

Hydroxypropylcellulose, a Thermotropic Liquid Crystal: Characteristics and Structure Development in Continuous Extrusion and Melt Spinning

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Synopsis

Hot-stage polarized light microscopy suggests that bulk hydroxypropylcellulose (Hercules Klucel E) is a cholesteric liquid crystal. Rheological measurements indicate this system exhibits shear viscosities similar to those of polyolefin melts except that it has a yield value comparable to suspensions. Birefringent characteristics were observed in shear flow between glass slides. No relaxation of birefringence is observed following flow. Extruded filaments (without applied take-up tensions) show high levels of birefringence and significant orientations from WAXS measurements. These have skin-core structures with highly oriented outer layers which are caused by the flow patterns in the reservoir and die preceding the extrudate. In the case of melt-spun filaments, where tensile elongation occurs, a highly oriented structure of uniform cross section is found.

INTRODUCTION

The history of the development of plastics and fibers from cellulose derivatives dates back more than a century.¹⁻³ The decline in commercial importance of cellulose from 1930 coincides with the growth of polymer physical chemistry and structural characterization techniques. Cellulose derivatives have not received the detailed study given to polyolefins, polydienes, etc. Liquid crystalline structure in polymer systems was first observed in concentrated solutions of polypeptides by Courtauld's investigators^{4,5} in the mid-1950s. Similar structures were found in solutions of para-linked aromatic polyamides⁶⁻⁹ and other relatively rigid aromatic polycondensates.^{10,11} Somewhat surprisingly, liquid crystalline structures were observed in hydroxypropylcellulose-water solutions by Werbowyj and Gray^{12,13} and others⁹ shortly thereafter. Liquid crystalline characteristics were reported in a wide range of cellulose derivative solutions by Panar and Willcox.¹⁴ These observations were extended to other cellulose derivatives by Aharoni¹⁵ and Bheda, Fellers, and White,^{16,17} The development of high levels of birefringence and orientation during flow of solutions of hydroxypropylcellulose has been described by Onogi, White, and Fellers¹⁸ and Asada et al.¹⁹ Similar studies for cellulose acetate butyrate solutions have recently been reported by Bheda et al.¹⁷

This report concerns our efforts to study structure development in processing of liquid crystalline cellulose derivatives. The first investigations in this direction were reported by Panar and Willcox¹⁴ in a patent application. More recently, wet spinning of liquid crystalline cellulose acetate butyrate and cellulose tricetate

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solutions have been reported by Bheda et al.¹⁷ Our interests have been directed toward thermotropic liquid crystalline polymers because solvents may be eliminated, thus avoiding problems of solvent toxicity and recovery and the vagaries of void structures formed during coagulation. The only known thermotropic polymer liquid crystals are aromatic polyesters.^{10,11} It is shown in this report that some hydroxypropylcelluloses (Fig. 1) exhibit liquid crystalline phases when they are in a fluid phase. Solid hydroxypropylcelluloses had been structurally characterized by Samuels,²⁰ and the existence of flow behavior similar to a polymer melt below their crystalline melting point has been discussed by Elliott.²¹ Our discovery led us to turn our attention to the processing of this system and in particular to orientation and structure development in melt spinning and extrusion. The present study thus represents a continuation of earlier studies by our group of structure formation in melt spinning.²²⁻²⁶ Recently, Horio and his co-workers²⁷ have reported that similar studies are in process in Japan. HPC would seem, however, to only be of interest as a model for thermotropic liquid crystal behavior and is not of obvious commercial importance itself. This is because of its excellent solubility in water, alcohols, ketones, and organic acids.

BACKGROUND

Crystalline Structure of Hydroxypropylcellulose

The crystalline structure of hydroxypropylcellulose (HPC) has been investigated by Samuels.²⁰ On the basis of wide-angle X-ray diffraction (WAXS) measurements, he indicates that it may be considered as a pseudotetragonal unit cell with dimensions

$$a = b = 11.33 \text{ \AA}$$

$$c = 15.0 \text{ \AA}$$

Here, c is the chain-axis repeat distance. For crystalline cellulose, the repeat distance is 10.3 Å, which corresponds to two anhydroglucose units. The repeat distance in HPC corresponds to three anhydroglucose units (which are oriented at 120° angles to each other).²⁰

Samuels²⁰ has classified the WAXS patterns of this polymer. The strongest WAXS reflection for HPC was found to be the (100), which is an equatorial reflection in a uniaxial film. This has a Bragg's law d spacing of 11.33 Å. The next weaker reflections are observed at d spacings of 7.49 and 4.98 Å. These correspond to the (002) and (003) reflections. Other weaker meridional d spacings related to (00 l) reflections are observed.

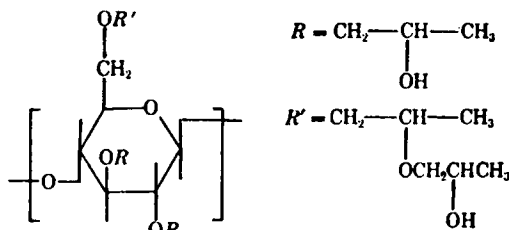


Fig. 1. Idealized structural unit of hydroxypropylcellulose with a degree of substitution of 4.

