Chiroptical Filters from Aqueous (Hydroxypropyl)cellulose Liquid Crystals

GÉRARD CHARLET* and DEREK GRAY, *Pulp and Paper Research Institute of Canada and Chemistry Department, McGill University, 3420 University Street, Montreal, Quebec, Canada H3A 2A7*

Synopsis

An experimental procedure has been designed for the preparation of aqueous mesophases of (hydroxypropyl)cellulose (HPC) exhibiting a stable low turbidity. Sandwich chiroptical filters have been made from these right-handed cholesteric liquid crystals confined between two parallel glass plates. Their optical properties, studied with new circular polarizers prepared from oriented polyethylene films, depend on the mesophase thickness. Thin filters (liquid crystal thickness ≤ 200 μm) reflect selectively up to 36% of normal incident light (i.e., 72% of the right-handed circularly polarized component) in a very narrow wavelength band (bandwidth ≤ 10 nm). An increase of the reflected intensity is observed at higher sample thickness, although it is accompanied by an increasing loss of selectivity of the filter toward circularly polarized light. However, a range of thickness exists where both selectivity and reflectivity are close to their optimum values. The availability, low cost, and UV resistance of (hydroxypropyl)cellulose make HPC–water liquid crystals attractive for optical applications.

INTRODUCTION

Cholesteric liquid crystals exhibit a layered structure where the long axes of the molecules are parallel in each layer but rotate from layer to layer. This generates a helicoidal supramolecular arrangement which possesses the distinctive property of reflecting light at a wavelength directly related to its pitch. When the mesophase is sandwiched between two parallel flat surfaces, a planar texture may develop in which the screw axis of the liquid crystal is perpendicular to the constraining planes over macroscopic dimensions. Under normal incidence, light of the same handedness as the cholesteric structure is then reflected in a narrow wavelength band while the other handedness as well as waves of any polarization at all other wavelengths are transmitted unaffected. Cholesteric liquid crystals appear to be ideally suited for optical applications, especially in laser systems,[1,2] because (i) they are fluid, being thus easily oriented, and (ii) their unique properties are based on reflection, allowing for the use of a high intensity light source without significant damage. Passive devices such as circular polarizers, bandnotch filters, or optical isolators are currently prepared from low molecular weight cholesterol derivatives.

---

*Present address: Chemistry Department, Université Laval, Quebec City, Quebec, Canada G1K 7P4.

CCC 0021-8995/89/092517-11$04.00

Cellulose derivatives form both lyotropic and thermotropic cholesteric liquid crystals.[3-5] Because cellulosics are readily available at low cost and exhibit a good stability toward UV light, they should offer an alternative to cholesteryl halides and esters, provided that a planar orientation of the mesophases can be achieved. Also, a study of the conditions for preparing planar lyotropic polymer liquid crystals is an important step toward the preparation of well-aligned free-standing cholesteric films. In this article, a procedure for preparation of highly reflective chiroptical filters from aqueous solutions of (hydroxypropyl)cellulose (HPC) is presented.

EXPERIMENTAL

Materials

A commercial sample of (hydroxypropyl)cellulose (Aldrich Chemical Co., nominal molecular weight 10^5 g mol^{-1}) was purified as described below. Filtration of the solutions was performed on glass microfibre filters (Whatman 934-AH, nominal retention: 1.5 μm). Chiroptical filters were prepared between microscope glass slides (Fisher Scientific, 75 $\times$ 50 $\times$ 1 mm^3) and subsequently sealed using either a UV-curing adhesive (Light-Weld F1B glue, Ferenczy Assoc., New York) or an epoxy resin (Spurr VCD, J.B. EM. services).

Polymer Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were measured with a Mattson Cygnus 25 instrument equipped with a TGS detector. Analysis of the insoluble material extracted from the polymer was performed on a ISI Model SS60 scanning electron microscope with a PGT Series 3 energy dispersive spectrometer.

