Solution Spinning of a Semirigid Chain Polymer Forming Ultrahigh Modulus Fibers

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Synopsis

Single filaments of the polyterephthalamide of p-aminobenzylhydrazide (X-500) were prepared by spinning X-500 solutions in dimethyl sulfoxide (DMSO) using water as a coagulating agent. The polymer is known for its ability to develop ultrahigh modulus fibers and for having a semirigid chain conformation with a persistence length of ~50 Å in DMSO. In the latter solvent, molecular rigidity appears to be just below that required for spontaneous formation of a nematic phase. The orientation of the fibers was performed in three different stages: during coagulation (I), in the washing bath following coagulation (II), and during postspinning treatments (III). Corresponding mechanical properties were determined. The results indicate that high elastic modulus (15 GPa) already appears during step I at very moderate pulloff ratios. Therefore, considerable orientation had already occurred in the flowing solution. Further increase of fiber orientation yields a large increase of modulus (from 22 to 67 GPa) during solid-state deformation (step III). The orientation of the flowing solution was monitored by viscosity and birefringence measurements. The results are discussed in terms of orientation due to elongational and shear flow and, possibly, a flow-induced transition to a nematic phase in the concentrated solution in which chain entanglement is shown to occur.

INTRODUCTION

Polymers such as poly(p-phenyleneterephthalamide) (PPD-T) and poly(p-benzamide) (PBA) exhibit lyotropic mesophases when polymer concentration exceeds a critical value.[1] Solution spinning from the nematic solution yields fibers which exhibit outstanding orientation and mechanical properties.[1] These properties have been related to the rigidity of PPD-T and PBA chains which have persistence lengths[2] in the order of 200 and 400 Å, respectively.

The polyterephthalamide of p-aminobenzhydrazide (X-500) does not readily form anisotropic solutions and its extensively characterized persistence length, ~50 Å in dimethyl sulfoxide (DMSO), falls between those of the above polyamides and those of typical randomly coiled molecules.[3,4] Yet solution spinning from isotropic solutions of X-500 yields fibers exhibiting mechanical properties comparable to those of the p-linked polyamides.[5,6] As is well known, conventional spinning techniques fail to produce high strength/high modulus fibers in the case of typical randomly coiled polymers.[7]

It thus appears that the attainment of high orientation and high modulus in polymers may be assisted by a relatively small degree of chain rigidity. In view of the high melting temperatures and poor solubilities of rigid polymers such as PPD-T and PBA, the latter conclusion is of considerable practical significance. The detailed mechanism by which the partial rigidity of the chain results in the formation of a well-oriented fiber is, however, unclear. Shear flow and elonga-

tional flow occur along the spinning line.[6] Orientation and chain extension may be so pronounced that a phase transition from isotropic to anisotropic solutions may actually occur under the flow field.[8] However, even if a transition does not occur, the degree of orientation achieved along the spinning line may be adequate to insure the attainment of high orientation during postspinning treatments. Although there is some evidence in favor of a phase transition occurring under flow for X-500 in DMSO,[6,9,10] a definite proof has not yet been obtained.

In the present work we analyze in detail the role of spinning variables and of postspinning treatments on the evolution of the orientation and of the mechanical properties of X-500.

EXPERIMENTAL

Materials

X-500 is the same sample used in previous investigations[3,4,6,9] (sample A). The intrinsic viscosity at 25°C in DMSO was 5.51 dL/g and the light scattering molecular weight was 45,500. The polymer was prepared by Preston et al., as described elsewhere.[11] The concentration of spinning dopes, C_p, was 10 g of X-500 in 100 mL DMSO. Dopes were filtered through a polypropylene gauze. DMSO was obtained from Hoechst and contained 0.03% water (Karl Fisher).