The degree of crystallinity in water-cast HPC films was estimated by density, calorimetry, and infrared measurements to be 15–20%.²⁰

Orientation Factors

The state of uniaxial polymer chain orientation in a filament may be represented in terms of the Hermans orientation factor f_c , defined as^{22–26,29,30}

$$f_c = \frac{3 \overline{\cos^2 \phi} - 1}{2} \quad (1)$$

where ϕ is the angle between the chain axis and the fiber axis. In a crystalline phase, we may express the state of orientation of the three axes of the unit cell using generalizations of eq. (1) of form³⁰

$$f_j = \frac{3 \overline{\cos^2 \phi_j} - 1}{2} \quad (2)$$

where j may be a , b , or c (chain axis), and ϕ_j represents the angle between the j crystallographic axes and the fiber axis. The f_j for the three crystallographic axes are referred to as the Herman–Stein orientation factors.

Hydroxypropylcellulose has a tetragonal unit cell. As the three crystallographic axes are orthogonal,

$$\overline{\cos^2 \phi_a} + \overline{\cos^2 \phi_b} + \overline{\cos^2 \phi_c} = 1 \quad (3)$$

and from eq. (2),

$$f_a + f_b + f_c = 0 \quad (4)$$

As the unit cell is tetragonal, the a and b crystallographic axes are equivalent. This leads to

$$f_a = f_b \quad f_c = -2f_a \quad (5)$$

WAXS Measurements of Orientation Factors

Samuels²⁰ has studied the crystalline orientation of HPC films using WAXS. He found that only the (100) reflection was strong enough and suitable for orientation measurements. We may determine the three crystalline orientation factors of a filament from

$$\frac{1}{\overline{\cos^2 \phi_a}} = \frac{\int_0^{\pi/2} I(\phi_{100}) \cos^2 \phi_{100} \sin \phi_{100} d\phi_{100}}{\int_0^{\pi/2} I(\phi_{100}) \sin \phi_{100} d\phi_{100}} \quad (6)$$

Then f_a may be computed from WAXS data using Eqs. (6) and (2), while f_b and f_c may be computed from eq. (5) for a tetragonal unit cell.

Interpretation of Birefringence

Birefringence Δn is related to crystalline orientation through the expression^{25,31–33}

$$\Delta n = X(f_c)_c \Delta_c^0 + (1 - X)(f_c)_{am} \Delta_{am}^0 + \Delta n_{\text{form}} \quad (7)$$

where X is the fraction crystalline, Δn_{form} is the form birefringence, and Δ^0 is the maximum (intrinsic) birefringence. The subscripts c and am refer to crystalline and amorphous regions. From the work of Samuels,²⁰ we may estimate X as 0.15 to 0.20. However, the values of Δ_c^0 and Δ_{am}^0 are not well established. The magnitude of Δ^0 was suggested by Onogi et al.¹⁸ to be of order 0.03 at room temperature.

EXPERIMENTAL

Materials

We have investigated a series of three different hydroxypropylcelluloses, Klucel E, G, and H, manufactured by Hercules, Inc. We designate these as HPC E, G, and H. HPC E has a nominal molecular weight of 60,000, HPC G of 300,000, and HPC H of 1,000,000. The most extensive investigations were performed on HPC E.

Hot-Stage Polarized Light Microscopy

The HPC series was investigated between glass slides on a Leitz Ortholux polarized light microscope with a hot stage. The studies were made between 20 and 240°C. Studies were made in which the HPC was sheared between glass plates in the field of the microscope.

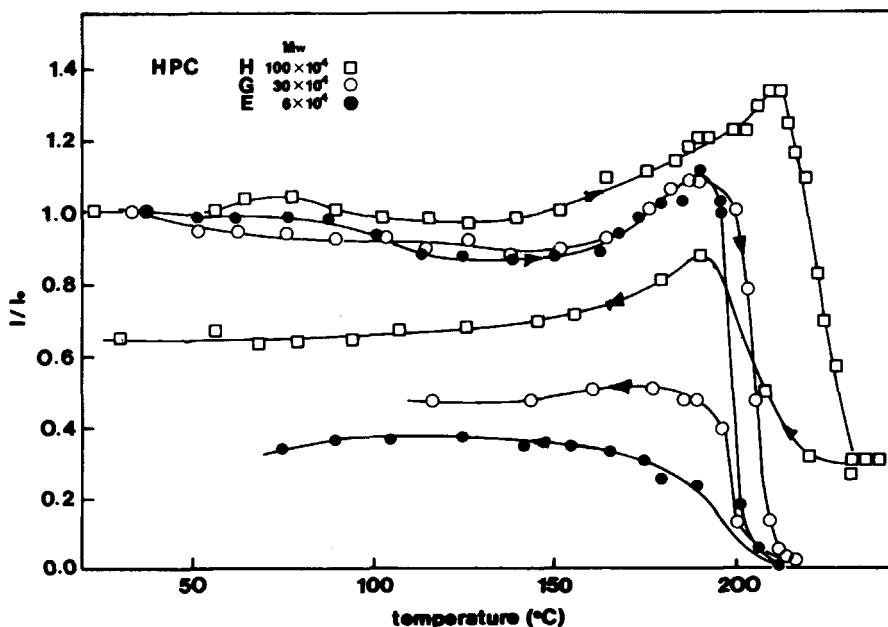


Fig. 2. Light intensity I/I_0 due to HPC between crossed polars as function of temperature.