Optical Properties

The selective reflection of light by cholesteric liquid crystals is ideally studied by spectropolarimetry. However, commercial instruments such as the Jasco J-500C spectropolarimeter used in this work are far too sensitive for highly reflective samples. The optical properties of HPC chiroptical filters were investigated by conventional UV-visible spectrophotometry with either a scanning (Pye-Unicam SP8-150; Figures 1, 5, and 6) or a photodiode array instrument (Hewlett-Packard 8450A; Figures 4 and 7). When required, the unpolarized source was converted into circularly polarized light by a combination of a linear polarizer and a quarter-wave plate, oriented at a 45° angle to each other and inserted in that order between the spectrophotometer source and the sample. The proper waveplate was prepared from oriented polyethylene, chosen because of its transparency over the whole UV-visible spectrum. Thin films were obtained by a uniaxial shear of the polymer melt pressed between two glass slides, followed by rapid cooling to room temperature. Two of these films were selected so that their thickness and birefringence provided for a retardation slightly larger than one fourth of the proper wavelength when they were combined with their shear directions parallel to each other. An exact quarter waveplate could then be obtained by a small twist in their

relative orientation. These adjustments were performed with the spectropo-
larimeter, taking advantage of the instrument's ability to measure the differ-
ential transmission of right- and left-handed circularly polarized light. The
waveplate was inserted between the spectropolarimeter source and a thin
HPC-water liquid crystalline test sample. The two polyethylene films were
then rotated with respect to each other, until the peak due to the circular
reflectivity of the sample completely vanished. In this orientation, the two
films constitute a quarter waveplate; i.e., the combination converts both right-
and left-handed circularly polarized light into plane polarized light. Finally,
the liquid crystalline test sample was again used, this time with the UV-visi-
ble spectrophotometer, to achieve a 45° or −45° orientation between the
linear polarizer and the quarter waveplate, a left- or right-handed circular
polarizer being obtained when the peak intensity of the test sample spectrum
was maximum or zero, respectively. The above combination was preferred to
commercial circular polarizers because it is very flexible (a precise circular
polarizer can be prepared at any wavelength), and it exhibits a continuous
UV-visible spectrum of low absorbance that can be easily subtracted. As a
proof of the overall accuracy of the optical setup, the UV-visible spectrum of a
given cholesteric sample measured with unpolarized light was observed to
match exactly that reconstructed by adding the two absorbance spectra
recorded with right- and left-handed circularly polarized light.

Optical Microscopy

The textures of the liquid crystals in the sandwich filters were examined
with a Reichert polarizing light microscope.

RESULTS AND DISCUSSION

Polymer Purification and Characterization

Isotropic solutions (5–10% polymer by weight) of HPC were prepared in
distilled water and allowed to dissolve for a few weeks with occasional
shaking. The resulting solutions exhibit a high turbidity. The transmission
spectrum recorded in the visible range against pure water for such a solution
is shown in Figure 1 (full line). The scattering of light at all wavelengths
suggests that suspended particles of micron size are responsible for the
turbidity. The solutions were submitted to centrifugation (about 20,000 g
acceleration for a few hours), which brings about a drastic improvement in
their transparency (Fig. 1, dashed line). The best results were obtained by
filtration (Fig. 1, dotted line). No change in the spectrum of the filtered
solution was subsequently observed over a period of months, which indicates
that the original turbidity originates from the presence of insoluble foreign
material rather than from reversible aggregation of the polymer in aqueous
solution. The solid matter extracted by centrifugation was rinsed several
times in distilled water and dried under vacuum. The resulting white powder,
which represents about 1% by weight of the original polymer, was analyzed by
FTIR (Fig. 2, dotted line). The spectrum of the original material is also given
for comparison (full line). The insoluble material shows a very intense absorp-
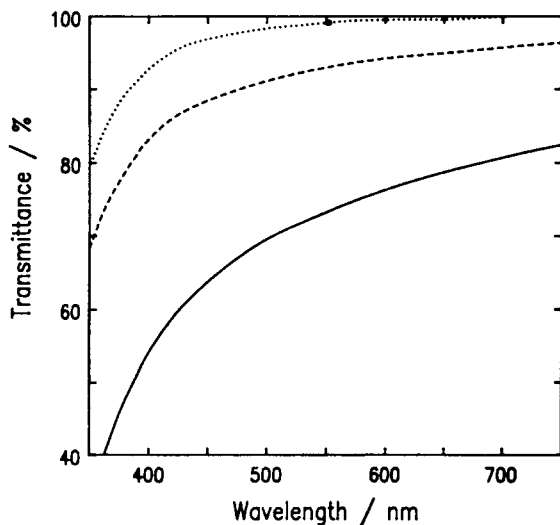tion band around 1100 cm^{-1} characteristic of a silicate bond. The presence of

