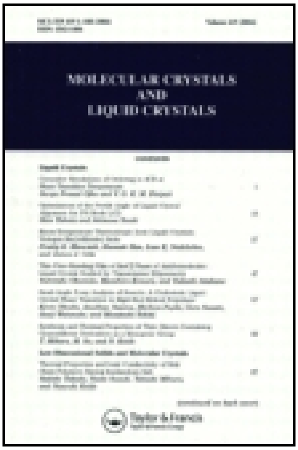

Molecular Crystals and Liquid Crystals

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Version of record first published: 18 Oct 2010

To cite this article: P. Prakasam & M. M. Labes (2002): Induction of Chirality in a Cationic Surfactant Nematic Phase by Hydroxypropylcellulose, Molecular Crystals and Liquid Crystals, 378:1, 51-58

To link to this article: http://dx.doi.org/10.1080/713738581

Mol. Cryst. Liq. Cryst., Vol. 378, pp. 51-58

1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290090020

Induction of Chirality in a Cationic Surfactant Nematic Phase by Hydroxypropylcellulose

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Addition of the water-soluble chiral polymer hydroxypropylcellulose (HPC) to a cationic nematic lyotropic phase induces cholesteric behavior. In this work, thirteen different well-characterized samples of HPC of known molecular weight and polydispersity were added to an N_D phase consisting of myristyltrimethylammonium bromide, 1-decanol, ammonium bromide, and water, and the fingerprint texture of the cholesteric phase was utilized to determine the helical twisting powers (HTPs) of the solutes. Samples with molecular weights ranging from 12,000 to 140,000 were soluble in the concentrated surfactant system. Above molecular weight 140,000 phase separation was observed. The HTP of HPC was found to be independent of both molecular weight and molecular weight distribution of the chiral polymer with a value of 11 ± 1 (μm wt fraction)$^{-1}$. HTP appears to depend only on the number density of chiral units in the phase and not on the polymer chain length.

Keywords: chirality, lyotropic, surfactant, hydroxypropylcellulose, cholesteric

INTRODUCTION

In previous work from this laboratory [1], the effect of chiral water-soluble polymers on aqueous lyotropic liquid crystals was surveyed. Chiral species in general are known to exert a cooperative effect on nematic media [2–4]. In the case of surfactant-based lyotropics [5–11], the extended micelles which normally show nematic ordering in a certain concentration range form a macroscopic twisted (cholesteric) array. In the limit of low concentration, the induced helix pitch P is inversely proportional to the concentration C of the chiral species and its "helical twisting power" β. Interpretation of β in terms of molecular structural parameters has been attempted by several investigators, but the problem still defies rigorous interpretation [12–17].

Received 18 September 2001; accepted 8 November 2001.

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In the preliminary work [1], several disklike and cylinder-like nematic phases were prepared using cationic and anionic surfactants. The cationic system was prepared using myristyltrimethylammonium bromide (MTAB). The two anionic surfactant systems investigated were based on sodium decyl sulfate (SDS) and cesium perfluorooctanoate (CsPFO). Ionic and nonionic cellulosic polymers were added to these phases. Out of seven cellulosic derivatives investigated, only hydroxypropylcellulose (HPC) was able to induce cholesteric phases in host disklike N_D nematics. HPC was not able to induce cholesteric phases in cylinder-like N_C phases. HPC was able to induce twist in both cationic and anionic micellar nematic phases. The twist was larger in anionic systems than in cationic systems. It was also reported that HTP decreases with increasing molecular weight for the range investigated. However, the polymers studied were of commercial grade, and no measurements were available of the polydispersities of the samples. Hence, the molecular weights and their distribution were not well defined. To understand clearly the relationship between HTP and polymer molecular weight, further molecular weight distribution and polydispersity work was carried out and is reported here.

EXPERIMENTAL

Materials

MTAB, ammonium bromide, and 1-decanol were purchased from Aldrich and used as received. HPC was procured from Polymer Standards Service, USA. These polymers were well characterized, their molecular weights having been determined using gel permeation chromatographic techniques. The molecular weights and polydispersities are reported in Table 1.

