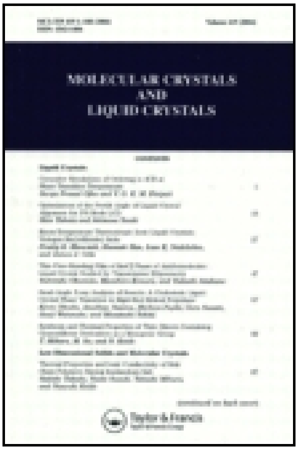

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The Cholesteric Pitch in Lyotropic Solutions of a Semi-Rigid Macromolecule: Hydroxypropyl-Cellulose

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The Cholesteric Pitch in Lyotropic Solutions of a Semi-Rigid Macromolecule: Hydroxypropyl-Cellulose[†]

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The cholesteric pitch P of lyotropic mesophases of hydroxypropyl-cellulose are determined from optical measurements, i.e., angular dependence of the scattered light intensity and transmission spectra. The observed results are explained with help of Pincus' theory for cholesteric liquid crystals. The variations of the twisting power with physical parameters such as polymer concentration C, nature of solvent, molecular weight, and ageing are investigated. The power law $P = P_0C^{-\alpha}$ is well satisfied for all polymer solvent combinations. It is proposed that the solvent could influence the cholesteric pitch not only through its intrinsic properties, but also through modifications of the macromolecular characteristics themselves.

INTRODUCTION

It is now well established[1] that highly concentrated solutions of cellulosic derivatives in a wide range of organic solvents give mesomorphic phases. The phase diagrams have been measured[2–4] and are shown in the first figure which illustrates the very broad range of critical concentrations for appearance of the mesophase.[‡] In contrast, little is known concerning the long

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[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

[‡] In this paper, the concentrations are given in weight ratios i.e.: polymer weight/solution weight × 100.

range orientational order. Nevertheless, the cholesteric character of the concentrated phases is shown by the iridescent colors, the circular dichroism peak, and the optical rotatory dispersion spectra;[5] also the degree of orientational order has been probed by N. M. R. measurements (nuclear splitting, chemical shift).[6]

The aim of this paper is the measurement of the cholesteric pitch and an investigation of the physical parameters which could influence the structure of the liquid-crystalline solution of hydroxypropyl-cellulose (HPC). Indeed, although the factors which govern the appearance of the mesophases are rather well investigated, both experimentally and theoretically,[7] the question of the nature (forces) and the characteristic physical parameters of the cholesteric phase are still a point of speculation. We measure here the variation of the helical pitch with various parameters such as the polymer concentration, the macromolecular weight, and the nature of the solvent using optical methods, i.e., the angular dependence of the scattered light intensity and the visible and IR transmission spectra.

EXPERIMENTAL

Hydroxypropyl-cellulose of molecular weight 100000, 300000, and 1000000 came from Aldrich laboratories, and HPC 60000 is a Klucel product. All solvents used are of spectroscopic grade—except the doubly distillated water—and are filtered prior to use. Concentrated solutions are prepared in cylindrical diffusion cells (ϕ = 20 mm) and centrifuged. All samples are matured for at least a few days or even for few weeks to allow a uniform organization of the phases.

Light scattering experiments are performed with the aid of a Sofica photogonio-diffusiometer modified to allow the use of a polarized incident laser beam (He-Ne laser: $\lambda_0 = 6328$ Å) with a scattering angle limited in the domain $0 - 110°$. The effects of cell form are diminished by immersing the cell in a bath of suitable refractive index (benzene).[†]

The optical transmission spectra are recorded with an automatic dual beam spectrophotometer (Cary 17) working with unpolarized incident light in the wavelength range 400–2500 nm. The solutions are deposited between flat glasses, separated by a 0.5 mm teflon spacer. Then they are to stand for at least 24 h to allow the relaxation of internal constraints.

[†] We wish to thank Dr. Bernango for having permitted us to perform these measurements with his apparatus.

