Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Hydrostatic pressure effects on polymer cholesteric liquid-crystalline structure. I. Equilibrium structure of hydroxypropyl cellulose aqueous solution

Yoshihiko Onogi[a][b]; Tsuneo Okubo[a]
[a] Department of Polymer Chemistry, Kyoto University, Kyoto, Japan [b] Department of Home Economics, Mukogawa Women's University, Nishinomiya, Japan

To cite this Article Onogi, Yoshihiko and Okubo, Tsuneo(1992) 'Hydrostatic pressure effects on polymer cholesteric liquid-crystalline structure. I. Equilibrium structure of hydroxypropyl cellulose aqueous solution', Liquid Crystals, 12: 5, 815 — 820

To link to this Article: DOI: 10.1080/02678299208029124

URL: http://dx.doi.org/10.1080/02678299208029124

LIQUID CRYSTALS, 1992, VOL. 12, NO. 5, 815–820

Hydrostatic pressure effects on polymer cholesteric liquid-crystalline structure

I. Equilibrium structure of hydroxypropyl cellulose aqueous solution

by YOSHIHIKO ONOGI*† and TSUNEO OKUBO

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan

(Received 14 February 1992; accepted 29 April 1992)

The effect of pressure on the polymer cholesteric liquid-crystalline structure of hydroxypropyl cellulose aqueous solutions was studied using reflection spectra measurements. Pressures applied to the polymer liquid crystals ranged from 1 to 2000 bar. The equilibrium reflection spectrum of the cholesteric structure shifted to longer wavelengths, showing that the cholesteric pitch of the liquid-crystalline structure increases as the applied pressure increases. At pressures higher than 200 bar the maximum wavelength of reflection shifted linearly with the increase in applied pressure. At lower pressures, the cholesteric structure was influenced by the surface plane of the quartz window.

1. Introduction

The structures of polymer liquid crystals have been studied intensively over the past decade with an interest in the development of new applications [1–3]. Polymer liquid crystals possessing a cholesteric nature are very interesting because the ordered orientation is constructed from much longer rigid chains than those of low molar mass liquid-crystalline molecules. The cholesteric structure is very sensitive to environmental conditions because of the relative weakness of the chiral interaction. The cholesteric pitch changes drastically with temperature [4]. In the case of lyotropic liquid crystals, the cholesteric pitch is also greatly affected by the concentration of polymer in the system and the properties of the solvents [5–8]. Consequently, cholesteric liquid crystals can change even the sign of their cholesteric sense under some experimental conditions [5, 9, 10]. Their liquid-crystalline structure is easily deformed by mechanical force, resulting in colour changes due to selective reflection of visible light from layered cholesteric planes [11, 12]. With these characteristics in mind, it is understandable that the cholesteric liquid crystal changes its cholesteric pitch due to variation of the chiral interaction caused by applied static pressure. However, it is very difficult to analyse experimentally the pressure effect on the cholesteric structure of liquid crystals. The pressure dependency of the helical structure of cholesteric liquid crystals was reported by Pollmann and Stegemeyer [13] for mixtures of small molecules, such as cholesterol derivatives. However, further study is needed of the pressure effect on polymer liquid crystals. Here we describe the static pressure effect on polymer cholesteric liquid crystals and compare the results with those of low molar mass liquid crystals.

---

* Author for correspondence.

† Present address: Department of Home Economics, Mukogawa Women's University, Nishinomiya 663, Japan.

2. Experimental

A lyotropic liquid-crystalline solution of hydroxypropyl cellulose (HPC) was chosen for the analysis of the pressure effect on the cholesteric structure of polymer liquid crystals. HPC dissolves in various solvents and forms cholesteric liquid crystals within certain concentration ranges [14–16]. Water was used as the solvent because the aqueous liquid-crystalline solutions selectively reflect visible light. HPC was purchased from Tokyo Kasei Co., Ltd., and was used without further purification. The molecular weight measured by viscometry was approximately 90 000 [17]. The degree of substitution of hydroxypropyl group per glucose unit was found by NMR spectroscopy to be about 4 [18]. As the concentration of HPC in the liquid-crystalline state was very high, it took more than three months to obtain the homogeneous liquid-crystalline solution required for spectroscopic measurements. The precise concentration of the liquid-crystalline solutions were determined from the average refractive index of the solution at 20·0°C. Liquid-crystalline solutions of 63 wt% and 67 wt% were used for this study. These solutions were completely monophasic and liquid-crystalline at this temperature.