Fig. 1.   UV-visible spectra of isotropic aqueous solutions of HPC (10% by weight) measured in 1 cm pathlength quartz cells, against pure water as reference: (——) original; (---) centrifuged; (· · ·) filtered solution. The shoulder observed at low wavelength for all solutions originates from the UV absorption of the polymer itself.
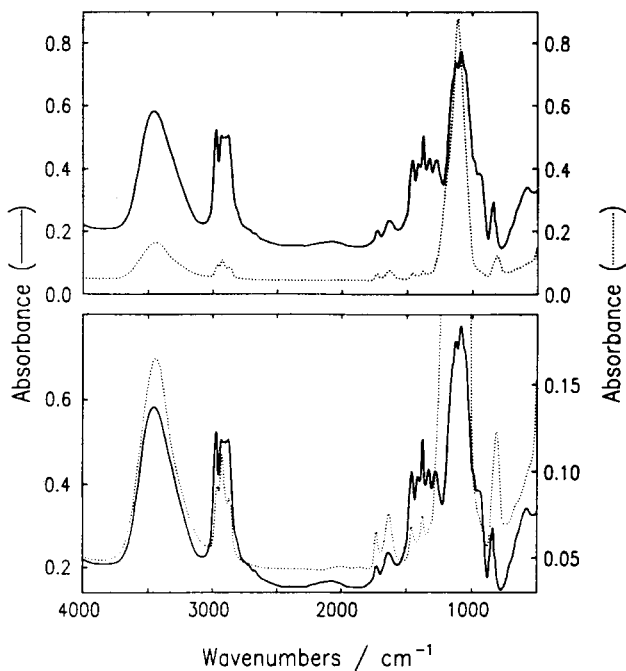

Fig. 2.   FTIR spectra of the original HPC (——, absorbance scale to the left) and the solid impurity recovered by centrifugation (· · · , scale to the right). Both spectra were recorded on the powders pressed with potassium bromide into a pellet form. The figure is drawn twice using different scales in order to facilitate the comparison.

silicon in the residue was confirmed by energy dispersive X-ray spectroscopy which revealed a peak at 1740 eV attributed to the silicon K_α doublet. The presence of such an impurity in commercial HPC is surprising, but, presumably, silica may have been added to the polymer powder by the manufacturer in order to improve its free-running properties. Other features of the FTIR analysis include bands present in both spectra at 3446, 2970, 2875, 1730, 1640, 1460, and 1376 wavenumbers. Therefore, the insoluble powder also contains some cellulosic material, probably HPC of a lower degree of substitution. A characterization[6] of the purified unfractionated HPC by size exclusion chromatography and ^{13}C-NMR showed that the polymer has a weight-average molecular weight of 4.1×10^5 kg mol^{-1}, a polydispersity index of 3.9, an average degree of substitution of 2.5 ± 0.1, and an average molar substitution $MS = 3.9 \pm 0.1$.

Mesophase Preparation

Aqueous mesophases were directly prepared from the filtered dilute solutions, by taking advantage of the liquid–liquid phase separation which occurs[7,8] upon heating aqueous solutions of highly substituted HPC (about 40°C for a polymer of MS = 4). The precipitating phase has a concentration well above the critical concentration for the formation of an anisotropic phase at room temperature, so that heating and decanting a 10% solution for a few days at 80°C allows the recovery upon cooling of a clear mesophase whose reflection wavelength varies between 600 and 900 nm, depending on the extent of the previous physical separation of the two phases. The concentration can then be adjusted to obtain the desired optical properties by dilution or slow evaporation of the mesophase. A summary of the above procedure is given in the sketch of Figure 3. Although the method leads to samples whose concentration has to be determined afterward, it has several advantages for the preparation of chiroptical filters. No drying and redissolving steps are involved, which diminshes the risk of contamination by dust particles. Starting from a
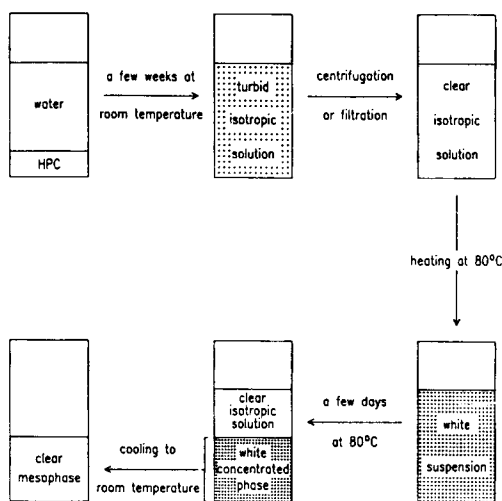

