

# A Comparison between Rheological Data for Polymer Melts and the Spriggs Four-Constant Viscoelastic Model

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An experimental and analytical study was made to determine how well the material functions, derived from the Spriggs four-constant viscoelastic model, could describe the rheological properties of polymer melts. Viscosity and elasticity of selected polymer melts were experimentally determined in the rotational and oscillatory modes using a Weissenberg Rheogoniometer. The Spriggs model was chosen for study because of its success in describing experimental data for polymer solutions and because of its uniqueness in combining results from molecular theory with results from the theories associated with continuum mechanics. It was found that the model provides a good description of the rheological data for polymer melts and that some of the model parameters depend upon the molecular characteristics of the polymer. Since this model contains a small number of well defined constants, it should be useful in developing dimensionless engineering correlations for the complex flows encountered in processes of industrial importance. Deviations between the theoretical and experimental results are discussed and deficiencies of the model noted.

In the two decades that have elapsed since the appearance of Oldroyd's (1, 2) classic papers regarding the formulation of a properly invariant constitutive equation for viscoelastic liquids, rheologists have directed considerable attention to the problem of developing an equation which would provide a precise mathematical description of the material functions associated with all liquids in this class. The motivation for seeking such an equation is due largely to two factors. First, this equation can be used to identify the significant rheological parameters and the experimental procedures for measuring them; these parameters could, in turn, then be related to molecular parameters and useful information obtained about molecular structure. Second, the equations could be used with the momentum equation to obtain either a mathematical description of simple flow fields, or the dimensionless groups that should be employed in developing empirical correlations for use in the engineering analysis of the complex flows encountered in processes of industrial importance.

In view of the uncertainties which have been associated with the amount of information that must be specified in the derivation of a generalized constitutive equation, the theoretical efforts of rheologists have led to the development of a multiplicity of constitutive equations, each of which reflects the views of a particular worker concerning the information that he thought needed to be included in his model. While most of these equations satisfied the invariance or material objectivity criterion, few of them, when evaluated by comparison with the available experimental data, were found to have the capability of describing the flow of real materials (3 to 8). At best, these equations could only describe the experimental data over limited ranges of shear rate or frequency, and, in some cases, required extensive modification.

A careful review of the literature (3 to 8) will reveal, however, that judgements concerning the relative merit of a given constitutive equation have been based solely on the equation's ability to describe experimental data for

polymer solutions. Notwithstanding that a constitutive equation must have the capability of describing the material functions for polymer solutions, it is generally recognized that it must also be capable of describing the material functions for polymer melts. Clearly then, attempts to modify any of the more promising models before testing their ability to describe experimental data for polymer melts would be premature. Heretofore, the lack of experimental data on polymer melts has presumably precluded comparisons of this nature. Thus, the research reported herein was initiated to obtain rheological data on polymer melts, and these data were then used to evaluate the material functions derived from a specific rheological equation of state, namely, the Spriggs four-constant viscoelastic model (9).

The reasons for restricting this study to the Spriggs viscoelastic model are as follows:

1. In the evaluations made by Spriggs (7), Spriggs, Huppler, and Bird (6), and Doughty and Bogue (5) it has been shown that the only models which show promise for providing a precise description of the experimentally observed material functions are those of Roscoe (10), Bernstein, Kearsley, and Zappas (11, 12), Spriggs, et al. (6), Bogue (13), Spriggs four-constant (9), and Spriggs six-constant\* (7).

2. The Spriggs four-constant model is unique in its use of results from molecular theory with results from the theories associated with continuum mechanics to reduce to four the number of constants appearing in the final equations. This, of course, makes the model attractive for use in developing dimensionless empirical correlations.

3. Since relationships may exist between molecular parameters and the rheological parameters in the Spriggs equation, a comparison between the results of this equation and the experimental results for different types of polymer melts might provide additional insight and useful suggestions regarding the incorporation of molecular concepts in the formulation of improved equations.

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\* Bird, et al. (14) have recently developed a six-constant model which also appears to have considerable promise for providing a precise description of the material functions.