The cholesteric pitch of the cholesteric liquid-crystalline structure can be calculated from the maximum wavelength of the selective reflection peak using the refractive index of the system [14, 19]. The spectra of the selective reflection were measured with a multichannel photodetector (MCPD, Model 110B, Union Engineering, Hirakata, Japan [20]). A Y-type cable of optical fibre was used to record the reflection spectra at the scattering angle of 180° and the instrument was operated by a microcomputer (MC800, Union Engineering). The apparent absorption spectra caused by the selective reflection were also measured using a Shimadzu double beam spectrophotometer (UV200S), for comparison with the reflection light wavelength of the same solution measured by the multichannel photodetector MCPD.

The liquid-crystalline solution was placed in a high pressure cell with a temperature-controlled jacket. The high pressure cell of stainless steel had a sample volume of 4 ml. The light intensity was monitored through quartz optical windows. In order to prevent leakage of the sample solution from the pressure vessel, rubber and teflon O-rings and back-up rings were used. The cell pressure was generated through an intensifier by means of an oil hand pump (1–5 bar). The intensity of the cell pressure was calculated from the known ratio of the areas of the pistons of the intensifier (8·8 ± 0·3) and the measured pressure in the hand pump. Throughout the experiment, the pressure was kept constant with no detectable leakage except during the initial period of the setting. The details of the high pressure cell have been described in other papers [21, 22].

3. Results and discussion

The liquid-crystalline solution of 63 wt% or 67 wt% was poured into the high pressure cell which was controlled at 25·0°C. It was allowed to stand for at least 15 h before measurement to allow relaxation of the flow orientation of the poured sample solution. It is very difficult to completely eliminate this orientation effect from the polymer liquid crystals. After relaxation for 15 h the reflection spectrum from the sample did not change any more. When the sample solution was suddenly subjected to a static pressure, the reflection spectrum from the sample changed rapidly toward the equilibrium profile. Therefore, in order to obtain the equilibrium spectrum, the reflection spectra were taken at least three minutes after the pressure application. The

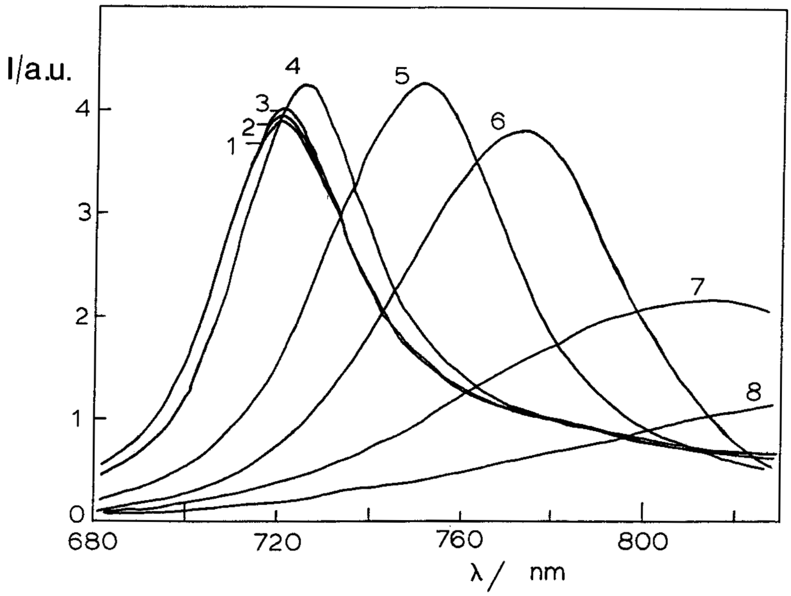

Figure 1. Pressure effect on the reflection spectrum of the 63 wt% aqueous HPC liquid-crystalline solution. Curve 1: 1 bar; 2: 50 bar; 3: 100 bar; 4: 200 bar; 5: 400 bar; 6: 600 bar; 7: 1000 bar; 8: 1500 bar.