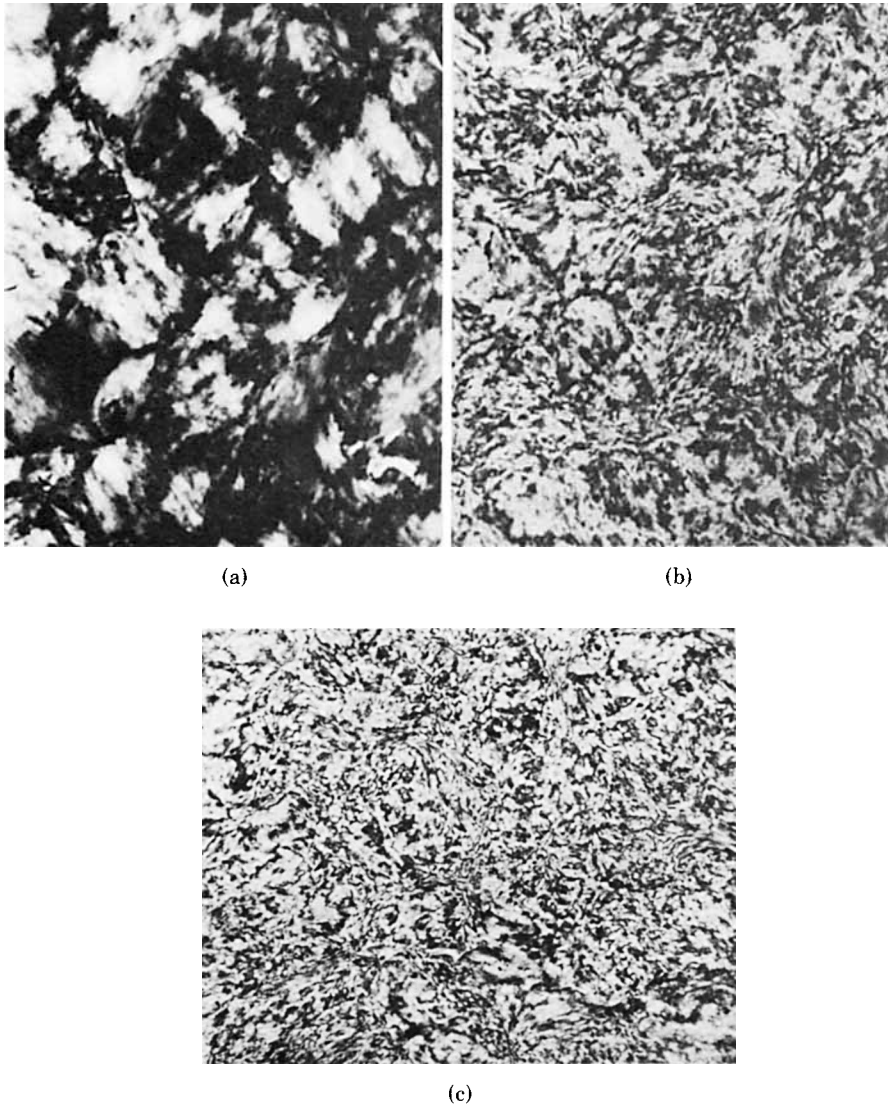


Fig. 3. Optical photomicrograph of HPC E between crossed polars at (a) 205°, (b) 190°, (c) 180°C.

Rheological Behavior

The viscosity of the HPC E “melts” were measured at 180°C in a Rheometrics mechanical spectrometer in the cone plate mode at low shear rates. Measurements were made in a Merz–Colwell Instron capillary at higher shear rates. Fully developed laminar shear flow across the instrument cross section in the direction of shear was presumed in determining the viscosity as is traditional with Newtonian fluids and molten plastics.^{34–36}

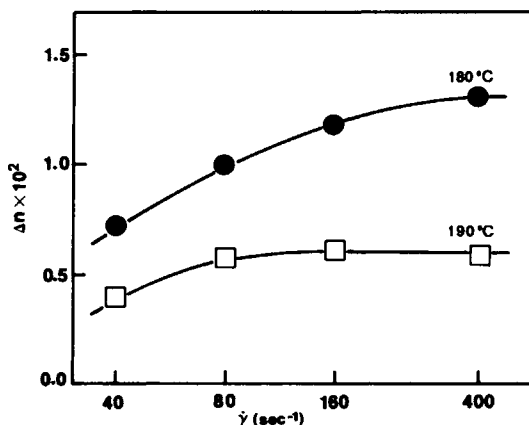


Fig. 4. Birefringence Δn as function of shear rate for HPC E at 180 and 190°C.

Extrusion and Melt Spinning

Filaments were extruded and melt spun from a Merz-Colwell Instron capillary rheometer with a die of diameter of 0.03 in. and L/D ratio of 20. The fibers were taken up on a rotating roll driven by a motor. Spinline tensions were measured using a Rothschild Tensionmeter.

Structural Measurements

WAXS fiber patterns were measured using a Philips X-ray generator with nickel-filtered $\text{CuK}\alpha$ radiation. Birefringence measurements on fibers were made with a Leitz Ortholux polarized light microscope equipped with a Berek compensator. SEM photomicrographs of fibers were made using an AMR high-resolution scanning electron microscope.

Mechanical Properties

Tensile stress-strain curves on melt-spun filaments were obtained using a table model Instron tensile tester. The filaments were dried in a vacuum oven prior to testing.

QUIESCENT AND RHEOPTICAL STUDIES

Hot-Stage Microscopy Studies

The various HPC samples were investigated over the range 20–240°C. We show a plot of transmitted light intensity I/I_0 through crossed polars as a function of temperature in Figure 2. Samuels²⁰ has interpreted from calorimetric measurements that HPC melts in the range 208–234°. We see the disappearance of all birefringence and occurrence of a dark field at 210°C for the E samples and the higher molecular weight G exhibits a dark field at 215°. H degrades before the dark field occurs.