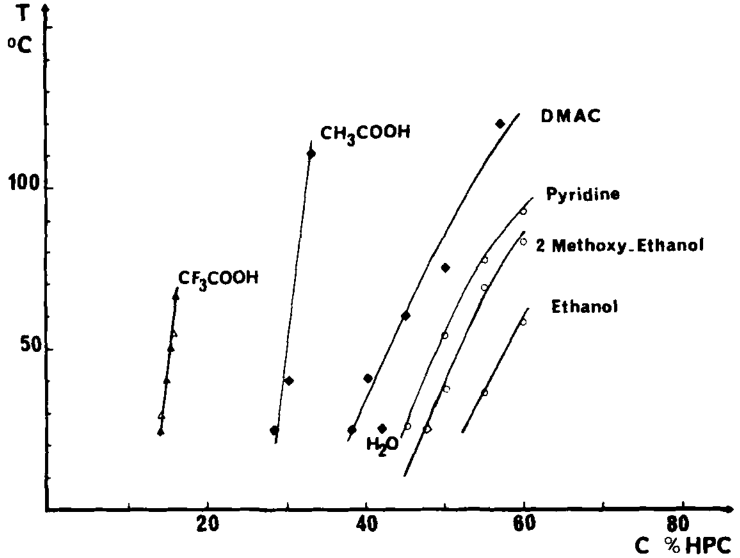

FIGURE 1 Phase diagrams for mesomorphic solutions of hydroxypropyl-cellulose: Curves ○ ○ ○ from ref (2) with HPC—M_w = 87000, $DS \simeq 3.5$ from Tokyo Kasei, Kogyo Co.; Curves ◆ ◆ from ref (3) with HPC Klucel L—M_w = 100000, $DS \simeq 3$ from Hercules. (◈:H_2O, ◇:Ethanol); Curves △ △ from ref (4) with HPC Aldrich M_w = 100000. The concentrations which were initially given in gm/ml and ml/ml have been converted to gm/gm %.

RESULTS AND DISCUSSION

Light scattering and transmission spectra

Figures 2 and 3 show the dependance upon polymer weight concentration of the spectra for static light scattering and transmitted IR and visible light at room temperature. The peaks that appear in both figures display the cholesteric character of the mesophase and arise from Bragg scattering due to selective reflections of light induced by the macromolecular suprastructure. The matching condition for the first order Bragg diffraction by the pseudo-planes of the medium of mean refractive index $\bar{n}$ is simply:

$$P \sin \frac{\theta_m}{2} = \frac{\lambda_0}{\bar{n}} \qquad (1)$$

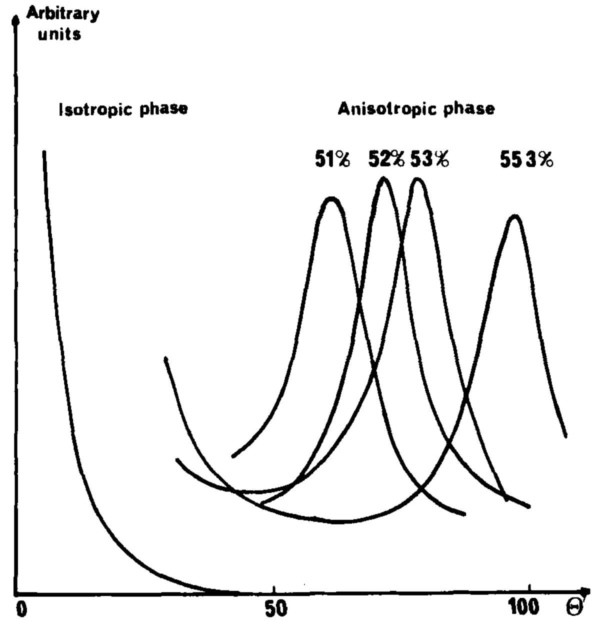

FIGURE 2 Light scattering spectra of aqueous solutions of HPC (M_w = 100000) at various concentrations in the anisotropic and isotropic phases.

where P is the pitch of the cholesteric structure, θ_m is the scattering angle, and λ_0 the light wavelength.