Fig. 3. Sketch of the procedure used to prepare nonturbid aqueous mesophases of HPC.

dilute solution leads ultimately to a mesophase where homogeneity in concentration is more easily achieved than by mixing directly the corresponding amounts of polymer and solvent. The long heating above the phase separation temperature removes dissolved gas, thus preventing formation of bubbles in the mesophase or the filter. Also, some separation between polymer species of varying molar substitution is known to occur during phase separation,[7] so that the procedure yields a concentrated phase of a more homogeneous polymer, with narrower reflection bandwidth than the original material.

Chiroptical Filter Preparation

Numerous factors affect the ultimate degree of order of a liquid crystal sandwiched between two parallel glass surfaces. These include the molecular interactions between glass and solution at the interface (and their response to chemical modification of the solid surface) and the mechanical history of the mesophase (i.e., any orientation imparted to the liquid phase in the course of the sandwich preparation). Lyotropic polymer liquid crystals show a strong tendency to align parallel to inert flat constraining surfaces.[9,10] However, (hydroxypropyl)cellulose interacts strongly with glass, probably through hydrogen bonding, since a polymer film cast on a slide from aqueous solution can seldom be removed. The effect is noticeable even with a solution: when a drop of the viscous lyomesophase is placed on one glass slide and then squeezed by applying the second plate, the original position of the drop before squeezing can still be located as it exhibits a lower degree of order and often a different reflection wavelength than the rest of the sample. This can be overcome by shear alignment of the mesophase, in agreement with results obtained on the thermotropic phase of the ethyl ether of (hydroxypropyl)cellulose.[11] Even when confined to a very small thickness between two glass slides, the (ethoxypropyl)cellulose cholesteric domains adopt a nearly random distribution of orientations with respect to the glass wall upon quiescent cooling from the isotropic melt.

In contrast, a highly ordered planar arrangement is recovered with gentle shear. The memory of the initial location of the HPC–water mesophase on the glass slide was erased by shearing the sample immediately after assembly at very high rates, by means of a manual parallel back-and-forth displacement of the slides at 1–10 mm s^{-1}. However, the samples remained oriented in the shear direction for a long time, and eventually formed only small areas of planar texture. The most effective method to rapidly induce a planar orientation in the highly sheared filters appeared to be a shear-flow alignment of the HPC liquid crystal at low constant rates (linear displacement of 2–5 mm at 10–20 μm s^{-1}). In these mild conditions, even the thicker filters (mesophase thickness up to 1 mm) could be oriented, as evident from the disappearance of the reflection color upon shearing. The thin sandwich filters, prepared without spacer, were finally sealed through filling by capillarity the empty gap around the mesophase with a UV curable glue. Filters thicker than 200 μm used spacers cut from polytetrafluoroethylene film. They were sealed with epoxy resin formulated for fast cure at room temperature. The adhesion at the glass–epoxy interface was unsatisfactory when curing proceeded in presence of water vapor from both the atmosphere and the HPC mesophase. For this

reason, the spacers were covered with a fine layer of vacuum grease prior to assembling the filter and the samples were cured in a dry environment. Samples prepared according to the above procedure still show no indication of water loss after more than 2 years. All results presented below have been obtained for filters at least three months old.

Mechanical treatment of the confining surfaces is commonly used[1,2] to induce a parallel orientation of liquid crystals. Preliminary experiments showed that a mechanical treatment of the glass, e.g., rubbing with a diamond paste, did not lead to reproducible optical properties, presumably because of a large variability in the treated surface quality. A more systematic study using suitable equipment will be needed to ascertain the efficiency of any physical modification of the surface. It was not undertaken here, in view of the good planar orientation (see below) obtained with untreated slides.

