



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl19>

Cholesteric Textures of Aqueous Hydroxypropylcellulose Solutions

S. Guido^a

^a Dipartimento di Ingegneria chimica, P.le V. Tecchio, Università
degli Studi di Napoli "Federico II", 80125, Napoli, Italy

Version of record first published: 23 Sep 2006.

To cite this article: S. Guido (1995): Cholesteric Textures of Aqueous Hydroxypropylcellulose
Solutions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals
and Liquid Crystals, 266:1, 111-119

To link to this article: <http://dx.doi.org/10.1080/10587259508033636>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any
substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,
systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation
that the contents will be complete or accurate or up to date. The accuracy of any
instructions, formulae, and drug doses should be independently verified with primary
sources. The publisher shall not be liable for any loss, actions, claims, proceedings,
demand, or costs or damages whatsoever or howsoever caused arising directly or
indirectly in connection with or arising out of the use of this material.

CHOLESTERIC TEXTURES OF AQUEOUS HYDROXYPROPYLCELLULOSE SOLUTIONS

S. GUIDO

Dipartimento di Ingegneria chimica, P.le V. Tecchio, Università degli Studi di Napoli "Federico II", 80125 Napoli, ITALY

Abstract Liquid crystalline textures exhibited by aqueous solutions of hydroxypropylcellulose were investigated by video-enhanced contrast polarized light microscopy. For the first time in this particular system, typical cholesteric structures, such as oily streaks and fingerprint lines, were resolved in close detail by light microscopy. Biphasic separation was observed even in samples of concentration well above the critical value generally accepted for mesophase formation at room temperature (~40% wt). The dependence of the helical pitch on polymer concentration was also studied, by Fourier transforming images of the cholesteric textures.

INTRODUCTION

Solutions of hydroxypropylcellulose (HPC) in water have been widely used as a model system for rheo-optical studies on liquid crystalline behavior in polymers. It is well known that HPC aqueous solutions form lyotropic mesophases displaying properties characteristic of cholesteric liquid crystals, such as the iridescent colors reflected when the sample is illuminated with white light and the peculiar optical rotary dispersion curve¹. A more direct evidence based on microscopic visualization of cholesteric stratifications was obtained by freeze-fracture electron microscopy^{2,3}. So far, the helical pitch for HPC in water has been considered not resolvable in light microscopy by several authors^{4,5}, and the dependence of the pitch on polymer concentration was studied by using indirect methods, such as spectrophotometric and optical rotary dispersion techniques^{4,6}. The results show an inverse third power dependence of the helical pitch on HPC concentration. Good agreement was found with the statistical theory for the ordering of an assembly of helical rodlike molecules developed by Kimura and co-workers⁷.

Images of typical cholesteric structures, including oily streaks and fingerprint lines, have been obtained in light microscopy only for a few solvents, such as acetic acid^{4,6}. For concentrated solutions of HPC in water a mosaic-like pattern of distorted black crosses was reported by several authors as becoming visible in thin samples between crossed polars several hours after loading^{1,4,5,8,9}. Since the texture was not resolved

in finer detail several interpretations have been proposed to explain the molecular arrangement underlying the observed pattern (see Meeten and Navard⁵ for a review).

In this study, by using a video-enhanced contrast (VEC) polarized light microscopy system, we were able to obtain high resolution images of the cholesteric textures exhibited by HPC aqueous solutions. The VEC technique allows dramatic improvement of the quality of microscopic images and has been used to resolve low-contrast features down to the theoretical limit of resolution¹⁰. Our observations are in agreement with the results of Meeten and Navard⁵, who explained the mosaic-like pattern in terms of a polygonal focal conics texture. Due to the improved optics, biphasic separation, in the form of tiny droplets, was observed for concentrations well above the reported critical value for mesophase formation¹¹. The ability of resolving fingerprint lines was exploited to study the dependence of the helical pitch on polymer concentration.

MATERIALS AND METHODS

HPC (Klucel E and EF, with nominal molecular weight of 60,000) was supplied by Aqualon. HPC samples were dried under vacuum at room temperature for three days before use. Aqueous solutions with concentration ranging from 39% to 50% wt were prepared using bi-distilled water and stirred daily by hand for a month prior to use to ensure complete dissolution.

