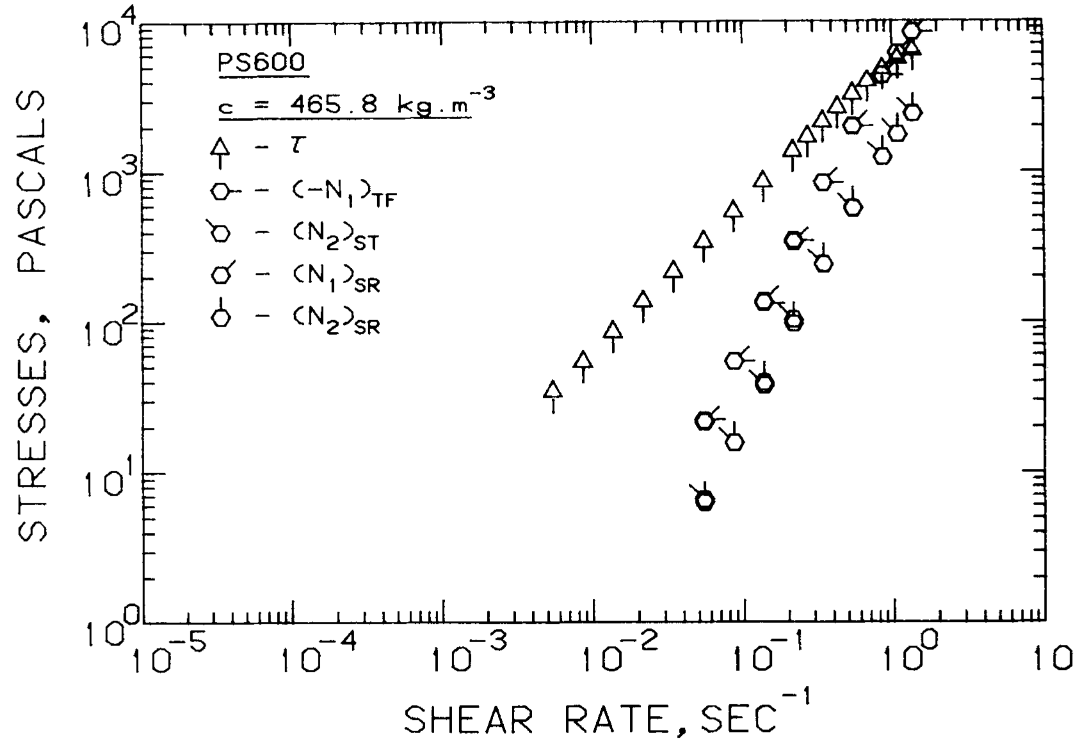

Figure 2. Steady shear data for solution as in Fig. 1; 2° cone angle, heavy spring.

$$R_i = R \exp\left(\frac{-\psi}{1+2\psi}\right) \qquad (6)$$

These relations are based on ideal shearing flow. Corrections must be made if such effects as surface tension, centrifugal force, etc., are not negligible. In Eq. 4, the isotropic pressure is assumed to be equal to the ambient pressure at the rim.

The viscosities were computed by means of Eqs. 1 and 2. Equations 3, 4, and 5 suggest alternate means for determining the normal stress differences, N_1 and N_2, two of which were used in

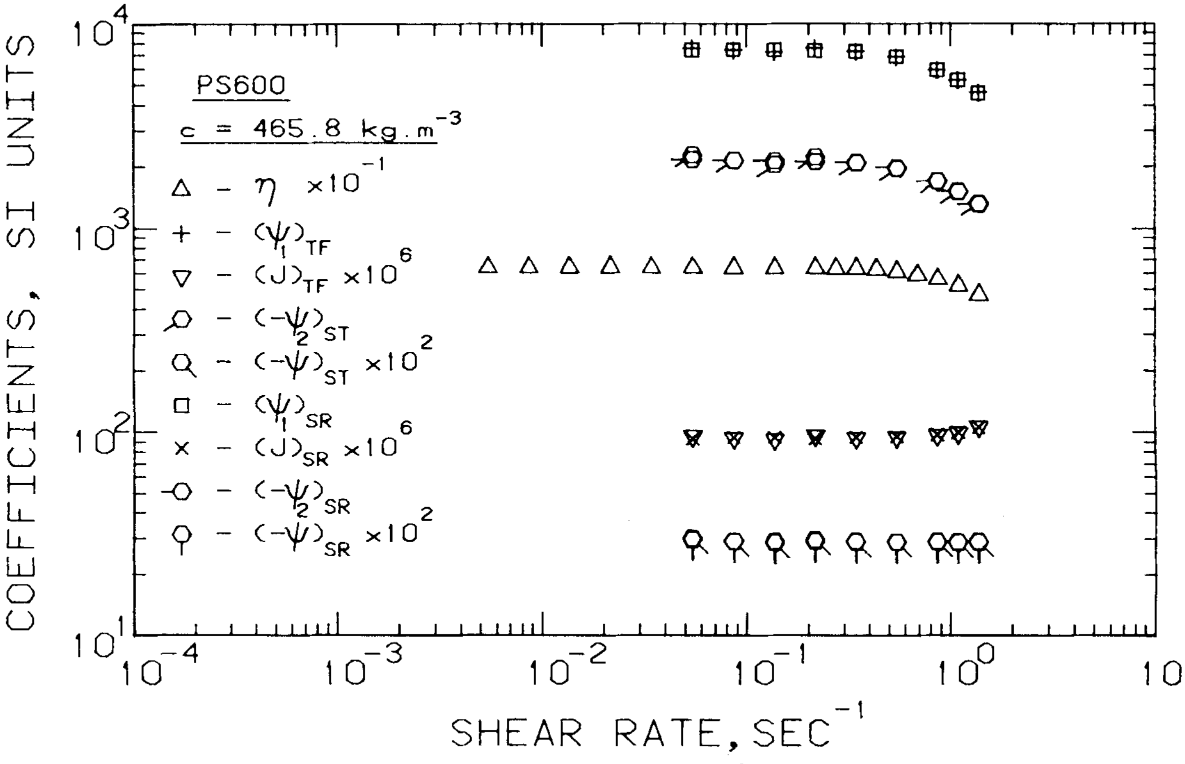

Figure 3. Steady shear data for solution as in Fig. 1; 2° cone angle, heavy spring.