Spinning

The wet spinning line,[12] manufactured by the School of Textiles, University of Bradford (U.K.), is schematized in Figure 1. A small amount of polymer solution (about 10 mL) is forced from a cylinder-piston unit to the spinnerette die through an adjustable length of tubing. The inner diameter of the cylinder was 12.7 mm. The spinnerette die had a diameter of 0.1 mm and length/diameter ratio equal to 1. The connecting tubing had an inner diameter of 1.16 mm and a length of 17 cm. The monofilament is extruded in H_2O at 18°C at a linear outflow rate V_0. By driving the piston at different rates, V_0 could be varied in the range 5–25 m/min. The monofilament is collected at the end of the coagulating bath (90 cm long) by a set of rollers (takeup rate V_1), continues into a washing bath (also 90 cm long), and passes through a second set of rollers having takeup velocity V_2. The V_1/V_2 ratio was invariably kept equal to 1. After about 100 cm in air, the filament is wound up by a bobbin operated at a takeup rate V_R. Fibers thus obtained were held in distilled water for about 24 h to eliminate traces of residual solvent, and then dried under vacuum at about 65°C. Fibers were stored over $CaCl_2$ until testing.
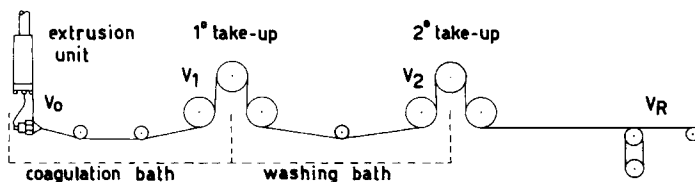

Fig. 1. Spinning line.

Fiber Properties

Fiber diameter (d) was determined with a Reichert—Zetopan Optical Microscope equipped with a micrometer eyepiece. Precision was ± 2%. The diameter was generally constant along an extended length of fiber, unless very low or very high V_1/V_0 or V_R/V_1 ratios were applied. The cross-sectional area was obtained using mean values of the diameter.

Mechanical properties were determined using an Instron Model 1122 Tensile Machine operated at room temperature. Initial deformation rate was 0.1 mm/min. Data reported are averages on three independent determinations performed on bundles of four untwisted filaments 50 mm long. The elastic modulus, the elongation to break, and the stress to break (strength) are indicated as E, ϵ %, and σ_b, respectively. Units are GPa which are related to g/den by the relationship

$$1 \text{ GPa} \simeq \frac{100}{9\,\rho} \text{ g/den}$$

where ρ is the polymer density (for X-500, 1 GPa ≈ 8 g/den).

Postspinning Treatments

Fibers to be later subjected to thermomechanical treatments were prepared as indicated above, using the following values of spinning variables: $V_0 = 6.5$ m/min; $V_1 = V_2 = 6.5$ m/min; $V_R = 6.5$ m/min; $V_1/V_0 = V_R/V_1 = 1$; $V_1/V_f = 1.44$. Each spinning operation yielded about 30 bobbins of fibers which exhibited uniform diameter and mechanical properties. The values were

$$\bar{d} = (25.6 \pm 1) \times 10^{-6} \text{ m}$$

$$\bar{E} = 14.65 \pm 0.05 \text{ GPa}$$

$$\bar{\epsilon}\,\% = 18 \pm 3$$

$$\bar{\sigma}_b = 0.50 \pm 0.04 \text{ GPa}$$

The thermomechanical treatment was performed using the line schematized in Figure 2. The bobbin was connected to a takeup unit in the spinning line and unwound at a rate V_A, which in most cases was equal to 3.4 m/min. The fiber passed over a hot surface and was wound up again by a bobbin operated at the rate V_R'. The V_A/V_R' ratios varied from 1 to the maximum value before rupture. The distance between the two bobbins was about 110 cm. The hot surface (halfway between the bobbins) was a large soldering iron with the surface covered by a thin and smooth aluminium sheet. The temperature of the hot surface was
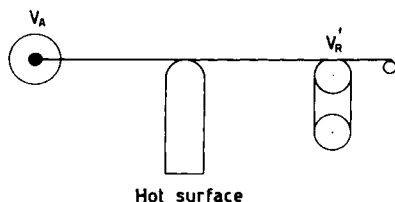

Fig. 2. Thermal treatment line.

maintained at a constant value (T = 200, 250, 300, 350, 400°C) using a series of adjustable resistors and calibration was performed with a Hewlett-Packard 2802 Athermometer.

Rheooptical Properties

Steady-shear rate measurements were performed at 20°C using a Model R18 Weissenberg Rheogoniometer equipped with a cone and plate. In some instances a cylinder–cylinder assembly was used. No difference in the results was observed. Torsion bars used had K_t = 0.097 × 10³ dyne cm/μ and K_t = 0.891 × 10³ dyne cm/μ for low and high X-500 concentration, respectively. Shear rate was $\dot{\gamma}$ = 4.4 s⁻¹ (Newtonian behavior prevailed in the low Cp range used in these experiments).

