Effect of Chiral Polymers on Lyotropic Liquid Crystals

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Abstract: Formation of the cholesteric phase in aqueous lyotropic liquid crystals doped with cellulose derivatives has been studied utilizing hot stage polarized microscopy. Three ionic surfactants—sodium decyl sulfate, cesium pentadecafluorooctanoate, and myristyltrimethylammonium bromide—were employed to obtain anionic or cationic lyonematics. After addition of chiral polymers (at polymer concentration $\sim$0.05−0.750 wt %) the samples were sealed in flat glass capillaries, and a magnetic field was applied to enhance the homogeneous orientation and formation of the fingerprint texture. Out of seven various cellulosic derivatives (five nonionic, one cationic, and one anionic), nonionic hydroxypropyl cellulose was the only compound that induced the cholesteric phase. The effective helical twisting power (HTP) of hydroxypropyl cellulose is 3−4 times higher in anionic lyonematics than in cationics. In both cationic and anionic media, the HTP decreases with an increase in the molecular weight of the chiral polymer. This behavior can be attributed to two factors: (i) inhomogeneous distribution of chiral centers (formation of polymer bound chiral micelle clusters) and (ii) the finite character of intermicellar chiral distortion forces. The pitch of the polymer-doped cationic chiral lyonematic decreases as the temperature rises, indicating a closer packing along the helical axis with an increase in the thermal motion of the system.

Introduction

When an optically active amphiphile is dissolved in a lyotropic nematic liquid crystal, a remarkable cooperative effect occurs: a macroscopic twisted array of micelles is established with a particular twist sense and repetition distance, referred to as the cholesteric (helix) pitch. Quantitatively, the magnitude of the induced helix pitch P is inversely proportional to the concentration C of the chiral species and its "helical twisting power" β. This phenomenon is in complete analogy with thermotropic mesophases, although the mechanism of the generation of a periodic helical structure in lyophases is somewhat different. It requires the presence of asymmetric long-range interactions between *molecular aggregates—micelles*—so that the correlated displacement of the major alignment axis of one micelle with respect to those of its neighbors results in the formation of a macroscopic twisted array. A review of cholesteric lyophases and recent studies of these systems are listed in refs 1−5.

Two models for the generation of twisted structure in lyonematic phases have been proposed. In the first, the pairwise asymmetric interaction between the chiral guest molecules incorporated into adjacent micelles perturbs the micelle parallel stacking and results in the formation of a helical array.[6,7] Taking into account that the aggregation number of extended micelles is on the order of 100, this approach may be justified by the consideration that even at the lowest concentration of chiral additives ($\sim$0.1 wt %) there is on average one chiral molecule per micelle. In the second model, the chiral guest induces a distortion of the symmetrical configuration of a micelle into a twisted propeller-like shape, and then the interaction of adjacent chiral micelles leads to the observed macroscopic twisted structure.[8−10] This model readily accounts for such experimental facts as low helical twisting power (HTP) of strongly hydrophilic chiral guests (weak interaction with micelles results in the weak distortion of the latter) and the increase of HTP with an increase in the hydrophobic character of optically active additives (hydrophobic character implies stronger association with micelles and hence its stronger chiral distortion). The second model implies a longer range cooperativity than the first one. Experimentally, a correlation between the twist of the mesophase and the alignment of chiral head groups on the micellar surface was observed using nuclear magnetic resonance spectroscopy in a system comprised of deuterated amphiphiles.[11] This observation presumably could support the second model, but subsequently it was found that the apparent connection between NMR quadrupole splitting and the bulk chirality twist is superficial.[12] Thus, there are still many aspects of cooperative chiral behavior in amphiphilic systems that are not well understood. It occurred to us that cooperative effects in macroscopic twist formation can be addressed by employing polymeric chiral solutes.

Such systems would be of considerable interest because compositions including water soluble polymers and surfactants are widely used to control the release rate of active substances to obtain suitable rheological properties, and to influence the solubilized state of drugs in various formulations. For that reason, the understanding of interactions between these two classes of compounds is of both applied and fundamental interest. It is apparent that a study of microscopic chiral perturbations induced by chiral polymers in concentrated surfactant media would also be a useful approach toward better understanding of the highly cooperative behavior of these systems.