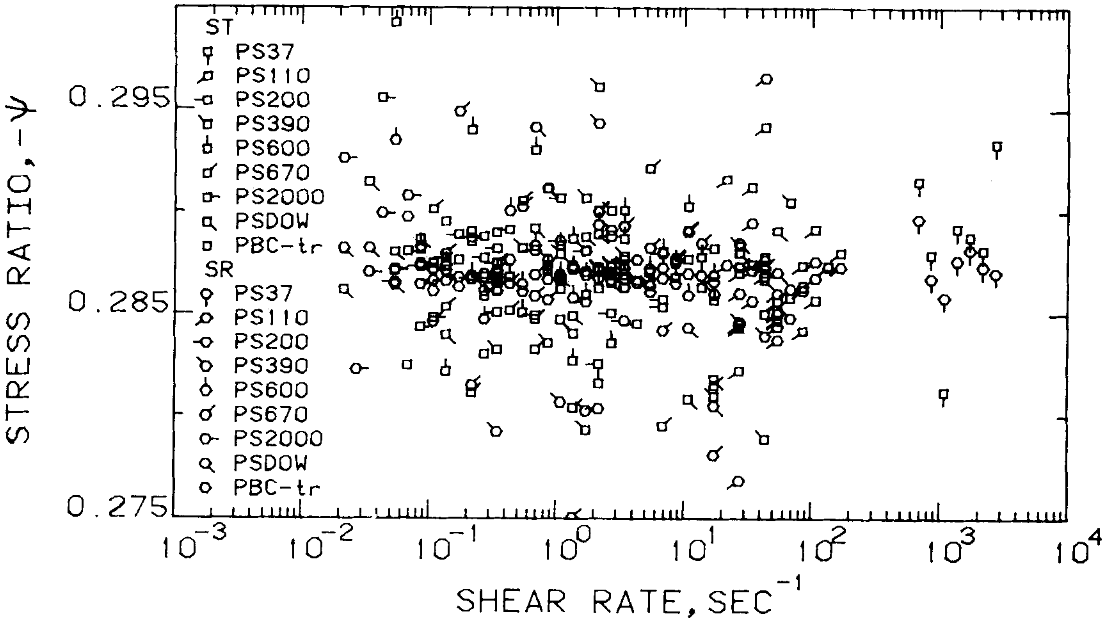

Figure 4. Ratio of N_2 to N_1, ψ, as a function of shear rate for concentrated solutions of linear polystyrenes and polybutadienes.

this study: (i) the slope total force (ST) method, in which N_1 was obtained by Eq. 3 and N_2 was obtained from Eqs. 3 and 5; and (ii), the slope rim (SR) method, in which N_1 and N_2 were obtained from Eqs. 4 and 5. Point and total centrifugal stresses were determined for glycerin as a function of Ω. These are represented well by Turian's (1972) relations, and normal stresses were corrected for centrifugal stress wherever these were significant.

RESULTS

A representative plate pressure distribution is shown in Figure 1. The straight lines were established by a least squares fit of the data. In general, the data fall within about 1% of such lines. By Eq. 5, these linear relations indicate that N_1 and N_2 and the shear rate are essentially constant in the shearing field. According to the adopted sign convention, Π_{22} at the rim is positive; consequently, by Eq. 4, N_2 is positive, and by Eq. 5, N_1 is negative.

By Eq. 6 and the abscissa intercept of $\Pi_{22}(\ln r)$ at $r = R_i$, ψ can be determined for a particular shear rate. And if, for a set of shear rates, the abscissa intercepts are the same, as in Figure 1, ψ is constant and independent of shear rate in that particular shear rate range.

The viscometric material functions $\tau(\dot\gamma)$, $N_1(\dot\gamma)$, and $N_2(\dot\gamma)$ and their coefficients for the linear monodisperse polystyrene solution