In cooling specimens from 210°C, the transmitted intensity is about one-third of that in heating. If however a slight shearing is applied, the light intensity is greatly increased.

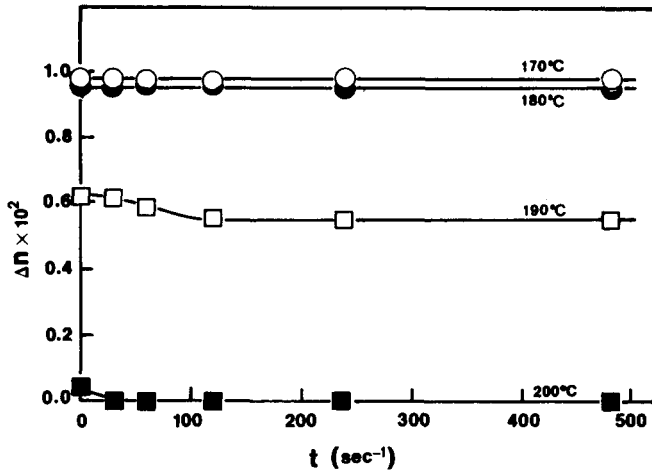


Fig. 5. Birefringence relaxation for HPC E at various temperatures.

Optical photomicrographs of the HPC E between crossed polars are shown in Figure 3 for 150, 190, and 205°C. The appearance at 205°C shows a two-phase morphology with birefringent and dark regions. At 190°C, the dark regions are greatly diminished. Below 190°C, the specimen shows a beautiful, colorful appearance implying a cholesteric liquid crystalline form. In the temperature range 190–210°C, the field is generally a light yellow.

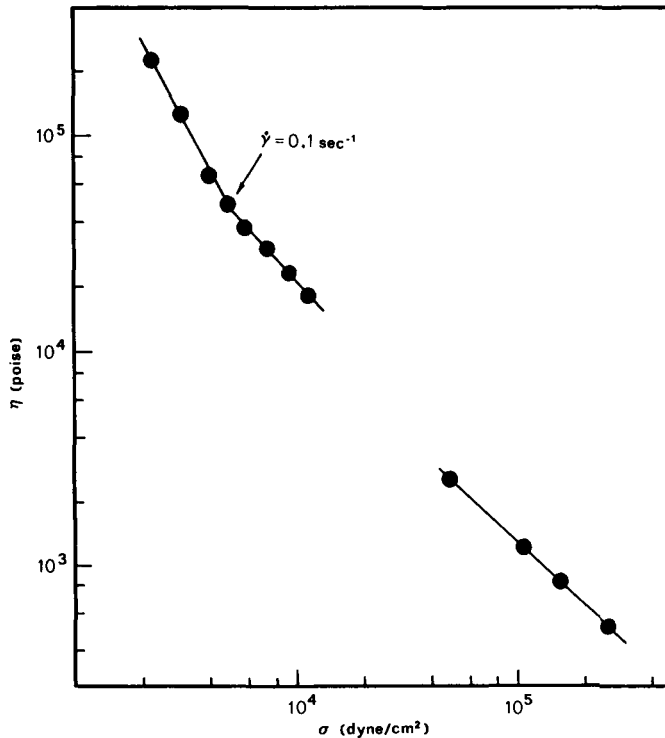


Fig. 6. Shear viscosity as function of shear stress of HPC E at 180°C.

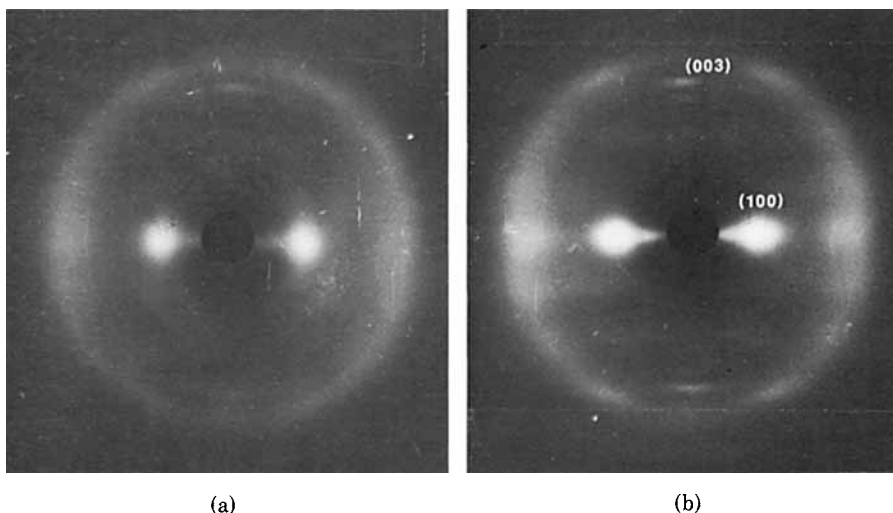


Fig. 7. WAXS patterns of an HPC E extrudate: (a) solidified extrudate; (b) extrudate annealed at 150°C for 3 h.

The HPC G and H samples appear to exhibit two-phase morphologies with what seems to be “gel” particles dispersed in a lower molecular weight phase. These appear to prevent the G and H from flowing.

We conclude that the E sample forms a liquid crystalline melt in the range of about 160–205°. The G and H samples contain both liquid crystalline phases and perhaps a second crystalline phase, which may be higher in molecular weight and/or lower in propylene oxide content. These were found to prevent it from forming uniform fibers and films.