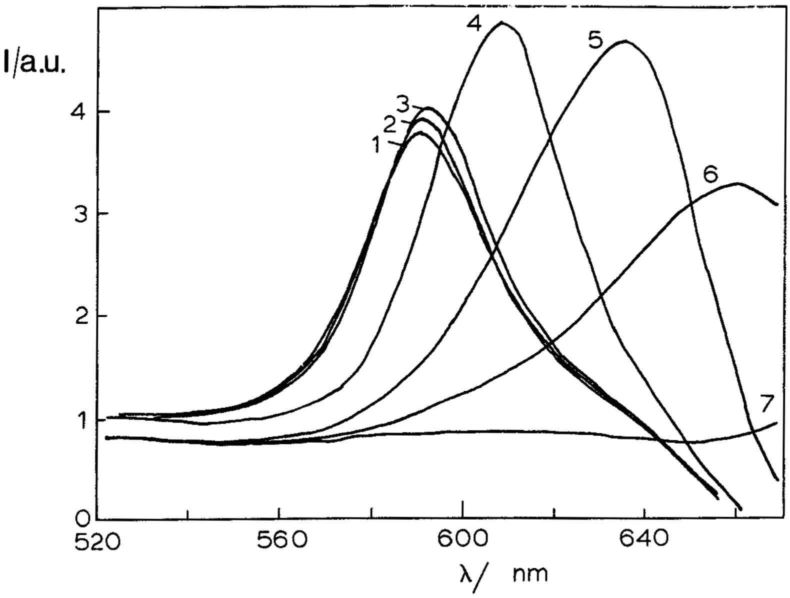

Figure 2. Pressure effect on the reflection spectrum of the 67 wt% aqueous HPC liquid-crystalline solution. Curve 1: 1 bar; 2: 100 bar; 3: 200 bar; 4: 400 bar; 5: 700 bar; 6: 1000 bar; 7: 1500 bar.

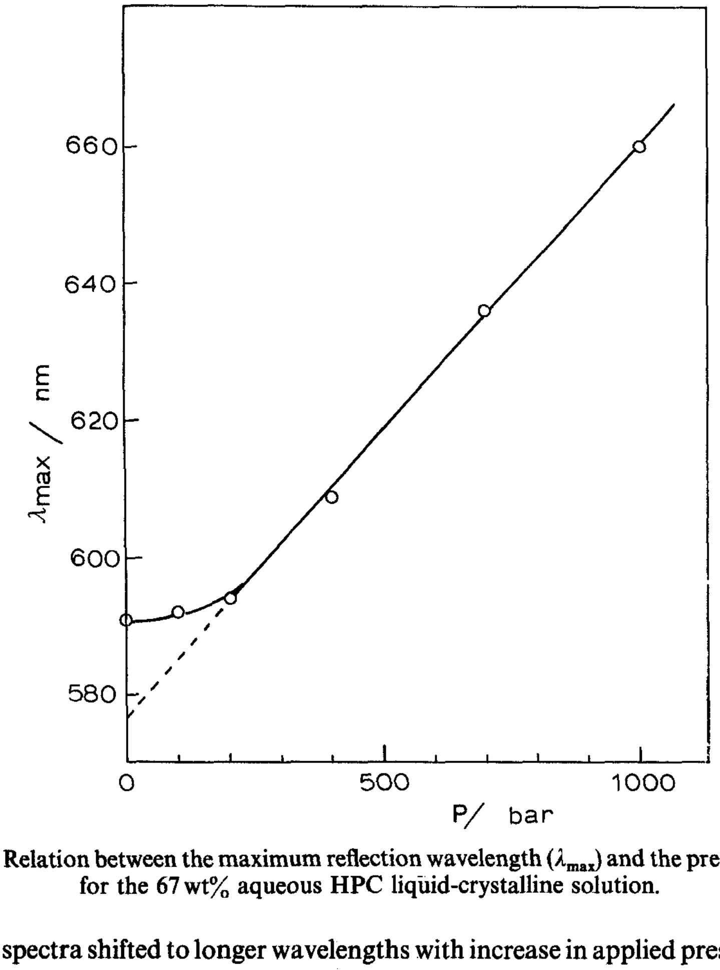

Figure 3. Relation between the maximum reflection wavelength (λ_{max}) and the pressure applied for the 67 wt% aqueous HPC liquid-crystalline solution.

reflection spectra shifted to longer wavelengths with increase in applied pressure. At the highest pressure (2000 bar), no selective reflection from the cholesteric structure was detected by our apparatus because of its low sensitivity for detecting light longer than 1000 nm in wavelength. The reflection spectra at several applied pressures are shown in figure 1 for the 63 wt% solution and the same result is shown for the solution of 67 wt% in figure 2. As no reflection was observed at 2000 bar, the reflection spectra were obtained by subtracting the reflection spectrum at 2000 bar from each, in order to correct for the background scattering. The red-shift of the reflection spectrum was observed for polymer liquid crystals on application of static pressure. The same observation was reported by Pollmann and Stegemeyer [13] for low molar mass liquid crystals (mixtures of cholesteroyloleylcarbonate and cholesterylchloride). The wavelength of the maximum reflection (λ_{max}) was obtained from the results shown in figures 1 and 2 and was plotted against the pressure (P) in figure 3 for the 67 wt% solution. When the applied pressure was greater than 200 bar, a linear relationship between λ_{max} and P was observed within the pressure range of this experiment. The deviation from this linear relation for lower applied pressures (1 to 200 bar) can be explained by the interaction effect of the quartz surface to which the cholesteric planes orient (wall effect).