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Table 1. Composition of Lyotropic Nematic Liquid Crystals

| | composition, wt % | | | | | temperature |
surfactant	surfactant	water	1-decanol	electrolyte	phase	range, °C
MTAB	30	60	3.8	6.2 (NH_4Br)	N_D	12−49
MTAB	39	61			N_C	18−54
SDS	35	55.3	6.8	2.9 (Na_2SO_4)	N_D	17.5−42
SDS	37	56	7.0		N_C	16−33
CsPFO	40	60			N_D	24−32

According to the theory of dilute polymer−surfactant water solutions, micelles tend to assemble on polymer chains, forming so-called "necklace" aggregates.[13] If this mechanism also holds for concentrated surfactant solutions, addition of macromolecules will lead to the formation of strings of bound chiral micelles, thus locally increasing the cooperativity in proportion to their chain length. As a result, one may expect to observe such effects as dependence of pitch on the molecular weight of a polymeric solute and unusual pitch−temperature dependence in such systems. Correlation of pitch with the molecular weight of chiral solutes has been studied so far only in mixtures consisting of polymeric species (poly(γ-benzyl glutamate)) and an aprotic solvent,[14] i.e., in systems very different from micellar solutions.

In this study a number of cellulosic derivatives of various molecular weight have been utilized in an investigation of induced cholesteric behavior in lyotropic mesophases composed of anionic and cationic amphiphiles.

Experimental Section

Materials. Myristyltrimethylammonium bromide (MTAB) was purchased from Aldrich and used as received. Sodium decyl sulfate (SDS) was bought from Acros Organics and recrystallized two times from 95% ethanol and two times from 100% ethanol prior to use. Cesium pentadecafluorooctanoate (CsPFO) was synthesized via neutralization of pentadecafluorooctanoic acid with cesium hydroxide (both from Aldrich) and then recrystallized from ethanol. Chiral polymers, nonionic−hydroxypropyl cellulose (HPC), ethyl hydroxyethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, methyl cellulose; anionic−carboxymethyl cellulose sodium salt; and cationic−hydroxyethyl cellulose reacted with trimethylammonium-substituted epoxide (polymer JR), were products of Aldrich, Polyscience, and Union Carbide, respectively, and used as received. Low molecular weight chiral compounds, (R)-(−)-mandelic acid, (S)-(−)-binaphthol, and (−)-N-dodecyl-N-methylephedrinium bromide, were acquired from Aldrich.

Mesophases. In a certain concentration range of surfactant, cosurfactant (1-decanol), electrolyte, and water, cationic surfactant MTAB and anionic surfactants SDS and CsPFO form nematic phases, comprised of disk-like (N_D) or cylinder-like (N_C) micelles.[7,15,16] The exact composition of the components in the preparation of the lyonematics is indicated in Table 1. Triply distilled water buffered to pH 7 (sodium phosphate buffer) was used in the preparation. The required amounts 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. Each phase was then characterized by its clearing point, the optical texture under a polarizing microscope, and the textural behavior in a magnetic field. The stock compositions were stored at room temperature (22 °C). No changes were detected over a period of several months. Chiral nematic phases were obtained by weighing the required amounts of dopant and host nematic phase (about 1 g) into 5 mL vials and stirring slowly at about 30 °C until complete dissolution of the dopant occurred.

Methods. Optical microscopy studies (phase identification and clearing points) were performed on samples introduced by vacuum suction into rectangular flat capillaries (Vitro Dynamics), varying in thickness from 150 to 600 μm. The ends of the capillaries were sealed with a rapid setting epoxy resin, and then the capillaries were affixed to conventional microscope slides. Magnetic field alignment was achieved by placing capillaries in a 6-in. electromagnet for a prescribed period of time in either the X (length) or Y (width) direction with respect to the field. Samples were thermostated in the magnet on a temperature-controlled brass stage which could be transferred to the optical microscope.

Host N_D nematic phases, based on MTAB and SDS, possess negative diamagnetic anisotropy (belong to type II DM) and hence align in an external magnetic field so that the bilayer normals are perpendicular to the field. Addition of chiral species to these disk-like micelles results in a cholesteric phase which aligns with the helical axis along the field, forming the so-called fingerprint texture (FPT). The lyonematic based on CsPFO possesses positive diamagnetic anisotropy (type I DM), and therefore formation of the FPT was allowed to occur spontaneously without a magnetic field. The pitch of the cholesteric phase was determined from measurements of twice the distance between adjacent stripes of the FPT using an eyepiece micrometer.

