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Cellulose-Based Liquid Crystalline Polymers; Esters of (Hydroxypropyl) Cellulose

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Propionic, *n*-butyric, isobutyric and phthalic acid esters of (hydroxypropyl)cellulose were prepared and characterized. The aliphatic esters were readily formed by reacting (hydroxypropyl)cellulose with the corresponding acid chloride at room temperature. The phthalic acid ester was formed by reacting phthalic anhydride with (hydroxypropyl)cellulose in pyridine at 45°C. The bulk aliphatic esters exhibit cholesteric reflection in the visible range of the spectrum. The wavelength of the reflection peak maximum, λ_o, was measured spectrophotometrically at different temperatures. Plots of λ_0^{-1} reached zero (i.e. the cholesteric pitch became infinite) at temperatures close to the anisotropic-isotropic phase transition temperatures. The latter temperatures were determined experimentally by polarizing microscopy and differential scanning calorimetry, and were in the range 165°C ±10°C for all cellulose derivatives studied in this work. The optical rotatory dispersion (ORD) and circular dichroism (CD) of thin layers of the planar cholesteric mesophase were also discussed.

INTRODUCTION

Cellulose[1–3] and its derivatives[4–22] often display liquid crystalline behavior. The formation of mesophases is attributed primarily to the limited flexibility of the cellulose chain, but flexible side chain substituents on cellulose may facilitate the orientation of the main chain by increasing its mobility and confering solubility. In a way, the molecular structure resembles a pipe cleaner, with the cellulose chain acting as the stiff core and the side chains as the fuzz. The presence of many large substituents on the cellulose backbone may also inhibit crystallization, increase the effective chain ra-

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dius and possibly change the chain conformation. The preparation of highly substituted cellulose derivatives was therefore undertaken to study the effects of side chain structure on the properties of the liquid crystalline phase. Here we report the preparation and characterization of propionic, *n*-butyric, isobutyric and phthalic acid esters of (hydroxypropyl)cellulose. This cellulose ether was selected as a parent compound because it is readily soluble in both aqueous and nonaqueous media, furnishing homogeneous reaction conditions.

EXPERIMENTAL PART

Preparation

The propionic, *n*-butyric, isobutyric and phthalic acid esters of (hydroxypropyl)cellulose were prepared. These esters will be referred to as PPC, BPC, IBPC and P*l*PC, respectively. The aliphatic esters were readily formed by reacting (hydroxypropyl)cellulose with the corresponding acid chloride at room temperature. A typical procedure is represented by the preparation of PPC; 20 mL of propionyl chloride was added to 10 g of dried (hydroxypropyl)cellulose (HPC) (nominal mol wt 100 000 from Aldrich Chemical Co.) without solvent at room temperature. The reaction was vigorous and exothermic. The final reaction mixture was a faint yellow viscous fluid. After 1 hr reaction time the mixture was poured into a large excess of cold distilled water. The PPC separated as a white sticky mass. It was washed several times with water to remove reactants and then purified by dissolution in acetone and reprecipitation in water. After drying under vacuum at 55°C for 48 hr, the yield was about 12 g. Two samples of PPC were also formed by allowing reaction for 4 and 10 min.

The phthalic acid ester of HPC (P*l*PC) was formed by reacting phthalic anhydride (26 g) with HPC (20 g) in pyridine (200 mL) at 45°C for 40 hr. The reaction mixture was cooled and poured into a large excess of ethyl acetate to precipitate the P*l*PC, which was repeatedly washed with ethyl acetate to remove reactant and solvent. The polymer was purified by repeated dissolution in methanol and reprecipitation in ethyl acetate. The product, after drying in vacuum at 55°C, was a fluffy mass which was easily powdered. P*l*PC, so formed, was soluble in acetone, chloroform, dioxane and methanol, and insoluble in water and benzene. It also dissolved in an aqueous solution of sodium hydroxide or sodium bicarbonate to give its sodium salt, which was isolated as a white powder. The salt is soluble only in water. Figure 1 shows a generalized scheme for the preparation of esters of (hydroxypropyl) cellulose.