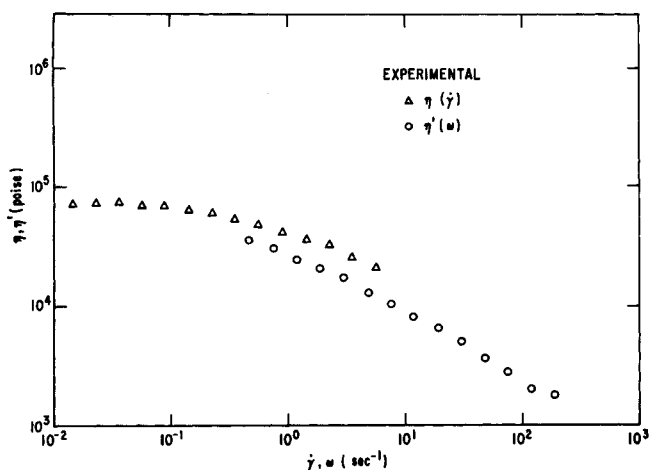


Fig. 1. Viscosity data for polyethylene at 200°C.

### MATERIAL FUNCTIONS FOR THE SPRIGGS FOUR-CONSTANT MODEL

The Spriggs four-constant constitutive equation (9) is based on a nonlinear extension of a generalized form of the Maxwell model

$$\tau_p + \lambda_p \frac{\partial \tau_p}{\partial t} = -2\eta_p \mathbf{e} \quad (1)$$

$$\tau = \sum_{p=1}^{\infty} \tau_p \quad (2)$$

The use of Equation (1) as a starting point in this derivation represents a significant departure from approaches used earlier in attempts to develop rheological models for viscoelastic liquids. Previous treatments considered nonlinear extensions of a generalized model consisting of a single high order differential equation, whereas in the Spriggs treatment, a nonlinear extension of a generalized model consisting of a set of first-order differential equations is considered.

The nonlinear extension of Equation (1) was realized by replacing the linear operator  $\partial/\partial t$  with a nonlinear operator  $F_e$  which, in addition to having the right invariance properties, contains terms that give rise to non-Newtonian viscosities and normal stresses. Hence, Equation (1) becomes

$$\tau_p + \lambda_p F_e \tau_p = -2\eta_p \mathbf{e} \quad (3)$$

The operator  $F_e$  is given by\*

$$F_e \tau = \frac{D}{Dt} \tau - (1 + \epsilon) \left[ \mathbf{e} \cdot \tau + \tau \cdot \mathbf{e} - \frac{2}{3} \text{tr}(\tau \cdot \mathbf{e}) \delta \right] \quad (4)$$

where

$$\frac{D}{Dt} \tau = \frac{\partial \tau}{\partial t} + \mathbf{v} \cdot \nabla \tau + \boldsymbol{\omega} \cdot \tau - \tau \cdot \boldsymbol{\omega} \quad (5)$$

Finally, it was noted that if some results from the molecular theories of Rouse (15) and Zimm (16) were utilized in specifying the form of  $\lambda_p$  and  $\eta_p$ ,

$$\lambda_p = \frac{\lambda}{p^\alpha} \quad (6)$$

$$\eta_p = \eta_0 \lambda_p \left/ \sum_{p=1}^{\infty} \lambda_p \right. \quad (7)$$

\* Appropriate definitions for the tensorial dot product and simple shearing flows are given elsewhere (7).

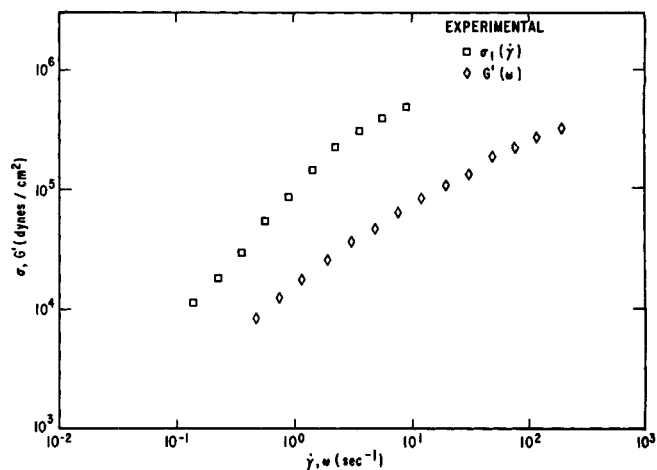


Fig. 2. First normal stress difference and dynamic storage modulus data for polyethylene at 200°C.

then the number of constants appearing in the expressions for the material functions could be reduced to four. Thus, for simple shearing flows

$$\frac{\eta(\dot{\gamma})}{\eta_0} = \frac{1}{Z(\alpha)} \sum_{p=1}^{\infty} \frac{p^\alpha}{p^{2\alpha} + (C\lambda \dot{\gamma})^2} \quad (8)$$

$$\frac{\eta'(\omega)}{\eta_0} = \frac{1}{Z(\alpha)} \sum_{p=1}^{\infty} \frac{p^\alpha}{p^{2\alpha} + (\lambda\omega)^2} \quad (9)$$

$$\eta''(\omega) = \frac{G'(\omega)}{\omega} = \eta_0 \frac{\lambda\omega}{Z(\alpha)} \sum_{p=1}^{\infty} \frac{1}{p^{2\alpha} + (\lambda\omega)^2} \quad (10)$$

$$\sigma_1(\dot{\gamma}) = \frac{2\gamma^2 \lambda \eta_0}{Z(\alpha)} \sum_{p=1}^{\infty} \frac{1}{p^{2\alpha} + (C\lambda \dot{\gamma})^2} \quad (11)$$

