A Rheological and Optical Properties Investigation of Aliphatic (Nylon 66, PγBLG) and Aromatic (Kevlar, Nomex) Polyamide Solutions

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Synopsis

An experimental study of shear viscosity $\eta(\dot{\gamma})$, principal normal stress difference $N_1(\dot{\gamma})$, storage modulus $G'(\omega)$, dynamic viscosity $\eta'(\omega)$, and filament elongation to break L_B is reported for solutions of several polyamides; namely, nylon 66 in sulfuric acid (H_2SO_4) and formic acid (HCOOH), poly(γ-benzyl-L-glutamate) (PγBLG) in *m*-cresol, Nomex in H_2SO_4 and dimethylacetamide (DMA)/5% LiCl, and Kevlar in H_2SO_4 at 25 and 60°C. The variation of properties with concentration, polymer backbone and chain configuration, and solvent type is emphasized. The nylon 66/H_2SO_4 solutions have higher viscosity, normal stresses, and storage modulus than the HCOOH solutions of equivalent concentrations. The Nomex/H_2SO_4 solutions have higher viscosity and higher normal stresses and storage modulus than the DMA/LiCl solutions at equivalent concentrations. The significance of polymer chain backbone rigidity in forming liquid crystalline phases in Kevlar and PγBLG solutions is discussed and its influence on flow properties is indicated. These systems allow polarized light to pass through crossed polarizers and show maxima in viscosity–concentration data. The 25°C Kevlar solutions are distinctive in that they exhibit apparent yield stress values. This gives distinctive shear flow and oscillatory data. Filament elongation-to-break data show Kevlar > Nomex > nylon 66 in H_2SO_4 solutions for the order of spinnability.

INTRODUCTION

The solution properties of polyamides have gained scientific attention as a result of interest in the characteristics of aromatic polyamides.[1-3] Poly(hexamethyleneadipamide) (nylon 66), and polycaprolactam (nylon 6), have been important commercial polymers for almost forty years. More recently, aromatic polyamides, notably Nomex and Kevlar fiber, have become important. While aliphatic polyamides are fusible and processed in the molten state to form fibers and molded parts, aromatic polyamides chemically degrade below their melting temperature and must be processed in the solution state. This has led to an increased interest in the solution properties of polyamides. Studies of aromatic polyamide solutions have turned up a number of striking experimental observations. Concentrated solutions of para-linked aromatic polyamides exhibit liquid crystalline behavior,[1-6] while solutions of meta-linked ones show complete association effects with salts in solution.[7,8] The liquid crystalline behavior is similar to that observed in concentrated solutions of polypeptides.[9-12]

The present authors and their co-workers have been concerned with the processing and properties of polyamides, including structure development in the melt spinning[13-15] and wet spinning[16] of nylon 6 and nylon 66 fibers as well as wet spinning Nomex and Kevlar fibers.[16,17] In related papers, new types of aromatic polyamides were synthesized and solution spun into fibers.[18,19] In this

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paper we investigate the rheological and optical properties of four polyamides of varying structure. We compare aliphatic, meta-linked and para-linked aromatic polyamides formed from diamines and dicarboxylic acids, specifically,
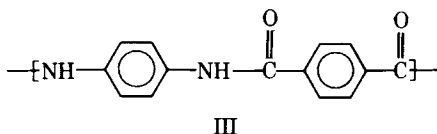
poly(hexamethyleneadipamide) (nylon 66),

$$\text{—}[\text{NH—(CH}_2)_6\text{—NH—C—(CH}_2)_4\text{—C}]\text{—}$$

I
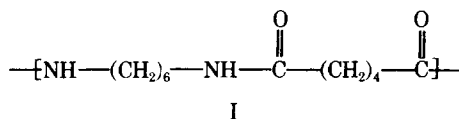
poly(m-phenyleneisophthalamide) (Nomex),⁻

$$\text{—}[\text{NH—}\bigcirc\text{—NH—C—}\bigcirc\text{—C}]\text{—}$$

II
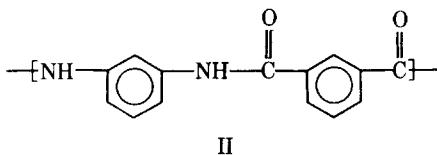
poly(p-phenyleneterephthalamide) (Kevlar):

$$\text{—}[\text{NH—}\bigcirc\text{—NH—C—}\bigcirc\text{—C}]\text{—}$$

III

These polymers differ considerably in chain flexibility, with polymer I being flexible and polymer III being rather rigid; polymer II is of intermediate flexibility. We also studied a polypeptide previously reported in the literature as liquid crystalline,[9-12]

poly(γ-benzyl-L-glutamate) (PγBLG),

$$\text{—}[\text{NH—CH—C}]\text{—}$$
$$\text{CH}_2$$
$$\text{CH}_2$$
$$\text{C}\!=\!\text{O}$$
$$\text{O—CH}_2\text{—}\bigcirc$$

IV
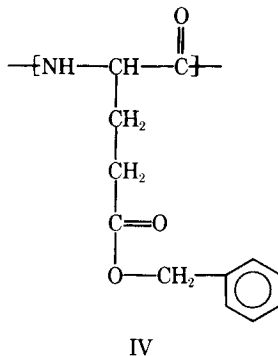
The rheological properties and possible onset of liquid crystalline character are studied in different solvents. In the case of polymers I, II, and III, we contrast their properties in H_2SO_4. Up to the present most such investigations were limited to shear viscosity,[1,3] but here we additionally consider normal stresses developed in shear flow, the stress response to sinusoidal oscillations, and apparent spinnability. In a sense, this paper specifically continues research described in two earlier papers. The polymer solvent systems wet spun by Hancock, Spruiell, and White[16] are included in the systems described here. The physicochemical properties including rheological and optical behavior of

poly(*m*-phenyleneisophthalamide) (II) in dimethylacetamide (DMA)/LiCl solvents have been investigated by Harwood, Aoki, Lee, Fellers, and White.[8] We shall contrast its rheological properties in H_2SO_4 solutions to its DMA/LiCl solution properties.

EXPERIMENTAL

Materials

Four polymers with structures indicated in I through IV above have been investigated in our studies. Their characteristics are summarized in Table I. Polymer I, poly(hexamethyleneadipamide), is a du Pont Zytel molding resin. Polymer II, poly(*m*-phenyleneisophthalamide), is a du Pont Nomex (Type 430) synthetic fiber. Polymer III is du Pont Kevlar synthetic fiber. Polymer IV is a PγBLG purchased from Sigma Chemical Company, St. Louis, Missouri.

The solvents used in this study were 100% sulfuric acid (H_2SO_4) obtained from Fisher Scientific Company, Fair Lawn, New Jersey; dimethylacetamide (DMA) obtained from Aldrich Chemical Company, Milwaukee, Wisconsin; lithium chloride (LiCl) from Fisher Scientific Company; and *m*-cresol from the Aldrich Chemical Company.

The polymer–solvent combinations studied were nylon 66 (I) with 100% H_2SO_4, 90% $HCOOH/H_2O$; Nomex (II) with 100% H_2SO_4, DMA with 5% LiCl; Kevlar (III) with 100% H_2SO_4; and PγBLG (IV) with *m*-cresol.

Optical Measurements

Each polymer–solvent system was studied in a transmission light microscope between crossed polarizer and analyzer. Specifically, the Kwolek DDA test was carried out.[1] Samples of polymer solution were placed between two glass slides separated from each other by Teflon tape of thickness 0.165 mm. The increase in I/I_0, the amount of light passing through the system with polymer solution present, where I_0 is the light intensity without the solution between the glass slides, was measured as a function of polymer concentration by means of a light meter (General Electric dc micrometer, Type DO-58).