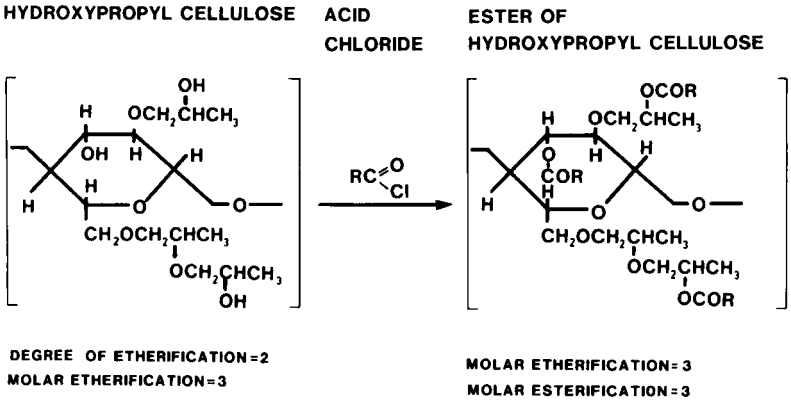

FIGURE 1 Generalized scheme for the preparation of esters of (hydroxypropyl)cellulose.

Characterization

The infrared spectra of the polymer samples of PPC, BPC, IBPC and P*l*PC were recorded on a Perkin-Elmer model 298 Infrared Spectrometer. The strong sharp band at about 1700 cm^{-1} is indicative of an ester function. The IR spectrum of HPC exhibits an exceedingly broad hydroxyl peak in the 3500–3400 cm^{-1} region (Figure 2, Curve I). This peak is insignificant for BPC (Figure 2, Curve II) suggesting complete esterification, but a small peak is shown by the IBPC sample, indicating incomplete esterification (Figure 2, Curve III). The PPC sample formed in 1 hr of esterification time seems to have a nearly complete esterification as its IR spectrum does not exhibit any significant hydroxyl peak. However, the samples formed during esterification times of 4 or 10 min show some evidence of hydroxyl groups in the range 3500–3400 cm^{-1}. In addition to a strong carbonyl peak at 1720 cm^{-1}, the infrared spectrum of P*l*PC also exhibited two bands at about 1600 cm^{-1} attributed to C=C stretching of the aromatic ring.

The degree of esterification was quantitatively determined by saponification. In a typical run, about 0.4 g of the dried polymer sample was dissolved in 75 mL of absolute ethanol and then 10 mL of normal NaOH was added. The hydrolysis was carried out for 4 hr at room temperature. The excess base was back titrated with standard aqueous sulphuric acid. Duplicate runs were made for each sample. The degree of esterification was ascertained using a value of 3.4 for the molar etherification of HPC.[22] The data are summarized in Table I.

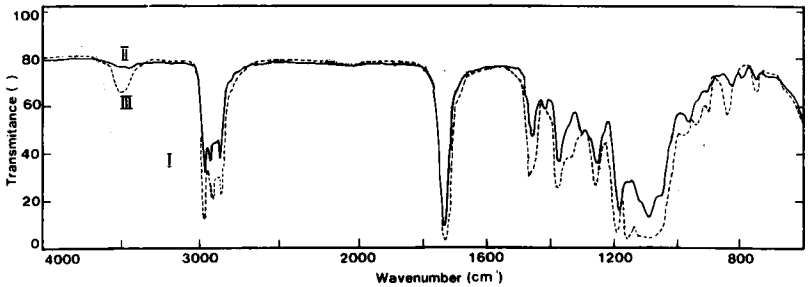

FIGURE 2 IR spectra of (I) (hydroxypropyl)cellulose (HPC); (II) *n*-butyric acid ester of (hydroxypropyl)cellulose (BPC); (III) iso-butyric acid ester of (hydroxypropyl)cellulose (IBPC).

The weight average molecular weights, $\overline{M}_w$ of the polymer samples were measured in acetone by means of a Chromatix KMX-6 low-angle laser light scattering photometer. The solutions were filtered with a 0.2 μm Millipore Type FG filter and then passed through the light scattering cell at a flow rate of 0.05 mL/min. Measurements of the Rayleigh factors for each solution were made at a scattering angle of 6–7°. The values for the specific refractive index increment, dn/dc, in acetone were determined with a Brice-Phoenix differential refractometer. The pertinent results are summarized in Table II which also includes limiting viscosity values determined in acetone at 25°C. The molecular weight of P*I*PC was measured in methanol.