Here, the shift factor  $C$  is related to  $\epsilon$ , the factor which accounts for deviations from the Weissenberg (17) hypothesis ( $\tau_{22} - \tau_{33} = \sigma_2 = 0$ ) by

$$C^2 = (2 - 2\epsilon - \epsilon^2)/3 \quad (12)$$

Spriggs (9) and Huppler, et al. (18) have pointed out that aside from being able to describe the more commonly observed phenomenon such as the shear rate dependence of viscosity, this model correctly predicts stress overshoot during stress growth at the onset of steady flow, a relaxation of normal stresses which is slower than the relaxation of shear stresses after the cessation of steady flow and a rate of decrease of the viscosity  $\eta$  which depends on the value of the shear rate prior to the cessation of steady flow. In addition, the model can accommodate deviations from the Weissenberg hypothesis. On the other hand, the model requires (a) a constant modulus  $G_p$ ; (b) an equality of slopes in the power law region for the shear stress and normal stress curves, and (c) the analogies between steady and dynamic behavior:

$$\eta(C\dot{\gamma}) = \eta'(\omega) \quad (13)$$

$$\frac{C^2}{2} \sigma_1(C\dot{\gamma}) = G'(\omega) \quad (14)$$

In connection with using the experimental results contained herein for relating the rheological parameters of the Spriggs model to molecular structure it is convenient to define a modulus  $G_s$  such that

$$G_s = \eta_0/\lambda \quad (15)$$

and, to examine the behavior of Equation (10) in the limit of low frequencies. Thus, after rearrangement, Equation

TABLE 1.

Material	$M_W$	$M_W/M_N$	Comment
Polyethylene	$2.3 \times 10^5$ *	6.1*	low density, branched, broad molecular weight distribution
Polypropylene	$5 \times 10^5$	5†	
Polyisobutylene	$5.9 \times 10^4$ ‡	<3.0	molecular weight distribution not considered to be broad
Polystyrene (26)	$1.8 \times 10^5$	2.6	commercial sample
Polystyrene (26)	$1.93 \times 10^5$	1.06	monodisperse
Polycarbonate	$2.8 \times 10^4$ §	2.5	

\* Typical value reported in the literature (23, 24).

† Estimated from zero shear melt viscosity and data of Grant (25).

‡ Viscosity average molecular weight calculated from an intrinsic viscosity in benzene of 0.26 dl/g.

§ Viscosity average molecular weight.

(10) becomes

$$\frac{G'(\omega)}{\eta_0^2 \omega^2} = \frac{\lambda}{\eta_0} \frac{Z(2\alpha)}{Z(\alpha)} = \frac{1}{G_s} \frac{Z(2\alpha)}{Z(\alpha)} (\omega \rightarrow 0) \quad (16)$$

The quantity on the left-hand side of Equation (16) occurs frequently in the linear theory of viscoelasticity and has been shown (19) to be equal to the steady state shear compliance  $J_E$ , a characteristic material property.

The similarity between Equation (13) and the expression for  $G'(\omega)/\eta_0^2 \omega^2$  in Rouse's molecular model

$$\frac{G'(\omega)}{\eta_0^2 \omega^2} = \frac{2}{5} \frac{M}{\rho RT} = \frac{2}{5} \frac{1}{G_R} \quad (17)$$

and, the fact that the results of the Rouse model are included as a special case in the Spriggs model ( $\alpha = 2$ ) suggests that  $G_s$  is the parameter that should be used in seeking correlations between the Spriggs rheological parameters and molecular weight, molecular weight distribution or molecular structure.

## EXPERIMENTAL APPARATUS AND PROCEDURE

A Weissenberg rheogoniometer (18, 20, 21), model R16, with cone and plate geometry (2.5 cm. cone diameter and 4 deg. cone angle) was used for the steady rotational and oscillatory shear measurements. Shear stresses and normal stresses in steady rotation were calculated from the measured deflections of a torsion bar ( $k_T = 1.61 \times 10^5$  dynes/in) and a normal-force spring ( $k_N = 3.47 \times 10^4$  dynes/in) respectively. The response of the normal stress system was checked using a Newtonian fluid (Aroclor 1260) of very high modulus; this material gave normal stresses which were more than an order of magnitude lower than the normal stresses for melts.

