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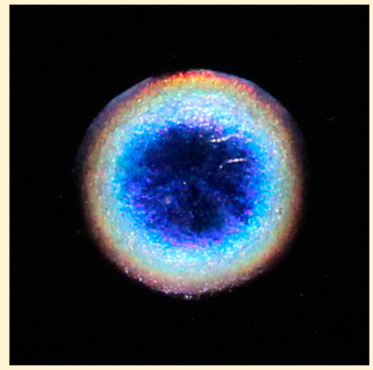
Formation of Chiral Nematic Films from Cellulose Nanocrystal Suspensions Is a Two-Stage Process

Xiaoyue Mu and Derek G. Gray*

Department of Chemistry, McGill University, Pulp and Paper Building, 3420 University Street, Montreal, QC, Canada H3A 2A7

Supporting Information

ABSTRACT: The evaporation of aqueous suspensions of cellulose nanocrystals (CNCs) gives iridescent chiral nematic films with reflection colors at visible wavelengths. A key problem is controlling the chiral nematic pitch, *P*, and hence the reflection colors of CNC films. By adding D-(+)-glucose to the suspension, we show that the change in *P* during evaporation occurs in two distinct stages. The first stage is the decrease in *P* as the concentration of CNC in the chiral nematic suspension increases due to evaporation; the addition of glucose causes a decrease in *P* at this stage. In a second stage, a concentration of CNC is reached where the formation of ordered gels and glasses prevents further major changes in *P*. The addition of glucose lowers the CNC concentration at which this occurs, leading to an increase in *P* and hence an overall shift to the red end of the spectrum in the final film.



INTRODUCTION

The hydrolysis of natural cellulose fibers with sulfuric acid leads to stable colloidal suspensions of cellulose nanocrystals (CNCs)[1,2] which display phase separation into an equilibrium ordered chiral nematic phase above some critical concentration.[3] The CNC nanoparticles are usually negatively charged due to sulfate half-ester groups on their surfaces, and increasing the ionic strength increases the critical concentration for ordered phase formation but decreases the pitch of the resulting chiral nematic structure.[4] The hydrolysis of the sulfate half-ester groups lowers the surface charge and increases the ionic strength of the suspension, and this influences the stability and redispersibility of the suspensions.[5] Isotropic and chiral nematic suspensions of pure, well-deionized CNC suspensions are stable, but interactions with ionic and polymeric species may result in flocculation or (noncovalent) gel formation. The gentle evaporation of water from chiral nematic CNC suspensions produces solid films in which the characteristic helicoidal chiral nematic arrangement of CNC is preserved.[6] The CNCs are organized in left-handed helicoids with pitch values typically around 1 to 2 μm, just above the pitch length where the reflection of visible light is expected. However, the addition of electrolyte to chiral nematic CNC suspensions is known to move the pitch to smaller values,[4] so by adding small quantities of NaCl to the suspension before film casting, the pitch values were reduced and colored iridescent films of CNC were obtained.[6] More recently, Beck and coworkers found that ultrasonication moved the reflection band of CNC suspensions and films to longer wavelengths,[7] thus demonstrating that iridescent films of any desired wavelength can be prepared from CNC suspensions by combining electrolyte addition with ultrasonication.

The formation of chiral nematic films from longer-pitch chiral nematic suspensions is not straightforward. The pitch of the suspension itself is controlled by the axial ratio and charge of the nanocrystals and by the ionic strength of the medium.[3,4] This is essentially an equilibrium process, complicated to some extent by the polydispersity of the CNC dimensions and the resulting tendency for the longer rods to migrate to the anisotropic phase. However, it is clear that as the concentration increases, a point must be reached where the mobility of the rodlike nanocrystals become severely constrained, resulting in gelation or glass formation.[8,9] As is often found with cellulose at larger length scales, drying from the wet state results in cooperative and essentially irreversible hydrogen bonding. For CNC, this irreversibility depends on the residual water content: below about 4% w/w water, the nanocrystals will not redisperse.[10] In interpreting the factors that control the pitch displayed by solid CNC films, there has been a tendency to ignore the kinetic factors that in essence control the chiral nematic pitch and liquid-crystalline texture during the latter stages of the drying process.[9] The factors that control the phase separation and chiral nematic pitch in suspension obviously are crucial, but a second set of variables come into play as the chiral nematic structure becomes locked into the film structure. This is important because control of the chiral nematic structure of CNC suspensions and films has become a key factor in their increasing use as templates for a wide range of organic and inorganic materials with chiral nematic structure and optical properties[11,12] that may be useful for photonic and plasmonic applications.[9]

