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Rheological Properties of Liquid Crystalline Solutions of Poly-*p*-Phenyleneterephthalamide in Sulfuric Acid*

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Synopsis

The steady state shear and linear viscoelastic properties of both isotropic and liquid crystalline solutions of the rigid chain polymer poly-*p*-phenyleneterephthalamide in sulfuric acid have been determined. Both the primary normal stress coefficient and the linear viscoelastic properties show the same characteristic concentration behavior as does the viscosity. The unique rheological properties of the anisotropic phase can be attributed to the formation of a suspension of highly ordered regions in a matrix of isotropic fluid. The rheological properties were compared against the Bird-Carreau model and Hand's anisotropic fluid theory. Remarkably good agreement was found between the Bird-Carreau model and data especially at high shear rates. This suggested that at high shear rates very little difference may exist between anisotropic and isotropic phases. Hand's model was more applicable to solutions which were only slightly anisotropic.

INTRODUCTION

There has been considerable interest in the last few years in the processing of polymers with liquid crystalline order. Systems such as poly-*p*-phenyleneterephthalamide (PPT) and poly-*p*-benzamide (PBA) in H₂SO₄ have been solution-spun to form ultra-high-strength fibers.^{1,2} Copolymers of polyethyleneterephthalate (PET) modified with *p*-hydroxy benzoic acid (PBH) have been injection molded to give samples which are extremely stiff in the flow direction but very flexible in the transverse direction.³ The fascinating aspect of these systems is that orientation and hence the exceptional physical

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properties are readily obtained without further processing steps because of orientation which is generated during the flow process.

In spite of the extensive interest in these fluids, there is very little known about their rheology.⁴ The most frequently published data consist of the concentration (C) and temperature (T) dependence of viscosity.⁴ The viscosity of systems such as PPT in H_2SO_4 (which are classified as lyotropic liquid crystalline systems) increases rapidly with concentration passing through a maximum with the onset of liquid crystalline order and then decreasing with further increases of C . The temperature dependence of viscosity of both the lyotropic and thermotropic (undiluted polymer) systems decreases with increasing T passing through a minimum. At this point the fluids become isotropic. η continues to increase with T until all parts of the fluid are isotropic.

The mechanism which accounts for these unique flow properties is somehow tied to the structure of the fluids. The nature of this structure is, however, unknown. They exhibit unique birefringence patterns under static conditions which suggests the fluids are inherently ordered and structured.⁵⁻⁷ It is believed that with the onset of liquid crystalline order, the solution becomes a suspension of highly ordered regions in an isotropic matrix (this concept is illustrated in Fig. 1). As the concentration increases the size and density of the ordered regions increase at the expense of the isotropic regions. During flow, the energy dissipated by these aggregates is considerably less than the collective sum of the energy dissipated by each individual

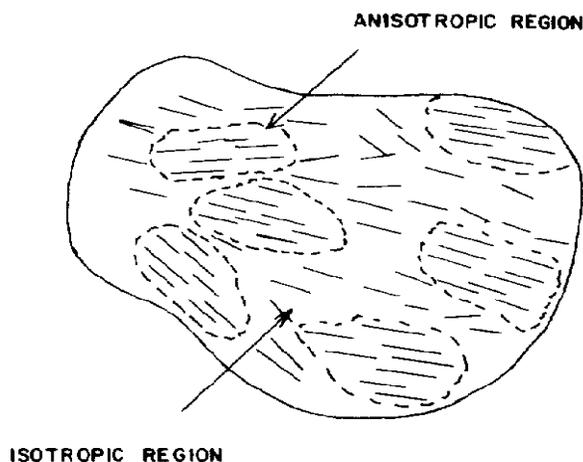


Fig. 1. Schematic drawing of the proposed suspension structure of polymer liquid crystals.

molecule. This may be a reasonable explanation to account for the decrease in η with C . There is also some evidence to support this mechanism since on centrifuging solutions of PPT and PBA the fluid separates into two phases.² It is not known how the other material functions might be accounted for through this model.

Although the viscous behavior of polymers with liquid crystalline order is well documented, there is little known about the elastic properties as determined by the primary normal stress difference (N_1) or the dynamic mechanical properties obtained from oscillatory measurements. In order to better understand the processing of these unique fluids it is necessary to completely characterize their rheological properties. One of the main objectives of this work is to study the rheological properties of solutions of PPT in 100% H_2SO_4 in steady shear and oscillatory flow over a wide range of temperatures and concentration. Another objective of this work is to determine whether the rheological properties of this system can be described by a simple fluid rheological model or whether one must consider the use of a model which incorporates the structure of the fluid. At the same time it is hoped to gain a better understanding of the structure of these fluids, and how this could account for the observed rheological properties.

EXPERIMENTAL

Solutions of 4, 6, 8, 10, 12, 15 wt % were prepared by mixing PPT with 100% H_2SO_4 in a Model 2 CV Helicone Mixer. The jacketed mixing bowl was maintained at 60°C and all mixing was carried out in a dry nitrogen environment. The weight average molecular weight (\overline{MW}) of the polymer sample was 40,100 as determined by light scattering.⁸ Negligible changes in \overline{MW} were observed as the result of mixing.