Because the polymer samples tended to crawl from the gap between the cone and plate at high shear rates, steady rotational measurements were limited to relatively low shear rates. The onset of this type of failure could be observed visually and usually was accompanied by an abrupt decrease in the measured torque. Not all samples failed abruptly, however, and at times measurements could be continued a fraction of a decade higher in shear rate. When failure was observed, the apparent viscosity decreased more rapidly than expected, while normal stresses continued to increase monotonically at the expected rate. Presumably, this is due to the fact that the normal stress is highest at the center of the cone and decreases exponentially with distance from the center. It is, therefore, less sensitive to the loss of material at the edge, whereas the torque, which is highest at the edge, is more sensitive to the loss of material.

In dynamic testing with the rheogoniometer, a low frequency phasemeter (22) was used to measure amplitude and phase angle. With large signals, phase angle measurements are accurate to within  $\pm 0.5$  deg. and the precision is limited only by the signal-to-noise ratio of the sine waves; amplitude meas-

urements were accurate to within 2%. The resulting precision of  $\eta'(\omega)$  and  $G'(\omega)$  was within 4% except when the phase angle is near 90 deg. where  $G'(\omega)$  is very sensitive to phase angle. The measured amplitude and phase angle were corrected to give the true values of strain and phase in the sample ( $C_1$  and  $C_2$  in reference 19) whenever necessary. In addition, corrections for phase shifts in the frequency filter were also applied. Calculations and data plotting were carried out using a General Electric 225 digital computer.

The materials used in this study are listed in Table 1.

## DISCUSSION OF RESULTS

An example of the type of experimental data obtained during the course of this work is shown in Figures 1 and 2. Figure 1 contains representative data for the non-Newtonian and dynamic viscosities, while Figure 2 contains data for the primary normal stress difference and dynamic storage modulus. Within the limited range of frequencies and shear rates reported, these data show that the non-Newtonian viscosity is larger than the dynamic viscosity and that the primary normal stress difference is larger than the dynamic storage modulus. Furthermore, these data suggest that at low shear rates, the recoverable shear strain  $\sigma_1^2/\tau_{12}$  is proportional to the shear stress  $\tau_{12}$  and, at the higher frequencies, the dynamic viscosity and storage modulus ostensibly have a power-law type dependence on frequency.

In order to make a comparison between the theoretical predictions of the Spriggs model and the experimental data, values for the four model constants  $C$ ,  $\eta_0$ ,  $\alpha$ ,  $\lambda$  must be determined. Thus,  $\eta_0$  was obtained by noting the asymptotic value of the non-Newtonian viscosity at low shear rates and the shift factor  $C$  was obtained by determining the extent to which the non-Newtonian viscosity data had to be shifted horizontally in order to superpose these data with the dynamic viscosity data. Figure 3 is an illustration of superposed viscosity data and was constructed by shifting the data shown in Figure 1. While it is recognized that a more precise method for determining  $C$  could have been used and a more conclusive demonstration of the analogy hypothesis [Equation (13)] could have been effected had non-Newtonian and dynamic viscosity data been obtained over a much wider range of shear rates and frequencies respectively, this was not possible since sample failure occurred at high shear rates and dynamic measurements were limited by low signals at low frequencies. Notwithstanding that these limitations existed, the resulting values of  $C$  were used to superpose the primary normal stress difference and the dynamic storage modulus data in the manner

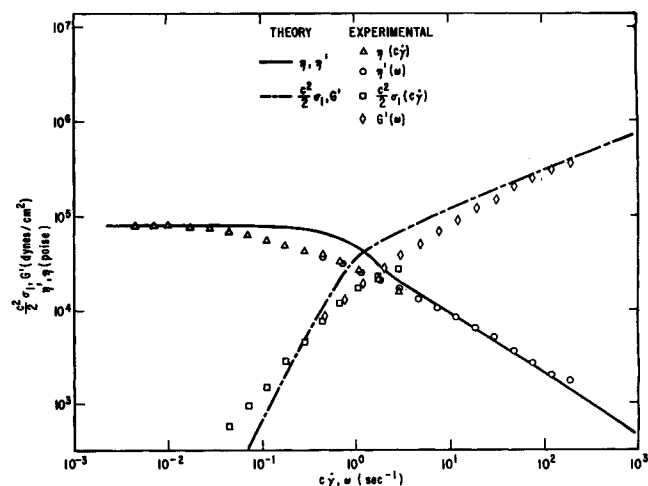


Fig. 3. Polyethylene at 200°C. Rotational data have been shifted using a  $C$  factor of 0.32.