Birefringence measurements were performed on the polymer solution at the exit of the connecting tubing and at the exit of the spinnerette, no pull being applied in both cases. The retardation was determined as a function of extrusion rate and of length/diameter ratio of the connecting tubing using an Heringaus compensator and monocromatic light ($\lambda \sim$ 5890 Å). Birefringence was calculated from the relation

$$\text{retardation/diam} = \Delta n$$

RESULTS AND DISCUSSION

Spinning

Due to non-Newtonian behavior, the radius of the extruded fluid just outside the spinnerette die increases, the velocity profile flattens, and the velocity decreases from the extrusion rate V_0 to the freely extruded velocity of the filaments (no takeup) V_f.[7,13] The variation of V_f with V_0 is illustrated in Figure 3. V_f was determined from the rate necessary to collect the filament at the first pickup,
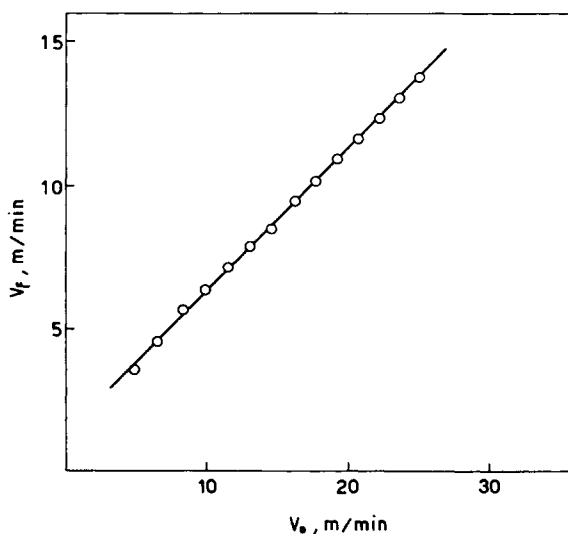

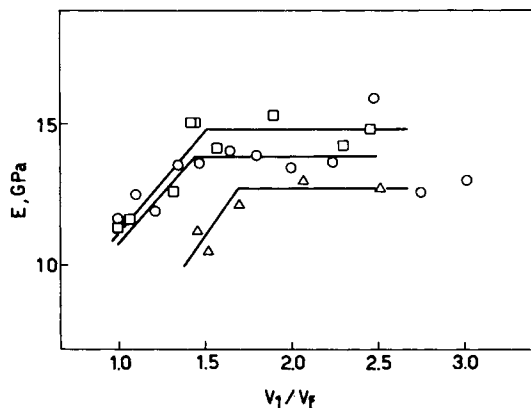Fig. 3. Variation of free velocity with extrusion rate.

Fig. 4. Effect of pulloff ratio during coagulation, V_1/V_f, on the elastic modulus of fibers. Only V_1 was varied while V_0 kept constant to the indicated values. ($\square$) $V_0 = 6.5$ m/min, ($\bigcirc$) $V_0 = 11.6$ m/min, ($\triangle$) $V_0 = 16.4$ m/min. V_f from Figure 3. $V_1/V_R = 1$.

no tension being applied to the fiber. The linear relationship between V_0 and V_f allows a simple determination of V_f corresponding to each V_0. The former value was used, instead of the latter, for calculating pulloff ratios. The effect of the pulloff ratio during coagulation (between V_0 and V_1), and subsequent to coagulation (between V_1 and V_R) on the elastic modulus of the fiber is illustrated in Figures 4 and 5, respectively. In the case of Figure 4, V_0 was kept constant, V_1 was varied, but V_R was kept equal to V_1. The elastic modulus is plotted as a function of V_1/V_f. The data show an initial increase of the modulus with pulloff during coagulation. However, above a certain value of V_1/V_f (between 1.4 and 1.6), E reaches a constant value which appears to decrease with an increase of extrusion rate. The value of 15 GPa, obtained when $V_0 = 6.5$ m/min, is already considerably higher (by about a factor of 3) than the value of the modulus of commercial fibers of flexible polymers. However, it is also considerably smaller (by about a factor of 3) than the modulus of as-spun fibers produced from anisotropic solutions of PBA (~ 50 GPa).[1]
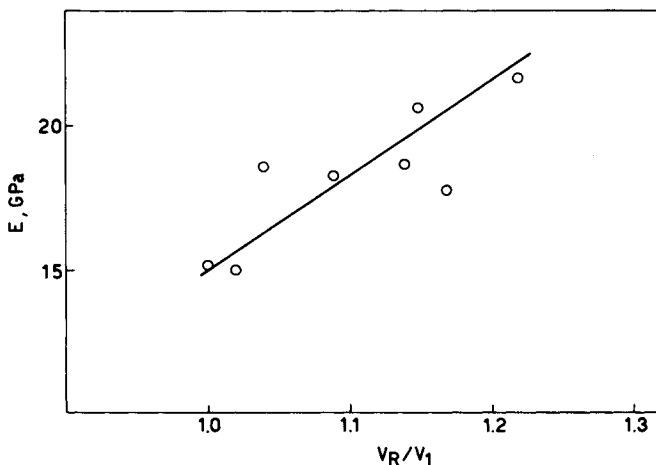