Rheological measurements were carried out using a Rheometrics Mechanical Spectrometer. Both the steady state shear using the cone-and-plate mode and the dynamic mechanical properties were measured at 35°C, 60°C, and 90°C. The cone angle was 0.04 rad and the plate diameter was 5 cm. Well known methods were used to reduce the torque and normal force data to various material functions.⁹

Because of the sensitivity of the anisotropic phase to moisture and the resulting change in rheological properties, special precautions were

taken to eliminate this problem. A dry box was constructed which covered the entire test chamber allowing us to keep the test sample in a dry nitrogen environment. An equally effective method consisted of covering the exposed test fluid surface with a thin film of low viscosity mineral oil. The success of these methods in giving dependable measurements is discussed elsewhere.¹⁰

The critical concentration (C^*) for the onset of liquid crystalline behavior is highly dependent on temperature. Although a sharp drop in viscosity is readily observed at C^* , the onset of liquid crystalline behavior was also identified using a polarizing microscope. The birefringent pattern is characteristic of the nematic mesophase, one of three liquid crystalline phases and has been described elsewhere.^{6,7}

RHEOLOGICAL MODELS

The rheological properties of solutions both in the isotropic and anisotropic state are compared against two types of models. On the one hand, we compare our data with a semi-empirical codeformational model (the Bird-Carreau model).¹¹ On the other, we selected one of the models which considers the microscopic structure of the fluid (the Hand model).¹² The Bird-Carreau model was chosen because it has been shown to fit the behavior of a number of polymer systems over a large range of conditions,¹³ and there are only five parameters in the model.

The following forms of the viscometric functions were used:

$$\eta = \sum_{k=1}^{\infty} \frac{\eta_k}{1 + (\lambda_k^{(1)} \dot{\gamma})^2} \quad (1)$$

$$\psi_1 = \frac{N_1}{\dot{\gamma}^2} = 2 \sum_{k=1}^{\infty} \frac{\eta_k \lambda_k^{(2)}}{1 + (\lambda_k^{(1)} \dot{\gamma})^2} \quad (2)$$

$$\eta' = \sum_{k=1}^{\infty} \frac{\eta_k}{1 + (\lambda_k^{(2)} \omega)^2} \quad (3)$$

$$\frac{\eta''}{\omega} = \sum_{k=1}^{\infty} \frac{\eta_k \lambda_k^{(2)}}{1 + (\lambda_k^{(2)} \omega)^2} \quad (4)$$

where

$$\lambda_k^{(n)} = \lambda_n \left(\frac{2}{k+1} \right)^{\alpha_n} \quad \text{for } n = 1, 2 \quad (5)$$

and η is the viscosity, η_0 is the zero shear viscosity, ψ_1 is the primary normal stress coefficient, and η' and η'' are the real and imaginary parts of the complex viscosity, respectively. Values of α_1 , α_2 , η_0 , λ_1 , and λ_2 were determined from viscosity versus shear rate data (η vs. $\dot{\gamma}$) and η' vs. angular frequency (ω). The functions in Eqs. (1) and (3) were fit to the experimental data in such a way as to minimize the sum of the squared differences between experimental points and theoretical predictions. The values of α , λ , and η_0 were then used to predict ψ_1 vs. $\dot{\gamma}$ and η''/ω vs. ω . A summary of the five parameters for solutions of different concentration and temperature is given in Tables I–III. Representative data and a comparison of the model predictions with experimental data are given in Figs. 2–9.

Polymer systems with liquid crystalline order are highly structured fluids as is evidenced by their ability to transmit polarized light under static conditions. For this reason, we compare the rheological

TABLE I
Bird-Carreau Model Parameters for Solutions of PPT in 100% H₂SO₄ at 35°C

Concentration (wt %)	n_0 (kg/m sec)	λ_1 (sec)	λ_2 (sec)	λ_1/λ_2	α_1	α_2	α_2/α_1
15 ^a	60,000	41.0	10.50	3.90	2.80	2.050	0.73
12 ^a	1,000	5.82	0.980	5.940	2.870	4.650	1.62
10 ^a	420	1.20	2.080	0.577	2.550	3.950	1.55
8 ^a	4,700	3.84	5.000	0.768	0.930	1.000	1.08
6	6,100	0.554	0.930	0.596	0.902	0.960	1.06
4	27	0.010	0.039	0.256	0.070	0.055	0.79

^a Optically anisotropic.

TABLE II
Bird-Carreau Model Parameters for Solutions of PPT in 100% H₂SO₄ at 60°C

Concentration (wt %)	n_0 (kg/m sec)	λ_1 (sec)	λ_2 (sec)	λ_1/λ_2	α_1	α_2	α_2/α_1
15 ^a	75.0	0.311	1.780	0.175	1.680	1.590	0.94
12 ^a	105	0.191	1.00	0.191	2.50	4.00	1.54
10 ^a	6,400	2.020	1.180	1.710	6.850	8.440	1.23
8	1,560	1.280	2.330	0.549	0.850	1.060	1.25
6	215	0.189	0.255	0.741	0.764	0.639	0.83
4	11.0	0.005	0.450	0.011	0.093	0.880	9.46

^a Optically anisotropic.

TABLE III
Bird-Carreau Model Parameters for Solutions of PPT in 100% H₂SO₄ at 90°C

Solution (% PPT)	η_0 (kg/m sec)	λ_1 (sec)	λ_2 (sec)	α_1	α_2	λ_1/λ_2	α_2/α_1
15 ^a	38	0.20	0.261	1.440	0.825	0.770	0.57
12 ^a	88	0.628	0.342	0.914	0.664	1.840	0.72
10 ^a	2,400	1.30	2.740	1.080	1.210	0.470	1.12
8	520	0.402	0.172	0.988	0.425	2.340	0.43
6	74	0.058	0.20	1.25	0.600	0.290	0.48
4	4	0.005	0.075	0.787	0.470	0.067	0.60

^a Optically anisotropic.

properties of these fluids against the predictions of a model which considers fluid structure. We have selected Hand's anisotropic fluid theory¹² for two reasons. First, it contains Ericksen's anisotropic fluid theory as a special case.^{12,14} Ericksen's theory was particularly constructed in an attempt to describe the rheological properties of liquid crystals.¹⁴ Second, Barthés-Biesel and Acrivos¹⁵ have shown that the exact analytical treatment of suspensions yields equations which are similar to the form predicted by Hand.