Birefringence Variation in Shear Flow

When one imposes a shear flow on the HPC E at a temperature of 180°C, through moving one glass slide parallel to the other, the birefringent field becomes homogeneous. At a shear rate of 400 s⁻¹, the fluid exhibits a birefringence of 0.015 in the 1–3 plane, where 1 is the direction of flow, 2 is the direction of shear, and 3 is the neutral direction (see Fig. 4).

It is difficult to estimate the actual level of orientation due to birefringence at 180°C. The birefringence is in large part determined by the orientation of the side groups. As birefringence decreases with temperature, it might be suggested that the side groups are orienting to become more perpendicular to the chain.

When the relative motion of the glass slides is ended, little tendency is found for the birefringence to decay away, although the stresses decay away in seconds (Fig. 5). Indeed, hours after the experiment, the shear flow-induced birefringence remains. Similar but less pronounced observations were made by Onogi et al.¹⁸ on HPC/water solutions where stresses decayed away in seconds and about one-half of the birefringence remained after a half-hour.

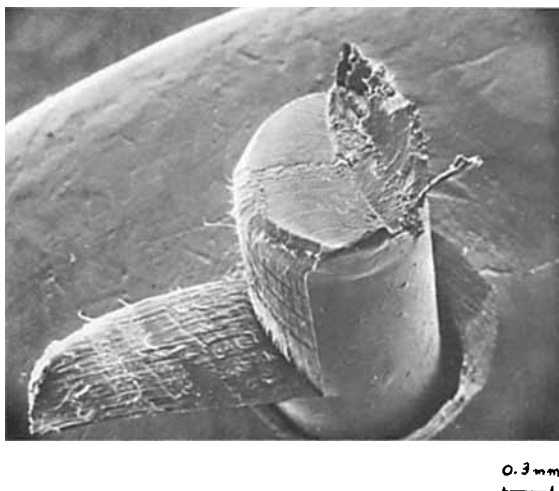
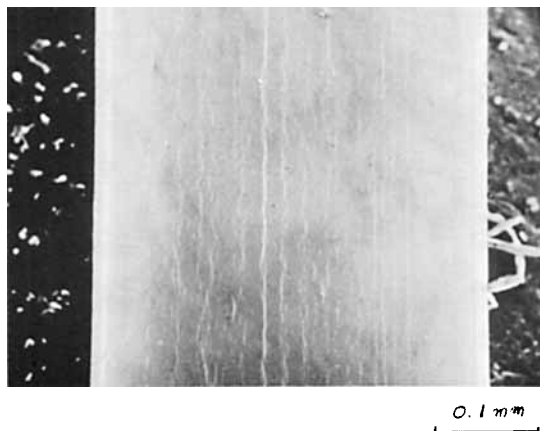


Fig. 8. SEM photomicrograph of HPC E extrudate.

Rheological Behavior

Viscosity measurements for the HPC E as a function of shear stress are shown in Figure 6. The viscosity shows a continuous decrease as a function of shear rate or stress. The viscosity is of order 20,000 poises at 10^4 dyn/cm². The viscosity continues to increase in an apparently unbounded fashion at low deformation rates and to exhibit a yield value of order 1000 dyn/cm². Our results are consistent with those of a decade-old study of the viscosity of HPC "melts" by Elliott²¹ at 190° who also seems to observe a yield value or at least no limiting zero shear rate viscosity.

Interpretation

The quiescent hot-stage microscopy and rheooptical studies suggest the HPC E is a cholesteric liquid crystal. This material responds to stress as a soft solid rather than a true fluid and exhibits a yield value above which it flows. During

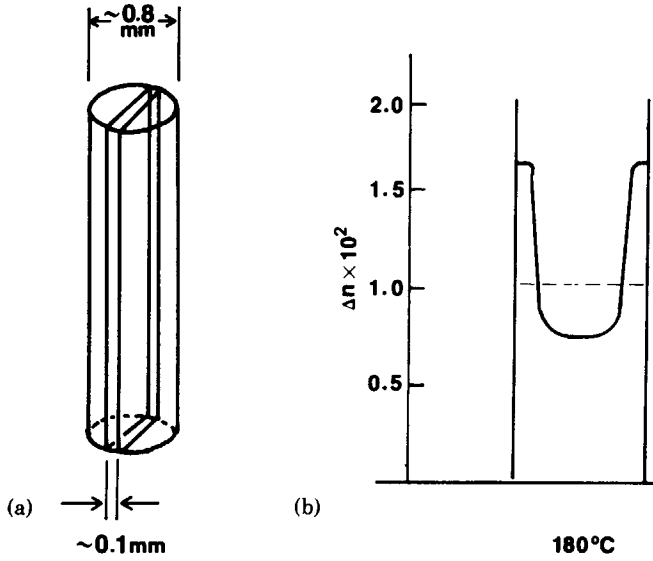


Fig. 9. Slicing of extrudates and birefringence variation in HPC E extrudate.

flow, very high levels of orientation are achieved which do not decay following flow.