All the observations were performed on a Zeiss microscope (Axioscop FS), both in polarized light and in bright field. Images of the samples were taken by a CCD video camera (Hitachi, model KPM-E1) and sent to an image analysis and processing system (based on a DT2867-LC frame grabber, controlled by Global Lab Image software, both by Data Translations Inc.), which allowed analog contrast enhancement by setting gain and offset of the incoming video signal. Images were further processed to subtract camera mottle and improve contrast via software. For each magnification selected, a calibrated reticule was used to determine scale factors ($\mu\text{m}/\text{image pixel}$), in order to measure the spacing of fingerprint lines, which is equal to half pitch.

The spacing can be measured directly by visual inspection of regions where the lines are well resolved, as reported by several authors^{6, 12}. Given the periodicity of the structure, an alternative, more efficient method used in this work is to perform the Fourier transform of the image and analyze the resulting pattern in the frequency domain. If the fingerprint lines are oriented randomly in the image, the Fourier spectrum shows a bright ring, whose radius is inversely proportional to the cholesteric pitch. The lowest measured value of the spacing was about $0.4 \mu\text{m}$ for the sample EF 50% (at higher concentrations, fingerprint lines could not be resolved). Temperature was controlled by

enclosing the microscope in a plexiglass box with a water-circulating radiator connected to a water bath acting as a cooling/heating element.

Samples for optical observations were prepared by placing a drop of solution between a microscope slide and a cover slip separated by a spacer. To avoid drying, samples were sealed with vacuum grease. Sample thickness ranged from 10 microns to 1 mm.

RESULTS

On standing for several hours at room temperature, all the samples examined showed a grainy morphology when observed in bright field with a low power objective, as shown in Fig. 1a (which was obtained by photographing the monitor, as all the other micrographs reported in this paper). At higher magnification, however, and by means of the VEC optics used here, the grainy texture turned out to be a dispersed phase made up of spherical droplets (see micrograph in Fig. 1b). The average drop diameter was found to diminish with increasing HPC concentration, down to about 10 μm for the more concentrated sample examined (50% wt).

To study the dispersed phase more closely, thin samples (less than 50 μm) were prepared and examined in polarized light. The micrograph reported in Fig. 2 shows the morphology displayed between crossed polars by a 10 μm thick sample (HPC-E 50% wt) at room temperature. In the continuous phase, oily streaks typical of cholesteric systems in a planar configuration¹³ are clearly visible, whereas no structure was apparent inside the droplets, even when the sample was rotated between crossed polars. The latter observation provides evidence that the material inside the droplets is isotropic (it should be noticed that some of the droplets in Fig. 2 don't have a spherical shape, because they happened to be squeezed between the two glass surfaces). By lowering the temperature, the isotropic droplets shrunk in size, until they totally disappeared and fingerprint lines became visible throughout the sample. The temperature transition from biphasic to fully anisotropic material was dependent on concentration.

In order to measure the pitch, images were recorded at a low enough temperature to ensure that all the samples examined were fully anisotropic. An example of image analysis is given in Fig. 3 for a HPC-EF 39% wt solution at 2°C (thickness was about 1 mm): a typical texture observed in the sample between crossed polars is shown in micrograph 3a and the corresponding Fourier spectrum is presented in Fig. 3b. The highest radius of the bright ring in the Fourier transform was used to calculate the helical pitch, as it will be discussed in the next section. In Fig. 4 the helical pitch P raised to the $-1/3$ power vs polymer volume fraction is reported for the HPC-EF solutions investigated