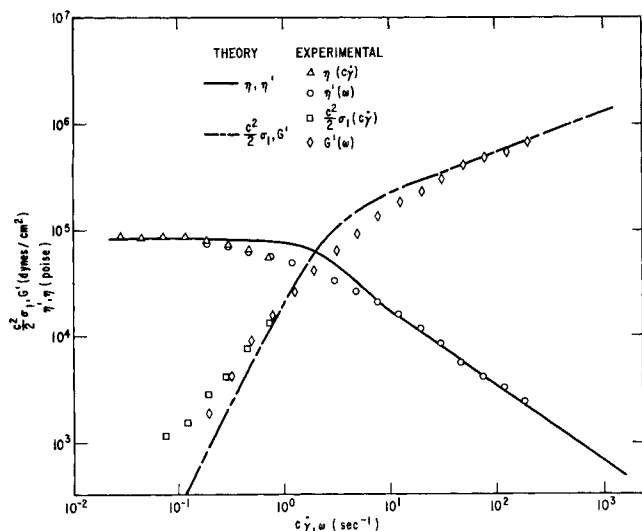


Fig. 4. Polystyrene (broad molecular weight distribution) at 199°C. Rotational data have been shifted using a C factor of 0.52.

suggested by Equation (14). Figure 3 is an illustration of how well the data of Figure 2 could be superposed using the value of C obtained from the viscosity data. It was subsequently found that for all materials considered in this work the shifted normal stress data fell within  $\pm 50\%$  of the dynamic storage modulus data at a given shear rate.

The two remaining constants,  $\alpha$  and  $\lambda$ , were determined in the following manner. For polyethylene, polystyrene, polyisobutylene, and polypropylene  $\alpha$  was obtained by measuring the slope S of the dynamic viscosity data at the higher frequencies where the data appeared to be following a power law type relation and  $\lambda$ , the leading relaxation time, was obtained by comparing the superposed experimental viscosity data with a dimensionless plot of  $\eta'/\eta_0$  vs.  $\lambda\omega$  for a given  $\alpha$  and calculating the value of  $\lambda$  which gave the best fit. For monodisperse polystyrene and polycarbonate a different procedure had to be used for determining  $\alpha$  and  $\lambda$ ; this was due to the fact that sufficient data for determining  $\alpha$  in the power-law region could not be obtained. This procedure was based on the observation that the dynamic storage modulus data for these materials followed the equation

$$G'(\omega) = K_1 \omega^2 \quad (19)$$

in the low frequency range. When Equations (16) and (19) are combined, an expression for calculating  $\lambda$  is ob-

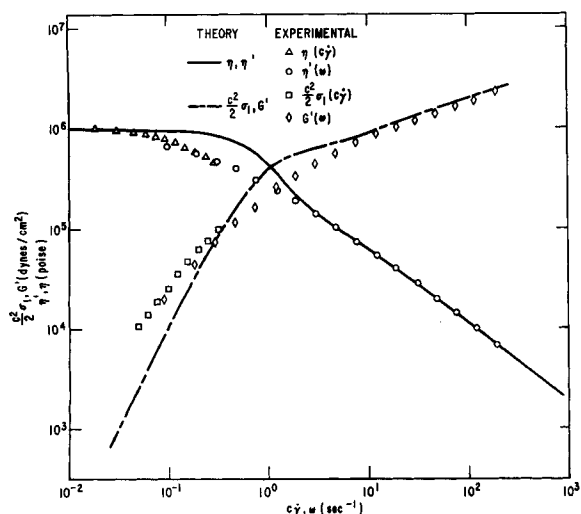


Fig. 5. Polyisobutylene at 25°C. Rotational data have been shifted using a C factor of 0.90.