The existence of such a Bragg peak in the depolarized light scattering spectrum of cholesteric liquid crystals was found by Pincus[8] who, following de Gennes' work[9] on nematic crystals, relates the differential cross section for scattering light to the thermal fluctuations in the orientation of the directors of the molecules, using the continuous theory of elasticity

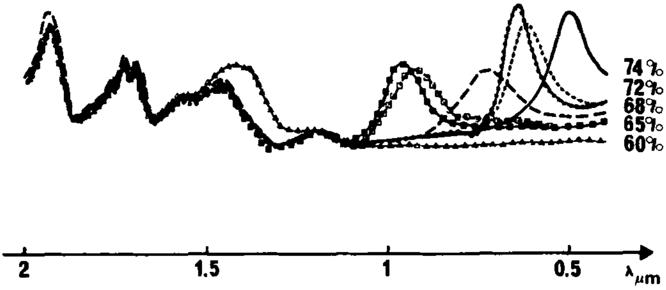

FIGURE 3 Absorption spectra of mesomorphic solutions of HPC (M_w = 100000) in ethanol. The dotted curves correspond to solutions after various delay times between preparation and study: — 8 hours, ---- 48 hours and —— 7 days.

developed by Oseen[10] and Franck.[11] In the special case when the fluctuations propagate along the cholesteric axis: $\vec{k} // \vec{q}_0$ the fluctuating modes are separated into two highly damped modes: a transverse mode described the twist elastic modulus k_{22} (phase fluctuations) and a longitudinal model related to the splay-bend modes of curvature with constants k_{11} and k_{33}. Then the total scattering cross-section is given by:

$$\frac{d\sigma}{d\Omega} = \left(\frac{\pi\varepsilon_a}{2\lambda^2}\right)^2 \frac{k_B T}{k_{22}} \left\{ \sin^2\frac{\theta}{2} \, \frac{k_0^2 \sin(\theta/2) + q_0^2}{(k_0^2 \sin^2(\theta/2) - q_0^2)^2} + \frac{1}{2}\cos^2\frac{\theta}{2} \left[\frac{K_{22}}{k_{11}(2k_0 \sin(\theta/2) + q_0)^2 + k_{33} q_0^2} + \frac{K_{22}}{k_{11}(2k_0 \sin(\theta/2) - q_0)^2 + k_{33} q_0^2} \right] \right\} \qquad (2)$$

where k_0 is the incident wave vector

$$k_0 = \frac{2\pi n}{\lambda_0}$$

θ is the scattering angle, and q_0 is related to the helical pitch:

$$q_0 = \frac{2\pi}{P}$$

In addition to the infinite scattering due to the transverse fluctuations at a wave vector satisfying the Bragg relation, the preceding equation displays the existence of a second scattering peak of finite intensity related to the longitudinal modes, at twice the Bragg wave vector. To our knowledge, there is no experimental evidence of the second peak. In Figure 4, we plot a light scattering spectrum, with reasonable, but speculative values for the elastic constants which gives an observable longitudinal peak. Because the rather low cholesteric pitch is of the same order of magnitude or even smaller than the wavelength, HPC solutions could be rather favorable for testing the Pincus theory. We have not observed the longitudinal peak with our experimental conditions, i.e., without any particular alignment of the medium relative to the diffusion vector required for the decoupling of the modes. The problem of anchoring the polymeric molecules to the glass surface to obtain uniformly oriented samples must be solved in order to investigate this problem further.

Nevertheless, even without macroscopic alignment of the twist axes relative to the wave vector, the transverse peaks are easily distinguishable (Figure 2). The helical pitch could be deduced from the maximum peak positions. On the same graph, we report the pattern observed for the isotropic phase where no diffraction peak appears. In both phases, isotropic