Similar yield values have been observed in liquid crystalline polymer solutions^{36,37} and in liquid crystalline polyester melts.³⁸

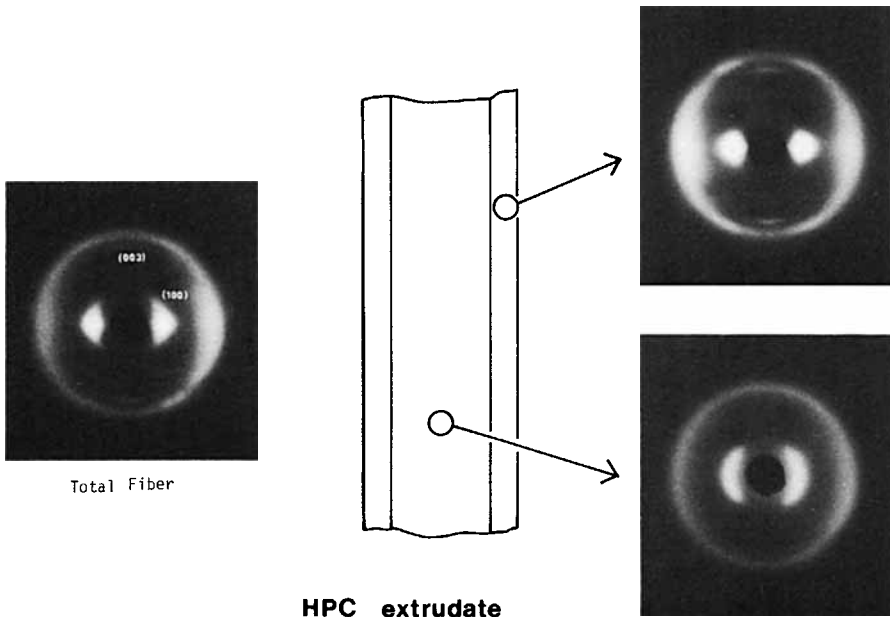


Fig. 10. WAXS patterns of outer layers and core of HPC E extrudate.

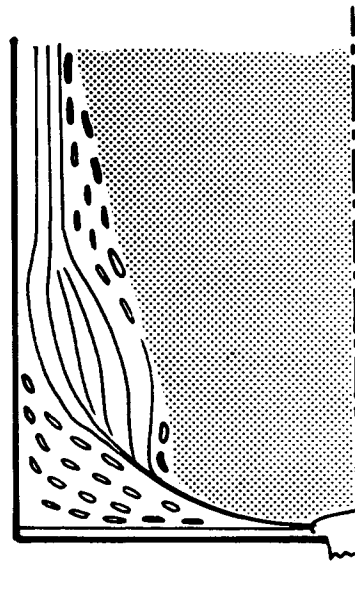
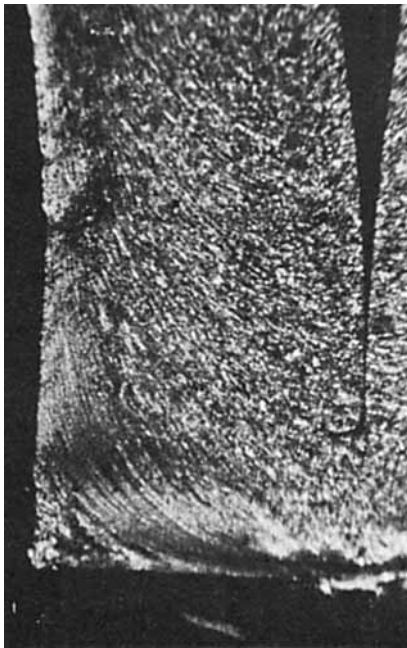
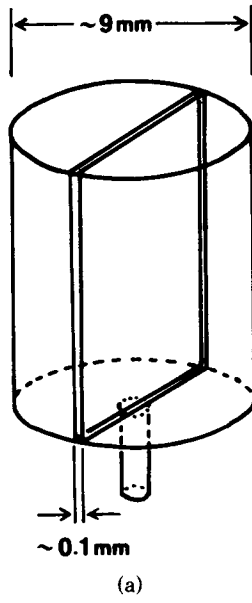


Fig. 11. Cross section of reservoir at die entrance: (a) sample preparation; (b) section between crossed polars; (c) schematic.

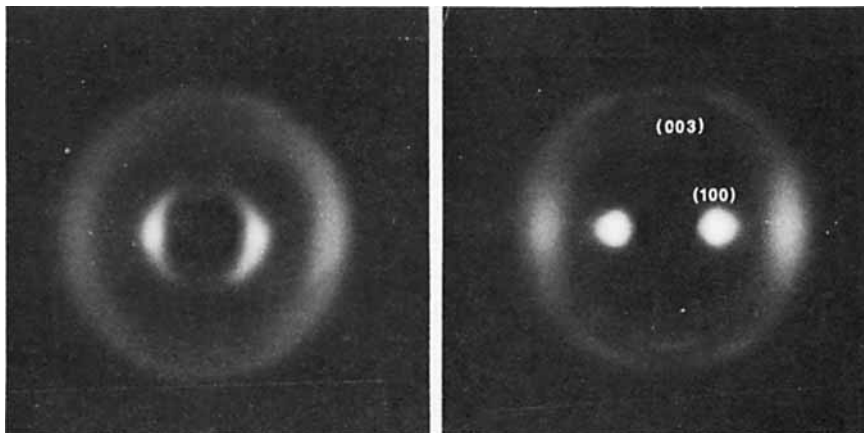


Fig. 12. WAXS patterns of HPC E melt-spun filaments. Left: extrudate. Right: fiber [drawdown ratio 17].

STRUCTURE OF EXTRUDATES

Initial Extrudate

Filaments were extruded from the E sample at a temperature of 180°C where they would be expected to be in a liquid crystalline form. No tension was exerted on the filaments, which solidified in air as they slowly descended vertically from the die.