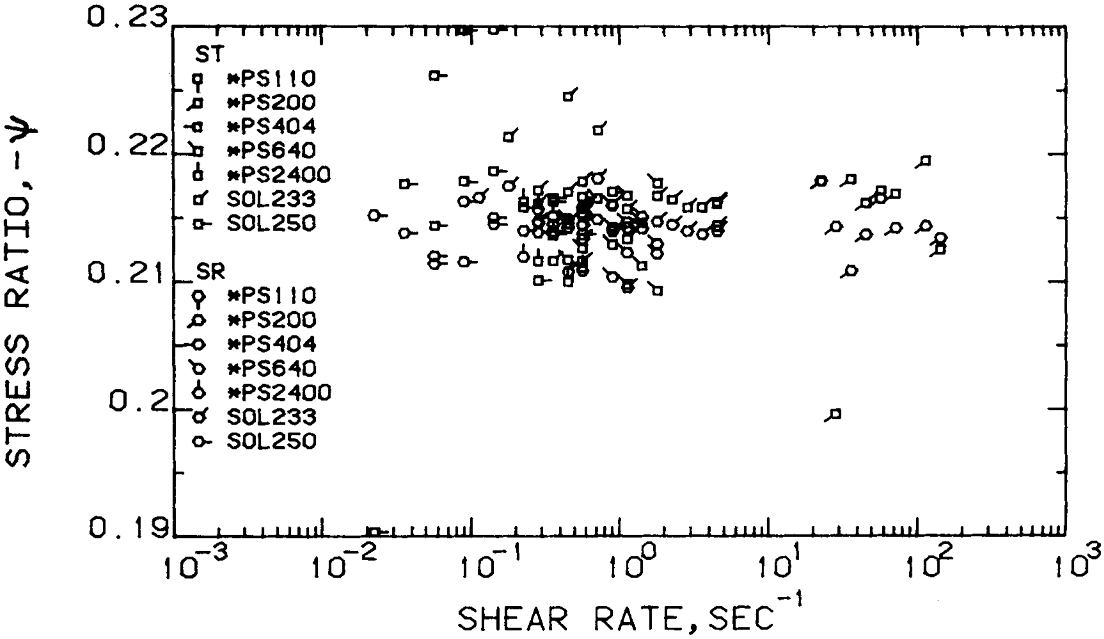

Figure 5. Ratio of N_2 to N_1, ψ, as a function of shear rate for concentrated solutions of four-arm star-branched polystyrenes (marked *) and polybutadienes in *n*-butylbenzene.

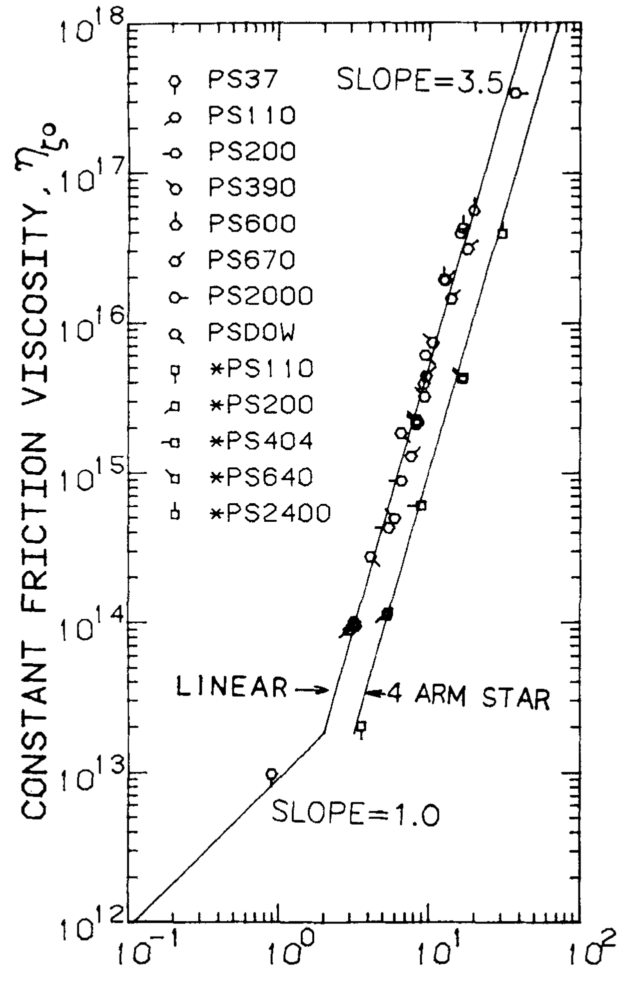

Figure 6. Constant-friction viscosity vs. entanglement density for concentrated solutions of linear and four-arm star-branched (marked *) polystyrenes in *n*-butylbenzene.

are plotted in Figures 2 and 3. These plots are typical of those for all linear polystyrene solutions. These functions extend from the linear "zero" shear rate region somewhat into the nonlinear shear-thinning range. However, in some cases flow instabilities occurred before the shear-thinning range was reached. In general, the onset of shear thinning occurred at progressively lower shear rates, with increase in concentration, molecular weight, and molecular weight distribution. The log-log plots of N_1 and N_2 vs. $\dot{\gamma}$ at low $\dot{\gamma}$ have slopes of 2, indicating that these quantities are proportional to $\dot{\gamma}^2$, as predicted by some theories and previously observed (Bird, et al., 1977; Gao, et al., 1981). Thus ψ_1 and ψ_2 are constant (equal to ψ_1^0 and ψ_2^0) in the linear low shear rate range. The onset of the effects of shear thinning for $N_1(\dot{\gamma})$ and $N_2(\dot{\gamma})$ occurs at about the same $\dot{\gamma}$ as in the case of $\eta(\dot{\gamma})$. It will be noted that the data determined by the ST and SR methods agree very well (within about 2%). Of particular interest, ψ does not vary significantly with shear rate. Also, $J(\dot{\gamma})$ increases with $\dot{\gamma}$ in the shear thinning region for these linear essentially monodisperse polymers, an observation to be considered later.

In general, the dependences of the flow functions on $\dot{\gamma}$ are qualitatively similar for the linear mono- and polydisperse and the branched mono- and polydisperse polymer solutions. In the low shear rate linear range, limiting behavior was exhibited: $\tau \alpha \dot{\gamma}$, $N_1 \alpha \dot{\gamma}^2$, and $N_2 \alpha \dot{\gamma}^2$ and $\eta(\dot{\gamma})$, $\psi_1(\dot{\gamma})$, $\psi_2(\dot{\gamma})$, and $J(\dot{\gamma})$ asymptotically approach the constant values η_0, ψ_1^0, ψ_2^0, and J_e^0. However, there are differences, e.g., in $J(\dot{\gamma})$, which will be discussed later.

