Nonflocculating and Chiral-Nematic Self-Ordering of Cellulose Microcrystals Suspensions in Nonpolar Solvents

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Nonflocculating and Chiral-Nematic Self-ordering of Cellulose Microcrystals Suspensions in Nonpolar Solvents

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Introduction

Cellulose is biosynthesized by numerous living species in the form of slender and nearly endless rods called microfibrils. Depending on their origin, these elements differ in lateral size, with diameter ranging from 2 to 20 nm. Upon the action of strong acids, these microfibrils break down into short crystalline rods or "cellulose microcrystals" whose diameter is the same as the parent microfibrils, but having shorter lengths, ranging from a few hundreds of nanometers to a few microns. In 1959, Marchessault et al.[1] reported the formation of birefringent aqueous gels of these cellulose microcrystals after an acidic treatment. The stability of these suspensions resulted from the grafting of ionic species (sulfate, phosphate, ...) during the acidic treatment.

More recently, Revol et al.[2] showed that microcrystals from bleached kraft wood pulp suspensions could spontaneously separate into a chiral-nematic liquid crystalline phase above a critical concentration. This organization is analogous to the structural organization of helicoids in nature. This self-organization has been observed with cellulose microcrystals extracted from wood or from cotton, in a concentration ranging from 2% w/w to 10% w/w, depending on the experimental procedure. Onsager[3] has predicted this liquid crystalline behavior in the general case of suspension of rods with a high aspect ratio. The critical concentration at which the rods self-organize depends on their aspect ratio and on the electrostatic repulsion,[4] if any. This general trend is also observed for other rodlike particles both organic (chitin,[5] tobacco mosaic virus,[6] DNA fragments[7,8]) or inorganic origin (vanadium oxide,[9] boehmite rods[10]) with either chiral-nematic or nematic order. In the case of cellulose, the effects of preparation conditions,[11] ionic strength[12] or counterions[13] have been extensively studied.

The ability of cellulose microcrystals to form stable aqueous suspension may lead to a number of potential applications. For instance, cellulose microcrystals from the mantle of the sea animal tunicate have been mixed with polymer latexes to yield nanocomposite materials with superior mechanical properties.[14] Aqueous suspensions of parenchymal cellulose microfibrils have been shown to exhibit interesting thickening and suspending properties.[15] All these properties rely on the individualization and good dispersion of the corresponding cellulose elements.

So far, the dispersion and self-ordering properties of cellulose microcrystals or microfibrils are restricted to aqueous suspensions or dispersions in a few organic solvents with high dielectric constant such as DMSO or ethylene glycol.[16] The main reason for such restriction is the electrostatic character of the suspension stability. In an apolar organic solvent, the electrostatic repulsion is inefficient and the establishment of strong hydrogen bonds between cellulose microcrystals leads to a rapid aggregation of the colloidal suspension. This phenomenon limits the applications and the studies of cellulose microcrystals suspensions to a few solvents.

Some attempts have been made to disperse cellulose microcrystals in organic solvents by chemical modification of the microcrystal surface. This method is still limited to the dispersion in acetone or acetic acid and requires controlled experimental procedures.[17] In another field, the dispersion of boehmite rods in cyclohexane has been reported by chemical grafting of poly(isobutene).[18] Again, these methods involve delicate chemical modifications of the surface of the rods. The aim of the present paper is to describe a new way to obtain stable dispersion of cellulose microcrystals in nonpolar solvents using surfactants as stabilizing agents. The dilute suspensions are briefly characterized, and some of the self-ordering properties of the concentrated suspensions are presented.

Materials and Methods

Preparation of Suspensions in Water. Initial suspensions of cellulose microcrystals were prepared by acid hydrolysis following the methods of Revol et al.[19] for cotton microcrystals (filter paper Whatman No. 1) and Sassi[20] for tunicate. The final concentrations of the samples were found to be 1.5% w/w and 0.3% w/w for the cotton and tunicate suspensions, respectively. Typical dimensions of the resulting microcrystals were about 10 nm wide and 300 nm long for the cotton and 15 nm wide for 1 micron or more for tunicate.