A thin film of the aliphatic ester polymers, placed between a microscope slide and a cover glass, and heated in a Mettler FP52 hot stage, displayed cholesteric reflection colors (Table III). However, a thin film of P*I*PC was strongly birefringent under the polarizing microscope but displayed no reflection colors. The birefringent pattern deformed under pressure or shear

TABLE I

The extent of esterification of acid esters of (hydroxypropyl)cellulose

Sample	Esterification time (min)	Ester content (wt%)	DS*	Reflection color at 25°C
PPC I	60	29.96	2.67	colorless
PPC II	10	27.43	2.36	colorless
PPC III	4	26.31	2.23	violet
BPC	60	34.03	2.59	violet
IBPC	60	27.41	1.90	red
PIPC	40(hr)	37.70	1.46	colorless

DS* calculated using a value of 3.4 for the molar etherification of (hydroxypropyl)cellulose.

TABLE II

Viscosity and light scattering data* of the esters of (hydroxypropyl)cellulose

Sample	$[\eta]_{25°C}$ (dL g^{-1})	dn/dc (mL · g^{-1})	$A_2 \times 10^4$ (mol · mL · g^{-1})	$\overline{M}_w \times 10^{-5}$ (g · mol^{-1})
PPC I	0.69	0.104	3.18	1.25
PPC II	0.84	0.104	2.06	2.08
PPC III	0.98	0.104	6.38	2.28
BPC	0.63	0.095	2.92	1.47
IBPC	0.63	0.092	4.88	1.63
PIPC	—	0.167	−12.60	1.11

*The solvent was acetone, except for PIPC which was dissolved in methanol.

TABLE III

The temperature range within which the cellulose based thermotropic polymer liquid crystals exhibit cholesteric reflection color

Sample	DS	Temperature range (°C)			
		Violet	Blue	Green	Red
PPC I	2.67	90	100	110	120
PPC II	2.36	70	80	90	110
PPC III	2.23	25	50	70	90
BPC	2.59	25	40	60	80
IBPC	1.90	—	—	—	25

and thus the microscopic texture differed from that of normal semi-crystalline polymers. The same behavior was observed for the benzoic acid ester of HPC.[18] The wavelengths of selective reflection colors at varying temperatures were recorded by means of a Pye-Unicam SP8–150 UV/VIS spectrophotometer with a modified Mettler FP52 hot stage as sample holder. A thin film of the sample, placed between a microscope slide and cover glass, was kept at the desired temperature in a Mettler FP52 microscope hot stage which was then placed vertically in the spectrophotometer beam. The optical rotatory dispersion (ORD) and circular dichroism (CD) of the polymer were measured as a function of wavelength with a Jasco model ORD/UV-5 spectropolarimeter. Thinner samples were essential in order to keep the maximum optical rotation within the range of the instrument. The thickness of the sample layer was obtained by measuring the thickness of the microscope slide, sample and cover glass with a precision micrometer and subtracting the thickness of the slide and cover glass. The

polymer film, sandwiched between the slide and cover glass was allowed to equilibrate for a few weeks.

The anisotropic-isotropic transition temperatures (i.e. clearing temperatures, T_c) of the polymers were measured by a Reichert polarizing light microscope equipped with a Mettler FP52 hot stage and also by a Perkin-Elmer DSC-2C differential scanning calorimeter as described previously.[18]

Results and Discussion

It is seen from Tables I and II that the extent of esterification increases with reaction time while the molecular weight of the resulting polymer decreases. Thus, the cellulose main chain suffers some chain scission during esterification with the bulk acid chlorides. The $\overline{M}_w$ for HPC was 2.1×10^5 g/mol.[23] The polymers, so formed, have the desired properties; they display thermotropic liquid crystalline behavior and the aliphatic ester polymers show selective cholesteric reflection colors (Table III). The reflectance spectra of thin layers of the polymers at different temperatures were recorded spectrophotometrically. Figure 3 shows typical spectra for the BPC sample. The wavelength of the reflection peak maximum, λ_0, due to the cholesteric structure, increases with increasing temperature. The peak wavelength occurs at about the same temperature on heating and cooling. Plots of inverse peak wavelength, λ_0^{-1} vs temperature are linear for all the aliphatic ester samples (Figure 4). The cholesteric pitch becomes infinite (λ_0^{-1} reaches zero) as the temperature approaches the clearing