The Ratio ψ

The ratio $\psi = N_2/N_1$ is plotted as a function of $\dot{\gamma}$ for a number of linear polymers in Figure 4. Data for the following are included: 1) solutions in normal butylbenzene of linear monodisperse polystyrenes of different molecular weights at concentrations of about 100 to 600 $kg \cdot m^{-3}$; 2) a 450.0 $kg \cdot m^{-3}$ solution of a linear monodisperse polystyrene PS200 in tri-cresyl phosphate; 3) solutions of a polydisperse polystyrene PSDOW in n-butyl benzene at three different concentrations; 4) a 304.4 $kg \cdot m^{-3}$ solution of a linear polydisperse cis-trans-polybutadiene in normal butylbenzene. The mean value of ψ for the solutions of linear polystyrenes (mono- and polydisperse) and the solutions of linear polybutadiene (polydisperse) are −0.287 (284 points) and −0.287 (14 points), respectively; the standard deviations are 1.12% and 0.75%, respectively. The maximum deviation from the mean value is 4.2%. The agreement between the ψ values from the SR (hexagons) and the ST (squares) techniques is within ± 1% except at low stress levels, where the agreement is within ± 2%.

Reptation models of Doi and Edwards (1978, 1979) and Curtiss and Bird (1981) for concentrated systems of linear, monodisperse polymers predict a low shear rate limiting value of $\psi_1^0 = -2/7 = -0.286$ and $\psi_1^0 -2/7 (1 - \epsilon)$, respectively. There is evidence that e must be near zero for reasonable representation of most of the flow functions in typical experimental ranges (Graessley, 1982; Lin, 1984), but there are dissenting views (Saad et al., 1982). However, both the Doi-Edwards and Curtiss-Bird theories predict that $-\psi(\dot{\gamma})$ decreases with shear rate. The predicted decrease by the Doi-Edwards theory for our data at the higher $\dot{\gamma}$ is significant but was not observed.

The ratio $-\psi(\dot{\gamma})$ for solutions of four-arm star-branched polystyrene and four-arm star-branched butadiene homopolymers in n-butyl benzene is shown in Figure 5. The data are for solutions having concentrations of about 200 to 550 $kg \cdot m^{-3}$. The mean values of the ratio for the four-arm polystyrenes (48 points) and the four-arm polybutadienes (70 points) are −0.214 and −0.216, respectively, with standard deviations of 1.5% and 2.4%, respectively. A maximum deviation of ±5% occurred at low stress values. Within the error of measurement, there are no significant differences in the ψ values between the branched-polybutadiene and branched-polystyrene solutions.

The mean value of ψ for solutions of four-arm star, random, and block copolymers of styrene and butadiene in normal butylbenzene (Ramachandran and Christiansen, 1983) is −0.214 (126 points) with a standard deviation of 1.5%.

The value of ψ for both the linear and the branched polymers does not vary significantly with M, MWD, concentration, composition, or shear rate and, in one case, is the same for a linear polymer in tricresylphosphate as in normal butylbenzene. In the case of the four-arm star copolymers, ψ does not vary with block structure. However, the mean value of ψ for all of the branched polymer solutions is −0.214, as compared with −0.286 for the linear polymer solutions—a significant 25% difference! The values for ψ are in the reported range but are unique in that they are sufficiently definitive to show a significant effect of branching. It is of interest that the Doi-Edwards theory predicts that if the number of entanglements per chain is sufficiently high, ψ for linear polymers is independent of concentration, molecular weight, and molecular weight distribution in agreement with our results but that ψ for linear and branched polymers is the same (Doi, 1984).

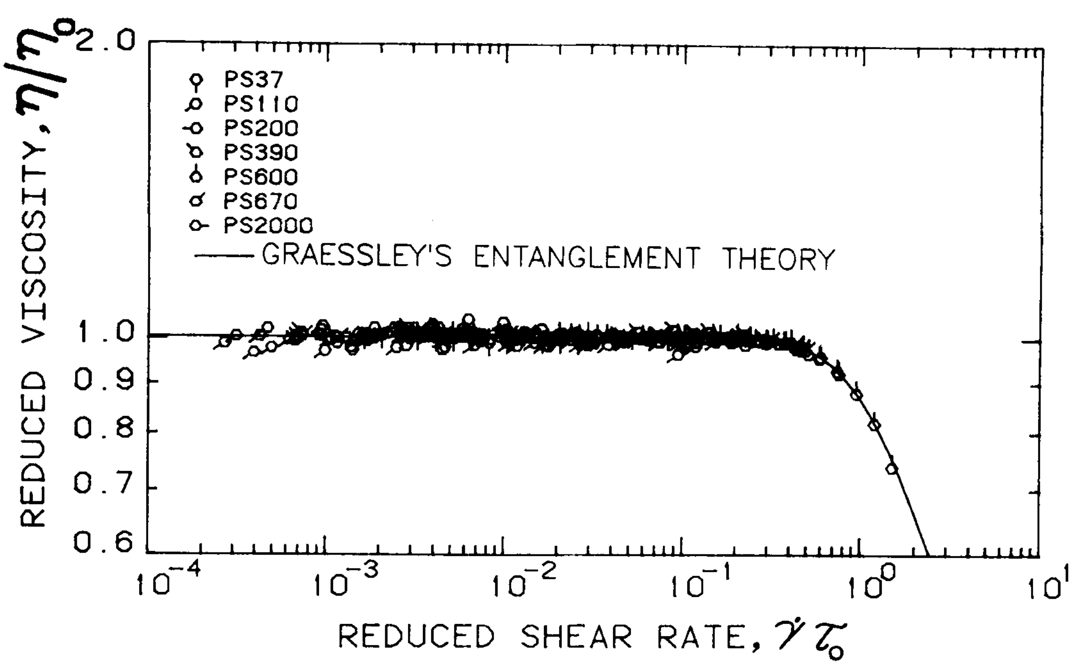

Figure 7. Reduced viscosity vs. reduced shear rate for concentrated solutions of linear monodisperse polystyrenes in *n*-butylbenzene.