Preparation of Suspensions in Nonpolar Solvents. Experimental details are also given in a pending patent.[21] The surfactant used in this study is the Beycostat NA (BNA) commercialized by the CECCA-ATO Co. The BNA surfactant is a phosphoric ester of polyoxyethylene(9) nonylphenyl ether. The initial suspensions were mixed with the surfactant in a proportion of 4/1 (w/w) of BNA to cellulose. Typically, a suspension of 50 mL of a cotton linters suspension 1% w/w was mixed with 2 g of BNA. A lower amount was not sufficient to obtain a good dispersion in the organic solvents, whereas a greater amount

(1) Marchessault, R. H.; Morehead, F. F.; Walter, N. M. *Nature* **1959**, *184*, 632.

(2) Revol, J.-F.; Bradford, H.; Giasson, J.; Gray, D. J. *Int. J. Biol. Macromol.* **1992**, *14*, 170.

(3) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.

(4) Stroobants, A.; Lekkekerker, H. N. W.; Odjik, T. *Macromolecules* **1986**, *19*, 2232.

(5) Revol, J.-F.; Marchessault, R. H. *Int. J. Biol. Macromol.* **1993**, *15*, 329.

(6) Bawden, F. C.; Pirie, N. W.; Bernal, J. D.; Fankuchen, I. *Nature* (*London*) **1936**, *138*, 1051.

(7) Robinson, C. *Tetrahedron* **1961**, *13*, 219.

(8) Livolant, F.; Leforestier, A. *Prog. Polym. Sci.* **1996**, *21*, 1115.

(9) Davidson, P.; Gabriel, J. C.; Levelut, A. M.; Batail, P. *Europhys. Lett.* **1993**, *21*, 317.

(10) Buining, P. A.; Lekkerkerker, H. N. W. *J. Phys. Chem.* **1993**, *97*, 11510.

(11) Dong, X. M.; Revol, J.-F.; Gray, D. G. *Cellulose* **1998**, *5*, 19.

(12) Dong, X. M.; Kimura, T.; Revol, J.-F.; Gray, D. G. *Langmuir* **1996**, *12*, 2076.

(13) Dong, X. M.; Gray, D. G. *Langmuir* **1997**, *13*, 2404.

(14) Favier, V.; Chanzy, H.; Cavaillé, J.-Y. *Macromolecules* **1995**, *28*, 6365.

(15) Dinand, E.; Chanzy, H.; Vignon, M. R. *Cellulose* **1996**, *3*, 183.

(16) Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1983**, *37*, 815.
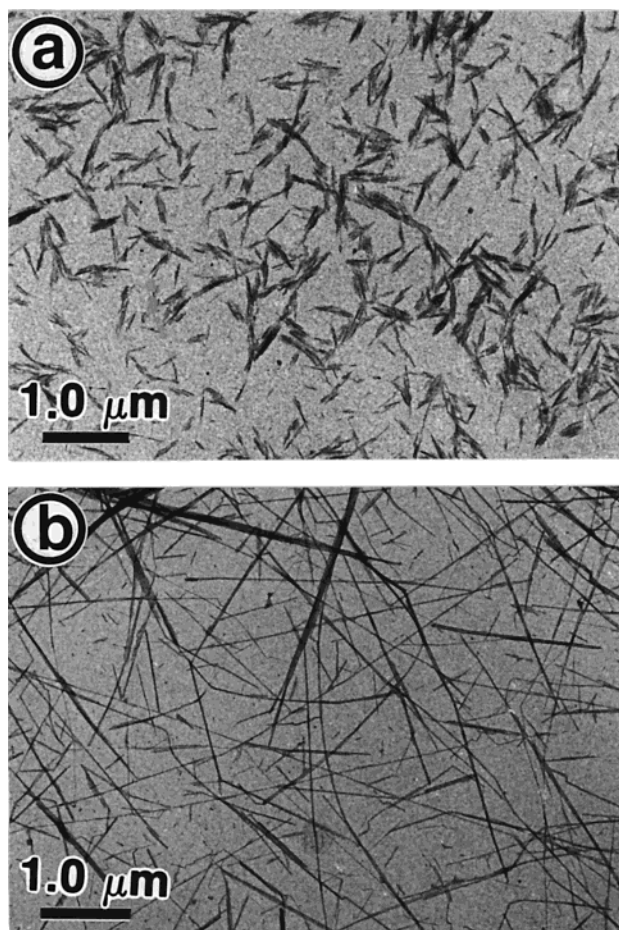
(17) Cavaillé, J.-Y.; Chanzy, H.; Fleury, E.; Sassi, J.-F. PCT Int. Appl. WO 97 12,917, **1997**.