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As evidence of this two-stage process, we here describe how a simple nonionic additive, D-(+)-glucose, acts independently on each process by decreasing the pitch in suspension but subsequently increasing the pitch on drying. This is clear, if qualitative, evidence for very different mechanisms in each stage of chiral nematic film formation from CNC and provides a practical approach to controlling the pitch of CNC-based chiral films. D-(+)-Glucose was chosen as an additive because the cellulose chain is composed of anhydroglucose units, so no specific interactions between cellulose and glucose were expected. Furthermore, D-(+)-glucose can exist as a glass at ambient temperatures.[13] Recently, glucose has been found to act as a plasticizer when added to CNC and sol−gel precursors, thus improving the physical properties of the resultant chiral nematic films.[14]

■ EXPERIMENTAL SECTION

Acid-form CNC suspensions (5.2 wt %) prepared from cotton cellulose were mixed with solid D-(+)-glucose to give samples with glucose concentrations of 1, 3, 5, 7, and 10% w/v. The suspensions and films cast from the suspensions were observed by polarized light microscopy, as described in the Supporting Information.

■ RESULTS

We consider first the effect on the phase behavior of adding glucose to liquid-crystalline suspensions of cellulose nanocrystals in water. A concentration of 5.2% w/w CNC in water was used as a stock solution, giving a predominantly (but not completely) anisotropic phase. Glucose was added to give concentrations from 1 to 10% w/v. The interface between the upper isotropic phase and the lower anisotropic phase was clearly visible when the samples were placed in sample tubes with rectangular cross sections. The fractions of the anisotropic phase in the samples were estimated from the heights of the menisci and phase boundaries in the samples. On average, the volume fraction of the anisotropic phase was 0.80 ± 0.04, independent of glucose content (Table 1). Thus, the glucose concentration has essentially no effect on the phase separation of the CNC. This is quite different from the effect of added electrolyte, which causes a marked decrease in the amount of anisotropic phase for a given CNC content: a concentration of 2.5 mM monovalent salt was sufficient to reduce the anisotropic volume fraction of a CNC suspension from ∼0.6 to 0.[4]

Table 1. Composition, Anisotropic Volume Fraction, and Chiral Nematic Pitch for CNC Suspensions Containing Increasing Amounts of D-(+)-Glucose

glucose content, w/v (%)	glucose added to each 5 mL CNC suspension (g)[a]	anisotropic vol fraction (ave 0.80)	chiral nematic pitch of suspensions, μm
0	0	0.82	10.9 ± 0.2
1	0.05	0.76	11.0 ± 0.2
3	0.15	0.87	5.7 ± 0.3
5	0.25	0.77	6.4 ± 0.2
7	0.35	0.82	7.4 ± 0.3
10	0.50	0.79	7.2 ± 0.3

[a]Each 5 mL sample also contains 4.74 g of H_2O and 0.26 g of CNC.

While the addition of glucose has no significant effect on the phase composition, it does influence the chiral nematic pitch of the suspensions. All of the samples contained regions where uniform extensive fingerprint textures could be discerned (Figure 1). The chiral nematic pitch for each sample was measured as twice the distance between the (dark or light) fingerprint lines. The pitch values were relatively constant for a given glucose concentration. All of the samples with more than 1% glucose showed significantly decreased pitch values (Table 1). The quantities of glucose added here are much larger than those of salts previously used to lower the pitch, and the mechanism for the increasing chiral nematic twist is not obvious here. The addition of chiral adducts to achiral nematic liquid-crystalline phases does result in chiral nematic phases.[15] D-(+)-Glucose is chiral and dextrorotatory in aqueous solution, so it is possible that it interacts to enhance the intrinsic twist of CNC suspensions. The fractionation of the polydisperse CNC in these biphasic samples may also result in the scattered pitch values. For the purpose of this communication, the important observation is that adding glucose to a CNC suspension causes a decrease in the pitch.