Optical Properties of Thin Filters

The UV-visible spectra of chiroptical filters prepared from various aqueous HPC mesophases and having thicknesses ranging from 100 to 200 μm are presented in Figure 4. All samples exhibit symmetrical narrow reflection bands (8–10 nm half-height bandwidth). In contrast, filters prepared using the same procedure from solutions of the untreated commercial polymer gave broader reflection peaks of a smaller absorbance at maximum, showing that the presence of solid particles constitutes the main impediment to ordering of the liquid crystal. The small value of the width of the reflection bands of Figure 4 is fairly close to the limit (2–5 nm, depending on wavelength) predicted from the de Vries theory,[12] for experimental data on the mean refractive index and layer birefringence of aqueous HPC liquid crystals.[13] This indicates that the liquid crystalline phase in the thin filters has adopted a nearly planar arrangement. Accordingly, microscopic observation under crossed polarizers with a white light source revealed a dark featureless texture of the same color as the reflected region of the visible spectrum. As shown in Figure 4, thin
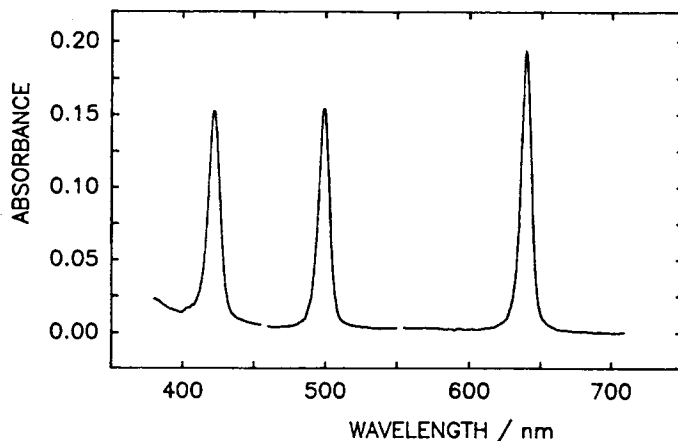

Fig. 4. UV-visible spectra of chiroptical filters made from aqueous HPC liquid crystals (mesophase thickness between 100 and 200 μm). The absorbance at the reflection maximum varies between 0.09 and 0.12, i.e., the filters reflect about 20–25% of the incident unpolarized radiation.
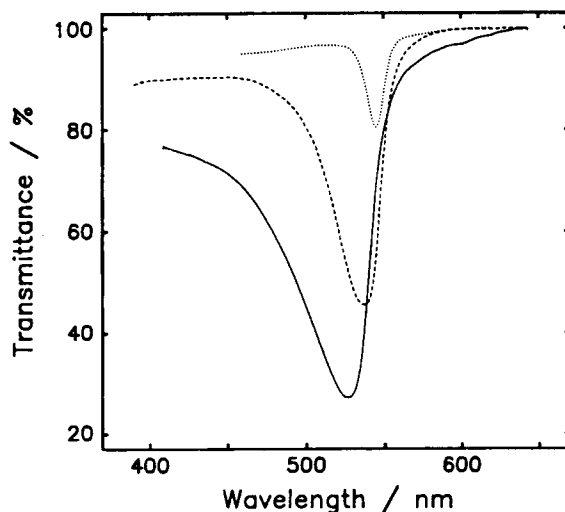
Fig. 5.   UV-visible spectra of HPC–water chiroptical filters prepared from the same HPC–water liquid crystal under identical conditions. The thickness of the mesophase is 160 (· · ·), 660 (---), or 860 (——) μm. The light source is unpolarized, and illumination is at normal incidence. The spectra were calculated from absorbance spectra arbitrarily shifted so that the absorbance is zero at 640 nm.

chiroptical filters transmit between 64 and 71% of the unpolarized incident light; i.e., they reflect more than about 60% of the circularly polarized component of the same handedness as the cholesteric helicoidal arrangement. For some applications, however, larger values of the reflected intensity may be desirable. In an attempt to improve the reflectivity, samples were prepared with thicknesses up to 1 mm.

Effect of Thickness on the Optical Properties

Figure 5 shows the UV-visible spectra measured for filters of different thickness prepared by the same procedure from a single HPC–water liquid crystalline solution. Several features appear to develop as the thickness increases. The absorbance at the maximum reflection wavelength increases drastically, and the maximum is slightly shifted toward lower wavelengths. Also, the reflection band broadens and loses its symmetry, exhibiting a tail on the low wavelength side. The most striking feature, however, is that the thicker specimens transmit *less* than half the incident light and must therefore reflect both hands of circularly polarized light.