(18) Buining, P. A.; Veldhuizen, Y. S.; Pathmamanoharan, C.; Lekkerkerker, H. N. W. *Colloids Surf.* **1992**, *64*, 47.

(19) Revol, J.-F.; Godbout, L.; Dong, X.-M.; Gray, D. G. *Liq. Cryst.* **1994**, *16*, 127.

(20) Sassi, J.-F. Ph.D. Thesis of Joseph Fourier University, Grenoble, France 1995.

(21) Bonini, C.; Heux, L. FR 99.07493 (France), 1999.

Figure 1. Transmission electron micrographs (a) cotton microcrystals and (b) tunicate microcrystals from toluene suspensions.

did not improve the quality of the dispersion. The suspensions were then vigorously stirred and their pH was adjusted to 9 by successive additions of aqueous sodium hydroxide (1% w/w). The optimal pH ranged from 7 to 10. For such values, the surfactant was in its alkaline form. The final suspension was freeze-dried and redispersed in as much organic solvent as the initial water content using an ultrasonic treatment in a Branson Sonifier (model 350) for 1 min. These suspensions were then centrifuged for 1 h at 20 000*g*. The resulting pellet was easily redispersed in the desired amount of organic solvent with an ultrasonic treatment of a few tens of seconds. The aim of this last operation was to remove the excess of surfactant and to adjust the final concentration to the desired one. The ratio of adsorbed surfactant to cellulose was found to be $\Gamma = 0.7$ for cotton and $\Gamma = 1.5$ for tunicate if $\Gamma = weight_{surfactant}/weight_{cellulose}$.

Observation of the Suspensions. The suspensions were characterized with an optical microscope (Axioplan, Zeiss) between crossed polars and a transmission electron microscope (CM200 Cryo, Philips). The liquid crystalline samples for optical microscopy were observed in a flat-sided capillary $0.2 \times 2.0 \times 50$ mm^3 (Microslides, VitroCom Inc.).

Results and Discussion

Observation of the Microcrystals. A first control of the dispersion quality is the visualization of the individualized microcrystals. Considering the microcrystals' size, this can only be achieved by transmission electron microscopy. To avoid the superposition of many layers of microcrystals, 0.1% w/w dispersions of tunicate or cotton microcrystals in toluene were deposited on a carbon grid and allowed to evaporate. Although this method can create some drying artifacts, it is commonly used for the observation of cellulose microcrystals. Figure 1, a and b, displays

the micrographs obtained by this method for cotton and tunicate suspensions in toluene, respectively. In the case of cotton suspensions (Figure 1a), we observed microcrystals of typical dimensions ranging mostly from 200 to 300 nm in length and around 8 nm in width. The preparation showed a good dispersion of the microcrystals. Some aggregates of a few microcrystals in the form of bundles were also present. This last feature is a general trend already observed for cotton microcrystals[22] in aqueous suspensions. For the tunicate suspension (Figure 1b), a good dispersion was also observed. The cellulose microcrystals were well individualized, with a typical lateral size around 15 nm and a large polydispersity in length, ranging from a few hundreds of nanometers to several micrometers. In both cases, the overall characteristics of these suspensions are very similar to what is obtained from the original aqueous suspensions (micrographs not shown). The presence of a skin of surfactant around the microcrystals could be not clearly observed.

Dilute Suspensions. Dilute suspensions of cellulose microcrystals were obtained in toluene and cyclohexane, at 0.3% w/w for tunicate and 1% for cotton. The appearance of the dispersion differed depending on the solvent. In the case of cyclohexane, a translucent dispersion is observed, whereas in toluene dispersion, a transparent solution is obtained. This is probably due to the difference in the refractive index of the solvent (1.43 and 1.50 for the cyclohexane and toluene, respectively) and the cellulose (mean value of 1.55). Both dispersions did not present any sign of sedimentation over several weeks. Indeed, in the case of aggregation, for example with lower content of surfactant, white aggregates sedimented quickly at the bottom of the tube.