This contrasts with the effect of added glucose in the pitch of films prepared by the evaporation of water from the suspensions. To observe the drying process, droplets of suspension were first placed on black acrylic sheeting and allowed to dry by evaporation under ambient conditions. After 4 h, the suspension with no glucose started to show a red iridescence. After another hour, the red iridescence had moved to shorter wavelengths for the glucose-free samples, and samples with glucose started to show iridescence, starting with the lowest glucose concentration. Eventually, all of the suspensions dried down to iridescent films, but the sample with the most glucose showed no visible color.

The effect of glucose was reproducible for droplets dried on acrylic or glass surfaces. The colors for each droplet were not uniform but showed rings of different colors. The colors observed for dry droplets are shown in Figure 2. Overall, the colors move to the red end of the spectrum with added glucose, but we found that the mass transfer of the rodlike cellulose nanocrystals within a droplet evaporating on a surface leads to a radial distribution of CNC, (analogous to the coffee-stain effect[16]), with a thicker ring of material at the outer edge (Supporting Information). Gelation occurs more readily in the ring so that the colors at the outer edge of the dried droplet are at the red end of the spectrum compared to the colors in the center. The reflection color patterns of the CNC−glucose droplets are shown more clearly by masking the center and outer ring of the dried droplets. While the colors are sensitive to the angle of incident light and the angle of observation, these were set as close as possible normal to the sample and are constant for a given photographic image.

■ DISCUSSION

The addition of glucose causes essentially no effect on the critical concentration for the formation of the chiral nematic phase but decreases the observed chiral nematic pitch in the suspensions and increases the (much smaller) chiral nematic pitch of the dry films. The decrease in pitch of the suspension at higher water contents mirrors the effect of added electrolytes

As the evaporation of water increases the CNC concentration to the point where gelation and eventually glass formation occur, the role of the added glucose changes. The added glucose is expected to lower the activity[17] and increase the viscosity[18] of the water, leading to an enhancement of gelation with increasing glucose concentration. If it is assumed that gelation prevents the further decrease in pitch expected for increasing CNC content, then the final reflection wavelength of

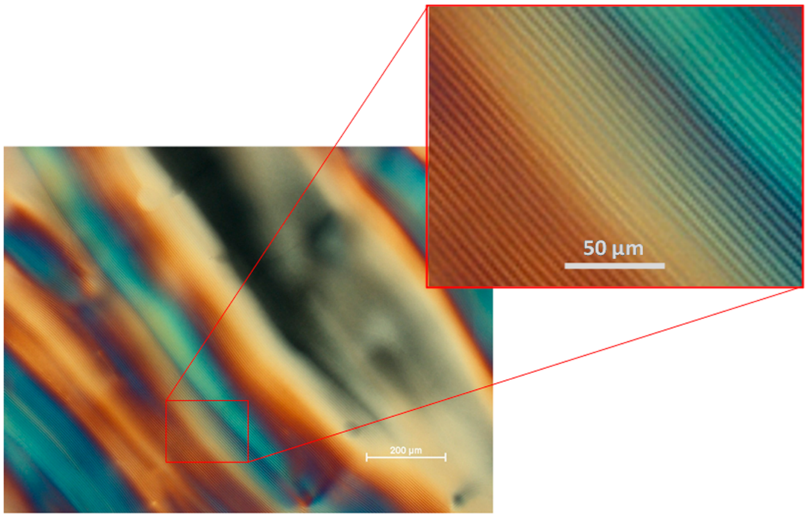

Figure 1. Polarized light microscope images of a 5.2% w/w CNC suspension in water. The magnified inset shows fingerprint lines with a spacing of $P/2$. Scale bars are 200 and 50 μm.