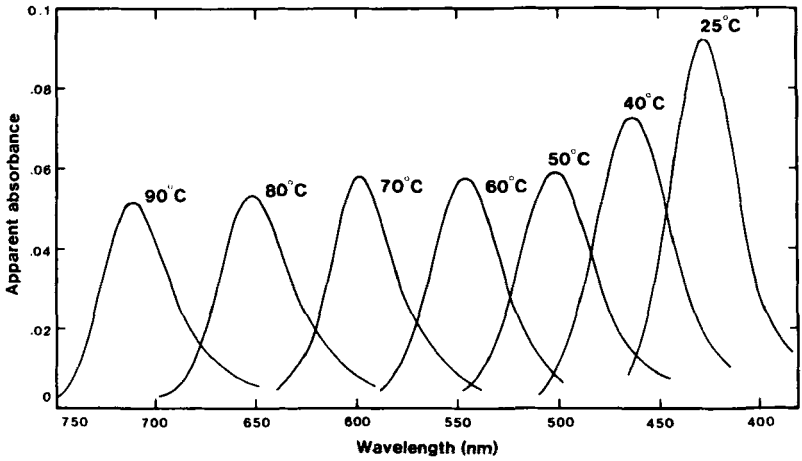

FIGURE 3 The apparent absorption spectra due to cholesteric reflection from film of BPC at different temperatures (film thickness, 70 μm).

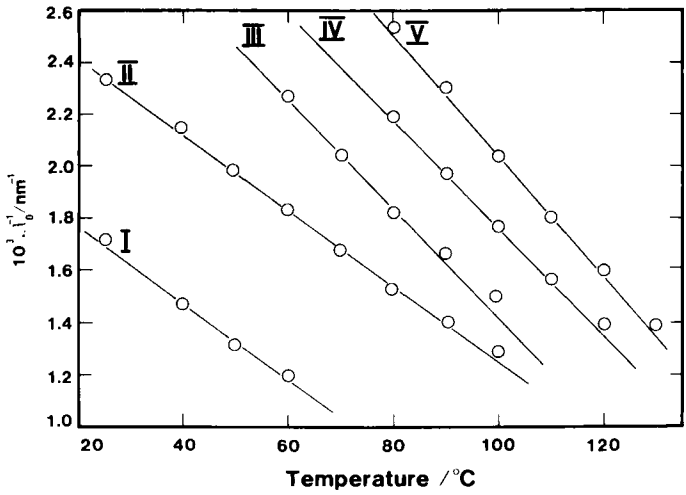

FIGURE 4 The plots of λ^{-1} (nm^{-1}) vs T(°C) for (I) IBPC; (II) BPC; (III) PPC (DS = 2.23); (IV) PPC (DS = 2.36), and (V) PPC (DS = 2.67).

temperature, T_c. The latter temperatures were measured experimentally by hot stage light microscopy and by differential scanning calorimetry. The results are summarized in Table IV. The peak wavelength, λ_0, is related to the cholesteric pitch, p, by de Vries' relationship;[24] $\lambda_0 = \bar{\mu}p$, where $\bar{\mu}$ is an average refractive index of the polymer. The helical pitch, p, of the cholesteric structure decreases with increasing temperature for most pure low molecular weight cholesteric liquid crystals,[25–27] while the increase in helical pitch, p, with temperature seems to be typical of liquid crystalline polymers.[28–29] At present, a unified theoretical interpretation of the tem-

TABLE IV

The anisotropic-isotropic phase transition temperatures of ester derivatives of (hydroxypropyl)cellulose (HPC)

	Transition temperature (°C)		
Sample	A	B	C
PPC I	160	163	185
PPC II	166	172	183
PPC III	165	170	166
BPC	163	165	178
IBPC	158	159	153

A–by differential scanning calorimetry
B–by hot-stage light polarising microscopy
C–by the extrapolation of curves of Figure 4.

perature dependence of the pitch, p, is still lacking although some theories have recently been reviewed.[30]

It appears that when the size of the substituent reaches that of the aliphatic esters of HPC in the present study, the pitch of the resultant cholesteric structure is in the range of the wavelength of visible light; consequently, the polymers show iridescent colors. On the other hand, the phthaloyl (and benzoate)[18] esters are larger than the aliphatic esters, and are not iridescent. The cholesteric pitch of these bulk esters may be too large ($\geqslant$800 nm) to exhibit selective reflection of visible light, but too small to be seen in the optical microscope. However, the concentrated solutions of P*I*PC in acetone ($\geqslant$50 wt.%) do display characteristic cholesteric finger print patterns similar to those previously reported for the benzoate ester.[18]