TABLE I
Polymers Used in This Study

Polymer designation	Polymer type	Supplier	Molecular weight $\times 10^{-3}$
I	nylon 66	du Pont	28.4[a]
II	Nomex	du Pont	89[a]
III	Kevlar	du Pont	~40[b]
IV	PγBLG	Sigma Chemical	150[c]

[a] As reported in ref. 16.

[b] As computed from ref. 35.

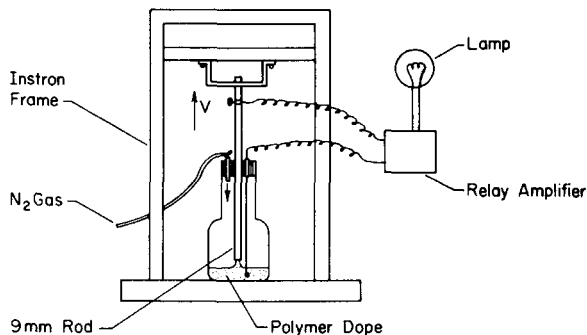[c] As reported by Sigma Chemical.

Fig. 1. Spinnability apparatus.

Rheological Measurements

Steady shear flow and sinusoidal oscillation experiments were carried out in a Model R16 Weissenberg rheogoniometer. A special Type 304 stainless steel cone–plate apparatus was designed and built in our shops for the H_2SO_4 experiments. It was checked and calibrated against the standard aluminum cone–plate with a noncorrosive polymer solution. This cone–plate fixture has an angle α of 2° and a radius R of 5 cm.

In a steady shear flow, the shear rate $\dot{\gamma}$ in a cone–plate geometry is

$$\dot{\gamma} = \Omega/\alpha \qquad (1)$$

where Ω is the angular velocity. The stress response involves a shear stress σ_{12} and three normal stresses, σ_{11}, σ_{22}, and σ_{33}, where 1 is the direction of flow, 2 is
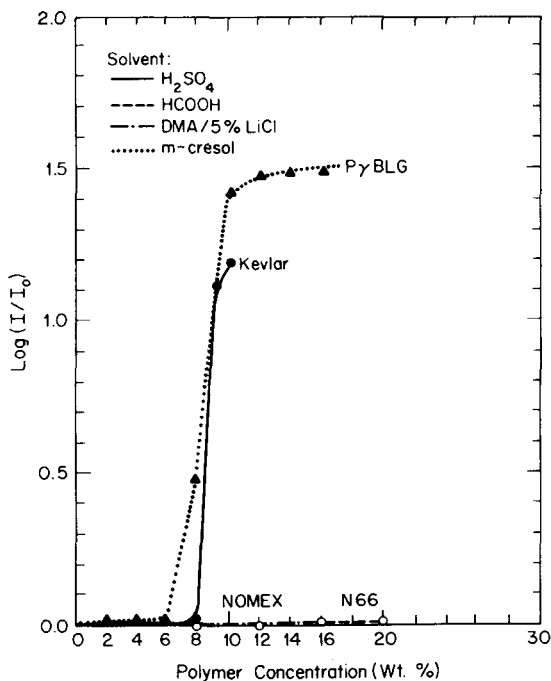
Fig. 2. Transmitted light I/I_0 as function of polymer concentration for polymers I–IV at 25°C.

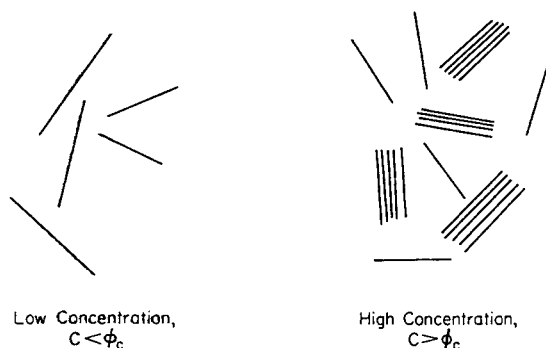Low Concentration,
$c < \phi_c$

High Concentration,
$c > \phi_c$

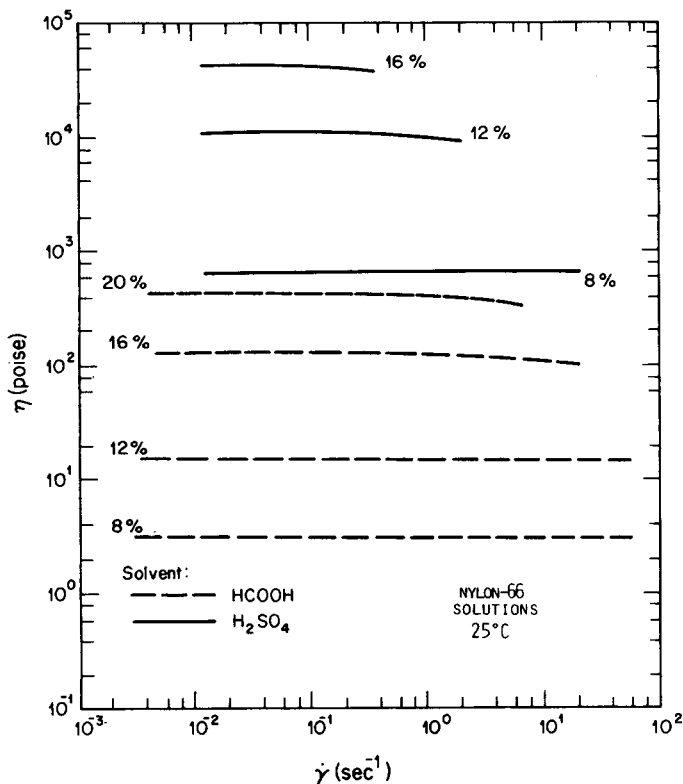Fig. 3. Mechanism of liquid crystal formation in solutions of rigid macromolecules.

Fig. 4. Plot of viscosity $\eta(\dot\gamma)$ as function of shear rate $\dot\gamma$ for nylon 66 in H_2SO_4 and 90% HCOOH at 25°C.

the direction of shear, and 3 is the neutral direction. The normal stresses are generally represented through an isotropic pressure p and two normal stress differences N_1 and N_2 defined as

$$N_1 = \sigma_{11} - \sigma_{22} \tag{2a}$$

$$N_2 = \sigma_{22} - \sigma_{33} \tag{2b}$$

Three rheological functions are defined by relating N_1, N_2, and σ_{12} to shear rate through the expressions

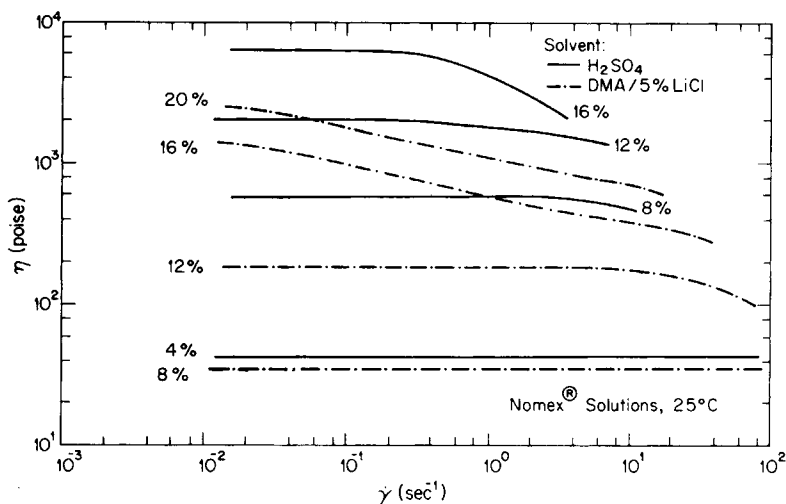$$\sigma_{12} = \eta\dot\gamma \tag{3a}$$

Fig. 5. Plot of viscosity $\eta(\dot{\gamma})$ as function of shear rate $\dot{\gamma}$ for Nomex in H_2SO_4 and dimethylacet-amide/5% LiCl at 25°C.

$$N_1 = \Psi_1 \dot{\gamma}^2 \tag{3b}$$

$$N_2 = \Psi_2 \dot{\gamma}^2 \tag{3c}$$

where η is the viscosity and Ψ_1 and Ψ_2 are normal stress coefficients.