Because the fingerprint method of pitch determination is very sensitive to boundary conditions,[17] special attention has been paid to possible effects of such variables as capillary thickness and washing solvent. Four capillaries of different thickness−150, 200, 400, and 600 μm−were employed to measure the pitch of the same sample: MTAB-based N_D nematic phase, containing 0.4 wt % of HPC (MW 100 000). All measurements gave consistent values falling into the range of 20.6 ± 1.0 μm. Thus, the value of the observed pitch was invariant to the thickness of the capillaries. Furthermore, it was observed that the FPT seemed more uniform in capillaries rinsed with ethanol, and so for all further preparations, the capillaries were treated in this way. The estimated error in pitch values is 5−10%.

The handedness of the twist was determined from contact preparations. Capillaries were initially partly filled with a chiral nematic of known helicity and then further filled with a test phase. When the test chiral nematic phase had helicity of opposite sign with respect to the reference phase, domains with twist compensation (no FPT) were observed in the contact area. As a reference chiral cationic phase, a left-handed 2.0 wt % solution of (R)-(−)-mandelic acid in the MTAB-based N_D phase was used.[5] The reference anionic chiral phases were left-handed 1.5 wt % solutions of cholesterol in SDS- or CsPFO-based N_D phases, respectively.[18]

Results and Discussion

Out of seven cellulose derivatives (five nonionic and two ionic), only HPC induced a cholesteric phase in host nematics, as was manifested by the formation of FPTs in samples initially showing the disk-like N_D phase. Other nonionic derivatives, though readily soluble (except for ethyl hydroxyethyl cellulose) in both anionic and cationic phases, did not induce a discernible macroscopic twist in either N_D or N_C phases. Two polyelectrolytes (anionic carboxymethyl cellulose sodium salt and cationic polymer JR) interacted strongly with oppositely charged surfactants (MTAB or SDS and CsPFO, respectively), resulting in a drastic thickening of the phase or gel formation. When small amounts (0.2−0.4 wt %) of carboxymethyl cellulose sodium salt or polymer JR were added to lyonematics based on similarly charged surfactants, the medium retained its nematic phase but did not become macroscopically twisted. The general features of the interaction of polymers with lyonematics are consistent with those surveyed in diluted surfactant solutions,[13] while the particular behavior of HPC as a nonionic polymeric chiral inducer requires special consideration. Cellulose itself is not soluble in water, but etherification with a degree of substitution as low as 1.6 yields water soluble polymeric

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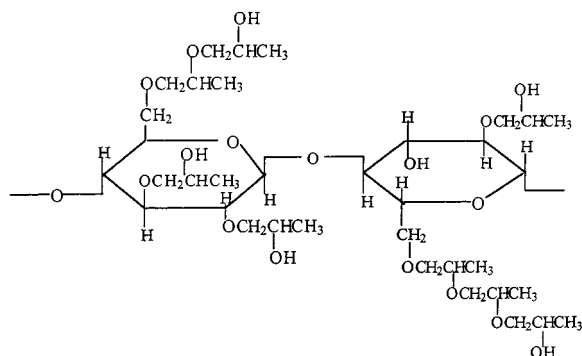(18) Alcantara, M. R.; Vanin, J. A. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 333.

Figure 1. Idealized structure of hydroxypropyl cellulose of molar substitution 4.0.[19]

Table 2. Helical Twisting Power of Some Chiral Solutes in Lyotropic Nematic Hosts Based on MTAB (Temperature 25 °C)

chiral compound	HTP, $(\mu m \times wt\ frac)^{-1}$	HTP, $(mm \times mol\ frac)^{-1}$	lit. data $(mm \times mol\ frac)^{-1}$
(R)-(−)-mandelic acid	−1.9	−347	−330[5]
(S)-(−)-binaphthol	+11.0	+3640	
(R)-(+)-binaphthol	−12.5	−4140	
cholesterol	+1.5	+670	1390[5]
DMEB[a]	+1.7	+830	