Mesophases

Nematic phases were formed with the compositions indicated in Table 2 [18,19]. Depending on the concentration of the components, the phases had either disklike (N_D) micelles or cylinder-like (N_C) micelles. Triply distilled water was used in the preparation. The required amount of each component were weighed into 50–100 ml flasks with pennyhead stoppers and stirred magnetically for 24–36 h at room temperature to ensure complete homogenization. The clearing point, optical texture under a polarizing microscope, and textural behavior in a magnetic field were utilized to characterize each phase. The stock compositions were stored at room temperature. No

TABLE 1 HTP of HPC samples

Sample number	M_n	M_w	*D*	*HTP* $(\mu m\ wt\ fraction)^{-1}$
1	7200	12,000	1.67	10.1
2	10,400	17,000	1.63	11.8
3	11,000	56,200	5.10	13.0
4	12,700	20,500	1.61	13.2
5	17,000	29,500	1.65	10.9
6	18,800	32,400	1.72	11.8
7	21,900	37,500	1.71	12.1
8	28,800	55,700	1.93	13.0
9	28,900	56,900	1.97	13.0
10	29,000	71,800	2.47	12.5
11	39,600	93,000	2.35	11.5
12	38,900	187,600	4.82	—
13	38,700	288,200	7.45	—

M_n, M_w are the number and weight average molecular weights, respectively. D is the polydispersity.

TABLE 2 Composition of lyotropic nematic liquid crystal phases

	Composition, wt%					
Surfactant	*Surfactant*	*Water*	*1-decanol*	NH_4Br	*Phase*	*Temperature range, °C*
MTAB	30	60	3.8	6.2	N_D	12–49
MTAB	39	61	0	0	N_C	18–54

changes were observed over a period of several months. Chiral nematic phases were obtained by weighing the required amount of dopant and host nematic phase (about 1 g) into 5 ml vials and stirring slowly at room temperature until complete dissolution of the dopant occurred.

Methods

Samples were introduced by vacuum suction into rectangular flat capillaries (Wale Apparatus Co. Inc.). The rectangular flat capillaries varied in thickness from 150 to 600 µm. The ends of the capillaries were sealed with a commercially available rapid-setting epoxy resin. The sealed capillaries were affixed to conventional microscope slides. Magnetic field alignment was achieved by placing capillaries in a 6-in electromagnet for a prescribed period in either the X (length) or Y (width) direction with respect to the field. Samples were then transferred to the optical microscope for phase identification and clearing point measurement.

MTAB-based N_D nematic phases possess negative diamagnetic anisotropy. They belong to type II diamagnetic anisotropic systems. Type II diamagnetic anisotropy arises when the diamagnetic susceptibility along the director, $\chi_{\|}$, is smaller than in the perpendicular direction, $\chi_{\perp}$, resulting in a negative diamagnetic anisotropy, $\Delta\chi = \chi_{\|} - \chi_{\perp}$. Hence they align in an external magnetic field so that the bilayer normals are perpendicular to the field. Addition of chiral species to these disklike micelles results in a cholesteric phase, which aligns with the helical axis along the field, forming the so-called finger print texture (FPT). The pitch of the cholesteric phase was determined from measurements of twice the distance between adjacent stripes of the FPT using an eyepiece micrometer.

Fingerprint methods of measuring pitch have been found to be very sensitive to boundary [20,21] conditions when the pitch approaches small multiples of the sample thickness. In this study, MTAB-based N_D phases were found insensitive to the capillary thickness. The fingerprints were found to be aligned better when the capillaries were rinsed with ethanol. The estimated error in pitch values are 5–10%.

RESULTS AND DISCUSSION

All the HPC polymer samples investigated in this study transfer their intrinsic chirality to the cationic disklike lyonematic system studied. The molecular weights and polydispersities are listed in Table 1.

Cellulose itself is not a water-soluble polymer, but etherification yields water-soluble materials. Of all the water-soluble cellulosic ether derivatives investigated, HPC was found to be the only material capable of inducing chirality in this surfactant system. The idealized structure of HPC of molar substitution 4.0 is shown in Figure 1 [22,23].