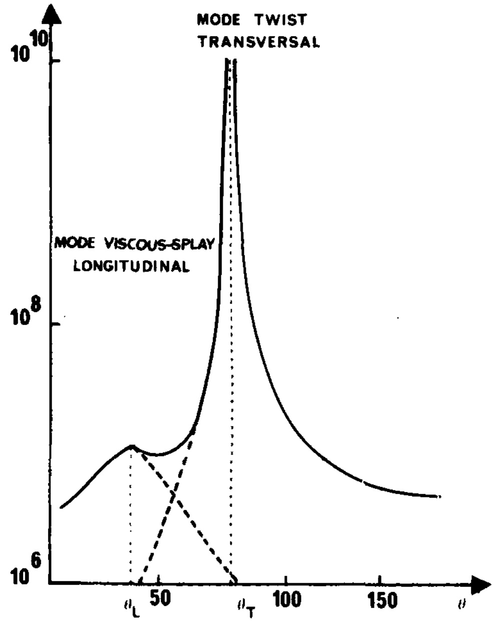

FIGURE 4 Theoretical spectrum of the intensity of the light scattered by a cholesteric medium; an application of Pincus' theory with the following parameters $\lambda_0 = 6328$ Å, $\bar{n}P = 9500$ Å and $k_o 11 = 5 \cdot 10^{-7}$, $k_{22} = 10^{-6}$, $k_{33} = 10^{-7}$ dyne.

and anisotropic, a strong diffusion is observed in the forward direction, i.e., for very weak scattering vectors. This intensity is thus associated with rather long-range inter-particle correlations due to optical inhomogeneities in the scattering medium, or possibly intermolecular aggregates also found in dilute solutions of cellulose tricarbanilate.[12]

Because of this forward diffusion and due to limitations in the scattering angle of the apparatus, the accessible range of pitch P (or precisely $\bar{n}P$) from light scattering experiments is 1,8 to 0.8 μm*, i.e., relating to solutions which do not give iridescent colors.

When the polymer concentration is raised, colors appear and the cholesteric pitch is then determined from the light transmission spectra (see Figure 3). The absorption of light is due to selective reflection by the medium as predicted by de Vries[13] from the equations of propagation of electromagnetic waves in a cholesteric slab with a planar texture. This Bragg peak is superposed on a background spectrum. The absorption lines in the region 1,3–2,5 μm may arise from vibrational excitation of the

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*We do not allow for the variation with concentration and solvent of the index $\bar{n}$, since very few experimental determinations exist and the error involved is less than 10%.

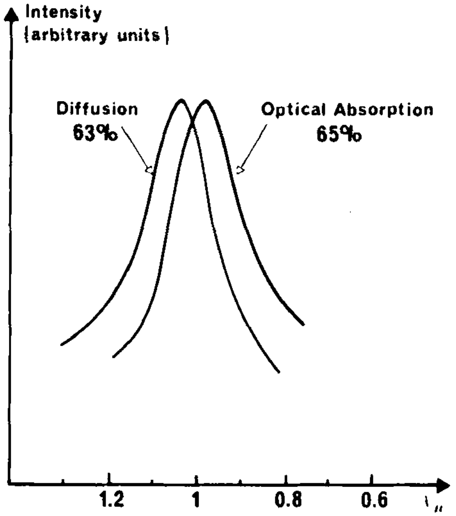

FIGURE 5 Comparison between spectra obtained from the angular dependence of the Bragg scattering and from light absorption. The wavelength scale for the scattering spectrum is deduced from the scattering angle by using the relation $\lambda = \lambda_0 \sin^{-1}(\theta/2)$. The slight shift between spectra is due to the slightly different polymer concentrations: 63 and 65% of HPC.

medium. The domain of validity for this method is restricted to visible and short IR wavelengths, i.e., 0,4 to 1,5 μm.

These methods are thus complementary, and the total domain of pitches $\bar{n}P$ is 0,4 to 1,8 μm. In the common wavelength range, the evaluated pitch is in good agreement. Figure 5 underlines the similarity of the profiles of the peaks obtained from Bragg scattering (after subtraction of the forward scattering) and absorption measurements (after subtraction of vibrational background). The full line width is rather large (of the order of 1700 Å) and may arise from various sources. Because of the finite size of the laser beam or of the visible light beam and of the finite collecting angle, reflections by cholesteric regions with slightly different pitches and orientations, but which fulfill the Bragg relation, contribute to the spectral intensity and broaden the line. In addition, due to the semi-flexible character of the HPC macromolecules, the mesophase is less well organized than liquid crystalline phases composed of small molecules; the configuration may, therefore, be described in terms of small domains of uniform orientation, their relative orientations varying either continuously or abruptly. The thickness of the pseudo-crystallites can be evaluated. Indeed, the light scattering by a liquid crystalline sample may be considered as analogous to X-ray scattering by a powder sample.[14] The width of the coherent scattering peak is related to the size L of the domains:[15]

$$\frac{L}{\lambda_0} \simeq \frac{1}{n\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)} = \frac{P}{d\lambda_0}$$

For example, assuming that the width of the line is entirely due to the finite thickness of the domains and in the case of the HPC-water ($C = 58\%$) solutions: $\theta = 70°$ and $\Delta\theta = 12°$ (see Figure 2), the size of the pseudo-crystallites is nearly 5 μm.