In Figure 7, we show WAXS patterns of the original and the annealed extrudate. A high level of orientation is observed. The WAXS patterns of the annealed fiber are more sharply defined and have narrower lines. Generally, polyolefin extrudates prepared under such conditions would exhibit complete Debye-Scherrer rings in a WAXS film pattern and no orientation.

The HPC extrudate exhibits a birefringence of 0.017 to be compared with Onogi et al.'s suggested Δ^0 of 0.03.

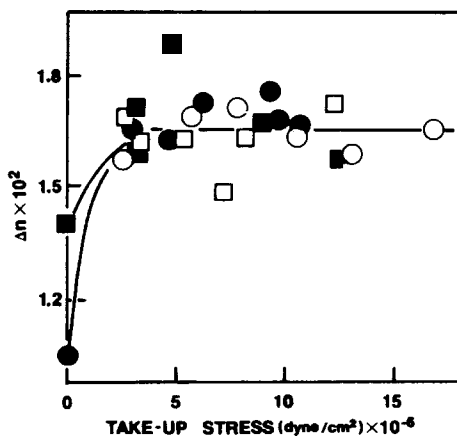


Fig. 13. Birefringence of HPC E filaments as function of take-up stress.

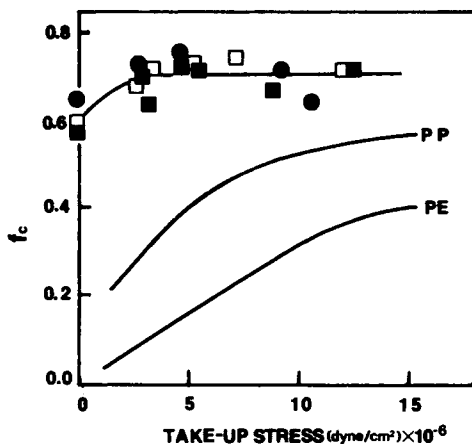


Fig. 14. Hermans orientation factors f_c as function of take-up stress.

We may determine Hermans–Stein orientation factors from these experimental results. From the WAXS pattern, we have for the crystalline regions

$$f_c = 0.65 \quad f_a = f_b \cong -0.33$$

From the birefringence data and Onogi et al.'s Δ^0 , we would surmise a mean Hermans orientation factor of

$$f_H = \frac{\Delta n}{\Delta^0} = 0.53$$

if we take Δ^0 to be 0.032. This should be compared to the WAXS f_c of 0.65.

An SEM photomicrograph of a peeled extrudate is shown in Figure 8. The fibrillar character of the outer layers is to be noted.

Annealed Extrudates

We annealed the extrudates at 150°C for 3 h. A WAXS pattern of the annealed extrudate is shown in Figure 7(b). The orientation is seen to be about the same or slightly increased. The (100) WAXS reflections are sharper, indicating larger crystallite sizes and more perfect crystalline structure.

Radial Variation of Extrudate Structure

Our SEM studies of peeled extrudates suggested strong radial variations in extrudate structure. This led us to slice the extrudates as shown in Figure 9(a) and determine birefringence distributions. It is apparent [see Fig. 9(b)] there is a strong radial variation in birefringence with the outer layers more highly birefringent than the inner regions. Figure 10 shows X-ray diffraction patterns of the extrudate as a whole, the outer layers, and the inner regions. Distinct differences in the orientation as indicated by (100) reflection correspond to the birefringence data.

Mechanism of Radial Variation

The radial variation in fiber structure must trace either to the stress and kinematic field within the capillary or to the prehistory in the barrel. From a force balance on rectilinear laminar flow in a tube,

$$\pi r^2 \Delta p = 2\pi r L \sigma_{12}(r)$$

$$\sigma_{12}(r) = \frac{R \Delta P}{2L} \frac{r}{R} \quad (8)$$

One should expect the maximum shear (and normal) stresses to be at large radii. The radial velocity gradient is zero at the center of a die and is a maximum at the die wall. This would tend to give a strong radial variation in birefringence.

However, certain experiments we have performed suggest to us that the orientation distribution develops in the die entrance region. It appeared to us that because the birefringence relaxation time is very long, the material in the Instron rheometer barrel should maintain its structure after having been cooled to room temperature. In Figure 11, we show a section of the reservoir (prepared as in Fig. 9(a) between crossed polars). The most birefringent regions are those from which fluid enters into the outer radii of the die.

The HPC E at 180°C is composed of a liquid crystalline domain structure. Above a certain set of deformation rate or stress conditions, the grains blend into uniform structure. Below these conditions, these grains persist. In Figure 11, we can see a fairly abrupt distinct change in domain structure and orientation along the radial direction. The material in the highly birefringent oriented region has merged into a continuous fluid. This is probably the region of highest stress and perhaps the only positions in the reservoir where the stresses exceed the yield value. Within the capillary, most of the granular core is brought above the yield stress. The radial variation in fiber structure is the result of these two processes.

Preheating Prior to Extrusion and Radial Variations

We have found that by heating the HPC in the reservoir up to 210°C for a period of 10 min and then cooling back to 180°C prior to extrusion, the birefringence of extrudates is much more uniform. Furthermore, the level of birefringence has increased to 0.0145 as compared to values of 0.0104 when the melt was not preheated.

MELT SPINNING

Results

Filaments were melt spun under the same conditions as used in the extrusion process. The range of operating conditions involved take-up velocities up to 24 m/min and tensions of 1.7×10^7 dyn/cm².