Constant Friction Factor Viscosities

In Figure 6, a constant friction-factor zero shear-rate viscosity is shown as a function of an entanglement density for a series of solutions of the linear and four-arm star-branched polystyrenes. A method employed by Lindeman (1967) was used in computing $\eta_{0\zeta}$ and $E = CM_w/\rho M_e$, where $\rho = 1{,}070$ kg/m^3 and $M_e = 15{,}600$ for polystyrenes. A linear least-squares fit of the linear polymer data for $E > 2$ has a slope of 3.5, as predicted by entanglement theories (Graessley, 1974), and is represented by

$$\eta_{0\zeta} = 1.61 \times 10^{12} E^{3.5}, \qquad (7)$$

This line also represents the polydisperse polystyrene data very well. The line of slope 1 was drawn through a point on the least-squares fit line at $E = 2$.

The line through the four-arm star-branched polymer solutions represents Eq. 7, but with E replaced with gE, where $g = (3f - 2)/f^2$, and f is the number of arms or branches. This result is in agreement with Bueche's (1964) predictions. Many branched polymer solutions and melts exhibit viscosity enhancement (Roovers and Graessley, 1981): i.e., η_o increases exponentially with branch length as predicted (Graessley, 1982), when the branch length is significantly greater than M_c, and η_o for the branched

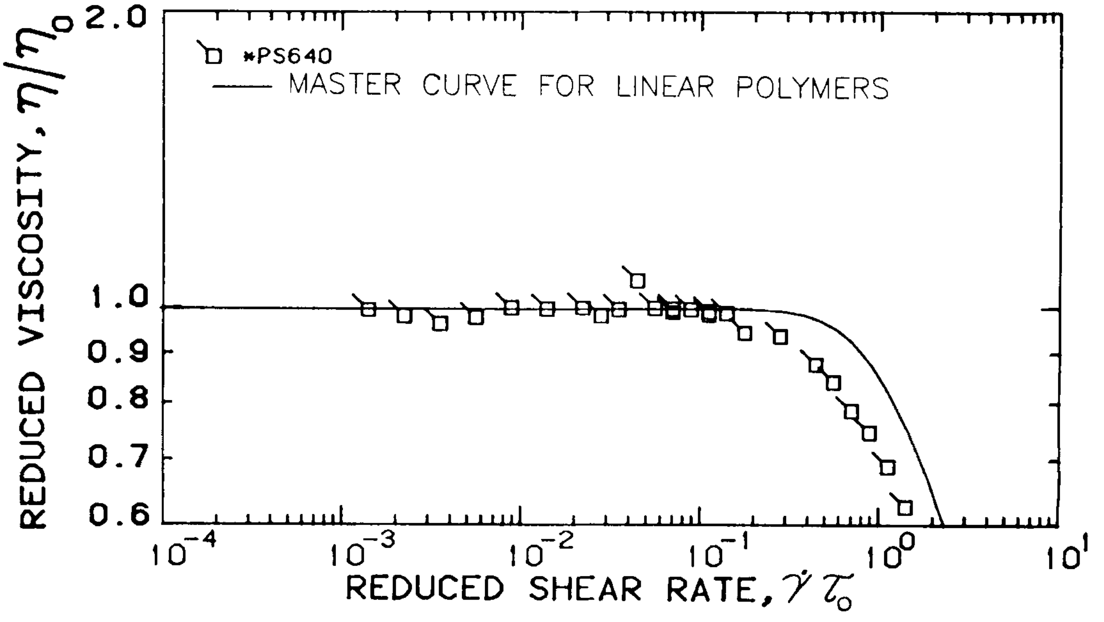

Figure 8. Dependence of viscosity on shear rate for a four-arm star-branched polystyrene solution (*) compared with the function for linear polystyrene solutions.