Pollmann and Stegemeyer [13] concluded from their experimental results that there is a limiting pressure, P, at which the cholesteric pitch of the liquid crystal

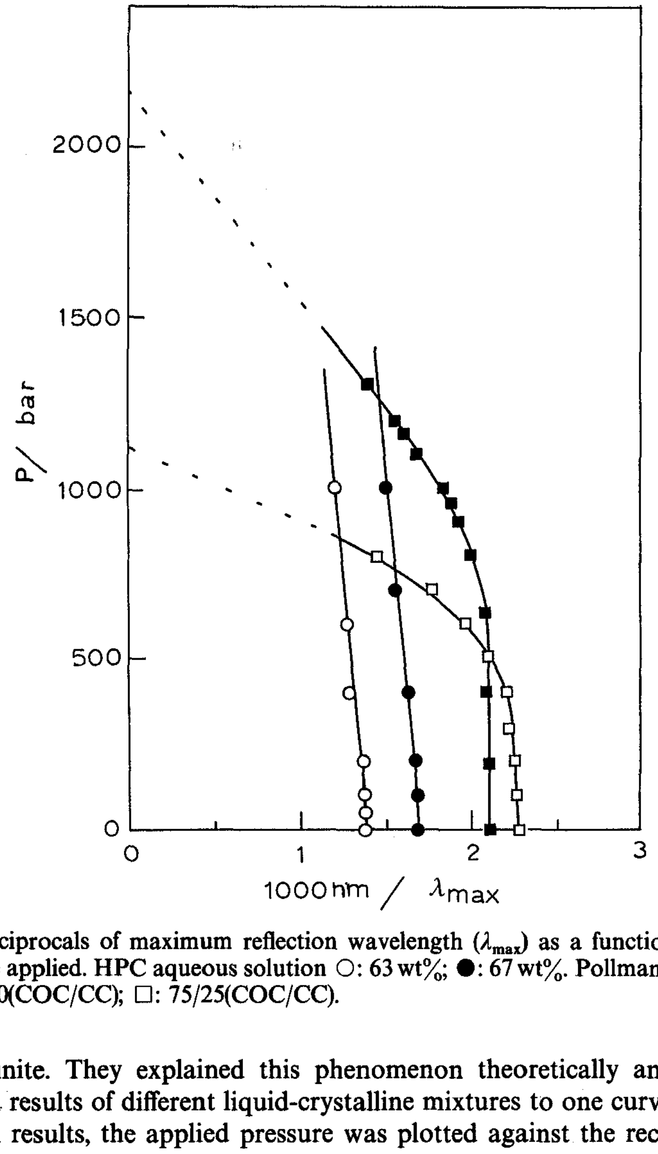

Figure 4. Reciprocals of maximum reflection wavelength (λ_{max}) as a function of the static pressure applied. HPC aqueous solution ○: 63 wt%; ●: 67 wt%. Pollmann's results [13] ■: 80/20(COC/CC); □: 75/25(COC/CC).

becomes infinite. They explained this phenomenon theoretically and fitted their experimental results of different liquid-crystalline mixtures to one curve. Using their experimental results, the applied pressure was plotted against the reciprocal of the wavelength of maximum reflection as shown in figure 4. Our results for polymer cholesteric liquid crystals were also plotted in the figure. As shown by the dotted lines, low molar mass liquid crystals seem to have some limiting pressure at which the cholesteric pitch becomes infinite. However, it is very difficult to conclude that there is a limiting pressure for polymer liquid crystals, which require much greater pressure to orient the rigid long chain nematically against the chiral force. As the cholesteric liquid crystals are very sensitive to pressure, they can be used as pressure detectors. According to our data, polymer liquid crystals would be suitable for detecting pressure higher than 200 bar. On the other hand, low molar mass cholesteric liquid crystals are very sensitive to lower pressures.