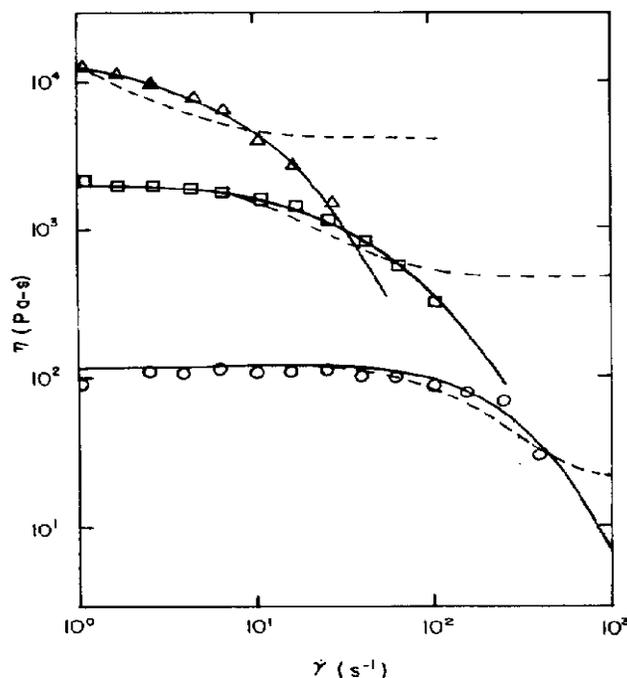


Fig. 2. Viscosity data for three isotropic solutions of PPT in H₂SO₄ at 60°C: Bird-Carreau model (—); Hand model (---); 4% (○), 6% (□), 8% (Δ).

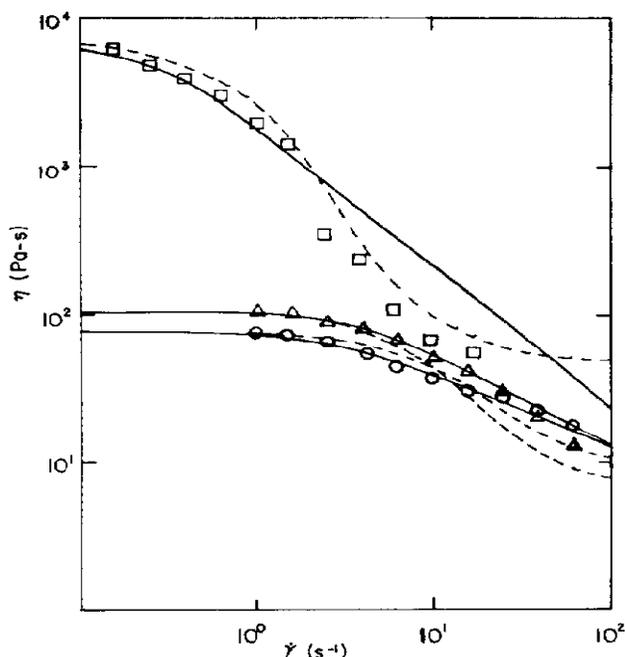


Fig. 3. Viscosity data for three anisotropic solutions of PPT in H_2SO_4 at 60°C : Bird-Carreau model (—); Hand model (---); 10% (\square), 12% (\triangle), 15% (\circ).

The basic concept proposed by Hand was that the stress at a point in a fluid which contains some anisotropy on the microscopic scale was a function of not only the rate of deformation tensor $\dot{\gamma}$, but a structure tensor \mathbf{A} : i.e. the stress tensor (σ) is given as $\sigma = \delta + \mathbf{f}(\dot{\gamma}, \mathbf{A})$ where δ is the unit tensor. The structure tensor is related to $\dot{\gamma}$ by $(D\mathbf{A}/Dt) = \mathbf{g}(\mathbf{A}, \dot{\gamma})$ where (D/Dt) is the Jauman derivative. The constitutive relations obtained by expanding these functions as polynomials and applying the principles of material frame indifference are given elsewhere.¹² Suffice it to say that these constitutive equations are rather complex and contain many material constants which are difficult to evaluate. In the most general form, Hand's constitutive equation cannot be classified as a simple fluid model.¹⁵ This theory predicts that stress is not only a function of the deformation history but of the initial anisotropy in the fluid.

The form of the constitutive equation used in this paper yields the following material functions in steady shear¹²:

$$\eta = \frac{m + n\dot{\gamma}^2}{p + q\dot{\gamma}^2} \quad (6)$$

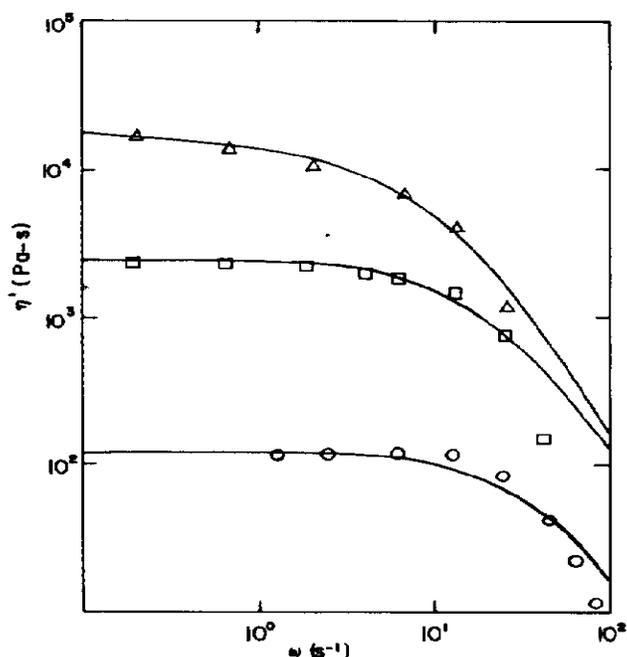


Fig. 4. Dynamic viscosity (η') data for three isotropic solutions at 60°C: Solid line represents Bird Carreau model; 4% (\circ), 6% (\square), 8% (\triangle).