All these dispersions exhibited strong birefringence between crossed polars under flow. In this situation, the cellulose microcrystals tend to align in the direction of the flow, as it has been demonstrated earlier for aqueous suspension.[23] This creates macroscopic domains where the microcrystals are parallel. As native cellulose is strongly birefringent ($n_{\parallel} \approx 1.58$ and $n_{\perp} \approx 1.53$), this macroscopic alignment gives rise to a macroscopic birefringence clearly visible between crossed polars. In the case of dilute suspensions, this birefringence vanishes after a few seconds. This phenomenon, already visible in water when the microcrystals were stabilized by electrostatic repulsion, is an indication of the dispersion quality. This is indeed observed for our suspensions in toluene and cyclohexane. For moderately concentrated suspensions, i.e., 1% w/w for tunicate microcrystals, this birefringence could persist for longer times as the viscosity rose for increasing concentration of microcrystals. Figure 2 shows a vial containing a 1% w/w tunicate microcrystals suspension in toluene visualized between crossed polars. The observation reveals a number of domains with a strong birefringence.

Concentrated Suspensions. As aforementioned, a concentrated assembly of rigid rods can spontaneously self-organize in liquid crystalline structures. For our suspensions of cotton microcrystals in nonpolar solvents, one can expect the same behavior. Nevertheless, Revol et al.[19] showed that for cellulose microcrystals originating from acid hydrolysis of wood, one has to account for an apparent effective diameter due to the electric double-layer. This lowers the critical concentration at which the microcrystals self-organize. In our particular case, this
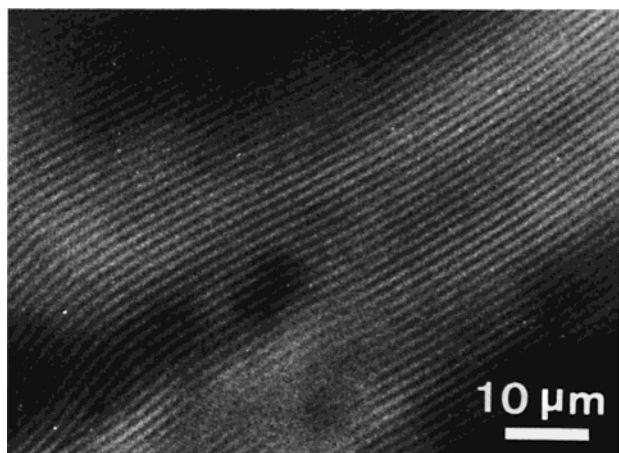
(22) Battista, O. A. In *Microcrystal Polymer Science*; McGraw-Hill Book Co.: New York, 1975; p 33.

(23) Orts, W. J.; Godbout, L.; Marchessault, R. H.; Revol, J. F. *Macromolecules* **1998**, *31*, +5717.
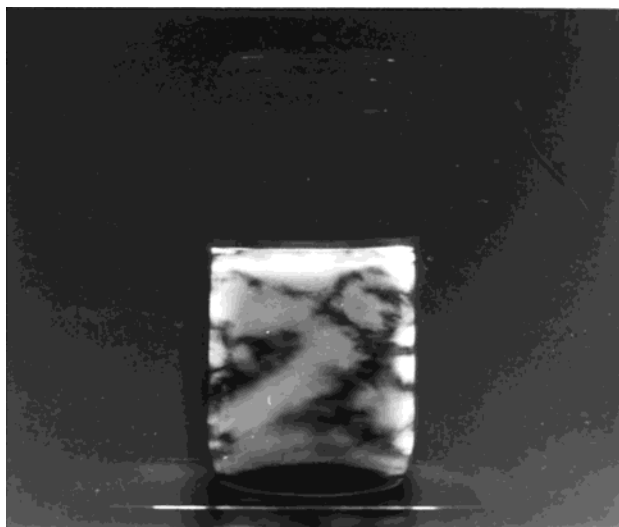
Figure 2. Dispersion of 1% (w/w) tunicate microcrystals suspension in toluene in a glass vial observed between crossed polars.