Fig. 5. Effect of pulloff ratio past the coagulation bath, V_R/V_1, on the elastic modulus of the fiber. Only V_R was varied. $V_0 = 6.5$ m/min; $V_1/V_0 = 1$, $V_1/V_f = 1.44$.

In the case of Figure 5, V_0 was again kept constant, V_R was varied, but V_1 was kept equal to V_0. Using the data of Figure 3, $V_1/V_0 = 1$ seems to correspond to $V_1/V_f = 1.44$, a situation under which a small tension is applied during coagulation. The latter condition was adopted to prevent morphological inhomogeneities which were found to occur when $V_1 \approx V_f$. The elastic modulus is plotted as a function of V_R/V_1. The lower value of E in Figure 5 (~ 15 GPa) corresponds to the maximum value observed under the conditions pertaining to the data in Figure 4 ($V_R/V_1 = 1$, $V_1/V_f \sim 1.4$). It is seen that the maximum modulus obtainable during coagulation can be increased by increasing the pulloff past the coagulation bath. Moduli up to 22 GPa were thus reached when $V_R/V_1 \sim 1.2$. For pulloff greater than the latter value, the fiber either breaks or develops macroscopic inhomogeneities. The effect of increasing V_0 on the data reported in Figure 5 is similar to the effect illustrated in Figure 4. E appeared to decrease with increasing V_0.

Figure 6 illustrates the variation of modulus and strength with elongation to break for fibers obtained under different values of V_1 and V_R, but for a constant value of V_0. As commonly observed, elongation to break decreases with modulus and strength. An increase of σ_b accompanies the increase of E.

It is to be noticed that the experimental data exhibited good reproducibility both for fibers obtained during a given spinning run or different runs performed under the same conditions. In order to explain the decrease of E observed with increasing extrusion rate (Fig. 5), we have investigated fibers obtained when the length of the coagulation bath was increased from 90 to 180 cm. The diameter of a given length of fiber was carefully measured in the swollen state at the exit of the coagulation bath (d_1) and after 48 h standing in H_2O at room temperature (d_2). Table I collects the variation in diameter (Δd %) observed in these experiments for different values of extrusion rate and pulloff ratio during coagulation. The data show that with the 180-cm coagulation bath Δd is essentially independent of V_0 and V_1/V_f. However, if the coagulation bath is 90 cm long, Δd increases with either V_0 or V_1/V_f. The result suggests that the decrease of E with extrusion rate may be simply related to a partial loss of orientation resulting from incomplete coagulation of the fiber core during the spinning run. The result supports the operational separation of the effects of pulloff ratios during and subsequent to coagulation performed here in the range $V_0 \leq 6.5$ m/min and $V_1/V_f \leq 2.5$ (cf. Fig. 4).
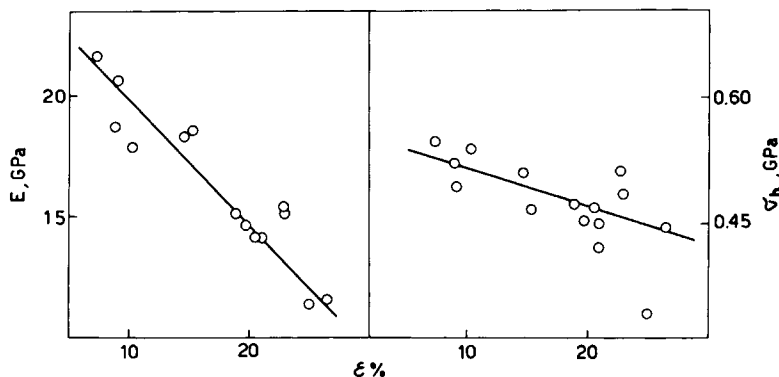

Fig. 6. Variation of modulus and strength with elongation to break. $V_0 = 6.5$ m/min.