The value of the line width therefore provides information on the degree of organization inside the sample.

The physical parameters influencing the cholesteric pitch

In Figures 6 and 7 are given the values of the cholesteric pitch determined as a function of the polymer concentration for the liquid crystalline phases of HPC. As can be seen from a logarithmic representation, the following law:

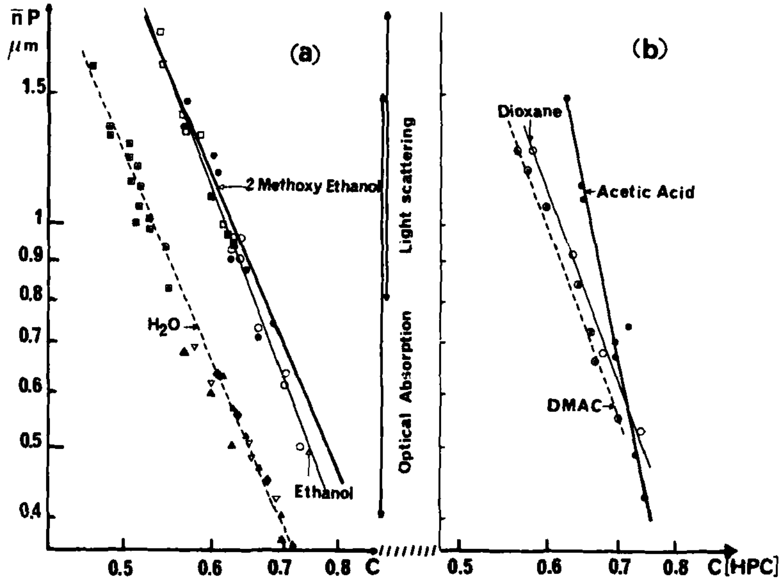

FIGURE 6 Change of cholesteric pitch with polymer concentration of mesomorphic solutions of hydroxypropyl-cellulose. For aqueous solutions, we also give the experimented determinations reported in the literature, i.e., ▽ ▽ ▽ from optical rotatory dispersion[1b] with HPC Klucel L; △ △ △ from absorption spectra[16] with HPC Klucel L; ▲ ▲ ▲ from dichroism peaks.[17]

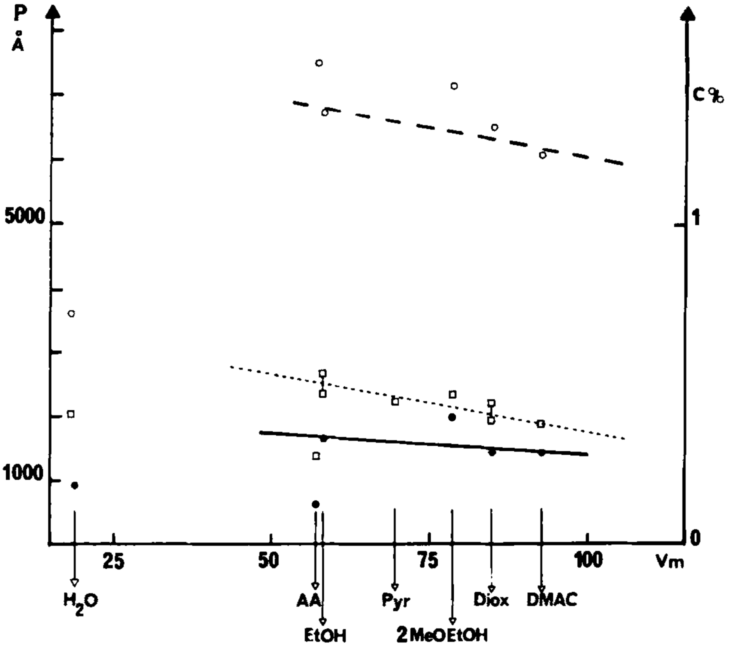

FIGURE 7 Dependence of the molar volume V_m ($=M/\rho$) of the solvent on the concentration for appearance of the mesophase C^* ⊟-⊟-⊟ and on the pitch$^{(i)}$ of a solution of 70% of HPC ⊖-⊖-⊖ and$^{(ii)}$ of the pure solute polymer (extrapolated values) -●-●-●-.