Experimental methods to calculate the exact degree of substitution have yet to be developed. Presumably, the additional hydroxyl groups associated with the ether moieties are sufficient to solubilize the polymer in water. The hydrophobic interaction between the polymer and the micellar core is the source of the interaction between the polymer and the micelles. The chiral centers of the polymers reside in the backbone of the chain as well as the side chains.

Figure 2 shows the relation between twist and the concentration of various polymers in the MTAB lyotropic nematic systems. The graph shows there is no perceptible difference in the relationship between twist and concentration, i.e., molecular weight of the polymer does not seem to affect the twist of the liquid crystal system. The HTP of all 12 polymer/surfactant samples (polymers numbered 1 to 12 in Table 1) investigated are of constant value. HTP was found to be 11 ± 1 (μm wt fraction)$^{-1}$.

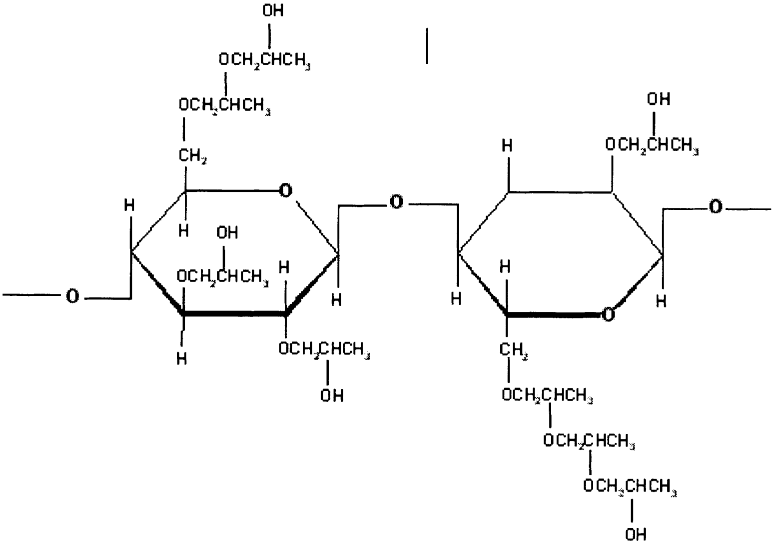

FIGURE 1 Idealized structure of hydroxypropylcellulose of molar substitution 4.0.

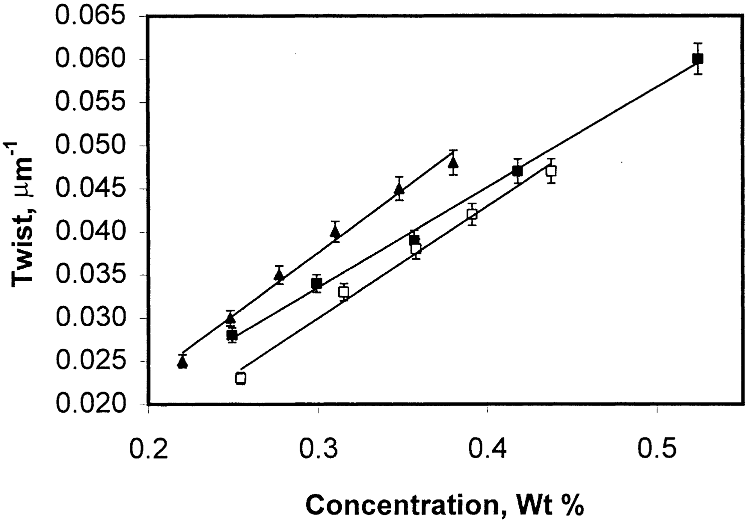

FIGURE 2 Twist versus concentration in wt% of various HPCs. ▲ = HPC $M_n = 10,400$, $M_w = 17,000$; ■ = HPC $M_n = 18,800, M_w = 32,400$; □ = HPC $M_n = 28,900, M_w = 56,900$.