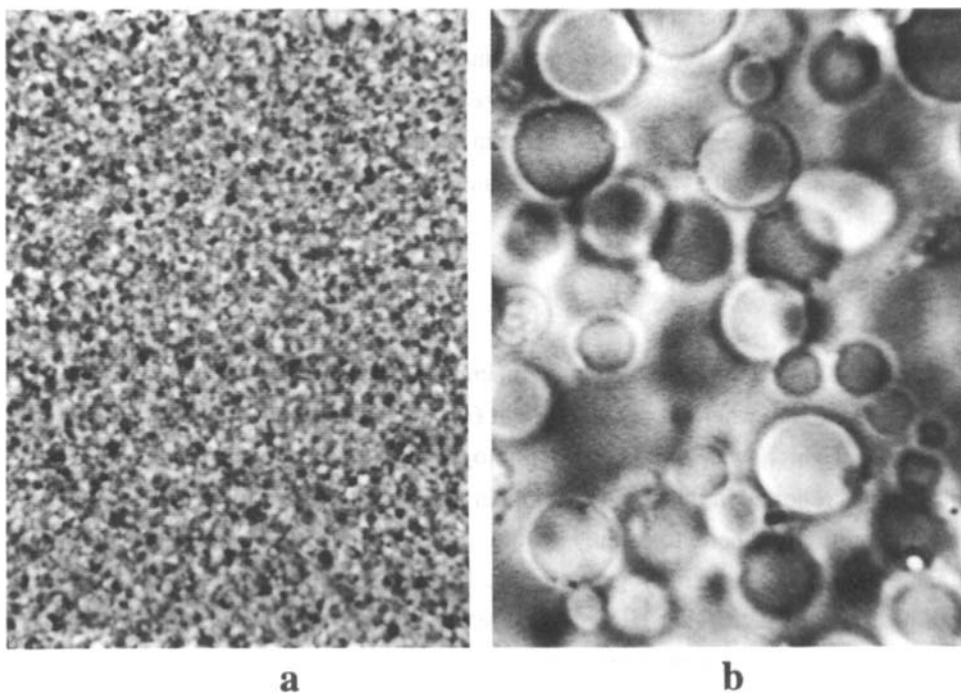


FIGURE 1 a) Grainy morphology displayed at low magnification by a 50% HPC sample at room temperature (200x); same sample observed at higher magnification (2000x).

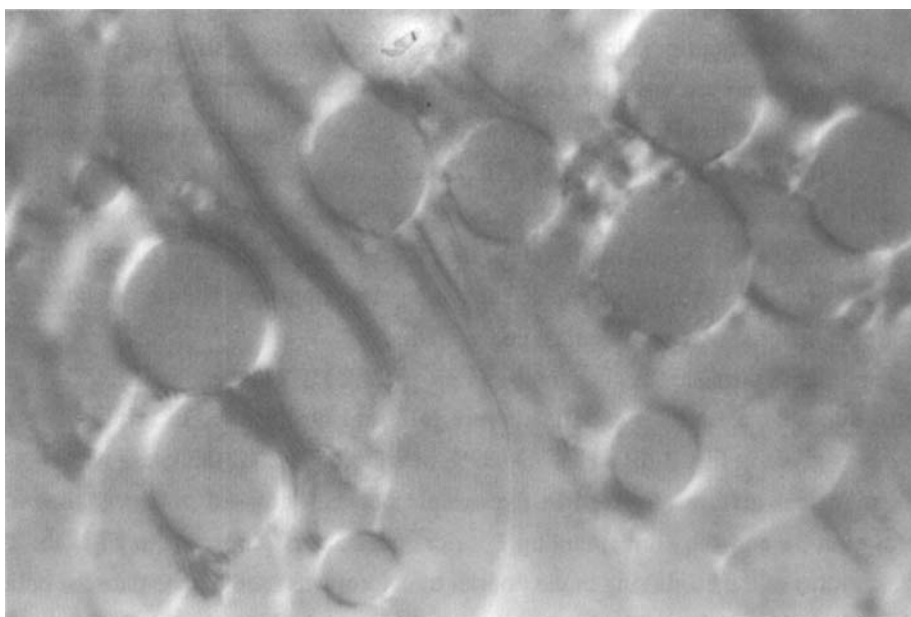


FIGURE 2 Oily streaks and isotropic droplets in a 10 μm thick 50% wt HPC-E sample between crossed polars at room temperature.