TABLE I
Effect of Extrusion Rate on Fiber Diameter

V_0, m/min	V_1/V_f	$d_1 \times 10^6$, m	$d_2 \times 10^6$, m	Δd %
		90-cm coagulation bath		
6.5	1.63	29.87	29.73	0.47
6.5	2.45	24.17	23.99	0.74
6.5	3.87	20.43	20.18	1.21
11.6	1.35	37.05	36.35	1.89
11.6	2.01	29.24	28.88	1.23
11.6	4.03	20.62	19.84	3.76
16.4	1.36	38.00	34.26	9.85
16.4	1.86	32.79	29.29	10.67
		180-cm coagulation bath		
6.5	3.87	19.97	19.97	0.00
11.6	1.35	35.28	35.07	0.59
11.6	2.01	28.80	28.43	1.28
11.6	3.66	20.69	20.61	0.39
16.4	1.36	35.74	35.57	0.48
16.4	1.86	29.47	29.35	0.41

Thermomechanical Treatments

Characterization of as-spun fibers prior to the postspinning treatment is reported under "Experimental." Preliminary attempts to perform postspinning treatments gave unsatisfactory results. An increase of modulus and strength and a decrease of diameter and extension to break were generally observed. However, no consistent trend of these values with the draw ratio V_R'/V_A or temperature of treatment was observed. Moreover, the appearance and homogeneity of fibers, which was optimal before treatment, worsened considerably subsequent to the application of a draw ratio at temperatures above 300°C. Sometimes, even an increase of diameter was observed. In order to explain this unsatisfactory behavior, we investigated the effect of the thermal treatment alone, no tension being applied to the fiber. Spontaneous elongation of unstressed fibers was noticed upon exposure to 250°C and 300°C for lengths of time up to 10 min. However, no increment of the mechanical properties of untreated fibers was observed. The effect of contact time between the fiber and the hot surface was also investigated. The position of the soldering iron was altered so that the fiber could remain in contact with it for lengths of time comprised between 0.02 and 1.5 s. No significant effect of the contact time on the modulus was observed. Eventually, we arrived at the conclusion that the unsatisfactory results indicated above were due to traces of moisture remaining in the as-spun fiber. Rapid evaporation of residual water above 300°C could have generated microvoids responsible for the worsened properties. As spun fibers were therefore maintained in vacuum oven at ~65°C for 7 days, and then transferred to a dessicator over $CaCl_2$ for at least 2 days. The results of the thermomechanical treatments performed on these fibers are collected in Table II. Draw ratios up to 1.7 could be applied before the fiber broke. The modulus of the treated fibers increases with both temperature and V_R'/V_A up to a maximum observed value of 67 GPa, which is about 4.5 times larger than the modulus of the corresponding as-spun fibers. A parallel decrease of diameter is observed. The appearance and homogeneity of the fibers was very satisfactory. The elongation to break decreased and the strength increased as a result of the

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TABLE II
Effect of Thermomechanical Treatments on Dried, As-Spun Fibers[a]

T, °C	$V_R{'}/V_A$	$d \times 10^6$, m	E, GPa	ϵ %	σ_b, GPa
200	1.23	22.36	19.0	12.8	0.63
	1.29	21.06	23.0	12.6	0.69
	1.35	21.05	26.0	10.0	0.76
	1.47	21.04	27.0	9.8	0.86
	1.53	21.03	28.0	9.3	0.88
250	1.23	21.06	38.0	7.3	0.66
	1.35	20.74	43.0	6.9	0.78
	1.38	19.71	44.0	6.5	0.80
	1.47	19.44	46.0	3.5	0.87
	1.59	19.44	48.0	2.5	0.96
300	1.23	22.36	33.0	6.0	0.75
	1.47	20.25	45.0	3.6	0.95
	1.53	19.50	48.0	3.3	1.02
	1.59	19.12	51.0	3.0	1.06
	1.65	19.12	53.0	2.1	1.10
350	1.23	22.68	49.0	2.7	0.89
	1.29	19.44	52.0	2.6	1.00
	1.35	19.22	55.0	2.5	1.07
	1.41	19.12	57.0	2.3	1.14
	1.47	19.12	58.0	2.2	1.19
	1.70	19.12	59.0	2.4	1.30
400	1.23	21.06	52.0	2.0	1.03
	1.35	19.44	58.0	2.3	1.15
	1.47	19.12	62.0	2.3	1.19
	1.59	18.63	64.0	2.4	1.27
	1.70	18.63	67.0	2.5	1.30