Figure 3. Optical micrograph between crossed polars of the anisotropic phase of a cyclohexane dispersion of cotton microcrystals (36% w/w).

electric double layer is not present due both to the presence of surfactant and the low dielectric constant of the solvents. One can then expect greater concentration for the appearance of the anisotropic phase.

Because of its lower toxicity, concentrated dispersions in cyclohexane were prepared, but the same general trend is observable also in toluene. A 36% w/w suspension of cotton microcrystals in cyclohexane was prepared, sealed in flat-sided capillary, and observed with optical microscopy between crossed polars. Immediately after the introduction, a mixed structure of isotropic and anisotropic phases was observed. After a slight centrifugation of the capillary at 500g during 3 min, we obtained a uniform anisotropic phase at the bottom of the capillary and a fully isotropic phase at the top without any sedimentation of the microcrystals. Figure 3 displays a micrograph of the anisotropic zone that exhibits fingerprint patterns. The alternating white and black lines are typical of the chiral-nematic structure. This texture arises from the regular change of the director of the microcrystals, which causes an alternance of extinction and illumination. The distance represented by two white and two black lines is equal to the pitch of the chiral-nematic order. In this particular case, we found a pitch of 4 μm. The volume fraction of anisotropic phase was about 80% v/v, and the
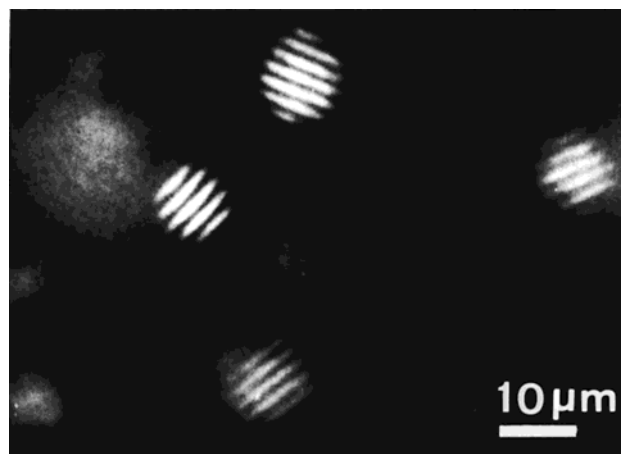
Figure 4. Same as Figure 3 but in the isotropic phase and after a few days.

respective concentrations were measured at about 37% w/w for the anisotropic phase and 32% w/w for the isotropic phase. The higher concentration in the anisotropic phase is also observed in water.[12]

The chiral-nematic structure is then preserved although a surfactant layer covers the rods. This supports the idea recently proposed by Orts et al.[23] that the chiral interaction is attributable to the packing of screwlike rods. Indeed, if the surfactant layers screen the sterical interaction between the cellulose chains, they preserve the global shape of the rods. Our results support the hypothesis of a chiral interaction arising from the shape of the rods and not from the chiral character of the cellulose chain. Moreover, the pitch measured in our case is 4 μm whereas typical values lying between 30 and 60 μm are found in aqueous suspensions.[12]

After a while, small birefringent droplets nucleated in the capillary within the isotropic phase (see Figure 4). Inside the droplets, alternating black and white lines were clearly visible. These droplets are similar to those observed in the case of an aqueous suspension of cellulose microcrystals from wood.[19] They correspond to a class of spherulites of an anisotropic chiral-nematic phase in an isotropic phase described for example by Bouligand and Livolant.[24]

The results presented in this study correspond, we believe, to the first description of stable dispersion of cellulose microcrystals in nonpolar solvents. The technique that we have described is easy to operate and reproduce. The preparations of these suspensions give access to a number of new studies that were so far impossible to achieve. The homogeneous dispersion of cellulose microcrystals and microfibrils in a number of polymer solutions and melts appears easily feasible. For instance, the dispersion of cellulose microcrystals in solvents of matching refractive indices, showing almost no diffusion from light scattering becomes also accessible etc. The results that we have presented are only preliminary. Work is in progress to characterize these systems in detail.

(24) Bouligand, Y.; Livolant, F. *J. Phys., Paris* **1984**, *45*, 1899.