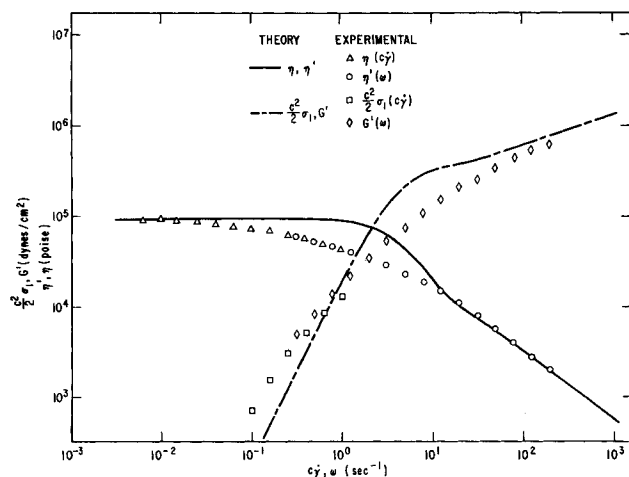


Fig. 6. Polypropylene at 200°C. Rotational data have been shifted using a C factor of 0.45.

tained.

$$\lambda = \frac{K_1}{\eta_0} \frac{Z(\alpha)}{Z(2\alpha)} \quad (20)$$

By assuming that the ratio  $Z(\alpha)/Z(2\alpha)$  was unity, a specific value for  $\lambda$  could be calculated and used to determine the value of  $\alpha$  giving the best fit of the data. After obtaining  $\alpha$ , the ratio  $Z(\alpha)/Z(2\alpha)$  was calculated, the value of  $\lambda$  recalculated, and  $\alpha$  properly adjusted.

Figures 3 through 6 graphically illustrate the ability of this model to describe the experimental data for polyethylene, polystyrene, polyisobutylene and polypropylene. These graphs show that the material functions for the viscosity provide an excellent description of the data except in the range of intermediate shear rates where the theoretical predictions deviate from the data by as much as 100%. In this shear rate range the experimental results for the non-Newtonian viscosity and dynamic viscosity indicate that these viscosities begin to decrease at a shear rate which is lower than that which the model predicts. Furthermore, the viscosities do not decrease as rapidly as the model predicts. With respect to the data for the dynamic storage modulus and the normal stress, the model describes these data reasonably well at high shear rates, but at intermediate shear rate, it gives values that are too high and, at low shear rates, values that are too low. Here, the theoretical predictions deviate from the data by as much as 100%.

The inability of the model to describe the viscosity data at intermediate shear rates and the dynamic storage modulus-normal stress data at both low and intermediate shear

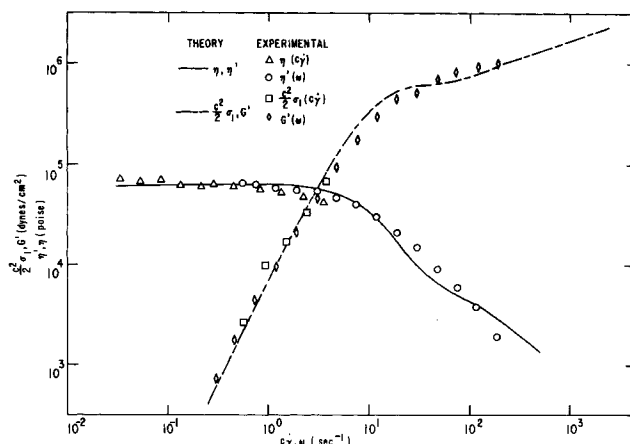


Fig. 7. Polystyrene (monodisperse) at 199°C. Rotational data have been shifted using a C factor of 1.0.

rates is believed to be due to the implicit assumption in the model that the modulus of elasticity for each element  $p$  is the same and is equal to:

$$G_p = \frac{\lambda_p}{\eta_p} = \frac{\lambda}{\eta_0} Z(\alpha) = G_s Z(\alpha) \quad (18)$$

The experimental data suggest, however, that the Spriggs model should incorporate a modulus  $G_p$  which increases with increasing  $p$ . This would provide a better fit of the dynamic storage modulus data at low frequencies and effect better agreement in the intermediate range for both the viscosity and dynamic storage modulus. We are pursuing this modification in our laboratory at the present time.

The experimental data and the theoretical predictions of the Spriggs model for monodisperse polystyrene and polycarbonate are shown in Figures 7 and 8, respectively. It will be noted that for these materials, the model provides a reasonably good description of the elasticity and viscosity data at low shear rates and frequencies, the deviation between the model predictions and the data being less than 50%. The excellent agreement between the model predictions and the elasticity data at low shear rates and frequencies is to be expected since polystyrene and polycarbonate exhibit linear viscoelastic behavior; in this same shear rate and frequency range, the predictions of the Spriggs model reduce to those derived from linear viscoelastic theory.