As shown in figures 1 and 2, the intensity of selective reflection increases with increasing applied pressure at pressures less than 400 bar. At higher levels, the reflection intensity decreased as the pressure increased, which can be explained by the dependence of reflection intensity on wavelength reported by Rayleigh [23]. This increase in the reflection intensity can be explained by the higher ordering of the cholesteric structure caused by static pressure in the cholesteric domains. This means that the polymer chain extends more than it does at atmospheric pressure. When the ordering of the orientation becomes higher, the reflection spectrum is expected to be sharper. As the reflection intensity was considerably weak, it was very difficult to precisely establish the baseline. Consequently, we could not determine whether the reflection spectrum became sharper as the applied pressure increased.

The pressure effect on HPC cholesteric structure is shown in figures 1 and 2. The results were measured at least 3 min after pressure was applied in order to obtain the reflection spectrum at the equilibrium state. When a sudden static pressure was applied to polymer liquid crystals, a much longer time elapsed, compared to low molar mass liquid crystals, before the equilibrium cholesteric structure was formed. Further study is continuing on these polymer liquid crystals.

4. Conclusion

When static pressure was applied to a polymer cholesteric liquid-crystalline sample, the reflection spectrum due to the cholesteric structure shifted toward a longer wavelength as the pressure increased. This means that the cholesteric pitch became larger as the applied pressure increased. Such behaviour is similar to that of low molar mass cholesteric liquid crystals reported by Pollmann and Stegemeyer [13]. However, no limiting pressure was detected in the case of polymer liquid-crystalline solutions. These results suggest that much higher static pressure is needed to overcome the chiral force of polymer cholesteric liquid crystals. If polymer cholesteric liquid crystals are used as a pressure sensor, they would be suitable for higher pressures, while low molar mass liquid crystals would be very sensitive to lower pressures.

References

[1] Ciferri, A., Krigbaum, W. R., and Meyer, R. B., 1982, *Polymer Liquid Crystals* (Academic Press).
[2] Blumstein, A., 1983, *Polymer Liquid Crystals* (Plenum).
[3] Chapoy, L. L., 1985, *Recent Advances in Liquid Crystalline Polymers* (Elsevier).
[4] Fergason, J. L., 1966, *Molec. Crystals liq. Crystals*, **1**, 293.
[5] Robinson, C., 1961, *Tetrahedron*, **13**, 219.
[6] Werbowyj, R. S., and Gray, D. G., 1976, *Molec. Crystals liq. Crystals*, **34**, 97.
[7] Gray, D. G., 1983, *J. appl. Polym. Sci. Appl. Polym Symp.*, **37**, 179.
[8] Fried, L., and Sixou, P., 1984, *J. polym. Sci. Polym. Chem. Ed.*, **22**, 239.
[9] Toriumi, H., Yahagi, K., and Uematsu, I., 1983, *Molec. Crystals liq. Crystals*, **94**, 264.
[10] Toriumi, H., Minakuchi, S., Uematsu, Y., and Uematsu, I., 1980, *Polym. J.*, **12**, 431.
[11] Pochan, J. M., and Marsh, D. G., 1972, *J. chem. Phys.*, **57**, 1193.
[12] Asada, T., Toda, K., and Onogi, S., 1981, *Molec. Crystals liq. Crystals*, **68**, 231.
[13] Pollmann, P., and Stegemeyer, H., 1973, *Chem. Phys. Lett.*, **20**, 87.
[14] Onogi, Y., White, J. L., and Fellers, J. F., 1980, *J. polym. Sci. Polym. Phys. Ed.*, **18**, 663.
[15] Gray, D. G., 1983, *J. appl. Polym. Sci. Appl. Polym. Symp.*, **37**, 179.
[16] Fried, F., Gilli, J. M., and Sixou, P., 1983, *Molec. Crystals liq. Crystals*, **98**, 209.
[17] Wirick, M. G., and Wadlman, M. H., 1970, *J. app. Polym. Sci.*, **14**, 579.
[18] Ho, F. F.-L., Kohler, R. R., and Ward, G. A., 1972, *Analyt. Chem.*, **44**, 178.
[19] Bhadani, S. N., and Gray, D. G., 1983, *Molec. Crystals liq. Crystals*, **99**, 29.
[20] Okubo, T., 1987, *J. chem. Soc. Faraday Trans. I*, **83**, 2487.
[21] Ise, N., Maruno, T., and Okubo, T., 1980, *Proc. R. Soc.* A, **370**, 485.
[22] Okubo, T., and Enokida, A., 1983, *J. chem. Soc. Faraday Trans. I*, **79**, 470.
[23] Lord Rayleigh, 1871, *Lond. Edinb. Dubl. Phil. Mag.*, **4**, 41, 107, 224, 447.