$$\psi_1 = \frac{1}{p + q\dot{\gamma}^2} \quad (7)$$

where m , n , and p , q are material constants determined as described below. Numerous assumptions were used to reduce the constitutive equation to a more tractable form. These assumptions include (i) that the secondary normal stress is negligible (i.e., $N_2 = 0$); (ii) the particles are initially spherical and become anisotropic as the result of flow; and (iii) σ is linear in $\dot{\gamma}$. In this form the theory must be considered as "pseudo-anisotropic" since the anisotropy is generated by flow.

In theory the four parameters in the simplified model can be evaluated by measurements of η and ψ_1 in the limit as $\dot{\gamma} \rightarrow 0$ and as $\dot{\gamma} \rightarrow \infty$ as follows:

$$\text{as } \dot{\gamma} \rightarrow 0 \quad 1/p = \psi_1^0, \quad (8)$$

$$m/p = \eta_0; \quad (9)$$

$$\text{as } \dot{\gamma} \rightarrow \infty \quad 1/q = N_{1,\infty}, \quad (10)$$

$$n/q = \eta_\infty. \quad (11)$$

Here ψ_1^0 is the zero-shear normal stress coefficient and $N_{1,\infty}$ is the

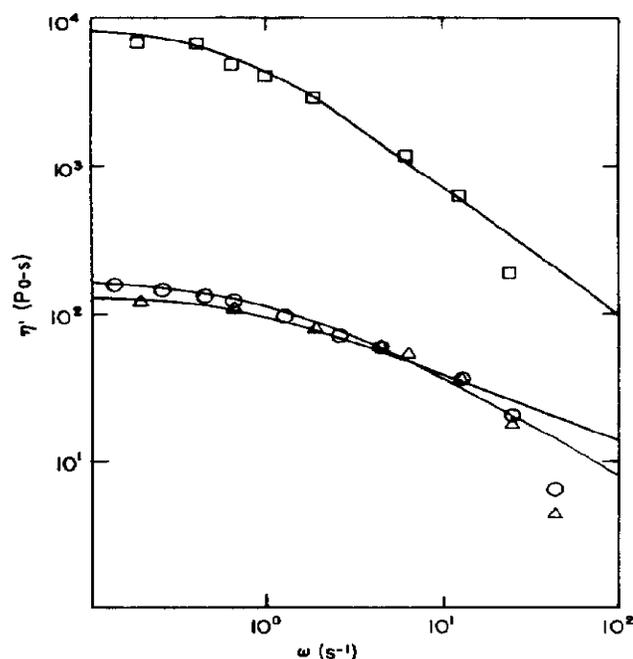


Fig. 5. Dynamic viscosity (η') data for three anisotropic solutions at 60°C: 10% (\square), 12% (Δ), 15% (\circ).

value of N_1 which is independent of $\dot{\gamma}$ at high $\dot{\gamma}$. In practice it is difficult to measure ψ_1^0 and η_∞ . Thus we fit the model using a least-squares analysis of data plotted as $1/\psi_1$ versus $\dot{\gamma}^2$. This yielded values of p and q . η_0 and hence m/p could be easily evaluated. A summary of these values is presented in Tables IV–VI. In some cases, data exhibited viscosity values (η_∞) which became independent of $\dot{\gamma}$. However, for the most part, η_∞ was used as an adjustable parameter to improve the fit of the model to the data. It is not possible at this time to compare predictions for oscillatory flow with experimental results because of the intractability of the theory. The model is compared with experimental data obtained in steady shear in Figures 2, 3, and 7.

RESULTS AND DISCUSSION

Rheological Properties

We first look at the other fluid properties to determine whether they might also show the same behavior as viscosity. As is observed in Figs. 10 and 11, the complex viscosity $|\eta^*|$ measured at $\omega = 2.5 \text{ sec}^{-1}$, the

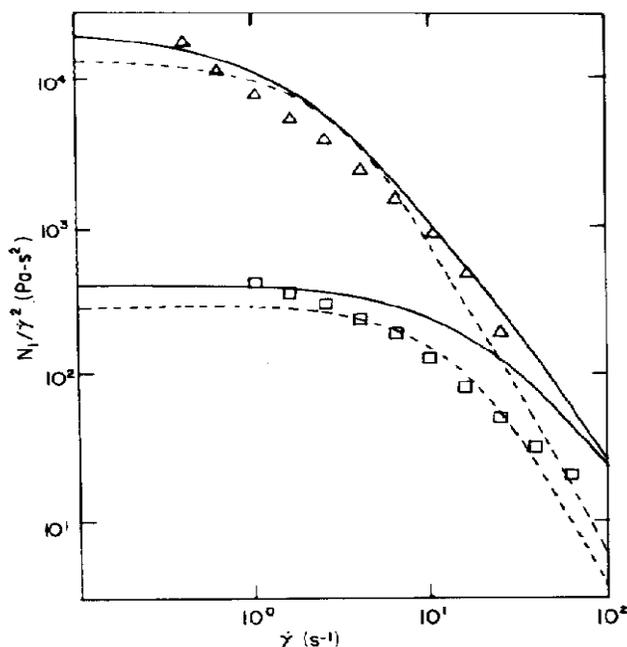


Fig. 6. Primary normal stress difference coefficient (Ψ_1) for two isotropic solutions: Bird-Carreau model (—); Hand model (---): 6% (\square), 8% (Δ).