Table 2 is a compilation of the material constants used to obtain the calculated material functions shown in Figures 3 to 8. Of particular interest are the values used for the shift factor  $C$ . When these values were substituted into Equation (12) and values of  $\epsilon$  calculated for polyethylene, polystyrene, and polypropylene, one positive and one negative value was obtained for each of these polymers; for each of the other polymers two negative values of  $\epsilon$  were obtained. Since the sign of the second normal stress difference depends on the sign of  $\epsilon$ , one is led to the conclusion that polyethylene, polystyrene, and polypropylene can have second normal stress differences which are both positive and negative. While there appears to be no dialectical way of determining the sign of the second normal stress difference, Tanner and Simmons (27) have shown that when the second normal stress difference is positive the Spriggs type of constitutive equations predict instabilities for flows in which simple shear and time-dependent shear are superposed; on the other hand, if the sign is negative,

TABLE 2.

Material	$C$	$\eta_0$ (poise)	$\alpha$	$\lambda$ (sec.)	$G_s$ (dynes/sq.cm.)	$T^\circ\text{C.}$
polyethylene	0.32	$8.2 \times 10^4$	2.8	1.0	$8.2 \times 10^4$	200
polystyrene	0.52	$8.6 \times 10^4$	3.2	0.33	$2.6 \times 10^5$	199
polyisobutylene	0.90	$1.0 \times 10^6$	3.8	1.3	$7.7 \times 10^5$	25
polypropylene	0.45	$9.0 \times 10^4$	4.0	0.25	$3.6 \times 10^5$	200
polystyrene (monodisperse)	1.0	$6.5 \times 10^4$	4.0	0.11	$5.9 \times 10^5$	199
polycarbonate	1.0	$6.5 \times 10^4$	2.0	0.04	$1.6 \times 10^6$	246

stable flows are possible. These findings suggest that if the polymers listed in Table 2 are to exhibit stable flows of the kind described above then only negative values of  $\epsilon$  are admissible. Clearly though, further experimental evidence is needed.

#### RELATION BETWEEN MODEL CONSTANTS AND MOLECULAR STRUCTURE

In order to obtain additional insight regarding the molecular concepts that should be incorporated in the formulation of a constitutive equation, it is of interest to examine the values of the Spriggs constants for the materials studied in terms of their molecular parameters: molecular weight, molecular weight distribution, chemical structure and chain structure.

Because measurements were not made on a given sample over a range of molecular weights for that sample, the results of this study cannot be used to determine the relationship between molecular weight and the model constants. However, previous work (28) has shown that when the sample molecular weight is above the critical molecular weight for entanglements, the zero shear viscosity follows the equation

$$\eta_0 = K M_w^{3.4} \quad (18)$$

Since the molecular weight of all samples considered in this research is above the critical molecular weight for entanglements, it is believed that Equation (18) would be valid for these samples. While  $G_s$ ,  $\alpha$ ,  $C$ , may be related to the molecular weight, the direct relationship is not known (29, 30).

The effect of molecular weight distribution on the model constants can be exemplified by the results for a polystyrene with a broad molecular weight distribution and a polystyrene with a narrow molecular weight distribution. The polystyrene with a narrow molecular weight distribution has a higher  $G_s$ , and a  $\eta'(\omega)$  which begins to decrease with shear rate at a higher value of shear rate than the polystyrene with a broad molecular weight distribution. Furthermore,  $\eta'(\omega)$  and  $G'(\omega)$  for the monodisperse polystyrene behave much like  $\eta'$  and  $G'$  for a Maxwellian fluid.

A comparison between the results for polystyrene (31) and polycarbonate of similar molecular weight distribution demonstrated the effect of chemical structure on the modulus of elasticity. Although the relation between modulus and chemical structure is not well understood, it is generally believed that elasticity of polymer melts is due to the deformation of segments of the chain between entanglements. It is useful to correlate chemical structure with the modulus through the entanglement molecular weight which for polystyrene, and polycarbonate, are  $3 \times 10^4$  and  $6 \times 10^3$  respectively. The moduli for these materials are  $2.6 \times 10^5$  and  $1.6 \times 10^6$  dynes/sq.cm. and vary inversely with the entanglement molecular weights.

The modulus is approximately proportional to absolute temperature as expected from its entropic origin and, therefore, measurements on different polymers require some