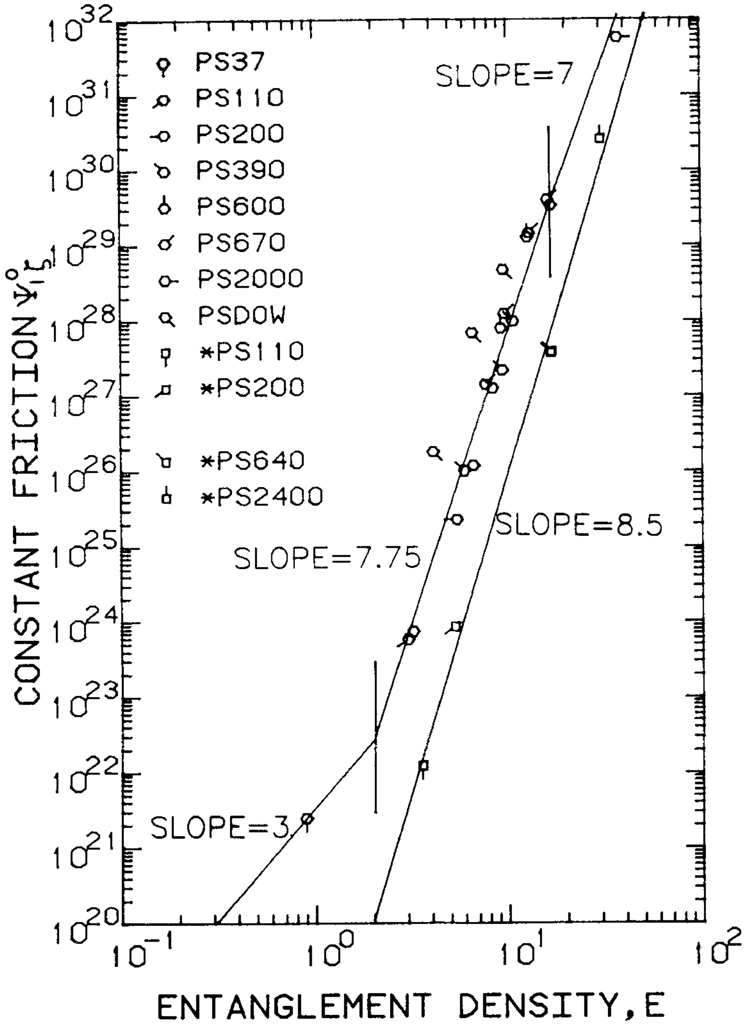

Figure 9. Constant-friction first normal stress difference coefficient vs. entanglement density for concentrated solutions of linear and four-arm star-branched (marked *) polystyrenes.

polymers may exceed that for linear polymers of the same M. It is clear that the branched polystyrene solutions studied did not exhibit viscosity enhancement, though $E > 20$. This observation agrees with other observations and Graessley's (1977) conclusion based on a reptation model that the molecular properties of star-branched polystyrene are less conducive to viscosity enhancement than the properties of many other polymers but do exhibit viscosity enhancement under some likely conditions. However, the four-arm, star-branched polybutadiene solution data do suggest viscosity enhancement as $\eta_0 \alpha M_w^7$, whereas, for the linear polybutadiene solutions, $\eta_0 \alpha M_w^{3.4}$.

In Figure 7, reduced viscosity data for linear monodisperse polystyrene solutions are plotted vs. a reduced shear rate and compared with the prediction of Graessley's (1974) entanglement theory. Much of the data do not extend far enough into the shear thinning region to estimate $\tau_0 = 1/\dot{\gamma}$ at $\eta = 0.8\eta_0$. For such data the τ_0 were estimated by fitting the data to Graessley's equations. A Gauss-Newton nonlinear least-squares program, based on the Bard algorithm (Kuester and Mize, 1973) and incorporating the Graessley equations, was used. This procedure explains in part the good fit of the data by the Graessley relation.

In Figure 8, reduced viscosity shear-rate data for a star-branched polystyrene solution are compared with the function for linear polymer solutions. While the form of the branched function is similar to that of the linear function, the onset of shear thinning occurs at a significantly lower shear rate.

Constant Friction Normal Stress Difference Coefficients

A constant friction coefficient, $\psi^0_{1\zeta} = 2\, J^0_e \eta^2_{0\zeta}$, is plotted vs. E in Figure 9 for the linear and branched polystyrene solutions. As indicated, monodisperse data between $E = 2$ and $E = 20$ are represented by $\psi^0_{1\zeta}\, \alpha\, E^{7.75}$ and may approach an asymptote $\psi^0_{1\zeta} \alpha\, E^7$ for $E > 30$. The line with a slope of 3 is drawn through the single low E datum and the point on $\psi^0_{1\zeta}\, \alpha\, E^{7.75}$ at $E = 2$. It is of interest that the linear polydisperse $\psi^0_{1\zeta}$ are significantly higher than those for the monodisperse polymers. Also, a least-squares fit for the four data points for the branched polymer solutions indicates that $(\psi^0_{1\zeta})_B\, \alpha\, E^{8.5}$ and that $(\psi^0_{1\zeta})_B$ will exceed $(\psi_{1\zeta})_L$ at a high value of E. Since $\psi = \psi_2/\psi_1$ is independent of M and concentration, the $\psi^0_{2\zeta}(E)$ will parallel $\psi^0_{1\zeta}(E)$ but will be lower for the same E by the value of the ratio, ψ_2/ψ_1.

Compliances

As shown in Figure 3, $J(\dot{\gamma})$ increases with $\dot{\gamma}$ in the shear-thinning region as observed by others (Graessley, 1974) and predicted (Doi