[a] For as spun fibers: $\bar{d} = 24.51 \times 10^{-6}$ m, $\bar{E} = 14.7$ GPa, $\bar{\sigma}_b = 0.56$ GPa.

treatment. However, while our maximum modulus is definitively in the ultra-high modulus range and favorably compares with those obtained in industrial laboratories (up to ~65 GPa),[14] tenacity and elongation to break exhibited by our fibers are rather poor. Apparently, high modulus is relatively simpler to achieve than high strength. A possible explanation of our modest strength values is the density of fibers which is considerably smaller (1200 kg/m³ vs. 1420 kg/m³)[14] than used for practical application. Microvoids resulting from residual moisture or inherently due to the fast coagulation in wet spinning could negatively affect the strength. The molecular weight is also a critical parameter. However, the molecular weight of our sample is similar to the one used by Preston,[14] who reported tenacity values up to ~2 GPa.

Fluid Orientation

The results illustrated in Figure 4 clearly reveal that an exceptionally high modulus (with respect to flexible polymers) can already be achieved during coagulation of the as-spun fiber with the application of rather small pulloff ratios. Since further increase of V_1/V_f does not produce additional increase of modulus, it would seem that the fluid jet leaving the spinnerette already possesses con-

siderable orientation. This observation is probably a most significant one for understanding the ability of semirigid polymers to develop ultrahigh modulus properties. The orientation already existing in the as-spun fiber may be the prerequisite necessary for the development of the ultrahigh modulus, and hence orientation, in the solid state during the postspinning treatment. Thus, once more,[6,8-10] the study of the flow of the X-500 solution appears to be of paramount significance. A marked ability of X-500 to develop orientation in the flow field could result in the occurrence of a flow-induced transition to a nematic state.[8] Some evidence in favor of a flow-induced transition for X-500 in DMSO has been presented.[8-10] It is also important to observe that X-500 in H_2SO_4[15] gives a nematic phase in the quiescient state, indicating that the solvent-affected rigidity is close to the critical limit for a spontaneous transition.

In order to shed additional light on the problem, we have extended our previous measurement[6,9] of the viscosity as a function of X-500 concentration at a low shear rate. Extensive determinations were performed in the three solvents: DMSO, DMSO+4% LiCl, DMSO+dimethylacetamide (DMAc) 1:1, covering the range from $Cp \sim 0.3$ to ~ 10 g/100 mL (which includes the ranges of concentration explored by Valenti and Ciferri[6] and by Chapoy and la Cour[10]). The results are shown in Figure 7. The η vs. Cp dependence can be described in terms of *three* segments exhibiting a change of slope at Cp_1^* and Cp_2^*. Actual slopes and Cp* values are listed in Table III, along with the inherent viscosity measured
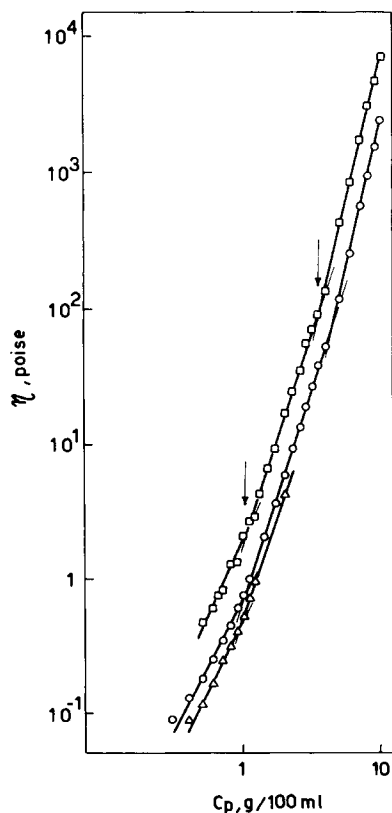

Fig. 7. Viscosity vs. polymer concentration for X-500 in three different solvents. $T = 20°C$; $\dot{\gamma} = 4.4$ s^{-1}. (□) DMSO + 4% LiCl, (○) DMSO, (△) DMSO + DMAc 1:1.