TABLE IV
Hand Model Parameters for Solutions of PPT in 100% H_2SO_4 at 30°C

Concentration (wt %)	$p \times 10^5$ (Pa sec ²)	$q \times 10^6$ (Pa ⁻¹)	m (sec ⁻¹)	$n \times 10^2$ (sec)
10	0.815	15.900	0.343	14.40
8	0.219	0.939	1.030	4.690
6	6.750	3.390	4.110	5.430
4	2370.000	6.450	64.000	0.452

primary normal stress coefficient (ψ_1) measured at $\dot{\gamma} = 2.5 \text{ sec}^{-1}$, $2\eta''/\omega$ where η'' is the imaginary part of the complex viscosity and ω is the angular frequency, and the relaxation time* (λ_1) all show behavior similar to that exhibited by η . On the other hand, the ratio $N_1/2\sigma$ (σ is the shear stress), which is related to the ultimate recoverable shear strain,¹⁶ is a monotonic increasing function of concentration. Except in the case of $N_1/2\sigma$, the structural changes which occur with the onset of liquid crystalline order seem to affect the other material functions in a manner similar to viscosity.

At low frequencies (ω) and low $\dot{\gamma}$ it has been observed that the

* λ_1 is the relaxation time in the Bird-Carreau model.

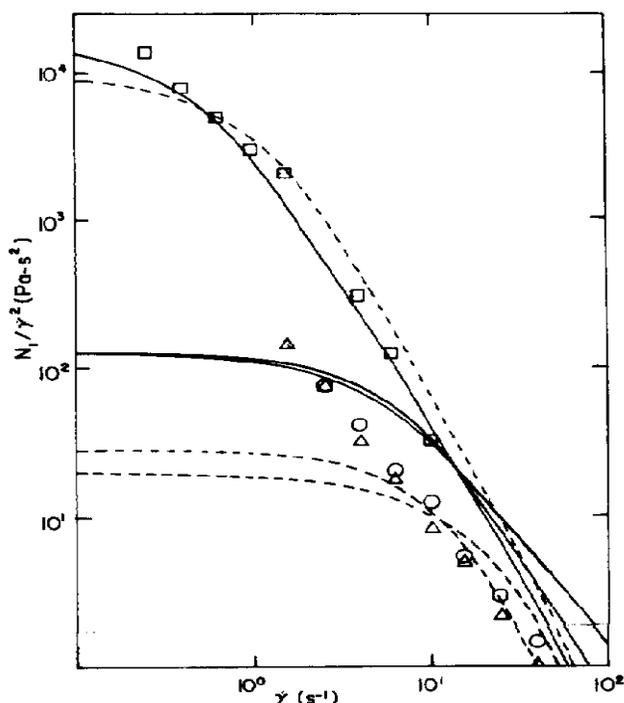


Fig. 7. Primary normal stress difference coefficient for three anisotropic solutions at 60°C: Bird-Carreau model (—); Hand model (---); 10% (□), 12% (Δ), 15% (○).

TABLE V
Hand Model Parameters for Solutions of PPT in 100% H₂SO₄ at 60°C

Concentration (wt %)	$p \times 10^4$ (Pa sec ²)	$q \times 10^6$ (Pa ⁻¹)	m (sec ⁻¹)	$n \times 10^3$ (sec)
15	5.510	3.510	4.130	3.51
12	29.30	5.350	30.800	4.01
10	9.01	1.540	0.709	7.72
8	0.079	1.610	1.260	64.60
6	3.870	2.760	8.310	13.80
4	1570.00	7.800	173.000	1.56

steady shear material functions and the linear viscoelastic properties are nearly identical for many polymers.¹⁷ For the isotropic solutions there is a good correlation between $|\eta^*|$, η and N_1 , $2G'$, where $\omega\eta'' = G'$. This is illustrated with representative data in Fig. 12. On the other hand, there is considerable difference between these same quantities for the liquid crystalline solutions (see Fig. 13). This difference is more noticeable at low $\dot{\gamma}$ rather than high $\dot{\gamma}$ which is