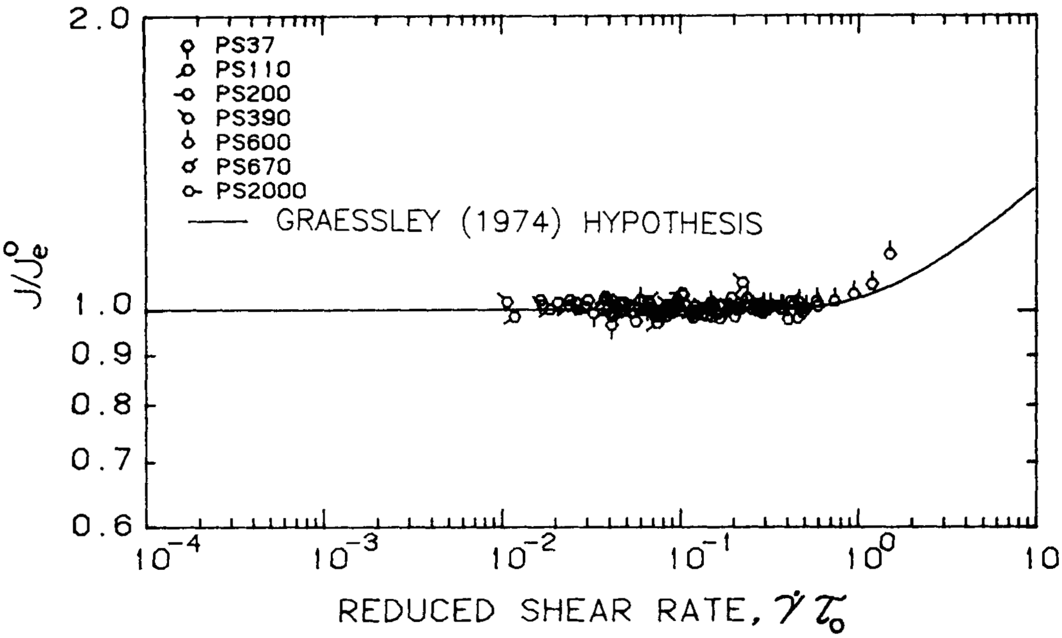

Figure 10. Reduced compliance J/J_e^0 vs. reduced shear rate for concentrated solutions of linear monodisperse polystyrenes in *n*-butylbenzene.

and Edwards, 1979; Graessley, 1974; Tanaka et al., 1970) for concentrated solutions of linear and monodisperse polymers. In Figure 10, $J/J_e^0(\tau_0\dot{\gamma})$ for concentrated monodisperse polystyrene solutions is compared with Graessley's (1974) entanglement reduction hypothesis. The increase in compliance starting in the shear-thinning region is greater than predicted. Also, in the case of the concentrated solutions of polydisperse polymer, J/J_e^0 decreases with $\tau_0\dot{\gamma}$ at the onset of shear thinning in agreement with the results of previous studies (Gao et al., 1981; Graessley, 1974). Also, in the case of the concentrated solutions of branched polymers, the $J(\dot{\gamma})$ for the monodisperse solutions increases; and the $J(\dot{\gamma})$ for the polydisperse polymers decreases with shear rate, starting with shear thinning. However, the increase with shear rate for the monodisperse branched polymers is not as clearly supported

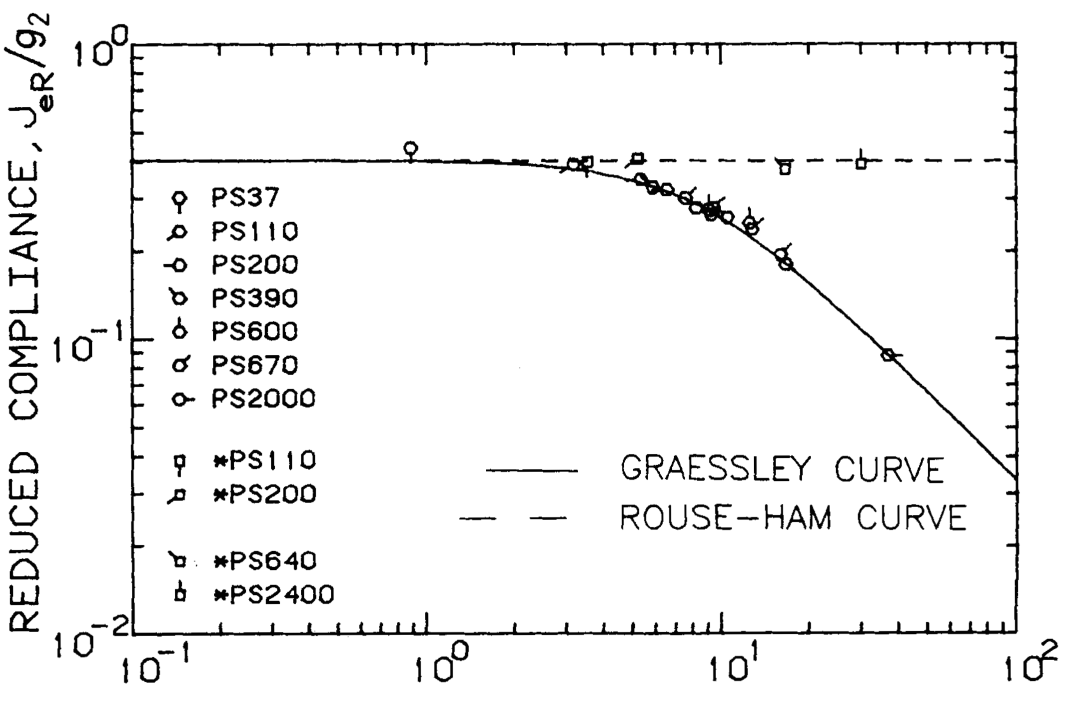

Figure 11. Reduced steady-state compliance J_{eR}/g_2 vs. entanglement density for monodisperse linear and four-arm star-branched (marked *) polystyrene solutions in *n*-butylbenzene.

by the data as in the case of the monodisperse linear polymers.