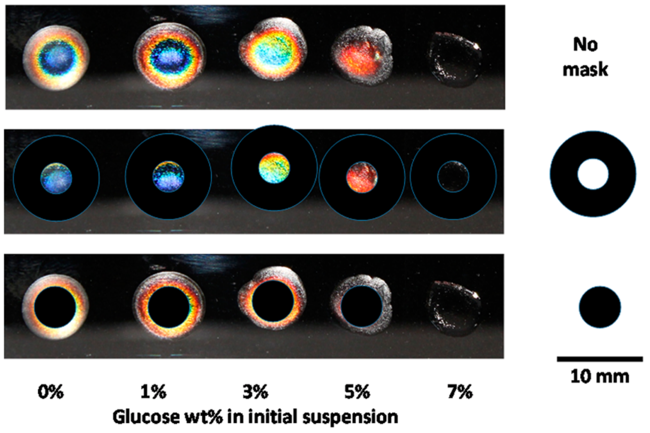

Figure 2. Reflection colors from dried droplets of 5.2% w/w CNC suspensions in water initially containing from 0 to 7 w/v % glucose. The lower two images are masked to show colors in the center and at the edge of dried droplets. In all cases, the colors move to longer wavelengths with added glucose.

the films should move to the red with increasing glucose content, as observed in Figure 2. The dependence of the chiral nematic pitch on the CNC concentration is illustrated schematically in Figure 3. At low concentrations, the suspension is isotropic. As the CNC concentration increases, the separation of an anisotropic phase first occurs at concentration C_a and is complete above C_i.[4] The pitch in the biphasic region (AB) is expected to remain almost constant. In general, for polymeric chiral nematic phases, $P \propto (C)^{-x}$, with exponent x between 1 and 3, at least over a moderate concentration range.[19] The lines BC and BC′ in Figure 3 imply this relationship between C_{CNC} and P. In this concentration range, the pitch values are usually longer than the wavelength of visible light and are measured by the spacing of the fingerprint lines (Figure 1). For a given CNC concentration, samples with added glucose (solid line) were observed to have shorter values of P than those with no added glucose (broken line). The onset of gelation at C_{gl} causes the pitch to deviate from the logarithmic relationship, and the formation of a solid film at C_{gs} essentially fixes the pitch in an ordered glass. Some decrease in pitch with concentration is expected as the gel loses water to form a glassy solid. If the aim is to make solid iridescent films, then the range of P values at which trapping occurs must correspond to those that give the reflection of visible light, as indicated by the rainbow region in Figure 3. The addition of glucose, which itself forms a glassy solid on evaporation,[13] lowers the concentration C_{gs} at which gelation and glass formation occur so that the observed final color for the glucose-containing sample (line DE) is shifted to the red compared to that for a glucose-free sample (line D′E′). In other words, the added glucose results in a red shift in the observed color, despite the decrease in pitch observed for the suspension at lower CNC concentrations.

In general, the freezing-in of the structure must occur over a relatively narrow compositional range if iridescent colors are to be observed. If gelation occurs at concentrations below C_a, then clear isotropic nonbirefringent films will result. If gelation occurs at pitch values above the rainbow region in Figure 3, then birefringent films with a chiral nematic structure will form but will lack reflection colors. Finally, if the suspension remains in a fluid state to very high concentrations, then the reflection band may move into the ultraviolet, and no visible iridescence will be observed.

In a recent communication that supplements this work, Dumanli et al.[20] followed the evaporation process from isotropic CNC suspensions to dry films under controlled humidity conditions. Both fingerprint spacing and reflection wavelengths were reported, with the latter showing an unexpected discontinuity in the time evolution of the reflection band wavelength prior to film formation. (These authors included the evaporation of the isotropic phase as one of their three stages of evaporation whereas we here consider only the two stages following chiral nematic phase formation.)