$$P = P_0 \cdot C^{-\alpha} \tag{3}$$

is well satisfied. The values of the parameters P_0 and α are reported in Table I for each polymer-solvent pair, together with the mean square deviation r^2 of the fit.

The parameter P_0 should be the pitch of the thermotropic phase extrapolated to room temperature. Since different values are obtained, we may question the validity of the simple extrapolation to pure solute. Unfortunately, this quantity has still not been measured for experimental reasons, *viz* the rather high critical temperature $T^*_{K\text{-}Ch} = 200°C$ of the thermotropic polymer.

A value of 2 for the second parameter α has been recently proposed[19] from a microscopic model of cholesteric mesophases composed of helical polymers with uniformly distributed electric dipoles along the long axes of molecules. (C is expressed as the number of molecules per unit volume). A nearly similar model has been proposed[20] which accounts for the chirality through the dielectric permittivity of the rods constituting the liquid crystal. A factor 2 is experimentally nearly verified for the mesophases of PBLG

TABLE I

Parameters describing the power law of the variation of the helical pitches $\bar{n}P$ (in Å) with the polymer concentration (in wt/wt) for appearance of the mesophase.

Solvents (Ref.)	V_m	C_A^*	α	P_0	$P(70\%)$	r^2
H_2O (Present work)	18.04	0.41 (3)	3.86	910	3610	0.93
(lb)			2.40	1185	4315	0.99
(16)			3.20	1180	3633	0.98
(17)			3.51	1160	4048	0.99
(Other work)			3.51	1114	3896	0.98
Ethanol	58.37	0.47 (3) 0.53 (2)	3.92	1665	6740	0.98
2-Methoxy-ethanol	78.78	0.47 (2)	3.56	2009	7153	0.90
Dioxan	85.25	0.42 ± 0.03*	4.20	1457	6518	0.98
D.M.A.C.	92.98	0.38 (3)	3.95	1487	6084	0.99
Acetic Acid	57.23	0.28 (3)	6.92	635	7486	0.98
Pyridine	69.77	0.45 (2)				
Trifluoroacetic acid	74.28	0.18 (4)				

*From our cross-polarized light microscopy observations.

with dioxan and *m*-cresol[21,22] However, higher values of the exponent have also been observed: $\alpha = 3$ in HPC-water[1b] and APC (acetoxypropylcellulose)-acetone[23] solutions. Here we find somewhat higher values for α which vary slightly with the solvent. In acetic acid solution, a very different power law is observed. We may also mention that the exponent α in polypeptide solutions has been found to be dependent on temperature.[24]

The question of the effect of the solvent on the cholesteric properties of the mesophase is an interesting but not trivial problem.

In the case of cellulose acetate, it was shown[1a] that, in weakly acidic solvents, the concentration for appearance of the mesophase, C^*, is simply inversely dependent on the molar volume of the solvent. We verify that this relation is again nearly satisfied (see Figure 7), except for water (probably due to H bonding) and acetic and trifluoroacetic acid (moderately and strongly acidic). Here, as in ref 1a, the stronger the acid, the lower the concentration C^*.

The relation between the cholesteric pitch and the solvent properties is not obvious, even if there exists a trend for the variation of $\bar{n}P$ with V_m for three of the six investigated solutions. From Table I, we remark that no evident relation can be found between $\bar{n}P$ and C^*.

No relation of the cholesteric twist to *simple* solvent properties is therefore found. Indeed, any statistical theory describing thermotropic cholesteric liquid crystals in terms of the anisotropic intermolecular potential can relate the pitch to, on the one hand, some molecular properties such as molecular shape asymmetry, anisotropic polarisability, and chirality, and on the other hand, to the orientational order parameter of the medium.[25] Any change of these molecular properties caused by the solvent molecules will produce marked effects in the cholesteric properties.