Reduced low-shear-rate compliances are shown for solutions of monodisperse linear and star-branched polystyrenes as a function of the entanglement density in Figure 11. As shown, J_{eR} for the linear polymers changes from a constant value of approximately 0.4 at low E, as predicted by the Rouse theory (Ferry, p. 195, 1980), to proportionality, to E^{-1} at $E \gtrsim 20$. Thus J_e^0 for the solutions of linear polymers is proportional to M at low M and is independent of M at higher M, as predicted by many theories (Graessley, 1982) and supported by much experimental data (Graessley, 1974). The solid line represents an empirical equation for linear polymers suggested by Graessley (1974). Based on the intersection of a line of slope $= -1$ through the data for $E \gtrsim 20$ and the line for $J_e^0 = 0.4$, $M_c'/M_e = 8.3$, and $M_c' = 8.3 \times M_e = 129{,}480$, which is in close agreement with a value of about 130,000 reported in the literature for polystyrene (Graessley, 1974). Doi (1981) predicted M_c'/M_e to be 7.2. At low E, J_e^0 is dependent on C^{-1}, and at high E, on C^{-2}, in agreement with experimental data for other systems (Graessley, 1974; Ferry, 1980).

The branched-polymer solution data shown in Figure 11 are well-represented by the Rouse-Ham equation (Ham, 1957),

$$(J_e^0)_B = 0.4 g_2 M/CRT$$

as has been found by others for concentrated solutions and melts (Graessley and Roovers, 1979). This proportionality to M was also predicted for star-branched polymers by Doi and Kusuu (1980) and Graessley (1982). The values of $(J_e^0)_B$ decrease rapidly with functionality which is embodied in g_2.

The zero shear compliances J_e^0, for solutions of a linear polydisperse polystyrene were found to be higher than those for the corresponding solutions of linear monodisperse polystyrene at the same molecular weight by a factor $(Mz/Mw)^d$, where d increases from 2.5 to 3.5 for a change in concentration from 250 kg·m^{-3} to 580 kg·m^{-3}. We have previously reported d to be equal to 3.5 for 450 kg·m^{-3} solutions of linear polydisperse polystyrenes in normal butylbenzene (Gao et al., 1981).

CONCLUSIONS

The viscometric material flow functions presented for concentrated solutions of linear, mono-, and polydisperse polystyrenes, polydisperse polybutadienes and four-arm, star-branched polystyrenes and polybutadienes support the following conclusions:

1. The viscosities and first and second normal stress differences are proportional to the 3.5 power and 7–8 power of the molecular weight, respectively, about as predicted by theory and as commonly observed.
2. The steady-state shearing compliance functions confirm previous results and the Graessley and Ham theories.
3. The normal stress difference ratio, $\psi = N_2/N_1$, for our data appears to be independent of M, MWD, solution concentration, polymer type, shear rate, and solvent for the variable range investigated.
4. Improved instrumentation for the measurement of plate normal pressure distributions enabled the unique finding that ψ is -0.287 and -0.214 for the concentrated solutions of linear and four-arm, star-branched polymer solutions, respectively.

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NOTATION

C = concentration, mass per unit volume
E = entanglement density, $CM_w/\rho M_e$, the number of entanglement junctions per molecule or number of entanglements per unit volume.
F = total normal or axial force exerted on plate
f = number of branches in star polymer
g = ratio of the mean square radii of gyration of the star-branched to the linear polymer at constant M, $\langle S^2\rangle_B/\langle S^2\rangle_L \simeq (3f-2)/f^2)$
g_2 $(15f-14)/(3f-2)^2 = (J_e^0)_B/(J_e^0)_L$
J_e^0 = steady-state zero shear compliance (in the zero shear rate limit), $\psi_1^0/2\eta_0^2$
$J(\dot{\gamma})$ = steady-shear compliance, $\psi_1(\dot{\gamma})/2\eta^2$
J_{eR} $= \dfrac{J_e^0 CRT}{M}\left(\dfrac{\eta_0}{\eta_0-\eta_s}\right)^2$
$(J_e^0)_B$ = 0.4 g_2M/CRT for branched polymers (Ham, 1957)
M = Molecular weight
M_c = characteristic molecular weight taken to indicate onset of "entanglement" $\eta_0(M)$ behavior, undiluted polymer, $C(M_c)_{\text{soln}}/\rho$
M_c' = characteristic molecular weight taken to indicate onset of "entanglement network" $J_e^0(M)$ behavior, undiluted polymer $C(M_c')$soln$/\rho$
M_e = average molecular weight between entanglement loci
M_n = number average molecular weight
M_w = weight average molecular weight
M_z = z-average molecular weight
N_1 = first normal stress difference, $\Pi_{11} - \Pi_{22}$
N_2 = second normal stress difference, $\Pi_{22} - \Pi_{33}$
p = pressure, isotropic
r = radial distance
R = radius of plate or universal gas constant
R_i = radial distance to intercept of $\Pi_{22}(\ln r)$ on abscissa for $\Pi_{22} - \ln r$ plot.
T = torque
t = time

Greek Letters

α = cone angle
$\dot{\gamma}$ or $\dot{\gamma}_{21}$ = shear rate
ϵ = link tension constant, Curtiss-Bird theory
η = apparent viscosity
η_0 = zero-shear-rate viscosity
η_s = solvent viscosity
η_ζ = constant friction viscosity
ρ = polymer density
ψ = N_2/N_1 or ψ_2/ψ_1
ψ^0 = N_2/N_1 in the limit of zero shear rate
ψ_1, ψ_2 = first and second normal stress difference coefficients, $-N_1/\dot{\gamma}^2$, $-N_2/\dot{\gamma}^2$.
ψ_1^0, ψ_2^0 = first and second normal stress difference coefficients in the limit of zero shear rate
$\psi_{1\zeta}^0$ = first normal stress difference constant friction coefficient, $2J_e^0/\eta_{0\zeta}^2$.
Ω = rotational velocity
π = Pi

Π_{ii} = total normal stress, $p\delta + \tau_{ii}$
τ_0 = a characteristic relaxation time.

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