Figure 6 gives the UV-visible spectra of the same samples illuminated at normal incidence with either right- (full line) or left-handed (dashed line) circularly polarized light. As already mentioned, the thin filter [Fig. 6(A)] exhibits a moderate reflectivity, but it is highly selective and reflects pure right-handed circularly polarized light. As the thickness of the mesophase increases, the reflectivity increases drastically, reaching a maximum close to 100% for a thickness of 660 microns [Fig. 6(B)]. At the same time, the selectivity is reduced, and an increasing amount of the left-handed component is reflected. The effect is particularly striking for the 860-μm filter [Fig. 6(C)], which reflects about 90 and 40% of the right- and left-handed incident
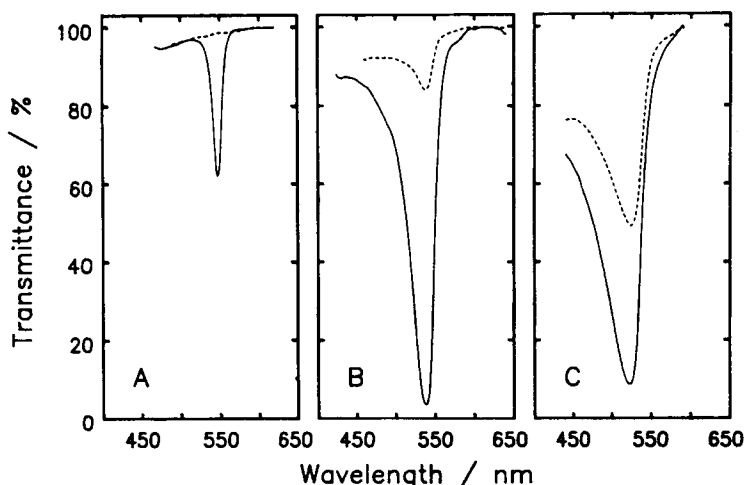
Fig. 6. UV-visible spectra of the same filters as in Figure 5, illuminated at normal incidence with either right- (——) or left-handed (---) circularly polarized light. Figures A, B, and C are for the 160, 660, and 860 μm filters, respectively.

radiation, respectively. The broadening of the reflection peak toward the low wavelength side, already observed under unpolarized illumination, is again apparent. Examination of the thick samples by light microscopy does not reveal any distinct texture, but the transmitted intensity under crossed polarizers is high, in contrast with thin filters.

These observations are consistent with a polydomain arrangement of the liquid crystal, i.e., a structure in which the optical axis adopts a variety of directions with respect to the glass wall. The interaction of a cholesteric liquid crystal with an oblique incident light beam must then be considered. A blue shift of the wavelength of maximum reflection has been measured[13] for a thin planar mesophase, in agreement with theoretical calculations.[14,15] In addition, a loss of selectivity, i.e., the reflection of both hands of circularly polarized light, is predicted[16-18] as the angle between the incident beam and the cholesteric optical axis increases. The effect has been observed experimentally[18,19] on a planar low molecular weight liquid crystal. The changes in the optical properties of the filters upon increasing the mesophase thickness, namely, blue shift of the reflection maximum, broadening of the reflection band toward low wavelengths, and loss of selectivity, therefore originate from an increasing deviation from the planar arrangement. The exact distribution of orientations of the cholesteric domains within the filters is difficult to appreciate from the present measurement alone, but it must still be quite far from random. Otherwise, all wavelengths below the reflection wavelength of the corresponding planar texture would be reflected to some extent, as observed for an extremely thick lyotropic mesophase[13] or a thin thermotropic phase of a cellulosic ether cooled from the isotropic melt.[11]