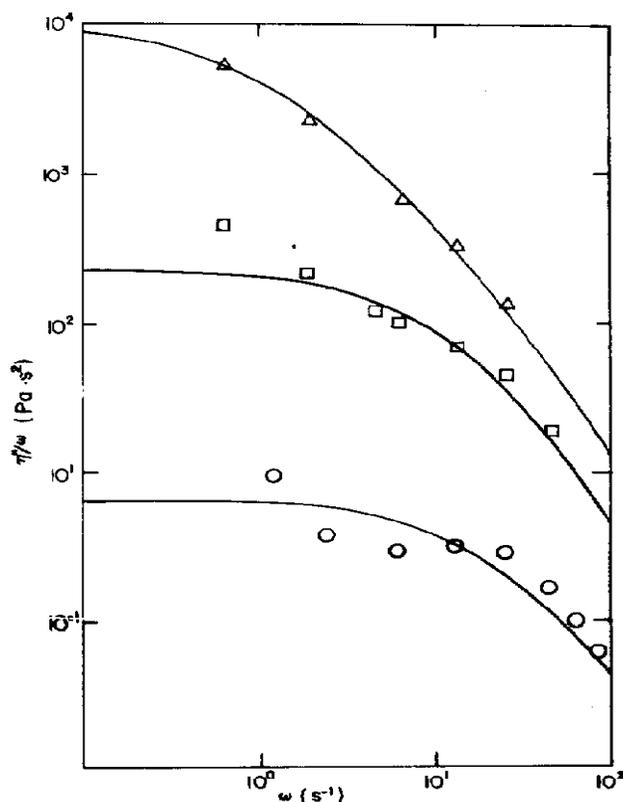


Fig. 8. η''/ω (or G''/ω^2 where G' is the storage modulus) for three isotropic solutions at 60°C: Bird-Carreau model (—), Hand model (---), 4% (○), 6% (□), 8% (△).

TABLE VI
Hand Model Parameters for Solutions of PPT in 100% H₂SO₄ at 90°C

Concentration (wt %)	$p \times 10^3$ (Pa sec ²)	$q \times 10^6$ (Pa ⁻¹)	$m \times 10^1$ (sec ⁻¹)	$n \times 10^2$ (sec)
15	1.060	8.410	0.403	1.010
12	0.588	4.330	0.517	0.347
10	0.0115	2.150	0.282	17.20
8	0.536	0.814	2.790	0.163
6	3.790	6.440	2.850	1.930
4	1430.000	8.510	57.100	0.0851

contrary to behavior exhibited by most polymers.¹⁷ The structure of the anisotropic fluids may be responsible for the poor correlation between steady state shear and linear viscoelastic properties at low $\dot{\gamma}$.

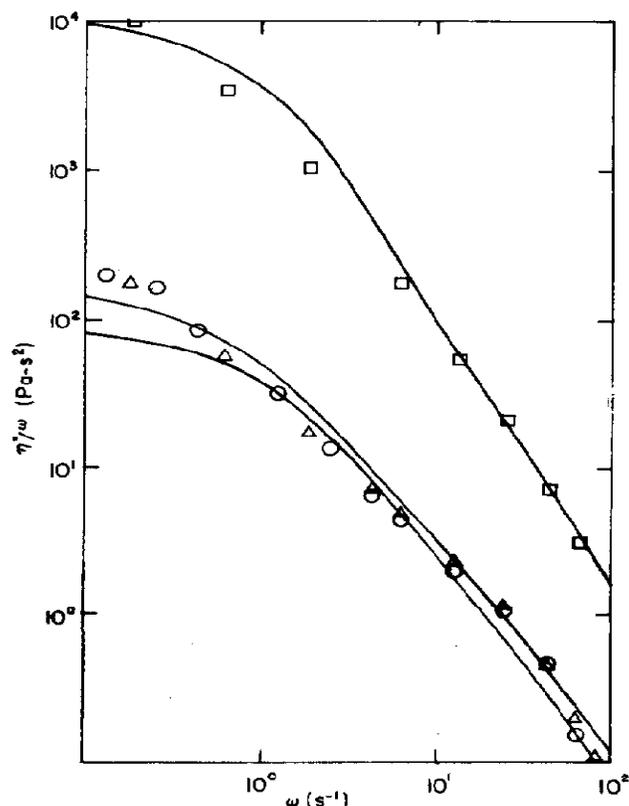


Fig. 9. η'/ω (or G'/ω^2) for three anisotropic solutions at 60°C: Bird-Carreau model (—), 10% (□), 12% (Δ), 15% (○).

Comparison of Data with Rheological Models

In this section we look at the ability of the two constitutive equations discussed earlier to describe the rheological properties of both the isotropic and anisotropic fluids. We are primarily interested in determining whether the structured fluids behave in a manner similar to isotropic fluids.

Representative η vs. $\dot{\gamma}$ data are presented in Fig. 2 for three isotropic solutions of PPT in 100% H_2SO_4 at 60°C. As one can see the Bird-Carreau model can be fit to this data quite successfully. On the other hand, the Hand model tends to level out too soon and does not fit the data well. In Fig. 3, representative data for anisotropic solutions are presented. With the onset of liquid crystalline behavior at $C = 10\%$ and for the 12% solutions, we see that the Hand model successfully fits the data whereas the fit is poor for the Bird-Carreau model. For the 15% solution, we observe that the Bird-Carreau model actually fits the viscosity data quite well.

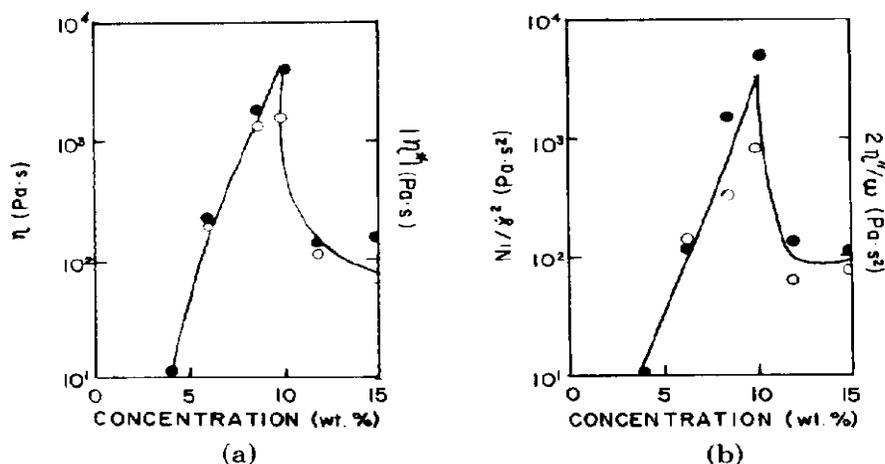


Fig. 10. (a) Steady shear (O) and complex viscosity (●) measured at $\dot{\gamma}$ or $\omega = 2.5 \text{ sec}^{-1}$ versus concentration (wt %) for solutions of PPT in 100% H₂SO₄ at 60°C. (b) Primary normal stress coefficient (ψ_1) (O) and $2\eta''/\omega$ (●) measured at $\dot{\gamma}$ or $\omega = 2.5 \text{ sec}^{-1}$ versus concentration for the same solutions as in (a).