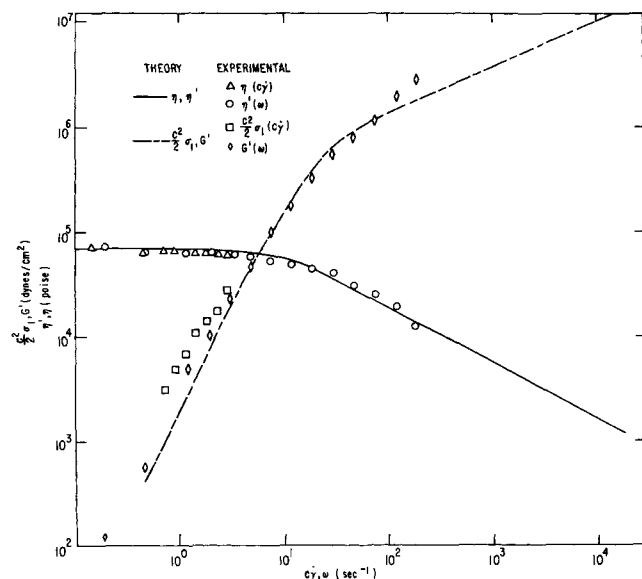


Fig. 8. Polycarbonate (Lexan) at 246°C. Rotational data have been shifted using a  $C$  factor of 1.0.

small corrections for the difference in temperature.

The combination of branching in the chain structure and broad molecular weight distribution gives values of  $G_s$  which are low. Since reactions which lead to branching in many cases also lead to a broadening of the molecular weight distribution, it is difficult to clearly ascribe the low modulus to one or the other effect. Low density polyethylene, Alathon 10, is an example of a polymer with a low modulus, branched structure and a broad molecular weight distribution. These effects probably dominate since on the basis of entanglement molecular ( $M_c = 4,000$ ) one would expect a relatively high modulus.

This discussion of the relation of model constants to molecular structure is semiquantitative at best, but it serves to illustrate the interrelations and the difficulty of separating some of the combined effects. The study of the rheological properties of well characterized polymers using a rheological constitutive equation which has a few significant constants will hasten the solution of this problem.

## CONCLUSION

In this study it has been shown that the Spriggs four-constant viscoelastic model can describe the rheological data on polymer melts with a degree of accuracy believed to be sufficient for the engineering analysis of industrially important processes.

Limited conclusions have been made concerning the relationships between selected molecular parameters for the polymer melts and the calculated model constants; however, these results are far from complete and further work needs to be done in this area.

Major discrepancies between the model predictions and the experimental data have been explained on the basis that the model does not contain a variable modulus  $G_p$ .

## NOTATION

$C$	= dimensionless parameter defined in Equation (12), shift factor
$C_1$	= rheogoniometer instrument correction constant
$C_2$	= rheogoniometer instrument correction constant
$e$	= $1/2 (\nabla v + \nabla v^T)$ , sec. <sup>-1</sup>
$F_e$	= operator defined in Equation (4)
$G'$	= dynamic storage modulus, dynes/sq.cm.
$G_p$	= modulus of elasticity of $p$ th Maxwell element, dynes/sq.cm.
$G_s$	= modulus of elasticity defined in Equation (15) for Spriggs model, dynes/sq.cm.
$G_R$	= modulus of elasticity defined in Equation (17) for Rouse model, dynes/sq.cm.
$K$	= constant in Equation (21)
$K_1$	= constant in Equation (19), dynes sec. <sup>2</sup> /sq.cm.
$M_c$	= critical molecular weight for entanglements, g./mole
$M_N$	= number average molecular weight, g./mole
$M_V$	= viscosity average molecular weight, g./mole
$M_W$	= weight average molecular weight, g./mole
$P$	= summation index
$R$	= gas constant, ergs/°K. mole
$S$	= slope of a plot of $\log \eta$ as $\log \gamma$ for large $\gamma$
$T$	= temperature, superscript which denotes transpose of a matrix, °K.
$t$	= time, sec.

## Greek Letters

$\alpha$	= $1/1 + S$
$\dot{\gamma}$	= shear rate, sec. <sup>-1</sup>
$Z(\alpha)$	= Riemann zeta-function
$\eta_0$	= zero shear viscosity, poise

$\eta_p$	= viscosity of $p$ th Maxwell element, poise
$\eta'$	= real part of complex viscosity, dynamic viscosity, poise
$\eta''$	= imaginary part of complex viscosity, poise
$\lambda$	= parameter, leading relaxation time, sec.
$\lambda_p$	= relaxation time of $p$ th Maxwell element, sec.
$\rho$	= density, g./cc.
$\sigma_1$	= first normal stress difference, $\tau_{11} - \tau_{22}$ , dynes/sq.cm.
$\sigma_2$	= second normal stress difference, $\tau_{22} - \tau_{33}$ , dynes/sq.cm.
$\tau$	= stress tensor, dynes/sq.cm.
$\tau_p$	= stress tensor of $p$ th Maxwell element, dynes/sq.cm.
$\omega$	= frequency of oscillation, or, $\frac{1}{2} [\nabla \vec{v} - (\nabla \vec{v})^T]$ , rad./sec.

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