[a] (−)-N-Dodecyl-N-methylephedrinium bromide.

ethers: methyl, ethyl, hydroxyethyl, hydroxymethyl, hydroxypropyl, etc. The idealized structure of HPC of molar substitution 4.0 is shown in Figure 1.[19] Presumably the additional hydroxyl groups associated with the ether moieties are sufficient to solubilize the polymer in water. Thus, when considering a probable model for the interaction between HPC and cationic or anionic micelles, one can reasonably assume that there is a hydrophobic interaction between the micelle cores and the polymer main chain. Since the chirality of all the employed cellulose derivatives resides in their main chain, it is indicative of the complexity of the interaction that even slight modifications of the side chains result in drastic changes in the ability of these derivatives to induce cholesteric phases.

The precision and reproducibility of methods employed in this study were tested by using several low molecular weight chiral dopants for the induction of the cholesteric phase in host lyonematics. Table 2 shows the results of doping the N_D host phases with these compounds. The consistency between these results and those reported in the literature confirms the validity of the adopted experimental techniques, which provide reliable measurements of pitch in the range 6−120 μm.

Using the method of contact preparation, it was determined that HPC induces a right-handed twist in all host N_D phases irrespective of their ionic nature. No indication of twist induction was observed in N_C phases. As shown in Figure 2, quantitatively the twist is roughly proportional to the concentration of HPC, although some obvious deviations from linearity, both positive (in MTAB and SDS systems) and negative (in CsPFO), are observed in the range of concentration 0.05−0.75 wt %. A positive deviation of the twist can be accounted for in terms of a decrease in average micelle size due to micelle−polymer interaction.[13,20] When smaller micelles are formed, the micelle number density increases and consequently the mean

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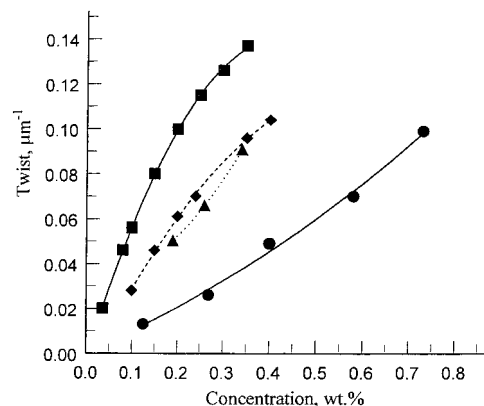

Figure 2. Variation of the twist (inverse pitch) versus concentration of HPC in chiral lyonematics: (■) CsPFO, HPC 60 000; (◆) CsPFO, HPC 100 000; (▲) SDS, HPC 60 000; (●) MTAB, HPC 100 000. Temperature 25 °C.

Table 3. Helical Twisting Power $(\mu m \times wt\ frac)^{-1}$ of HPC of Different Molecular Weights in Nematic Hosts

MW of HPC	MTAB	CsPFO	SDS
60 000		56	30
80 000	10		
100 000	12.0	32	
140 000	11.0	12	
300 000	3.3		
1 000 000	1.9		

micelle distance is reduced, leading to a shorter pitch.[5] This behavior was noted in MTAB and SDS host phases. In the lyonematic based on CsPFO, one observed an opposite trend: HTP decreased with increasing polymer concentration. Since the nematic phase of the CsPFO/H$_2$O system is bordered by the lamellar phase on the lower temperature side, this behavior can be attributed to pretransitional effects caused as one approaches this phase, in accord with an earlier interpretation by Acimis et al.[21] Further noteworthy results are (i) HTP (determined from initial segments of the twist−concentration curves) is much higher in anionic nematics (CsPFO, SDS) than that in a cationic system (MTAB) and (ii) HTP decreases with increasing molecular weight of the polymer. Table 3 gives the HTP of HPC samples of various molecular weights in host lyonematics.

The higher values of HTP observed in anionic media obviously reflect a much stronger interaction between HPC and anionic micelles.[13] In the case of SDS, induction of macroscopic twist occurs only when HPC with the lowest molecular weight (MW 60 000) is employed. Dopants with higher molecular weights caused formation of a biphasic system; none of the phases showed FPT. Fluorinated surfactant (CsPFO) micelles, which interact with a polymer presumably only via Coulombic forces, lend themselves to a macroscopic twist array with chiral polymers of higher molecular weights, although forming less twisted helices as the molecular weight of HPC increases. The same tendency is also observed in the MTAB-based N_D phase.