The shear stress σ_{12} and N_1 were determined from rheogoniometer torque M and vertical thrust F measurements. This was carried out using the expressions[20]

$$\sigma_{12} = 3M/2\pi R^3 \tag{4a}$$

$$N_1 = 2F/\pi R^2 \tag{4b}$$

N_2 was not measured.

In the oscillatory shear flow, a sinusoidal strain $\gamma(t)$ is imparted to the fluid between the cone and plate. We may express this as

$$\gamma(t) = \gamma_0 \sin \omega t \tag{5}$$

where ω is the frequency and γ_0 is the shear strain ampiltude. The shear stress response is out of phase with the strain. It may be represented as

$$\sigma_{12}(\omega) = G'(\omega)\gamma_0 \sin \omega t + G''(\omega)\gamma_0 \cos \omega t \tag{6a}$$

$$\sigma_{12}(\omega) = G'(\omega)\gamma(t) + \eta'(\omega)\frac{d\gamma}{dt} \tag{6b}$$

where $G'(\omega)$ is the dynamic storage modulus, $G''(\omega)$ is the loss modulus, and $\eta'(\omega)$ is the dynamic viscosity. In-phase and out-of-phase stress components were obtained using eq. (6a) by taking Lissajous patterns from the oscilloscope and then converting to $G'(\omega)$ and $\eta'(\omega)$.

Spinnability Experiments

An apparatus was designed to estimate the spinnability of polymer solutions. Its principle and design are summarized in Figure 1. A rod is initially in contact with the surface of a polymer solution. It is withdrawn at velocity V inducing a cylindrical liquid filament of length L, equal to Vt, where t is the time elapsed to form the filament between the surface of the liquid and the moving member. The existence of the filament is measured by electrical conduction. When the filament breaks at length L_b, the contact is broken. The apparatus is similar to an instrument described by Sherr[21] more than a generation ago.

OPTICAL STUDIES

Results

Measurements of transmitted polarized light I/I_0 in the Kwolek DDA test are shown as a function of concentration for the polymers studied in Figure 2. At low concentrations, essentially no light is transmitted. At high concentrations, the solutions of Kevlar and PγBLG transmit significant quantities of light, while the other solutions do not. The transition occurs at concentrations of 9.5% for the Kevlar and at 9% for the PγBLG.
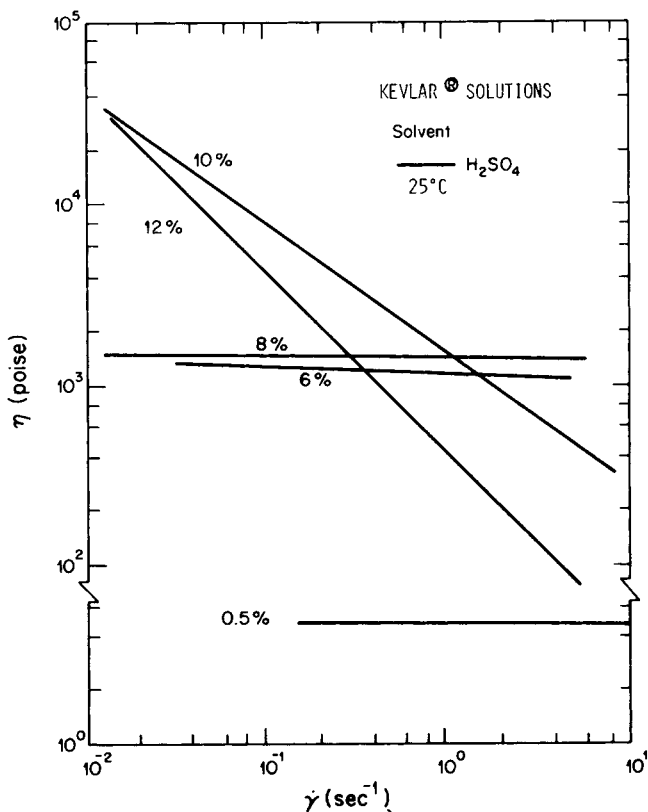

Fig. 6. Plot of viscosity $\eta(\dot{\gamma})$ as function of shear rate $\dot{\gamma}$ for Kevlar in H_2SO_4 at 25°C.
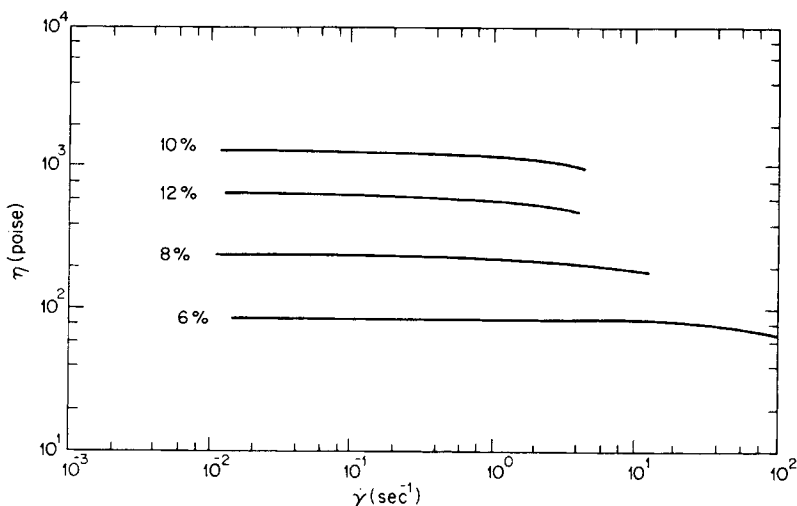
Fig. 7. Plot of viscosity $\eta(\dot{\gamma})$ as function of shear rate $\dot{\gamma}$ for Kevlar in H_2SO_4 at 60°C.
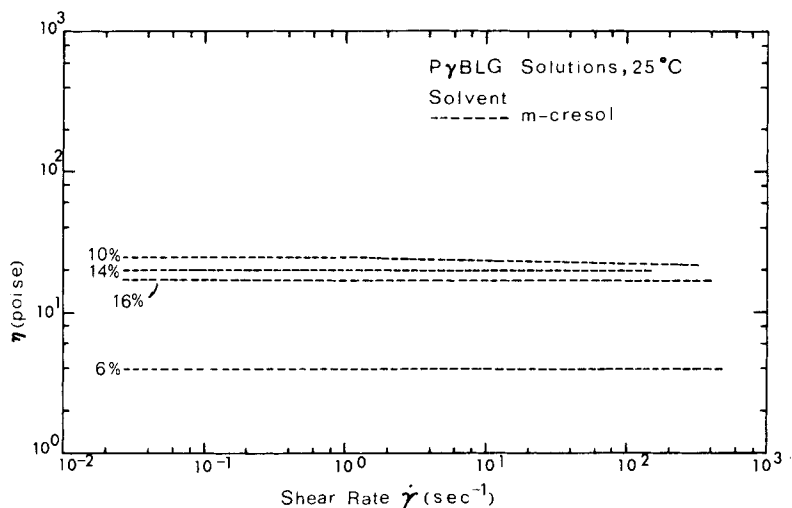

Fig. 8. Plot of viscosity $\eta(\dot{\gamma})$ as function of shear rate $\dot{\gamma}$ for PγBLG in m-cresol at 25°C.