The added glucose acts as a diluent, which also will prevent the CNCs from attaining their short-pitch state. The idea that a neutral additive can move reflection bands to longer wavelengths by enhancing gelation, essentially trapping the chiral nematic structure and preventing attainment of the equilibrium pitch, may also provide an explanation for the results reported by Beck and Bouchard;[7] the ultrasonication required to disperse CNC might also liberate sugars and sugar acids in sufficient quantities to influence the pitch of the final films.

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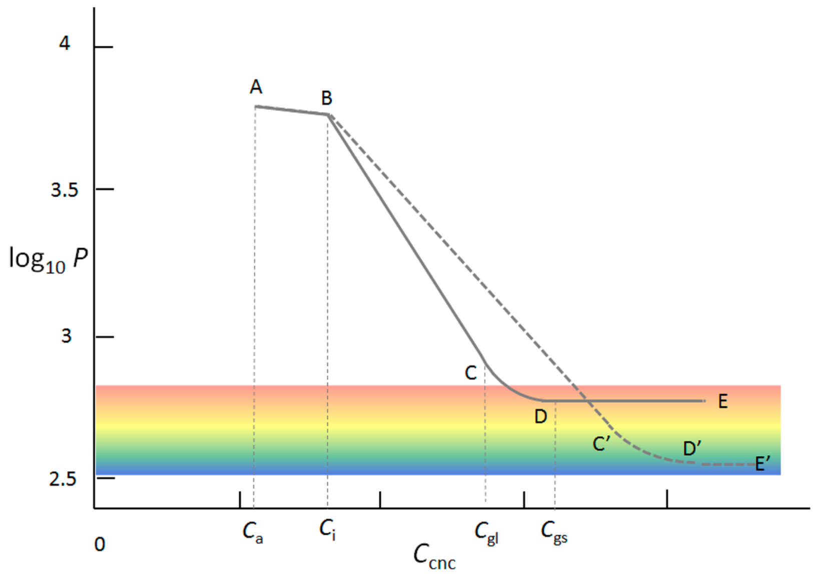

Figure 3. Schematic illustrating the observed dependence of the chiral nematic pitch, P, as a function of CNC concentration, C_{cnc}, as water evaporates to form a solid film. Solid and broken lines are for suspensions with and without added glucose, respectively. The rainbow area represents the range of P values that reflect visible light. C_a and C_i represent critical concentrations for the onset and completion of the chiral nematic phase separation, respectively, and C_{gl} and C_{gs} represent concentrations for gel and solid glass formation, respectively. Points on the curves are described in the text.

OUTOOK

While the observations in this letter are qualitative, they clearly show that the addition of D-(+)-glucose causes the pitch of chiral nematic long-pitch suspensions to decrease but shifts the (much shorter) pitch of the dry films to longer values, thus moving the iridescent reflection of the films to the red end of the spectrum. The results support the proposition that two distinct mechanisms operate as chiral nematic films form by evaporation, with the addition of glucose enhancing the tendency to gel and hence inhibiting further decreases in pitch as the suspension dries. D-(+)-Glucose was chosen as a relatively inert and benign additive. The range of possible additives is very large, encompassing any water-soluble compound that does not cause flocculation of the CNC suspension; polysaccharides and surfactants have recently been shown to cause the gelation of CNC suspensions, but chiral nematic order was not detected.[21] Given the current state of the theory, it is difficult to predict the effect of additives on P in the equilibrium region, but the onset of the CNC gelation process is accessible by rheological measurements.[22] Lower concentrations of water-soluble gel-forming polymers would make more effective gelling additives than simple sugars, while the addition of appropriate cosolvents might allow shorter pitch values to be attained before gelation. The two-stage approach should facilitate the control of reflection bands not only in chiral nematic films of cellulose nanocrystals but also in the burgeoning field of organic and inorganic film prepared with CNC templates.[12]

ASSOCIATED CONTENT

Supporting Information

Experimental details and information on the topography of dried films. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: derek.gray@mcgill.ca.

Notes

The authors declare no competing financial interest.

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