To rationalize the reduction of HTP with an increase in polymer molecular weight, a model based on two well-grounded assumptions can be considered. First, one can assume that the interaction of ionic surfactants with neutral HPC proceeds through the formation of associates described as necklace aggregates.[22] In general, there is also a possibility that the polymer acts like a template, forming a mixed supermicelle.

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However, such formations have been observed only in systems comprised of oppositely charged surfactants and ionic polymers or in surfactants with low molecular weight (425 and 1000) poly(propylene glycol),[23] and therefore they are not likely to be present in homogeneous systems containing dissolved HPC of molecular weight ranging from 60 000 to 250 000. Second, one can assume that the overall twist of the mesophase is proportional to the chiral distortion of individual micelles and, in turn, the micellar chiral distortion is proportional to the degree of the association between a micelle and a chiral polymeric inducer. Studies performed with both hydrophilic and hydrophobic chiral guests confirm this model for low molecular weight dopants,[5] and therefore it is logical to suggest that it also holds in the case of chiral polymeric inducers.

The molecular weight of the idealized repeating segment of HPC of molar substitution 4.0 is ~700, and its approximate length is ~10 Å (Figure 1). Presumably HPC macromolecules are sufficiently stiff so that their molecular rigidity accounts for the formation of a cholesteric phase in concentrated water solutions.[24] It is reasonable to assume that in surfactant solutions a HPC molecule also retains its rigidity and takes on a stretched rather than coiled configuration. For HPC of molecular weight 100 000, the number of segments is about 140 and the expanded length of this chiral macromolecule is approximately 1000 Å. By comparing the dimensions of a micelle and a macromolecule, one can readily estimate the number of micelles directly interacting with one macromolecule. The typical dimensions of ionic micelles range from 40 to 100 Å.[25] Assume for simplicity the average size of a micelle is ~100 Å. Then, taking into consideration the intermicellar distance, one can estimate the number of bound micelles (n_B) at about 10 per $HPC_{MW\ 100\ 000}$ molecule. It is apparent that $n_B = 1$ for $HPC_{MW\ 10\ 000}$ and $n_B = 100$ for $HPC_{MW\ 1\ 000\ 000}$.

At 1.0 wt % concentration of polymer in lyonematics, there is approximately one $HPC_{MW\ 100\ 000}$ molecule per 100 micelles (if one assumes that the average aggregation number for MTAB, SDS, and CsPFO is about 100). Thus, in a chiral lyonematic doped with 1.0 wt % $HPC_{MW\ 100\ 000}$, the ratio of bound and free micelles is 1/10 assuming the expanded length of the polymer molecule is ~1000 Å. As long as the weight concentration of HPC dopant is constant (i.e., 1.0 wt %), the ratio of bound to unbound micelles in a unit volume is invariant with the molecular weight of the polymer, although the spatial distribution of bound (chirally distorted) micelles is essentially different in media doped with polymers of different molecular weights.