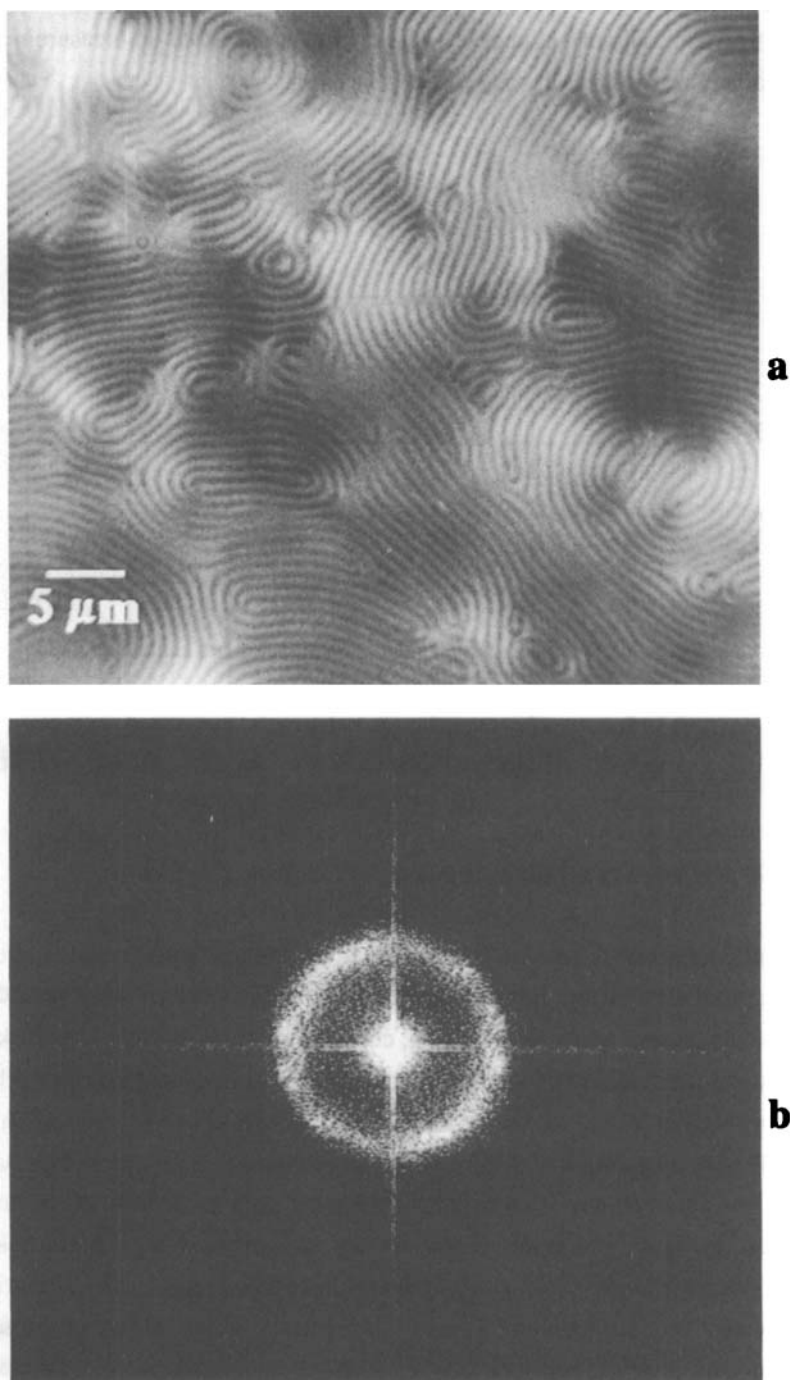


FIGURE 3 a) Morphology observed in a HPC-EF 39% wt sample (thickness 1 mm) at 2°C between crossed polars; b) Fourier transform of the image in a).

(the volume fractions were calculated using a value of 1.20 g/mL for the HPC density and assuming additivity of volumes¹¹). The error bars are based on measurements of the pitch performed on different images at each concentration.