Interpretation

The dilute solutions of all polymers studied are optically isotropic in a state of rest. However, optical anisotropy arises in solutions of Kevlar and PγBLG. Such anisotropy may be due to stress induced birefringence[22,23] or to liquid crystalline character.[1-6,9-12] If it is due to the former, it should decay with time in a solution until it disappears. However, if the solution is a soft gel rather than a true fluid, some of the birefringence could be permanent.

The two polymer solutions found to transmit polarized light have both been reported as liquid crystalline by earlier investigators. The behavior seems associated with the lack of polymer chain flexibility as these systems are also the most rigid of the macromolecules investigated. The para-linked phenyl groups makes the Kevlar a rigid chain. The rigidity of the PγBLG follows from the chain having the configuration of a helix. The infrared spectra,[24] optical rota-
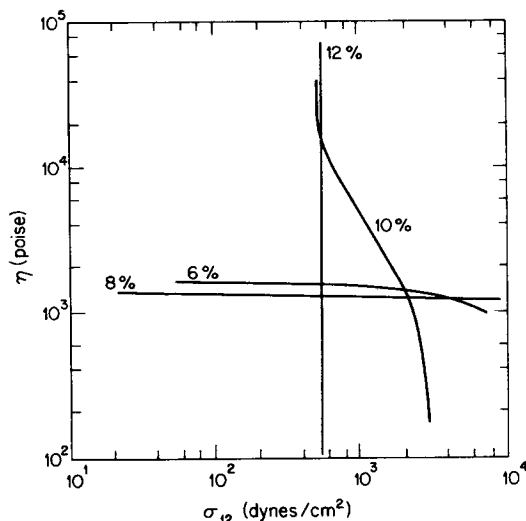
Fig. 9. Plot of viscosity η for Kevlar/H_2SO_4 at 25°C as function of shear stress σ_{12}.
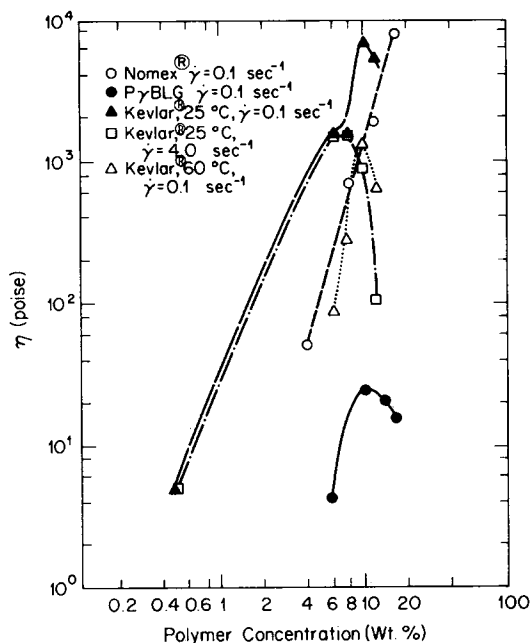

Fig. 10. Viscosity as function of concentration for Kevlar/H_2SO_4 at 25°C (0.1 and 4.0 sec^{-1}), Kevlar/H_2SO_4 at 60°C, PγBLG/m-cresol, and Nomex/H_2SO_4 at 25°C.

tion,[25] and dilute solution viscosity[26] characteristics prove the existence of the helical chain conformation. The solutions of Kevlar are also reported as liquid crystalline by du Pont investigators.[1,2] PγBLG solutions are a classical case of liquid crystalline behavior in polymers.[9-12]

The formation of liquid crystalline phases in these systems has been theoretically linked by Flory[27] and others to polymer chain rigidity using a statistical thermodynamic theory. Essentially, it is argued that rigid rods, unlike flexible
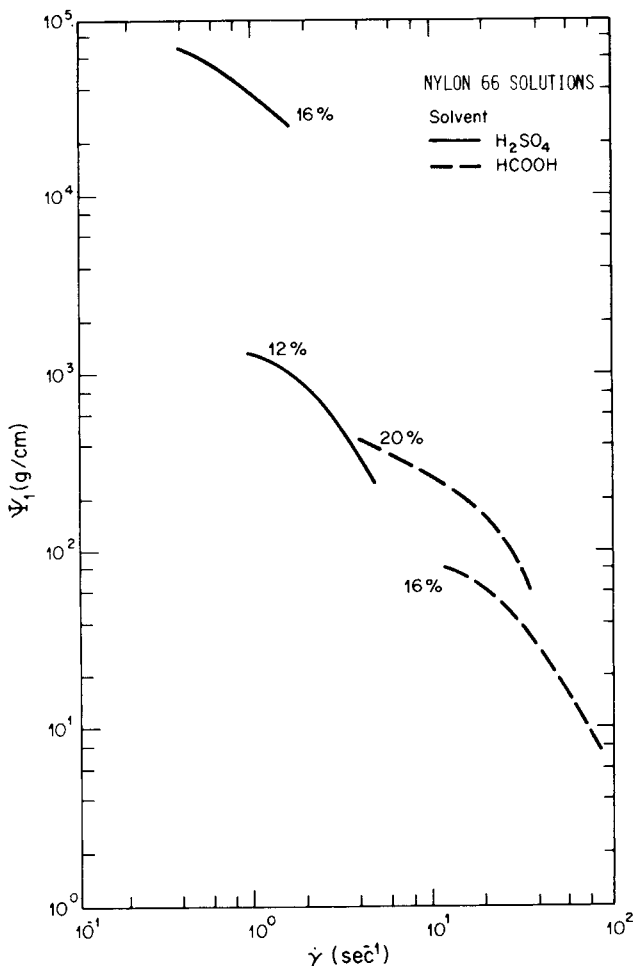
Fig. 11. Principal normal stress difference coefficient $\Psi_1(\dot{\gamma})$ as function of shear rate and concentration for nylon 66 in H_2SO_4 and HCOOH/10% H_2O at 25°C.

chains, cannot pack together in concentrated systems. This is illustrated in Figure 3. The theory, however, can only be reviewed as approximate, as evidence exists[1] that the critical polymer concentrations required for liquid crystalline phase formation is solvent dependent. The solvent character may be involved in "chain straightening" processes.

VISCOSITY STUDIES

Results

Plots of viscosity η as a function of shear rate $\dot{\gamma}$ are shown for the solutions of nylon 66 at 25°C in Figure 4, Nomex at 25°C in Figure 5, and of Kevlar at 25°C in Figure 6 and at 60°C in Figure 7. It is clear that solvent quality has a strong influence on viscosity in these systems. At any concentration, the H_2SO_4 solution data are the highest for both nylon 66 and Nomex. Of all the solvent systems used, Kevlar is only soluble in H_2SO_4.