There are two models in the literature to explain these interactions. The first one is based on the formation of associates described as necklace aggregates [24–27]. The polymer wraps around the micelles forming a necklace-like formation. The second model is one where the polymer acts like a template, forming a mixed super micelle [28]. In the molecular weight range from 12,000 to 300,000, the first model seems to be more appropriate. These models have been predicted for systems with dilute polymer-surfactant water solutions. In this study the lyotropic systems have high surfactant concentrations. At these concentration levels, micelles, which are formed at low concentrations aggregate to form nematic systems with large cylinder-like and disklike structures [29,30].

The dimensions of the disklike nematic systems is given by $d_{\mathrm{n}} = a(n)^{1/2}$, where d_{n} is the diameter of the disks, a is the height of the disks and n is the micelle aggregation number [31]. The typical dimensions of micelles range from 40 Å to 100 Å, and the average aggregation number, n, is approximately 100. Using the values of a as 100 Å and n as 100, the diameter of the disks can be calculated to be approximately 1000 Å. The dimensions of the cylinder-like nematic system are given by $\mathrm{l_n} = 2(\mathrm{n} - 1)\mathrm{a}/3$, where $\mathrm{l_n}$ is the length of the cylinders, a is the diameter of the cylinder, and n is the micelle aggregation number [31]. Using the values of a as 100 Å and n as 100, the length of the cylinders can be calculated to be approximately 6600 Å.

The molecular weight of the idealized repeating segment of HPC of molar substitution 4.0 is ~700, and its approximate length is ~10 Å. HPC molecules are rigid rodlike structures. They form cholesteric phases in concentrated water solutions. It is reasonable to assume HPC exists as rigid-rods in surfactant solutions and is in stretched form rather than in coiled form. For HPC of molecular weight 10,000, the number of segments is about 14. The expanded length of this chiral molecule is approximately 100 Å. For HPC of molecular weight 100,000, the number of segments is about 140 and the expanded length of this chiral molecule is approximately 1000 Å.

From the structure of HPC molecules and the shape of the cylinder-like nematic structures it is obvious why no cholesteric phases are observed in cylinder-like systems. The polymer is a rigid-rod type of polymer. The curvature of the cylinder-like nematic is not compatible with the polymer adsorbing significantly onto the cylinder surface. This leads to minimal chiral interaction between the polymer and the cylinder-like structures. Hence, chiral induction is not observed in cylinder-like nematic phases. This is, however, not the case with disklike nematic structures. At 1.0 wt% concentration of polymer of molecular weight 100,000 in the cholesteric phase, there is approximately one $\mathrm{HPC}_{\mathrm{MW}\,100{,}000}$ molecular per disklike micelle. Assuming x chiral centers in each monomeric unit, $\mathrm{HPC}_{\mathrm{MW}\,100{,}000}$ has $140x$ chiral centers per disklike micelle. At 1.0 wt% concentration of polymer of molecular weight 10,000 in the cholesteric phase, there are approximately ten $\mathrm{HPC}_{\mathrm{MW}\,10{,}000}$ molecules per disklike micelle. $\mathrm{HPC}_{\mathrm{MW}\,100{,}000}$ has $14x$ chiral centers per disklike micelle and hence the cholesteric phase has $140x$ chiral centers per disklike micelle. This simple approximation shows that for the same concentration in weight percentage, as HPC of different molecular weight contributes the same amount of chiral centers per micelle for the twist formation. This results in the HTP being independent of the molecular weight and its distribution in the cholesteric phase. Lyonematic systems with HPC molecular weights greater than 140,000 showed phase separation. The phase separation occurs because of the rigid-rod nature of the HPC; hence a single HPC cannot wrap itself around many micelles. This leads to phase separation.

CONCLUSIONS

HPC is able to induce twist in MTAB-based lyonematic phases. Formation of the cholesteric phase is observed only in disklike nematic phases. No discernible cholesteric phase is observed in the cylinder-like nematic. The HTP (expressed in terms of twist per weight fraction) is higher than that observed in low molecular weight chiral dopants, and is invariant with the molecular weight of the polymers investigated up to a molecular weight of 140,000. Above this range, the system phase separates into surfactant-rich and polymer-rich regions.

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