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TABLE III
Viscosity-Concentration Dependence for X-500 in Three Solvents

Solvent	Cp_1^*, g/100 mL	Cp_2^*, g/100 mL	Slope	η_{inh}, 25°C
DMSO	0.97	4.28	1.79	4.17
			3.09	
			4.30	
DMSO + 4% LiCl	1.08	3.50	2.18	5.22
			3.15	
			4.18	
DMAc + DMSO 1:1	0.94		2.04	4.32
			2.94	

at Cp = 0.5 g/100 mL in the different solvents. The results indicate that Cp_1^* can be associated with the occurrence of entangled systems, as suggested by Chapoy and la Cour,[10] while Cp_2^*, as previously discussed,[6,9] may be associated with the onset of the transition[8] to a nematic phase under the shear flow.

Additional investigation on the orientation acquired by the X-500 solution within the spinning unit was made by analyzing the birefringence of the fluid jet *before* it entered the spinnerette die. To this end, the connecting tubing was disconnected from the spinnerette. The retardation was measured as a function of the rate of shear at the wall of the tube, $\dot{\gamma} = 4 \, Q/\pi R^3$, under free falling conditions just below the region of the swelling at the exit of the connecting tubing. Q is the volumetric flow rate and $\dot{\gamma}$ was varied by changing the extrusion rate. The experiment was repeated using tubes having diameters $(2R)$ and lengths different from those employed during the spinning runs. The effect of capillary diameter and capillary length is illustrated in Figures 8 and 9, respectively, for a 10% X-500 solution in DMSO (the amount of die swelling was found to be essentially unaffected by $\dot{\gamma}$). At a given $\dot{\gamma}$, the birefringence increases with the
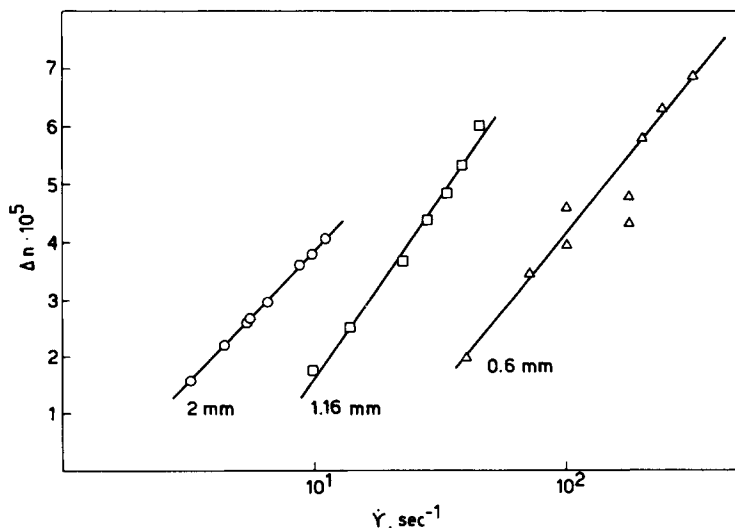

Fig. 8. Birefringence vs. shear rate for 10% X-500 solutions in DMSO at the exit of capillaries 17 cm long and the indicated diameters. $T \sim 20°C$.
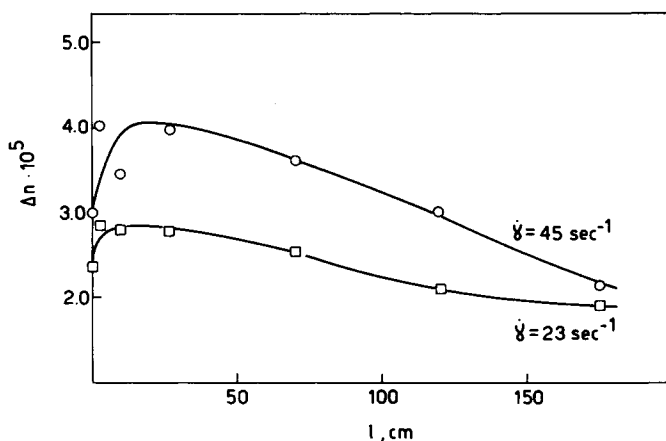
Fig. 9. Birefringence vs. capillary length for 10% X-500 solutions in DMSO at the exit of connecting tubing having a diameter of 1.16 mm. Shear rates are indicated. $T \sim 20°C$.

diameter (Fig. 8) and, therefore, with a decrease of the flow time (t) of the solution through the capillary ($t = 4l/\dot{\gamma}R$).