Figure 5 shows ORD (Curve I) and CD (Curve II) spectra for the bulk BPC sample with a violet reflection color at room temperature. The dextro structure reflects right-handed circularly polarized light without reversal of handedness and transmits only left-handed circularly polarized light. The levo structure exhibits the reverse effects.[26,31] The negative CD band in Figure 5 therefore suggests that the liquid crystal possesses a right-handed twisted planar structure. The optical rotatory power arises from the supermolecular helicoidal structure and not from the optical activity of individual polymer molecules. On the basis of his model for cholesteric structure, de

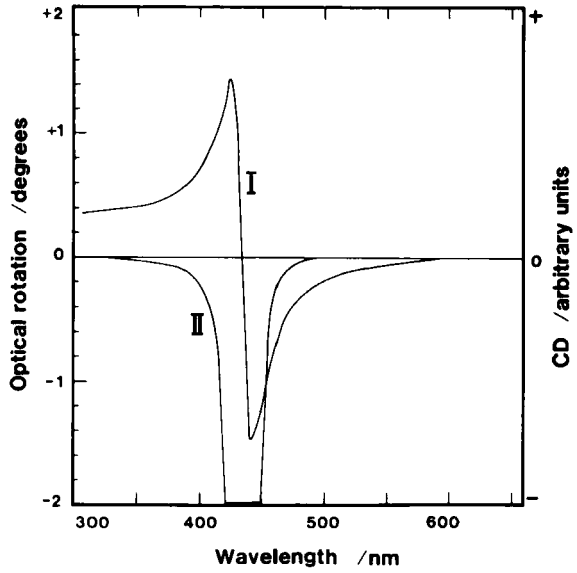

FIGURE 5 ORD (Curve I) and CD (Curve II) for a planar cholesteric layer of BPC at room temperature.

Vries[24] predicted that the optical rotatory power, θ, along the helicoidal axis is given as a function of wavelength, λ, by

$$\theta = -\frac{\pi(\Delta\mu)^2\lambda_0}{4\lambda^2\bar{\mu}[1 - (\lambda/\lambda_0)^2]} \quad (1)$$

where $\Delta\mu$ is the birefringence of an individual layer in the untwisted cholesteric structure, and λ_0 is the wavelength of reflected light at which the optical rotation changes sign. Here λ_0 is the same as the wavelength of the maximum reflection peak in the apparent visible absorption spectrum (Figure 3). The plot of θ vs $[\lambda^2(1 - \lambda^2/\lambda_0^2)]^{-1}$ is expected to be linear with the slope

$$\frac{\pi(\Delta\mu)^2\lambda_0}{4\bar{\mu}}$$

The ORD curve I of Figure 5 was fitted to Eq. (1) and the resulting plot is illustrated in Figure 6, which is linear, in accord with de Vries' equation.

From the slope of Figure 6, an average value of 1.465 for $\bar{\mu}$ measured from an Abbé refractometer and sample thickness of 60 μm, the birefringence of the BPC sample was estimated to be 4.6×10^{-3}. The orientation of the polymer mesophase may not be perfectly uniform, so the above birefringence value may be less than the true value.

In summary, the aliphatic acid esters of (hydroxypropyl) cellulose show cholesteric reflection colors while the aromatic esters form a long pitch cholesteric structure.

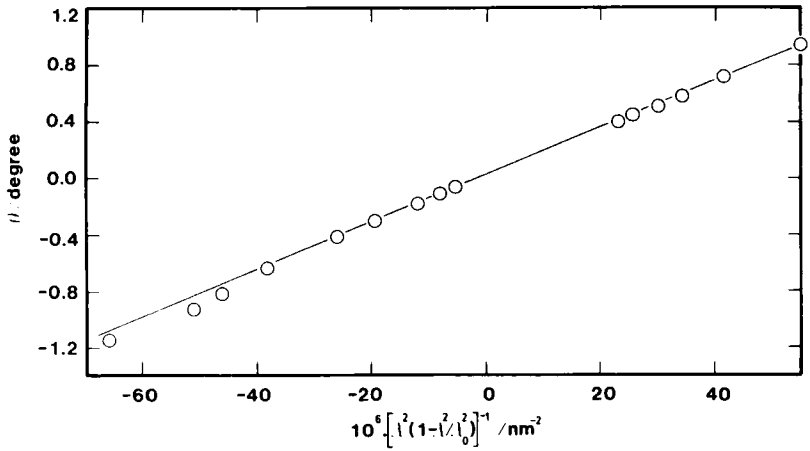

FIGURE 6 Plot of θ vs $[\lambda^2(1 - \lambda^2/\lambda_0^2)]^{-1}$ for BPC ($\bar{\mu}$ = 1.465, λ_0 = 434 nm, sample thickness = 60 μm).