The general behavior of the viscosity–shear rate–concentration relationship for solutions of polymers I, II, and III differ.   In the case of nylon 66 and Nomex, the response is Newtonian at low shear rates.   For dilute solutions of these polymers, the behavior is Newtonian at all shear rates studied.   For Kevlar at 25°C (Fig. 6), the response is qualitatively different.   The low concentration (6% and 8%) solutions do exhibit Newtonian behavior.   The 10% and 12% solution viscosities do not show Newtonian behavior even at the lowest shear rates, and the data continue to increase with a slope of 45° on logarithmic coordinates. Furthermore, the viscosity in this system, especially at high shear, does not increase monotonically with concentration.   Instead, the viscosity strikes a maximum and then decreases at high concentration.

Figure 7 shows the response of the same system at 60°C.   The low shear rate response differs from that observed at 25°C, and the solutions are close to Newtonian.   However, the viscosity–concentration dependence still exhibits a maximum.

The viscosity–shear rate behavior of PγBLG in m-cresol is contained in Figure 8.   The PγBLG solutions possess a Newtonian character similar to the nylon 66 solutions, but the viscosity–concentration dependence clearly exhibits a maximum.
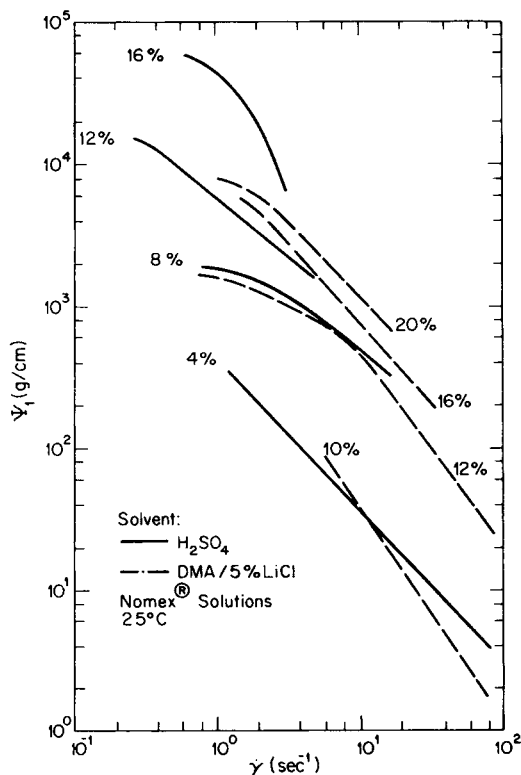

Fig. 12. Principal normal stress difference coefficient $\Psi_1(\dot{\gamma})$ as function of shear rate and concentration for Nomex in H_2SO_4 and DMA/5% LiCl at 25°C.
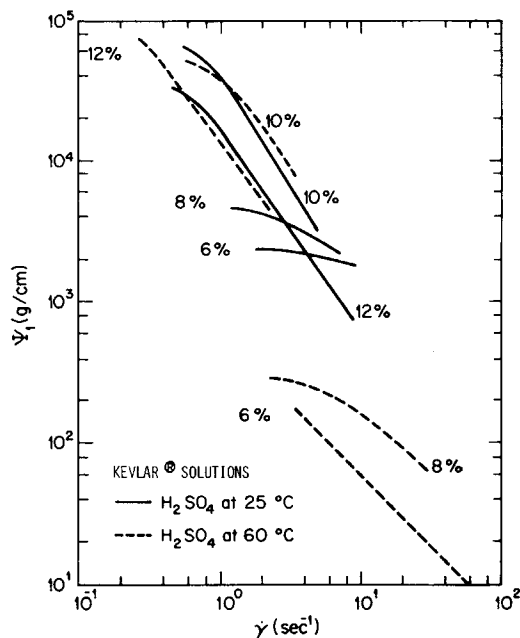
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Fig. 13. Principal normal stress difference coefficient $\Psi_1(\dot{\gamma})$ as function of shear rate and concentration for Kevlar/H_2SO_4 at 25 and 60°C.
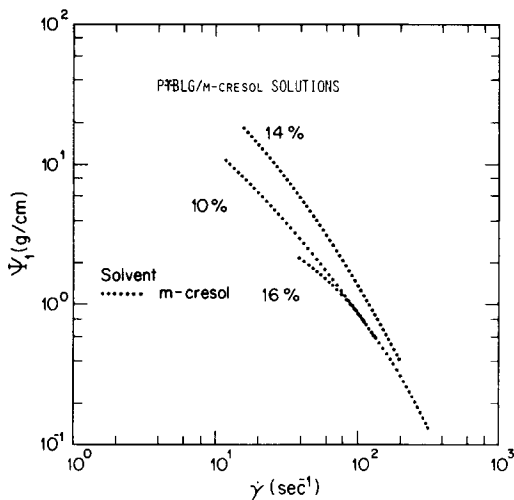

Fig. 14. Principal normal stress difference coefficient $\Psi_1(\dot{\gamma})$ as function of shear rate and concentration for P_γBLG in m-cresol at 25°C.

Interpretation

Certain aspects of the experimental results require expanded consideration. First we note the unusual $\eta(\dot{\gamma})$ behavior of the concentrated Kevlar/H_2SO_4 solutions at 25°C. This type of response has been found in other polymer systems, usually in polymer melts or solutions containing particulate fillers.[28-30] It is considered to mean that the material exhibits a yield value. This is illustrated in Figure 9, where we plot viscosity as a function of shear stress σ_{12}. It can be
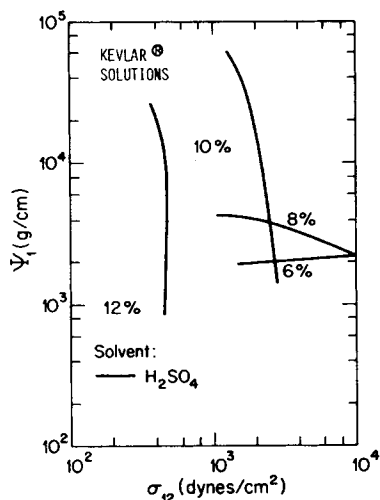
Fig. 15. Principal normal stress difference coefficient plotted as function of shear stress σ_{12} for Kevlar/H$_2$SO$_4$ solutions at 25°C.
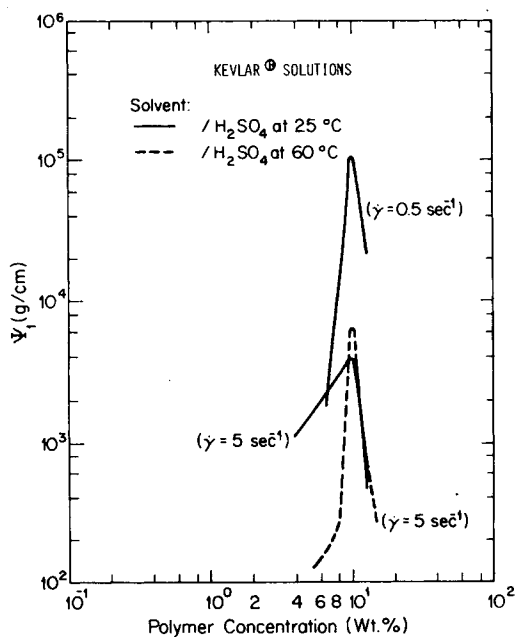

Fig. 16. Principal normal stress difference coefficient as function of concentration for 25 and 60°C Kevlar/H$_2$SO$_4$ solutions.