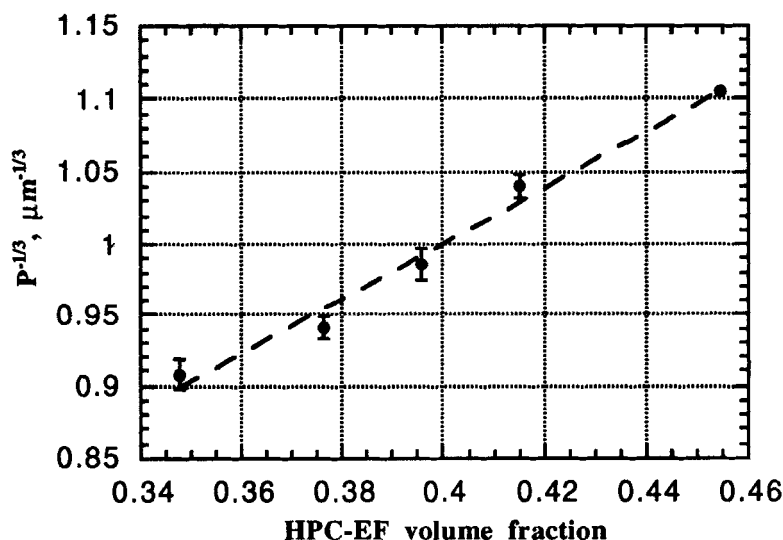


FIGURE 4 Variation in helical pitch P with HPC volume fraction.

In fully anisotropic samples (i.e., at low enough temperatures), and at intermediate thicknesses (between 10 and 100 μm), a peculiar, transient texture was observed between crossed polars several hours after loading, consisting of a mosaic-like network of black lines (in some areas elongated draughtboard patterns, already observed for other liquid crystalline polymer solutions¹⁴, were also noticed). A typical low magnification image of a HPC-EF 50% wt solution at 7°C between crossed polars is shown in Fig. 5a (sample thickness was about 50 μm). It should be mentioned that the periodicity of the grid pattern depends on the depth within the sample. In fact, the image in Fig. 5a was taken about halfway between the glass slides. By focusing close to the glass walls, the grid pattern was still visualized, but with half as many dark lines as in the middle of the sample, in agreement with previous observations^{5, 8, 9}. When specimens were examined at high magnification, fingerprints lines were clearly resolved and were arranged in round spirals surrounding the centers of black crosses, as shown in Fig. 5b for a HPC-EF 48% wt solution at 15°C. After several days, the mosaic-like morphology turned into a planar