The Bird-Carreau model is also fit to η' vs. ω data. In Figs. 4 and 5 representative data for the isotropic and anisotropic solutions, respectively, are presented. For the isotropic solutions, the Bird-Carreau model is quite successfully fit to the data, but for the anisotropic fluids the agreement is poor for $\omega > 10 \text{ sec}^{-1}$. From these two sets of experimental data (i.e., η vs. $\dot{\gamma}$ and η' vs. ω), values of α_1 , α_2 , λ_1 , λ_2 , and η_0 are determined and are summarized in Tables I, II, and III.

These values were then used along with Eqs. (2) and (4) to predict

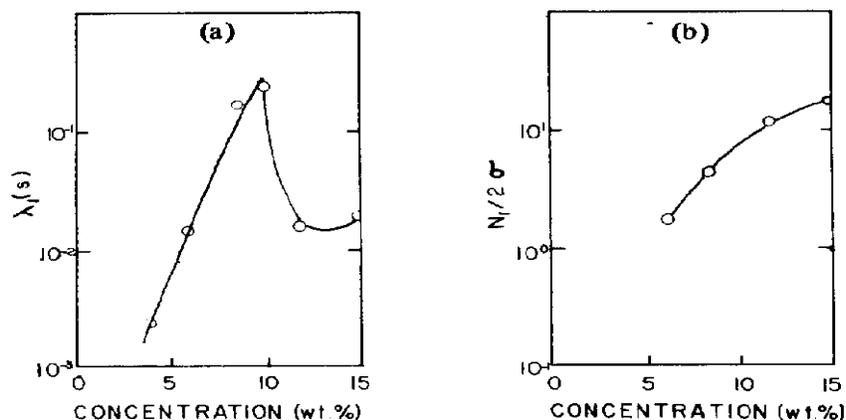


Fig. 11. Values of (a) relaxation time (λ_1) and (b) $N_1/2\sigma$ (recoverable shear strain) versus concentration for same solutions as in Fig. 2.

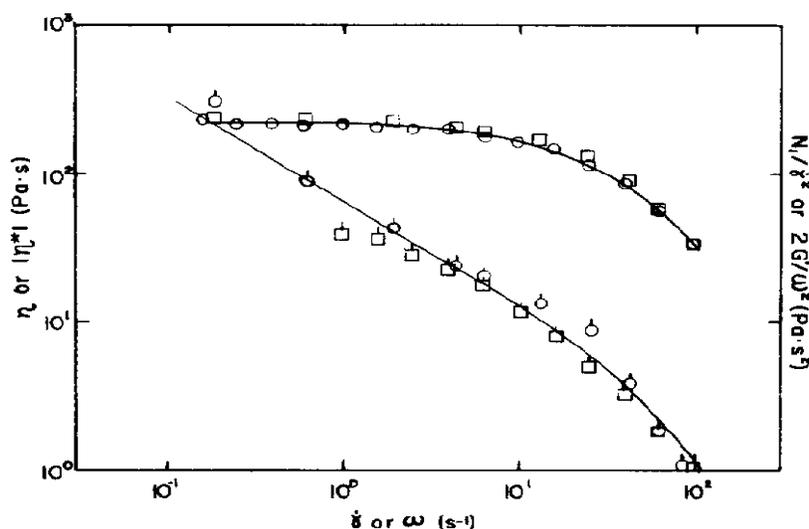


Fig. 12. Comparison of η (\square) versus $\dot{\gamma}$ with $|\eta^*|$ (\circ) versus ω and comparison of $N_1/\dot{\gamma}^2$ (\square) versus $\dot{\gamma}$ with $2G'/\omega^2$ (\circ) versus ω for a 6% isotropic solution of PPT in H₂SO₄ at 60°.

values of $N_1/\dot{\gamma}^2$ vs. $\dot{\gamma}$ and η''/ω vs. ω . In Fig. 6 experimental values of $N_1/\dot{\gamma}^2$ vs. $\dot{\gamma}$ are compared with the model predictions for isotropic solutions while similar comparisons for the anisotropic solutions are presented in Fig. 7. For the 6% solution, the Bird-Carreau model is in poor agreement with the experimental data, while for the 8% so-