seen that the viscosity tends to infinity for the 10% and 12% solutions at a finite nonzero shear stress. This implies that there will be no flow in these systems below a critical shear stress of 700 dynes/cm^2. The Kevlar/H$_2$SO$_4$ becomes a gel. Papkov et al.[4] report similar behavior in poly(p-benzamide) solutions. It is possible that the system is, however, a fluid rather than a gel and the viscosity eventually becomes a constant. This might be observed if the shear rates were lowered far enough. We have not however observed this.
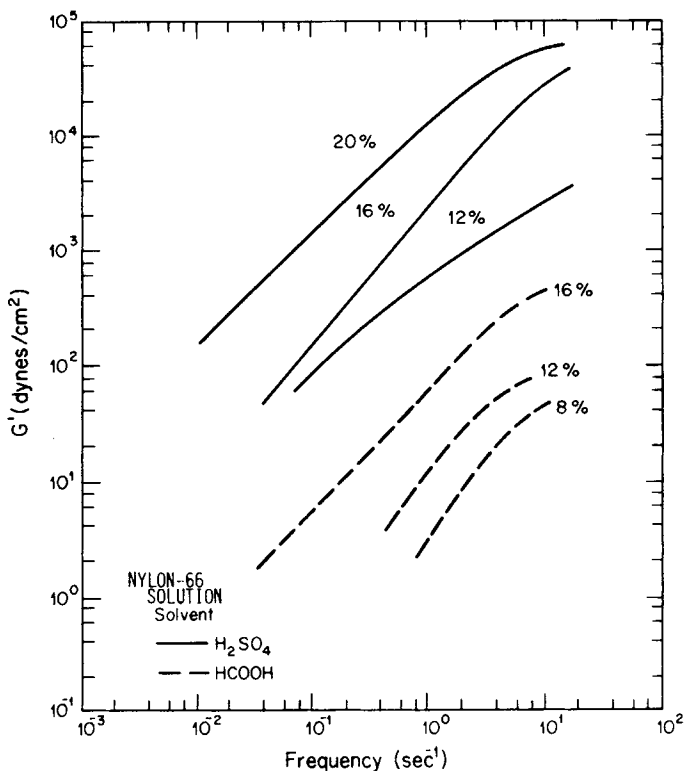
Fig. 17. (a) $G'(\omega)$ as function of frequency for nylon 66 solutions in HCOOH/10% H_2O at 25°C. (b) $\eta'(\omega)$ as function of frequency for nylon 66 solutions in HCOOH/10% H_2O at 25°C.

The viscosity–concentration behavior of the Kevlar and PγBLG solutions deserves special attention as they exhibit a maximum at intermediate concentrations. This is shown in Figure 10 for Kevlar at 25°C (at $\dot{\gamma} = 0.1$ and 4.0 sec^{-1}), Kevlar at 60°C, and PγBLG at 25°C. We also include Nomex in H_2SO_4 for comparison. The Kevlar and PγBLG solutions show viscosity maxima. The concentration dependence of η at different shear rates is to a large extent influenced by the existence of a yield value. The position of the viscosity maxima in PγBLG solutions has been previously noted by Hermans[10] and in para-linked aromatic polyamides by Kwolek and her co-workers[1-3] and by Papkov et al.[4] It has been associated with the formation of liquid crystalline regions in these solutions, which generally occurs at about the same concentration as the rise in transmitted light I/I_0 described in the previous section. As we have noted earlier, such liquid crystalline character is associated with solutions of polymer chains with rigid backbones.

The viscosity–concentration–shear rate behavior of the nylon 66 and Nomex solutions is typical of that of solutions with flexible chains. This may be seen by comparing the behavior to that of polystyrene solutions.[31]

It is of interest to the above considerations that similar viscosity decreases have been found associated with the formation of nematic liquid crystalline phases in low molecular weight organic compounds.[32] These organic compounds exist
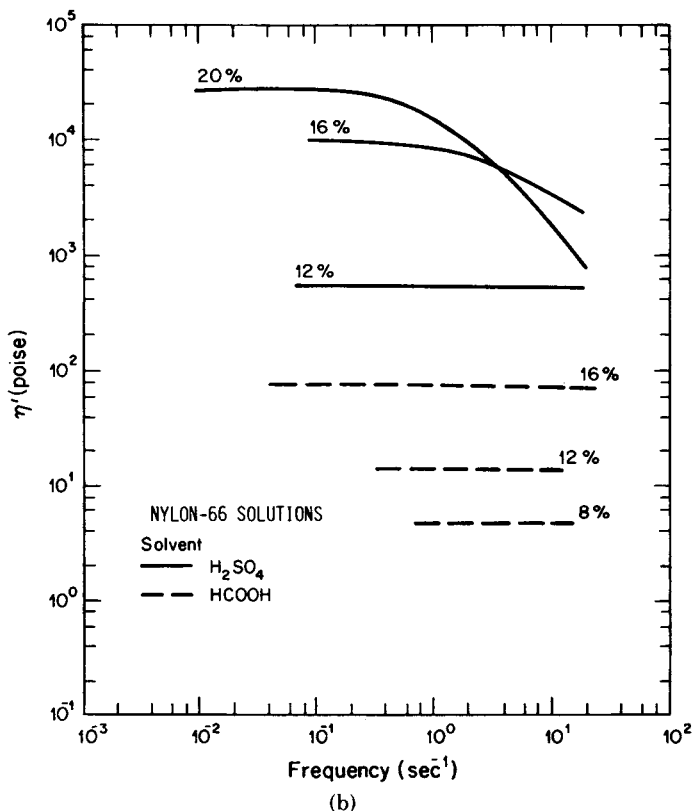
Fig. 17. *(Continued from previous page.)*

as isotropic liquids at high temperatures and solid crystals at low temperatures. In an intermediate temperature range, they behave as nematic liquid crystals. It was found by Porter and Johnson[32] that in the isotropic liquid state the viscosity increases as temperature decreases, as would be expected in normal liquids. However, when the transition temperature to the liquid crystalline state was reached, there was a substantial *drop* in viscosity.