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References

1. H. Chanzy, A. Peguy, S. Chaunis and P. Monzie, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1137 (1980).
2. P. Navard and J. M. Haudin, *Br. Polym. J.*, **12**, 174 (1980).
3. D. L. Patel and R. D. Gilbert, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1231 (1981).
4. R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst. (Lett.)*, **34**, 97 (1976).
5. J. S. Aspler and D. G. Gray, *Macromolecules*, **12**, 562 (1979).
6. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
7. J. S. Aspler and D. G. Gray, *Macromolecules*, **14**, 1546 (1981).
8. J. Bheda, J. F. Fellers and J. L. White, *Colloid Polym. Sci.*, **258**, 1335 (1980).
9. Y. Onogi, J. L. White and J. F. Fellers, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 663 (1980).
10. Y. Onogi, J. L. White and J. F. Fellers, *J. Non-Newt. Fluid Mech.*, **7**, 121 (1980).
11. T. Asada, K. Toda and S. Onogi, *Mol. Cryst. Liq. Cryst. (Lett.)*, **68**, 231 (1981).
12. T. Tsutsui and R. Tanaka, *Polym. J.*, **12**, 473 (1980).
13. S. M. Aharoni, *Mol. Cryst. Liq. Cryst. (Lett.)*, **56**, 237 (1980).
14. P. Navard, J. M. Haudin, S. Dayan and P. Sixou, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 379 (1981).
15. S. Dayan, P. Maissa, M. J. Vellutini and P. Sixou, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 33 (1982).
16. D. L. Patel and R. D. Gilbert, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1449 (1981); D. L. Patel and R. D. Gilbert, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1019 (1982).
17. S.-L. Tseng, A. Valente and D. G. Gray, *Macromolecules*, **14**, 715 (1981).
18. S. N. Bhadani and D. G. Gray, *Makromol. Chem. Rapid Commun.*, **3**, 449 (1982).
19. J. Bheda, J. F. Fellers and J. L. White, *J. Appl. Polym. Sci.*, **26**, 3955 (1981).
20. S. M. Aharoni, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 495 (1981); S. M. Aharoni, *J. Macromol. Sci. Phys.*, **B21**, 287 (1982).
21. K. Shimamura, J. L. White and J. F. Fellers, *J. Appl. Polym. Sci.*, **26**, 2165 (1981).
22. S.-L. Tseng, G. V. Laivins and D. G. Gray, *Macromolecules*, **15**, 1262 (1982).
23. R. S. Werbowyj, Ph. D. Thesis, McGill University (1982).
24. A. de Vries, *Acta Crystallogr.*, **4**, 219 (1951).
25. S. Chandrasekhar, "Liquid Crystals", Cambridge University Press, Cambridge, 1977, p. 267.
26. P. G. de Gennes, "The Physics of Liquid Crystals", Clarendon Press, Oxford, 1974, Chapter 6.
27. Y. S. Freidzon, A. V. Kharitonov, V. P. Shibaev and N. A. Plate, *Mol. Cryst. Liq. Cryst.*, **88**, 87 (1982).
28. V. P. Shibaev, H. Finkelman, A. V. Kharitonov, M. Portugall, N. A. Plate and H. R. Ringsdorf, *Polym. Sci. (USSR)*, **23**, 1029 (1981).
29. S. Sikasuya, S. Sasaki, J. Watanabe, Y. Fukuda and I. Uematsu, *Polym. Bull.*, **7**, 241 (1982).
30. G. S. Chilaya and L. N. Lisetskii, *Sov. Phys. Usp.*, **24**, 496 (1981).
31. W. Elser and R. D. Ennulat, "Advances in Liquid Crystals", edited by G. H. Brown, Academic Press, New York, 1976, Vol. 2, p. 77.