Spectral Uniformity of the HPC Filters

Uniform optical properties over large distances were difficult to achieve for thin filters (mesophase thickness ≤ 200 μm), probably because of a large sensitivity to the presence of irregularities and defects in the glass surface.
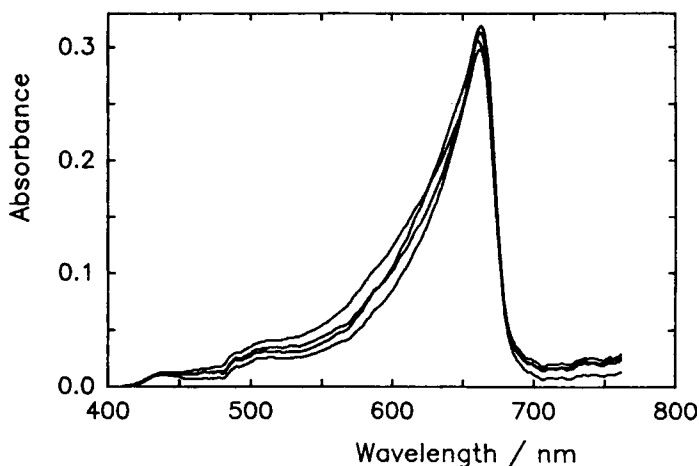
Fig. 7.   UV-visible spectra recorded at different locations on a 440 μm filter.

Also, thin filters were prepared without spacer, introducing variations in the glass–glass distance along the sample. A careful polishing of the substrate surface and the use of thin calibrated spacers should improve the homogeneity in optical properties. Thicker specimens were free of such shortcomings. A 440-μm filter was prepared from an aqueous HPC mesophase reflecting in the red region of the UV-visible range. The central 8×10 mm^2 area was divided into ten 4×2 mm^2 regions whose optical properties were studied independently by masking the rest of the sample. Negligible changes in the wavelength of maximum reflection are observed. On the other hand, only small variations of the absorbance at the reflection maximum (range 0.277–0.314; average 0.294; standard deviation 0.013) and the half-height bandwidth of the reflection peak (range 43–58; average 49; standard deviation 5) are observed over the 0.8 cm^2 aperture. Figure 7 gives typical reflection spectra recorded at four of these different locations.

CONCLUSION

Careful preparation of HPC solutions yields highly transparent mesophases which can be oriented into planar liquid crystals between two glass plates. The efficiency of uniaxial shear deformation and/or confinement between parallel plates in inducing a planar orientation is observed to diminish when the distance between the glass slides increases. However, a range of thickness exists where the reflectivity is close to maximum while the selectivity is still fairly high, making aqueous HPC mesophases an attractive alternative to low molecular weight cholesteric liquid crystals for optical applications.

References

1. S. D. Jacobs, *J. Fusion Energy*, **5**(1), 65 (1986).

2. S. D. Jacobs, *Handbook of Laser Science and Technology*, M. J. Weber, Ed., CRC Press, Cleveland, OH, 1986, Vol. IV, Part 2.

3. D. G. Gray, *J. Appl. Polym. Sci., Polym. Symp.*, **37**, 179 (1983).

4. R. D. Gilbert and P. A. Patton, *Prog. Polym. Sci.*, **9**, 115 (1983).

5. D. G. Gray, *Faraday Discuss. Chem. Soc.*, **79**, 257 (1985).

6. S. Fortin and G. Charlet, unpublished results.

7. E. D. Klug, *J. Polym. Sci., Polym. Symp.*, **36**, 491 (1971).

8. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).

9. R. B. Meyer, in *Polymer Liquid Crystals*, A. Cifferi, W. R. Krigbaum, and R. B. Meyer, Eds., Academic, New York, 1982.

10. T. Odijk, *Macromolecules*, **20**, 1423 (1987).

11. A. M. Ritcey and D. G. Gray, *Macromolecules*, **21**, 1251 (1988).

12. H. de Vries, *Acta Crystallogr.*, **4**, 219 (1951).

13. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **17**, 1512 (1984).

14. J. L. Fergason, *Mol. Cryst. Liq. Cryst.*, **1**, 293 (1966).

15. T. Asada, in *Polymer Liquid Crystals*, A. Cifferi, W. R. Krigbaum, and R. B. Meyer, Eds., Academic, New York, 1982.

16. V. A. Belyakov and V. D. Dmitrienko, *Sov. Phys. Solid State*, **15**(9), 1811 (1974).

17. E. I. Kats, *Sov. Phys. Jept.*, **32**(5), 1004 (1971).

18. D. W. Berreman and J. Scheffer, *Mol. Cryst. Liq. Cryst.*, **11**, 395 (1970).

19. H. Takezoe, Y. Ouchi, M. Hare, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.*, **22**, 1080 (1983).