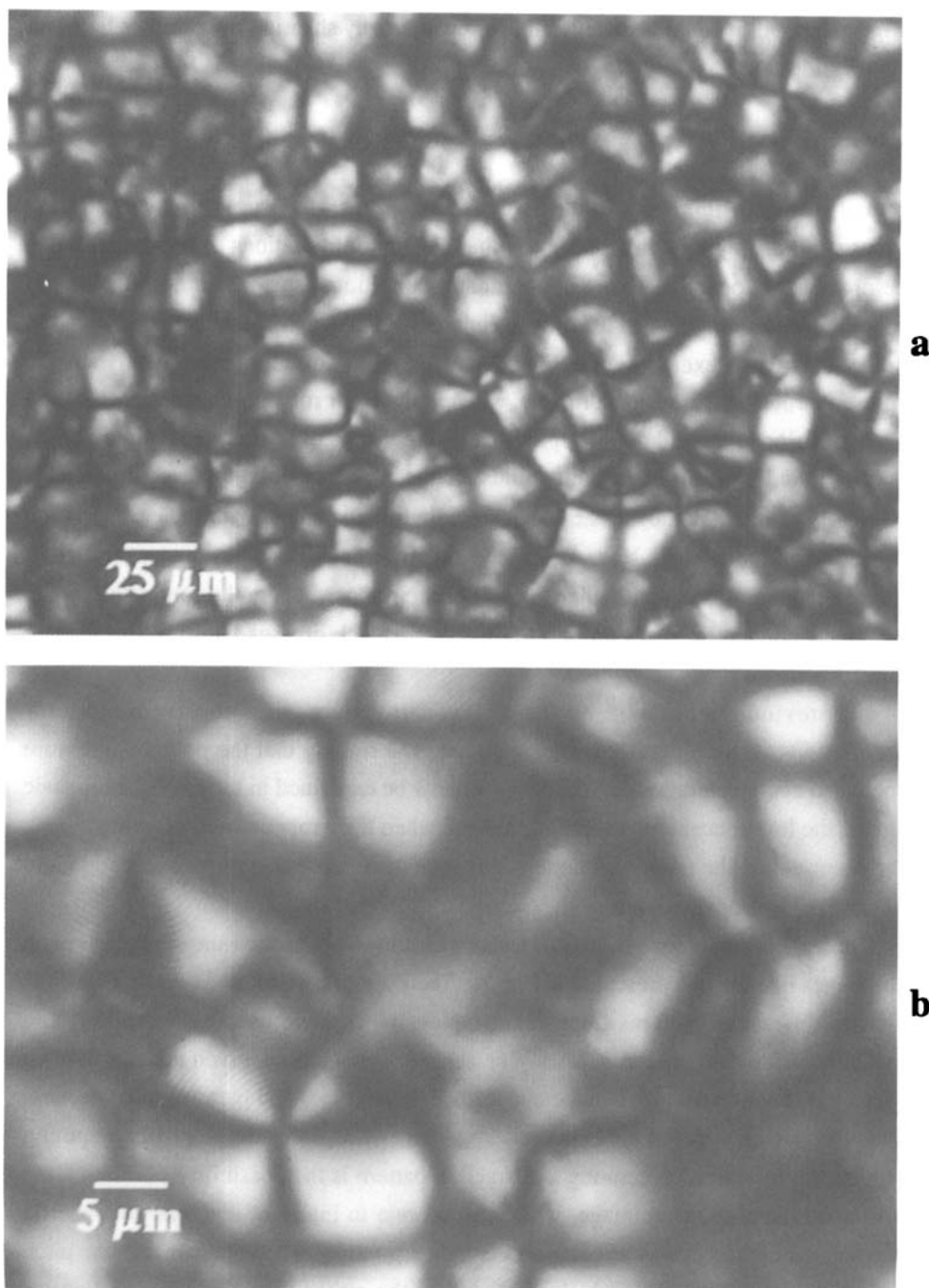


FIGURE 5 a) Mosaic-like pattern in a HPC-EF 50% wt sample at 7°C (thickness about 50 μm) as observed at low magnification between crossed polars; b) higher magnification image showing the round spirals starting from the centers of the black crosses of the polygonal texture in a HPC-EF 48% wt sample at 15°C. Polarizer axis is horizontal.

configuration, but it could be recovered in a few hours by shearing the samples between the glass slides.

DISCUSSION

The main result of this work is the visualization of the cholesteric textures of HPC aqueous solutions by light microscopy. Either planar configurations or polygonal fields were observed depending on the experimental conditions, such as sample thickness, temperature, concentration and loading procedure. A high density of defects was found in both the textures, as exemplified in Figs. 2 and 3a; in the former numerous oily streaks are present around the isotropic droplets, while in the latter rotation-dislocations ($-\pi$ and $+\pi$), edge-dislocations and double-spirals can be recognized. In samples with thickness between 10 and 100 μm , the round spirals characteristic of polygonal focal conics¹² were clearly resolved in the mosaic-like texture, in full agreement with the interpretation proposed by Meeten and Navard⁵, based on low magnification images and light scattering patterns (see in particular Fig. 1B of their paper, where the round spirals are sketched as concentric rings around the distorted black crosses forming the mosaic texture).

In previous reports^{5,8,9}, the polygonal texture was observed only for concentrations above 50% at room temperature. The finding that the polygonal texture formed also at concentrations below 50% can now be explained in terms of the biphasic nature of the less concentrated samples. Indeed, when the temperature was brought back to the room value, the polygonal texture was seen to collapse due to the nucleation and growth of the isotropic droplets.