NORMAL STRESSES

Results

The principal normal stress difference coefficient Ψ_1 for the polymer solutions is plotted as a function of shear rate $\dot{\gamma}$ in Figures 11 to 14. The magnitude of normal stresses varies considerably with solvent for any particular polymer and with polymer type. For the nylon 66 system, the H_2SO_4 Ψ_1 values are higher than the HCOOH results at the same concentration and shear rates. For the Nomex solutions, the Ψ_1 is larger in the H_2SO_4 solutions at equivalent concentrations and shear rates. The Kevlar Ψ_1 data are generally higher than those of Nomex and nylon 66 but seem to exhibit a maximum with respect to concentration. The Ψ_1 values are larger at 25°C than at 60°C, except for the 10% and 12% cases, where Ψ_1 values seen unchanged with temperature. The normal
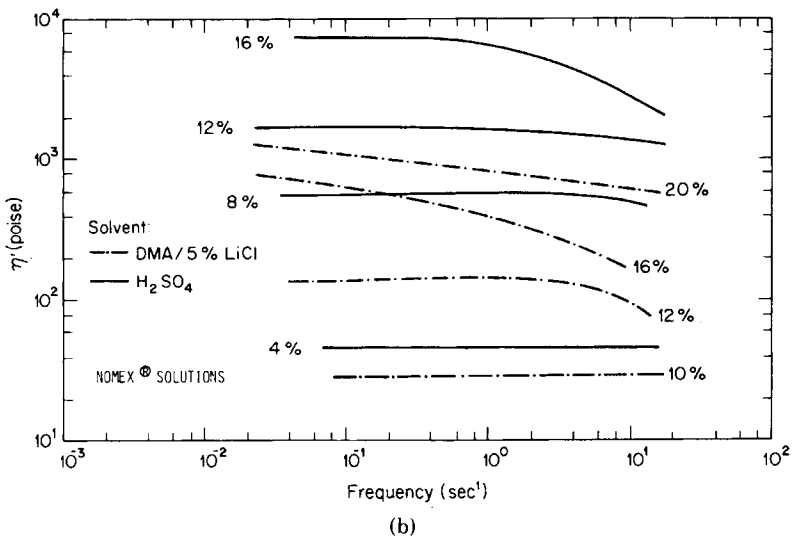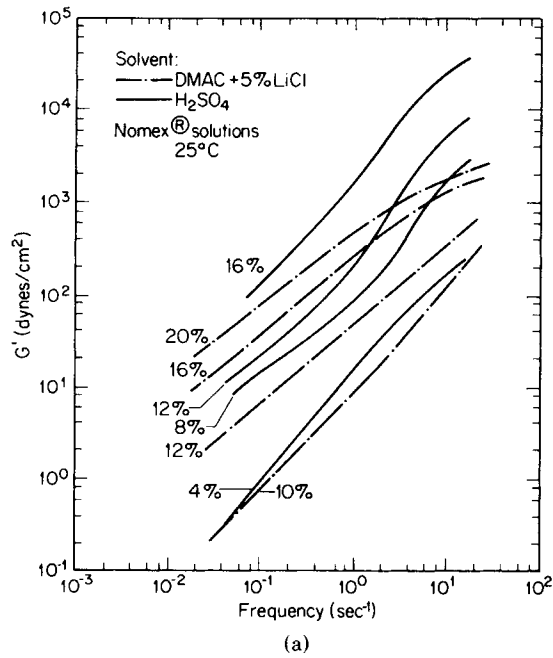
Fig. 18. (a) $G'(\omega)$ as function of frequency for Nomex solutions at 25°C. (b) $\eta'(\omega)$ as function of frequency for Nomex solutions at 25°C.
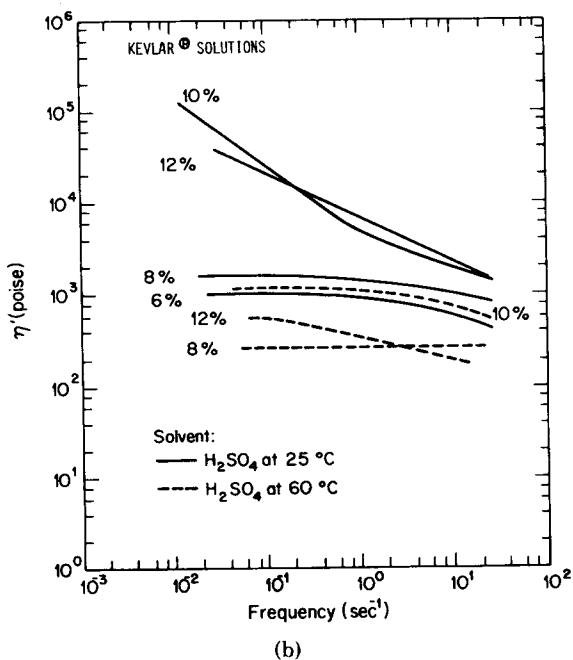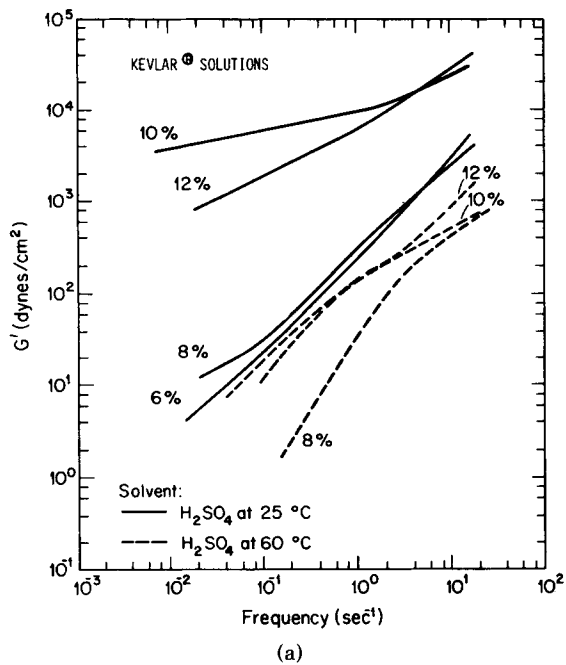
(a)

(b)

Fig. 19. (a) $G'(\omega)$ as function of frequency for Kevlar in H_2SO_4 at 25 and 60°C. (b) $\eta'(\omega)$ as function of frequency for Kevlar in H_2SO_4 at 25 and 60°C.
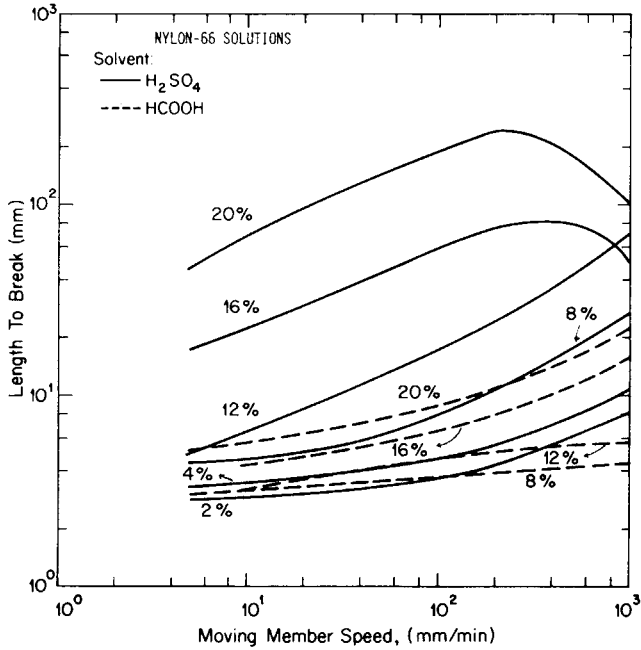
·Fig. 20. Length of threads to break for the nylon 66 in H_2SO_4 and HCOOH spinnability experiments as function of moving member speed and concentration at 25°C.
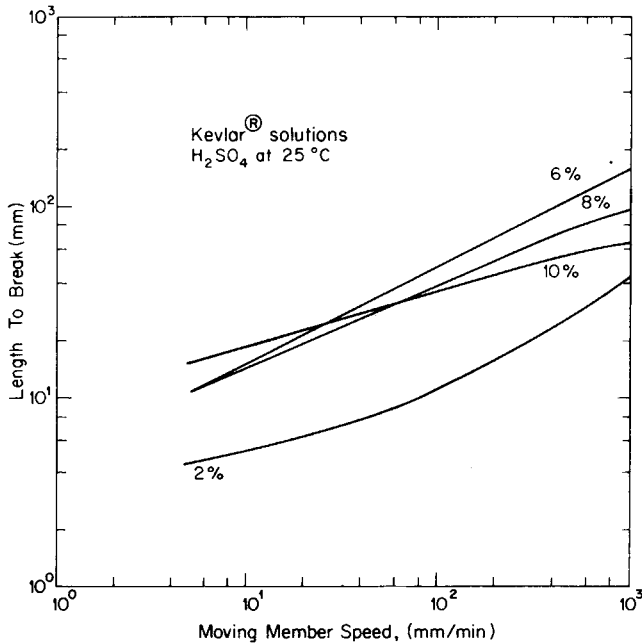

Fig. 21. Length of threads to break for the Kevlar/H_2SO_4 as function of moving member speed and concentration at 25°C.

stresses in PγBLG solutions are quite small and can only be observed at the highest concentrations.