The above speculations are schematically illustrated in Figure 3 for two samples of HPC with MW 10 000 ($n_B = 1$) and MW 100 000 ($n_B = 10$) (parts a and b, respectively). The circles centered on chirally distorted (bound) micelles represent the areas of effective chiral correlations. Since the induction of a macroscopic twist in lyotropic nematics has not been observed at a concentration of a chiral monomer dopant lower than 1 chiral guest molecule per 10 host micelles, one may reasonably assume that the chiral distortion force field is confined to only several intermicellar distances due to the field screening (interruption) by water compartments. When the regions of effective chiral correlations cover the larger part of the sample
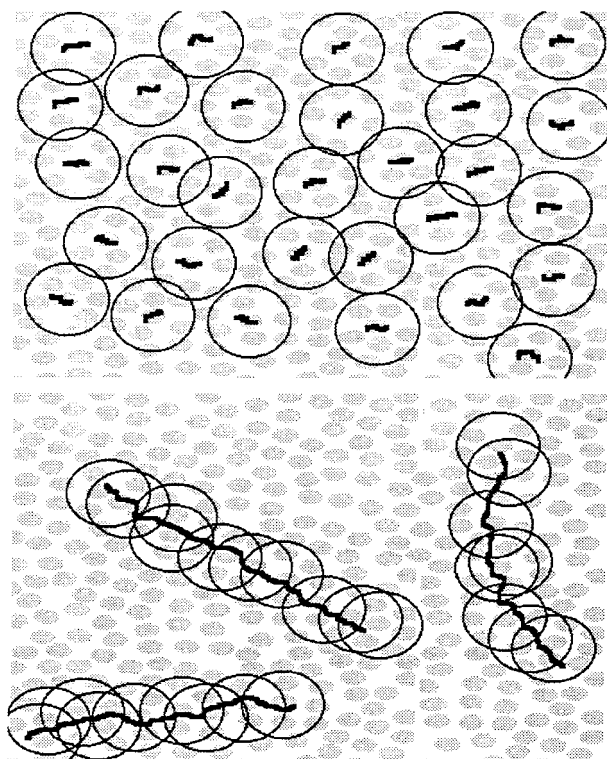
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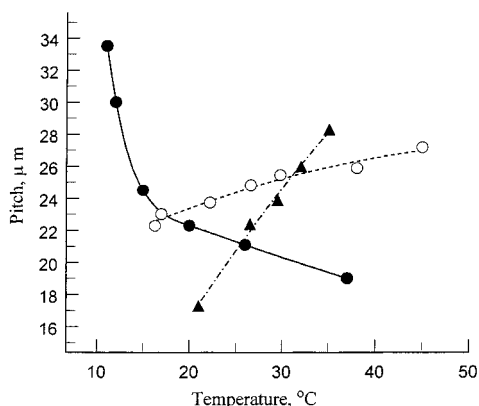

Figure 3. 2D schematic view of lyonematics doped with polymers of molecular weight (a, top) 10 000 and (b, bottom) 100 000. Each rectangle contains 300 micelles. There are 30 polymer molecules of MW 10 000 in (a) and 3 molecules of MW 100 000 in (b). The circles around bound micelles represent areas of effective chiral correlation beyond which chiral information from a distorted micelle is not translated into the medium.

(as in Figure 3a), the nematic medium becomes macroscopically twisted. With an increase in the polymer molecular weight, the total area covered by these regions decreases due to the less uniform distribution of chirally distorted micelles (Figure 3b), and therefore the overall macroscopic twist diminishes, in accord with experimental observations.

The proposed model is based on the idealized representation of HPC (Figure 1). Indeed, the molecular substitution levels of the HPC polymers used in this study fall in a range of 3.5−4.5, and the polydispersity is not at all narrow (~8 as reported by the manufacturers). Therefore, only a qualitative conclusion correlating molecular weight with HTP is possible. Clearly, the degree of branching and the degree of molecular substitution can also contribute to the HTP of macromolecules. These factors may account for the smaller twisting power of HPC of MW 80 000 as compared to that of MW 100 000. However, by employing a rather wide range of molecular weights, one can discern a clear-cut trend in the dependence of the twisting power on the molecular weight.

Pitch−Temperature Dependence. The temperature dependence of pitch in induced cholesteric phases has an opposite sign in anionic and cationic media. As illustrated in Figure 4, $dP/dT > 0$ in the SDS-based chiral nematic and $dP/dT < 0$ in the cationic host, based on MTAB. A positive sign of pitch−temperature dependence is also observed in CsPFO/H$_2$O systems (not shown in Figure 4). Typical P_o values at room temperature are 17.5, 18, and 22 μm, respectively, for SDS, CsPFO, and MTAB. The relative pitch expansion (contraction) coefficients $dP/(P\ dT)$, as determined from the linear segments of the pitch−temperature plots, were as follows: +4.6, +3.1, and −0.9%/°C for SDS, CsPFO, and MTAB phases, respectively. Although the temperature behavior of the pitch in lyotropic cholesterics

Figure 4. Temperature dependence of the pitch in chiral lyonematics based on (●) MTAB doped with 0.4 wt % HPC$_{MW\ 100\ 000}$, (○) MTAB doped with 3.3 wt % (−)-*N*-dodecyl-*N*-methylephedrinium bromide, and (▲) SDS doped with 0.2 wt % of HPC$_{MW\ 100\ 000}$.