In Figure 12, we show a WAXS pattern of melt spun fiber. Compare this to Figure 7. The birefringence of the melt spun fibers is shown as a function of take-up stress in Figure 13. The surface of the melt-spun fibers shows a fibrillar structure like the extrudate.

Interpretation

In Figure 14, we plot the Hermans–Stein orientation factor f_c , which was determined as described earlier as a function of spinline stress. Such plots are suggested by earlier melt spinning studies from our laboratories^{22–26}; f_a and f_b are given by eq. (5). At zero take-up tension, we have the high levels of orientation described in the previous section. Some increase in orientation occurs with increasing drawdown, but this is modest. We also present in Figure 14 experimental data for polyethylene²² and polypropylene.^{23,25} This is found to go through the origin at zero stress unlike the unique characteristics of HPC and to generally exhibit lower values except at the highest stresses.

We have studied radial variations in birefringence using the method of Figure 9. The birefringence of the fibers is found to be independent of radius, unlike the extrudates. Radial variations of fiber structure found in extrudates are eliminated by the drawdown. This indicates an interesting interaction of the influence of flow in the die system and subsequent postdie processing on the solid state structure of liquid crystalline fluids.

MECHANICAL PROPERTIES

From Instron tensile tests, the HPC fibers are found to have a moderately high modulus and are brittle. The Young's moduli of the samples are all in the range $2\text{--}3 \times 10^{10}$ dyn/cm². The elongations to break are 2–5%. The tensile strengths are of order 8×10^8 dyn/cm².

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References

1. J. W. Hyatt, *Ind. Eng. Chem.*, **6**, 158 (1914).
2. E. C. Worden, *Nitrocellulose Industry*, Van Nostrand, New York, 1911.
3. W. Haynes, *Cellulose, the Chemical That Grows*, Doubleday, Garden City, N.Y., 1953.
4. C. Robinson, *Trans. Farad. Soc.*, **52**, 571 (1956).
5. C. Robinson, *Tetrahedron*, **13**, 219 (1961).
6. S. L. Kwolek, U.S. Pat. 3,671,542 (1972).
7. P. W. Morgan, *Macromolecules*, **10**, 1381 (1977).
8. M. Panar and L. F. Beste, *Macromolecules*, **10**, 1401 (1977).
9. Y. Onogi, J. L. White, and J. F. Fellers, *J. Polym. Sci. Polym. Phys.*, **18**, 663 (1980).
10. W. J. Jackson and H. F. Kuhfuss, *J. Polym. Sci. Polym. Chem.*, **14**, 2043 (1976).
11. W. R. Krigbaum and F. Salaris, *J. Polym. Sci. Polym. Phys.*, **16**, 883 (1978).
12. R. S. Werbowyj and D. G. Gray, *Mol. Liq. Cryst.*, **34** (Letters), 97 (1976).
13. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
14. M. Panar and O. B. Wilcox, *Offenlegungsschrift* (German Federal Republic) 2705381 (1977).
15. S. Aharoni, *Mol. Liq. Cryst.*, **36** (Letters), 237 (1980).
16. J. Bheda, J. F. Fellers, and J. L. White, *Coll. Polym. Sci.*, **258**, 1335 (1980).
17. J. Bheda, J. F. Fellers, and J. L. White, unpublished research, 1978–80.
18. Y. Onogi, J. L. White, and J. F. Fellers, *J. Non-Newt. Fluid Mech.*, **7**, 121 (1980).
19. T. Asada and S. Onogi, unpublished research.
20. R. J. Samuels, *J. Polym. Sci.*, A-2, **7**, 1197 (1969).
21. J. H. Elliott, *J. Appl. Polym. Sci.*, **13**, 755 (1969).
22. J. R. Dees and J. E. Spruiell, *J. Appl. Polym. Sci.*, **18**, 1053 (1974).
23. J. E. Spruiell and J. L. White, *Polym. Eng. Sci.*, **16**, 550 (1975).
24. V. G. Bankar, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 2341 (1977).

25. H. P. Nadella, H. M. Henson, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 3003 (1977).
26. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 53 (1978).
27. M. Horio, paper presented at the American Chemical Society, Division of Cellulose, Paper and Textile Chemistry Meeting, Houston, March, 1980.
28. P. H. Hermans and P. Platzek, *Kolloid Z.*, **88**, 68 (1939).
29. J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger, *Rec. Trav. Chim.*, **65**, 427 (1946).
30. R. S. Stein, *J. Polym. Sci.*, **31**, 327 (1958).
31. P. H. Hermans, J. J. Hermans, D. Vermaas, and A. Weidinger, *J. Polym. Sci.*, **3**, 1 (1948).
32. G. R. Taylor and S. R. Darin, *J. Appl. Phys.*, **26**, 1075 (1955).
33. R. S. Stein and F. H. Norris, *J. Polym. Sci.*, **21**, 381 (1956).
34. K. Walters, *Rheometry*, Chapman and Hill, London, 1975.
35. B. L. Lee and J. L. White, *Trans. Soc. Rheol.*, **18**, 467 (1974).
36. H. Aoki, J. L. White and J. F. Fellers, *J. Appl. Polym. Sci.*, **23**, 2293 (1979).
37. S. P. Papkov, V. G. Kulichikhin, V. D. Kalmykova, and A. Ya Malkin, *J. Polym. Sci. Polym. Phys.*, **12**, 1753 (1974).
38. K. F. Wissbrun, unpublished research, 1980.

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