Generally, the normal stress coefficient is a decreasing function of shear rate
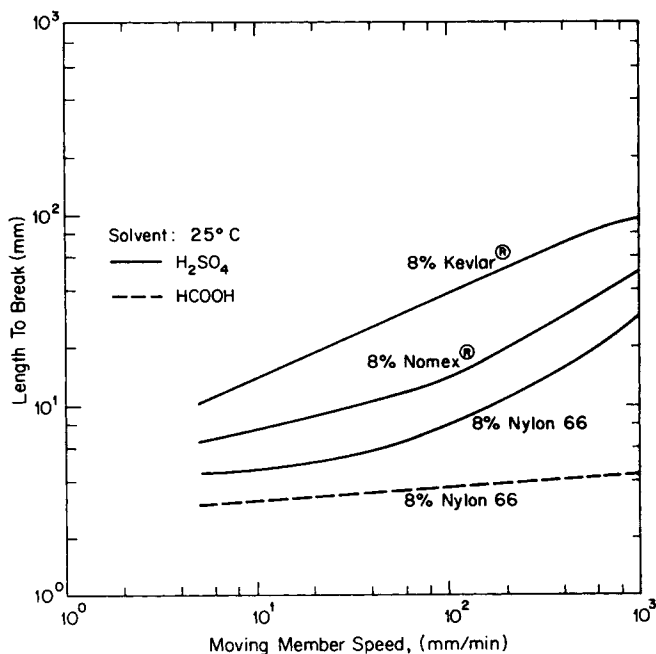
Fig. 22. Comparison of length to break for nylon 66, Nomex, and Kevlar 8% solutions.

and tends to become constant at low shear rates. An exception would seem to be the Kevlar solutions.

Interpretation

The dependence of Ψ_1 in Kevlar solutions on shear rate, shear stress, and concentration is of special interest. In Figure 13 we see that at low shear rates the Ψ_1 values for 10% and 12% solutions are significantly larger than those of the 6% and 8% solutions but decrease rapidly with shear rate. This is to be compared with the viscosity–shear rate behavior at the same concentration. In Figure 15 we plot Ψ_1 as a function of σ_{12} at 25°C. The shapes of the 10% and 12% solution data seem consistent with the idea of a yield value in the more concentrated solutions, though the data at 60°C would not do so. Figure 16 plots Ψ_1 as a function of concentration evaluated at 0.5 and 5 sec^{-1} for 25°C and at 5 sec^{-1} for 60°C. Maxima are observed at both temperatures.

For the nylon 66 solutions the Ψ_1 data for H_2SO_4 systems are, like the viscosity, higher than for the HCOOH solutions. It is similar for the case of the Nomex solutions. Here, the H_2SO_4 solutions are more viscous than the DMA/LiCl solutions and have higher normal stress coefficients.

OSCILLATORY EXPERIMENTS

Results

This experimental investigation was not so extensive as the shear flow studies. Figures 17 and 19 show typical plots of $G'(\omega)$ and $\eta'(\omega)$ as functions of frequency and concentration. The data of Figure 16 are for nylon 66, those of Figure 18

for Nomex solutions, and those of Figure 19 for Kevlar in H_2SO_4 at 25° and 60°C. The curves of the latter at 25°C are rather different from the former, with $\eta'(\omega)$ becoming indefinitely larger at low frequency and $G'(\omega)$ having a finite, rather than zero, asymptote.

Interpretation

The experimental data of Figures 17 and 18 are very typical of isotropic viscoelastic fluids. Generally, in comparing the dynamic viscosity $\eta'(\omega)$ and the steady shear viscosity $\eta(\dot\gamma)$, one has

$$\lim_{\omega \to 0} \eta'(\omega) = \lim_{\dot\gamma \to 0} \eta(\dot\gamma) = \eta_0 \qquad (7a)$$

and

$$\eta(\dot\gamma) > \eta'(\omega = \dot\gamma) \qquad (7b)$$

Similar experimental results have been reported for other concentrated polymer solutions.

The behavior of the Kevlar solutions is similar at low concentrations. At high concentrations the response changes considerably. At low ω, $\eta'(\omega)$ increases indefinitely as ω decreases, and

$$\eta(\dot\gamma) < \eta'(\omega = \dot\gamma) \qquad (8)$$

for Kevlar at 25°C. The shape of the $G'(\omega)$ curves are different from those of Figures 17 and 18 for the nylon 66 and Nomex.

Consider

$$\tan \delta = \frac{G''(\omega)}{G'(\omega)} = = \frac{\omega\eta'(\omega)}{G'(\omega)} \qquad (9)$$

which represents the ratio of dissipated to stored energy.[23] The 10% and 12% Kevlar solutions at 25°C have a much lower value of $\tan \delta$ at any frequency than the other solutions in this study. This indicates a more elastic solid-like response. We suggest that the different linear viscoelastic characteristics of the 25°C Kevlar solutions are associated with existence of the gel structure discussed in connections with our observations of the viscosity function $\eta(\dot\gamma)$.

The $G'(\omega)$ data are higher for the H_2SO_4 solutions of Nomex and nylon 66 than they are for the DMA/LiCl solutions as are the normal stress coefficients, $\Psi_1(\dot\gamma)$. The dynamic viscosities $\eta'(\omega)$ for the H_2SO_4 solutions are larger than for the DMA/LiCl solutions, as are the shear viscosities $\eta(\dot\gamma)$. This is to be expected from the second-order fluid theory of nonlinear viscoelasticity[33] where it is shown that

$$\lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} = \frac{1}{2} \Psi_1(0) \qquad (10)$$

and the limit of $\eta'(\omega)$ at low ω is given by eq. (7a).

SPINNABILITY

Results

Figures 20 to 22 plot filament length to break L_b as a function of Instron cross-head velocity for the various solutions investigated at 25°C. It is seen that the thread length which we interpret as spinnability varies considerably with polymer and solvent type. For the nylon 66, the H_2SO_4 solutions have greater L_b than the HCOOH solutions. With the exception of the Kevlar, L_b increases with concentration. Comparison at 8% concentration shows an ordering of Kevlar > Nomex > nylon 66 in H_2SO_4.

Interpretation

The experiment reported here is similar to that analyzed by Ide and White,[34] except that the elongation rate

$$E = V/L(t) \tag{11}$$

decreases with time rather than being constant. However, the same mechanisms of failure—capillarity, ductile failure, and cohesive fracture—occur and should interact similarly. From our observations, the dominant failure mode appears to be capillarity at low concentrations and cohesive fracture at high concentrations.

It is of interest to compare the experimental observations made here with the wet-spinning spinnability observations of Hancock, Spruiell, and White,[16] These authors found for any particular system that spinnability increases with concentration. We observed a similar variation of L_b. They found the nylon 66-HCOOH solutions most difficult to wet spin in comparison to Nomex and Kevlar solutions. The best spinnability was found in the Kevlar solutions. This is supported by Figure 22. At the same concentration Kevlar shows the greatest L_b among the polymers studied here, with the order being Kevlar > Nomex > nylon 66.

At higher extension rates, both Kevlar/H_2SO_4 and nylon 66/H_2SO_4 show decreasing L_b. This may be due to high elongational viscosity induced brittle fracture. This type of phenomenon is predicted by Ide and White.

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