has not been studied as extensively as in thermotropic systems, all previous studies consistently indicate a positive sign of the $P-T$ dependence in these systems.[12,26−28] The reported changes in the pitch were on the order of 2−10%/°C. Thus, the pitch−temperature correlation in the HPC-doped anionic lyophases is in conformity with earlier findings. However, the temperature behavior of the pitch in the HPC−MTAB cationic phase is fundamentally different. It is similar to that of a typical thermotropic cholesteryl ester: on cooling the sample, a slow linear growth is observed followed by a sharp exponential increase in the pitch, characteristic of helix unwinding due to pretransitional phenomena. When the cationic host is doped with a low molecular weight chiral surfactant, (−)-*N*-dodecyl-*N*-methylephedrinium bromide, one observes a conventional positive pitch−temperature dependence (Figure 4, ○). Therefore, the unusual response of the pitch to variation of the sample temperature in the HPC−MTAB system can be attributed to a specific interaction between cationic micelles and a nonionic chiral polymer.

The main difference between HPC−MTAB and HPC−SDS (or CsPFO) systems is in the charge of the surfactant. It is known that nonionic polymers interact much more strongly with *anionic* than *cationic* surfactants,[13] and consequently one can justify higher HTP values of HPC in anionic phases as being due to this stronger interaction. Apparently the weaker interaction between HPC and MTAB also may lead to a change in the mechanism of twist−temperature dependence as compared with anionic phases.

In analogy with thermotropic cholesteric liquid crystals,[29] the pitch−temperature dependence in lyocholesterics can be understood as follows. When the temperature of a lyotropic system rises, the increased thermal motion results in an expansion of the molar volume and can affect the twist of the helical axis by either (i) increasing the intermicellar distance along the helical axis or (ii) increasing the average displacement angle of one micelle with respect to its neighbor. The first process leads to a decrease in the twist (a positive $P-T$ dependence) as seen in HPC−SDS (CsPFO) systems, and as also observed in a number of lyotropic cholesterics. The second process will result in an increased twist (a negative $P-T$ dependence) and has not been previously reported. To account for the pitch−temperature behavior in the HPC−MTAB system, one can assume that cationic micelles have a higher degree of motional freedom due to weaker interaction with the repeat units of HPC, and when the temperature rises, they are therefore more liable to change the average displacement angle than their anionic counterparts.

There is an additional factor which should be considered for lyotropic systems; namely, the possibility of temperature-induced changes in the micellar size. In general, a decrease in the micellar size with an increase in temperature might be responsible for the observed pitch contraction of lyocholesterics, since smaller micelles can more easily pack in a twisted array. However, since neither MTAB phases doped with low molecular weight (−)-*N*-dodecyl-*N*-methylephedrinium bromide nor anionic systems based on SDS or CsPFO doped with HPC exhibit negative pitch−temperature dependence, it is unlikely that this factor can solely govern the behavior of the MTAB−HPC system.

Conclusions

The chiral interaction of lyotropic nematics with various derivatives of cellulose has been investigated. Formation of the induced cholesteric phase in lyonematics based on MTAB, SDS, and CsPFO surfactants is observed when the disk-like nematic phase is doped with nonionic hydroxypropyl cellulose. The HTP (expressed in terms of twist per weight fraction) of HPC is several times higher than that typical of low molecular weight chiral dopants. Stronger interaction between the surfactant and polymer leads to higher values of HTP as manifested in a comparison between HTP in cationic MTAB and anionic SDS and CsPFO lyonematics. The HTP of HPC decreases with increasing average molecular weight. This behavior can be ascribed to two factors: (i) inhomogeneous distribution of chiral centers (formation of polymer bound chiral micelle clusters) and (ii) the finite character of intermicellar chiral distortion forces.

The negative temperature dependence of the pitch ($dP/dT < 0$) in the induced cationic cholesteric phase is fundamentally different from that of most lyocholesterics and may be attributed to a weaker interaction between cationic micelles and hydrophobic units of HPC. The closer packing along the helical axis with an increase in thermal motion of this system can be explained as being due to an increase in the average displacement angle between chirally distorted adjacent micelles.

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