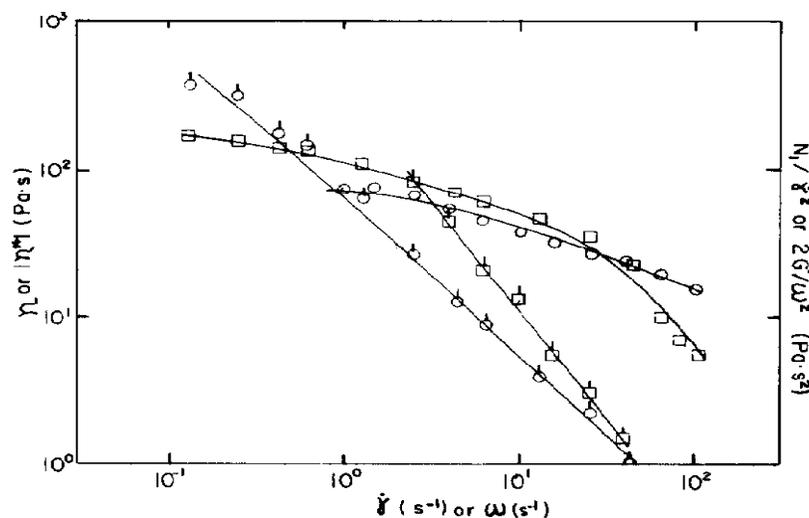


Fig. 13. Comparison of the same functions as in Fig. 4 for a 15% anisotropic solution of PPT in H₂SO₄ at 60°C: η (\square), $|\eta^*|$ (\circ), $N_1/\dot{\gamma}^2$ (\square), $2G'/\omega^2$ (\circ).

lution the agreement is quite good. For the anisotropic solutions we see that Hand's theory fits the data quite well at high $\dot{\gamma}$, but at low $\dot{\gamma}$ the model levels off too soon. For the data available for the 10% solution, the agreement is good for both models. It is interesting to note that the Hand model at least predicts the correct shape of $N_1/\dot{\gamma}^2$ versus $\dot{\gamma}$ curves at high $\dot{\gamma}$ for the anisotropic fluids.

Finally, in Figs. 8 and 9 values of η''/ω vs. ω are compared with predicted values of η''/ω from the Bird-Carreau model. For the isotropic solutions the agreement between the predicted and experimental values is quite good over the full range of ω . Even for the anisotropic solutions, the agreement is quite good at high ω , but at low ω values of η''/ω continue to increase with ω .

CONCLUSIONS

It is somewhat remarkable that even with onset of liquid crystalline order, the Bird-Carreau model for most part successfully fits the steady shear and oscillatory data. The Bird-Carreau model actually does quite well at predicting η''/ω values for both the isotropic and anisotropic solutions. However, there are some significant differences between predicted and measured values of $N_1/\dot{\gamma}^2$. The agreement is usually better at high $\dot{\gamma}$ and ω . These results suggest that the inherent anisotropy of the fluids with liquid crystalline order may only be a significant factor in the rheological properties at low $\dot{\gamma}$. At high $\dot{\gamma}$ the flow induced orientation may dominate or erase the thermodynamically induced order. In fact, as has been reported elsewhere¹⁸ for liquid crystalline solutions of a synthetic polypeptide in dimethylformamide the difference between the isotropic and anisotropic phase disappears at high $\dot{\gamma}$. The data presented in Fig. 14 show that the concentration dependence of η tends to decrease with increasing $\dot{\gamma}$, i.e., at high $\dot{\gamma}$ the characteristic behavior observed at low $\dot{\gamma}$ is beginning to disappear.

The Hand model successfully fits the normal stress data for the anisotropic solutions at high $\dot{\gamma}$ and the viscosity data at concentrations at which the solutions have just become anisotropic. The lack of fit of the normal stress data at low $\dot{\gamma}$ may be associated with the simplifications used to make the theory tractable. For the model in the form used here, the fluids are considered to be isotropic at rest and become anisotropic during flow. The optical behavior of the anisotropic fluids indicates they are structured at rest. Hence, part of the

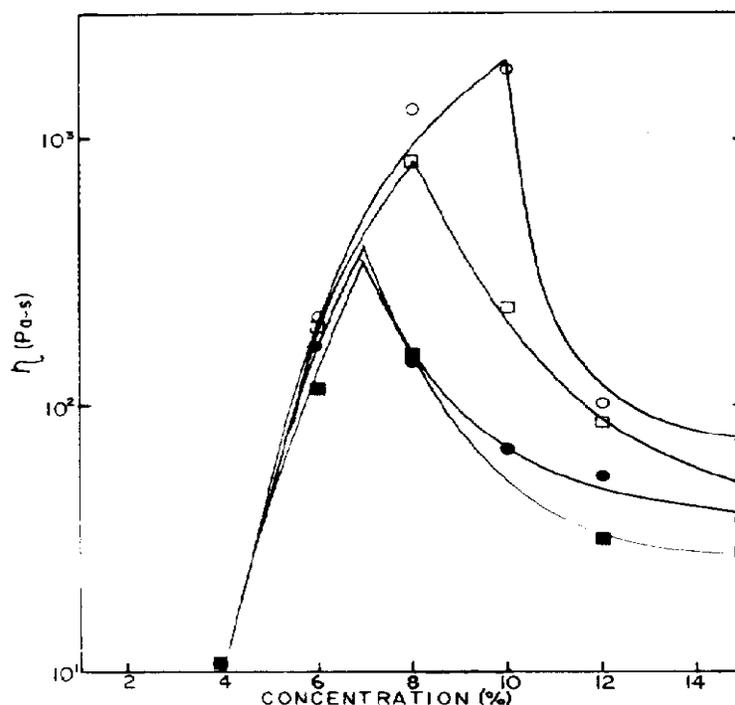


Fig. 14. Dependence of η versus concentration on shear rate for solutions of PPT at 60°C: $\dot{\gamma} = 25$ (■), 10 (●), 4 (□), 1 (○) sec^{-1} .

lack of agreement at low $\dot{\gamma}$ may be due to neglecting the anisotropy of the fluid at rest.

In this paper, we have considered only the steady state shear and linear viscoelastic properties. Other rheological measurements such as extensional viscosity, entrance/exit pressures, and transient normal stresses are needed in order to better understand the processing characteristics of these unique fluids.

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