It has been shown[26] that the molecular rigidity of cellulosic derivatives, as measured by their persistence length q, is influenced by the solvent. The macroscopic orientational order is also dependent on the chain flexibility through the persistence length[7] and we expect a similar effect for the cholesteric pitch. The persistence length q of the HPC–ethanol solution, estimated by applying Yamakawa's theory[27] to intrinsic viscosity determinations,[28] together with a reasonable value[29] of 8 Å for the hydrodynamical diameter, is 107 ±2 Å.[30] Polypeptides have persistence lengths ten times larger[32] and have also higher cholesteric pitches.

Interactions of solvent molecules with side chains, through solvatation or H-bonding, could modify the local chirality of the substituent. This effect was shown for polypeptide liquid crystals.[30]

We must also mention that the cholesteric pitch can be related[25] to the twist elastic modulus k_{22}.[25] This parameter has been measured using polypeptide solutions[22] and also depends on the solvent properties. At this time, it is difficult to test these features, even qualitatively, since no systematic experimental determinations of the parameters influencing the pitch have been made.

The influence of the macromolecular weight on the cholesteric pitch is weak. The range of weight accessible to experiment is limited.* In the case of aqueous solutions of HPC, results appear in Figure 8 where the pitch seems uninfluenced by the molecular weight. Different variations of P (M_w) have been reported: constant,[21] decreasing,[22] or increasing.[5b]

The ageing effect is more clear. As seen in Figure 3, a red shift of the cholesteric peak is recorded when the delay time between the sample preparation and the observation is increased; sometimes, this is masked by an evaporation process which leads to an opposite variation. The shift is accompanied by a narrowing of the line. Due to the relaxation of the internal constraints, the texture becomes better organized, as the size of the pseudo-domains together with their relative alignment increases with time. No degradation process has been observed.

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*Concentrated, homogeneous solutions with the highest weight (M_w = 10^6) are difficult to prepare at room temperature due to the very high bulk viscosity of the sample. The solutions with the smallest weight (M_w = 60000) cannot be directly compared, since the product was obtained from a different source.

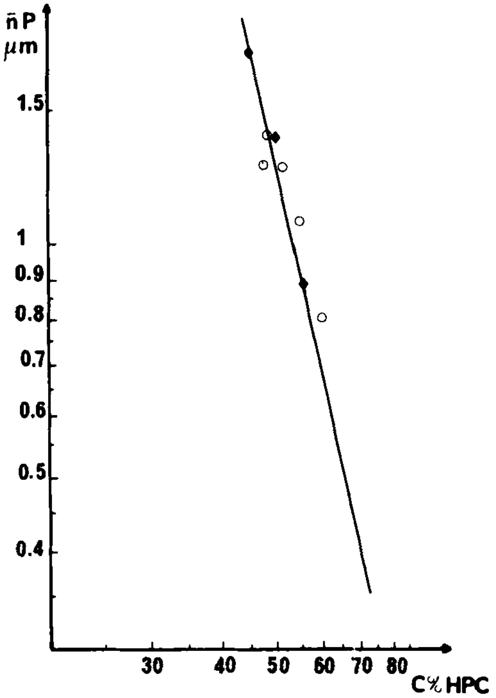

FIGURE 8 Influence of the macromolecular weight on the cholesteric pitch of aqueous solutions of HPC: M_w = 100000: ——, M_w = 300000: ◆◆◆ and M_w = 60000 ○∪○.

CONCLUSIONS

Optical absorption and light scattering provide complementary tools for studying the helical pitch of cholesteric materials over a wide range of concentration. In this paper, they have been applied to lyotropic solutions of HPC in various solvents as a function of polymer concentration. A power law $P = P_0C^{-\alpha}$ has been observed in all cases, but the value of the exponent depends on the nature of the solvent. The influence of various physical parameters which modify the asymmetry of the interactions between the semi-rigid macromolecules in the cholesteric medium has been investigated. Further experimental work—in particular using mixed solvents and with variable temperature—and theoretical investigations are required to further clarify this problem.

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