This behavior can be interpreted in terms of an orientation due to elongational flow occurring at the capillary entrance,[16] when a variation of section occurs. Due to the large relaxation times involved, the orientation persists for some time in the capillary where the prevailing shear flow should not greatly contribute to orientation.[7,17] When flow time increases, the orientational effect of the elongational flow decreases. A similar interpretation was advanced by Baird et al.[9] to explain the observed increase of the viscosity of X-500 solutions with capillary length (at given diameter and $\dot{\gamma}$). The trend of the data appears more complex in Figure 9. Straightforward extension of the above interpretation would require that the birefringence decreases with capillary length (l). However, a maximum is observed for shorter capillaries. Only when l is larger than that used in the spinning runs (17 cm), Δn decreases with l. This behavior suggests a reinforcement by the shear flow of the orientation caused by the extensional flow at the capillary inlet, provided l is not so great as to dissipate the effect of elongation flow. This suggestion is in agreement with the experimental observation that, with a connecting tubing 60 cm long E of as-spun fibers reaches at most a value of 12 GPa rather than 15 GPa. Unusual rheological behavior for shorter capillaries was also noticed by Baird et al.[9] An interaction between the effects of shear and elongational flow for an *entangled* system is not unexpected.[6,8]

The behavior described above clearly suggests a peculiar response of semirigid chains to orientation in the flow field. The qualification of the "nature" of the orientation remains to be discussed. The data appears to be in line with the hypothesis of a phase transition to a nematic phase beginning at the capillary inlet, continuing into part of the capillary and possibly evolving in a flow instability.[6,9] Alternatively, partial rigidity could enhance orientation without, however, the attainment of a true phase transition (an effect for which a theoretical treatment is not yet available).

When the tube is connected again to the spinnerette, a great increase of the birefringence of the fluid extruded from the latter is observed. The data are shown in Figure 10. The shear rate reaches extremely high values (10^4–10^5 s^{-1})
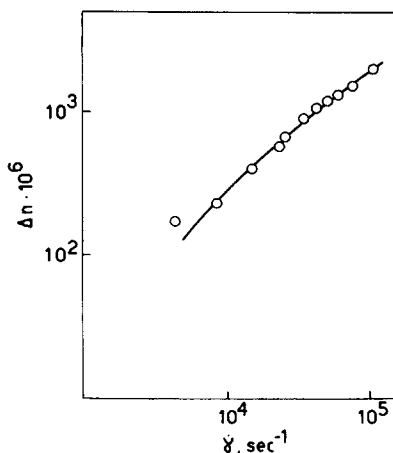
Fig. 10. Birefringence vs.shear rate for 10% X-500 solution in DMSO at the exit of the spinnerette just below die swelling and under free falling conditions. $T \sim 20°C$.

and the flow time t becomes extremely small ($\sim 10^{-4}$ s). Apart from the different entry geometries, qualitatively similar effects should occur in the capillary sections of the connecting tubing and of the spinnerette, but dissipation of orientation in the latter should be minimal.

CONCLUDING REMARKS

For a typically flexible polymer (e.g., polyethylene) the modulus of as-spun fibers, in the order of 3 GPa, may be increased to about 70 GPa as a result of mechanical treatments.[18] For a typically rigid polymer (e.g., PBA) the modulus of an as-spun fiber may be as high as 50 GPa, and may reach 100 GPa following treatment.[1] The present results indicate that for a semirigid polymer such as X-500 the modulus of as spun fibers is in the order of 15 GPa and may reach 67 GPa after thermal treatment. Thus X-500 is similar to a flexible polymer in that a severalfold increase of the as-spun modulus can only be obtained by solid-state deformation, and it is similar to a rigid polymer in that a high modulus is already attained for the as-spun fiber. Moreover, the present results (cf. Fig. 4) clearly indicate that the orientation responsible for the high modulus of as spun fibers is a property of the flowing solution, and *can only be associated with the semirigid nature of the X-500 chain*. The rheological study indicates that already in a 1% X-500 solution entanglement of a semirigid chain occurs. Moreover, strong evidence indicates that the rigidity of X-500 in DMSO is close to the value at which a nematic phase can spontaneously occur.[4,15] Although circumstantial evidence certainly supports the formation of a flow-induced nematic phase,[6,8–10] flow-induced orientation without a transition, and slow dissipation of such orientation when the gradient is attenuated, could be strongly enhanced by the semirigid character of the chain.

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