The application of image analysis techniques allows one to measure the helical pitch from images like the one presented in Fig. 3a. The Fourier transform shown in Fig. 3b is similar to diffraction patterns from thin samples, which were used by Werbowyj and Gray⁶ to measure the cholesteric pitch. The analogy is not casual, given the equivalence between a diffraction pattern, like the one formed in the back focal plane of the objective, and the Fourier spectrum of the corresponding image. The main advantage of computing the transform instead of generating a diffraction pattern is the possibility of relating the spectrum to the real-space image, which allows one to interpret and analyze specific features in a more direct way as compared to light scattering. The uncertainty in the pitch value at each concentration, which is related to the rather broad ring in the Fourier transform, is due to deviations of the cholesteric axis from the horizontal plane¹⁴. The pitch was therefore calculated for the highest value of the ring radius, which corresponds to the smallest spacing of the fingerprint lines in the real-space image. The inverse third

power dependence of the helical pitch on HPC volume concentration is in agreement with previous results⁶.

The ability of resolving structural defects in light microscopy is in principle a powerful tool to elucidate some aspects of the complex flow behavior of liquid crystalline polymers. Much attention has been recently devoted to the role of defects in the rheology of these materials¹⁵. In particular, the occurrence of a shear thinning viscosity at low shear rates (Region I of the viscosity curve, according to the terminology introduced by Onogi and Asada¹⁶ in 1980) has been interpreted as the result of an "anchoring effect" of defects on tumbling liquid crystalline polymers¹⁵.

Another result of this work is the observation of a biphasic separation at room temperature for concentrations that were considered to be well above the critical value for mesophase formation. The high density of defects found in this study is likely to be related to the presence of isotropic droplets, since the droplets can act as walls for the growth of cholesteric structures and distort the surrounding texture. A more detailed investigation of the phase behavior of HPC aqueous solutions is in progress and will be presented elsewhere.

ACKNOWLEDGEMENTS

Financial support from the European Economic Community under the contract BREU-CT92-0213 in cooperation with Profs. G. Marrucci and N. Grizzuti is gratefully acknowledged. The author wishes to thank Dr. F. Greco for critical reading of the manuscript.

REFERENCES

1. R. S. Werbowyj and D. G. Gray, Mol. Cryst. Liq. Cryst., **34**, 97 (1976).
2. R. J. Spontak, M. A. El-Nokaly, R. G. Bartolo, and J. L. Burns, in Polymer Solutions, Blends, and Interfaces, edited by I. Noda and D. N. Rubingh (Elsevier, Amsterdam, 1992), pp. 273-298.
3. F. Livolant and Y. Bouligand, Mol. Cryst. Liq. Cryst., **166**, 91 (1989).
4. F. Fried and P. Sixou, J. Polym. Sci., Polym. Chem. Ed., **22**, 239 (1984).
5. G. H. Meeten and P. Navard, J. Polym. Sci., Polym. Phys. Ed., **26**, 413 (1988).
6. R. S. Werbowyj and D. G. Gray, Macromolecules, **17**, 1512 (1984).
7. H. Kimura, M. Hosino, and H. Nakano, J. Phys. Soc. Jpn., **51**, 1584 (1982).
8. K. Shimamura, Makromol. Chem., Rapid Commun., **4**, 107 (1983).
9. A. M. Donald, C. Viney, and P. Ritter, Liq. Cryst., **1**, 287 (1986).
10. D. G. Weiss and W. Maile, in Electronic Light Microscopy, edited by D. Shotton (Wiley-Liss, New York, 1993), Ch. 5, pp. 105-140.
11. R. S. Werbowyj and D. G. Gray, Macromolecules, **13**, 69 (1980).
12. Y. Bouligand, J. Phys. (Paris), **33**, 715 (1972).
13. Y. Bouligand, J. Phys. (Paris), **34**, 1011 (1973).
14. F. Livolant, J. Phys. (Paris), **47**, 1605 (1986).
15. G. Marrucci and F. Greco, Adv. Chem. Phys., **58**, 331 (1993).
16. S. Onogi and T. Asada, in Rheology, edited by G. Astarita, G. Marrucci, and L. Nicolais (Plenum Press, New York, 1980), vol. 1, pp. 127-147.