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Self-Organization of Cellulose Nanocrystals Adsorbed with Xyloglucan Oligosaccharide−Poly(ethylene glycol)−Polystyrene Triblock Copolymer

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Highly crystalline cellulose particles can be produced by acid hydrolysis through partially dissolving cellulose fibrils.[1−4] Such cellulose crystals have a rod or whisker shape with a diameter from 3 to 20 nm and a length from 100 nm to several μm depending on the hydrolysis conditions and the nature of the cellulose resource.[5,6] Because they are biodegradable and biocompatible and have a high stiffness, high aspect ratio, low density, and a reactive surface that facilitates grafting chemical species to achieve different surface properties, cellulose nanocrystals reinforced nanocomposite materials are attracting increasing attention.[7,8] A specific challenge to overcome for broader application and to achieve maximum performance of such materials is the difficulty of obtaining well-dispersed, stable suspensions of cellulose nanocrystals in organic solvents and hydrophobic polymer matrices.

Some attempts have been made to disperse cellulose whiskers in organic media by coating the cellulose nanocrystals with a surfactant[9−11] or surface chemical modification, e.g., partial silylation.[12,13] Controlled polymer grafting by living polymerization techniques, such as atom transfer radical polymerization (ATRP), reversible addition−fragmentation chain transfer polymerization, and ring-opening polymerization, have been carried out on cellulose fibers. The initiators were specifically immobilized on cellulose fibers through multivalent hydrogen-bonding interactions using the xyloglucan/xyloglucan endotransglycosylase technique[14−16] or the covalent linkage by direct chemical modification.[17−20] In these approaches, cellulose fibers were purified after the initiator immobilization. In addition, monomers and unbound polymers were carefully removed after the graft polymerization. Such purification processes are tedious and difficult, especially with cellulose nanocrystals.[21,22]

The lignin−carbohydrate copolymer, hydroxypropyl lignin-*block*-cellulose propionate, has previously been used as a compatibilizer in composites of hydroxypropyl lignin and cellulose propionate.[23] Further, pullulan abietate, a model copolymer representing the lignin−carbohydrate complex, was applied to modify the cellulose model surface (Langmuir−Blodgett thin films of regenerated cellulose).[24] Glycopolymers, e.g., linear block copolymers of polystyrene and polysaccharides including dextran, maltodextrin, and maltoheptaose, have been synthesized by block synthesis methods using end-functionalized polystyrene.[25−28] Such glycopolymers exhibited enhanced structural and physiological properties, e.g., blood anticoagulant activity, cell depletion, targeted drug delivery, etc. However, they have not previously been used for cellulose fiber surface modification.

Herein, we report a new route for the surface modification of cellulose nanocrystals using a xyloglucan oligosaccharide-based triblock copolymer (Figure 1). Chiral nematic self-ordering of the cellulose nanocrystals with adsorbed copolymer was investigated in nonpolar solvent.

Xyloglucan oligosaccharides (XGOs) were prepared from deoiled tamarind kernel powder (300 mesh, Maharashtra Traders, India) using endoglucanase digestion.[14] Carboxylic acid-terminated polystyrene was synthesized using ATRP with 4-(1-bromoethyl)benzoic acid as the initiator[29] and had a weight-average molecular mass (M_w) of 4572 and a polydispersity index (M_w/M_n, where M_n is the number-average molecular mass) of 1.08. The xyloglucan oligosaccharide−poly(ethylene glycol)−polystyrene (XGO−PEG−PS) triblock copolymer was synthesized by coupling prefabricated linear blocks, i.e., reductive amination of XGOs with *O*,*O*′-bis(3-aminopropyl)poly(ethylene glycol) and subsequent carbodiimide-mediated N-acylation with carboxylic acid-terminated polystyrene. PEG was used as a compatible block between the carbohydrate (XGO) and hydrophobic (PS) blocks and to increase the hydrophilicity of the copolymer. A diblock copolymer of XGO and PS precipitated from water and failed to stabilize the cellulose nanocrystals.

The XGOs (2 g) and *O*,*O*′-bis(3-aminopropyl)poly(ethylene glycol) (amino-terminated PEG, Fluka 14535, $M_r \sim 1500$, 8 g) were dissolved in water (50 mL). Following the addition of sodium cyanoborohydride (2 g), the reaction was stirred at room temperature in the dark for 3 days. Acetic acid was then added until the solution reached pH 3.5. After evaporation and coevaporation with methanol (3 × 50 mL), the reaction solution was concentrated in vacuo. The crude product was redissolved in 10 mL of deionized water and purified on a cationic exchange column (Resin Dowex 50WX4-400, gradient 0−5% $NH_{3(aq)}$) for the removal of unreacted XGO. The product was then further purified on a size exclusion column (Biorad, Bio-Gel P2, 5 cm × 22 cm) to remove the excess of amino-terminated PEG. Fractions containing the product XGO−PEG−NH_2 were pooled and concentrated to dryness, yield 2.5 g. Syntheses and purification were monitored by analytical thin-layer chromatography on silica gel 60 F254 precoated plates (Merck, Darmstadt) and ^{1}H NMR (Supporting Information).

N-Ethyl-*N*′-(3-(dimethylamino)propyl)carbodiimide (EDC, 0.2 mL) and carboxylic acid-terminated polystyrene (0.75 g) were dissolved in *N*,*N*-dimethylformamide (DMF, 5 mL) and stirred at room temperature for 30 min. A solution of XGO−PEG−NH_2 (0.50 g) and 4,4-(dimethylamino)pyridine (DMAP, 12 mg) in DMF (5 mL) was then added. The mixture was stirred at 22 °C for 16 h, followed by the addition of methanol (200 mL). The resulting precipitate was collected on Whatman GF/A glass microfiber filters, vacuum-dried, and redissolved in 3 mL of DMF (DMF is the common solvent for the PS block and XGO−PEG diblock), followed by adding 300 mL of hot water. The excess of carboxylic acid-terminated polystyrene was removed by filtration using Whatman 541 filter papers. The filtrate, i.e., aqueous colloidal solution of XGO−PEG−PS, was dialyzed against deionized water using Spectra/Por 3 dialysis membrane (MWCO: 3500) for 7 days and then freeze-dried on a Christ Alpha 2-4 LDplus freeze-dryer at 0.021 mbar, yield 0.60 g. Figure S6 shows the ^{1}H NMR spectrum of the triblock copolymer XGO−PEG−PS in DMF-d_7 at 25 °C. The disappearance of the carboxylic acid at 13.12 ppm and the presence of the XGO and PEG blocks at 3.0−5.75 ppm were identified. Because of the intensive dialysis, the presence of remaining uncoupled XGO−PEG diblock is unlikely. Hence, it can be concluded from

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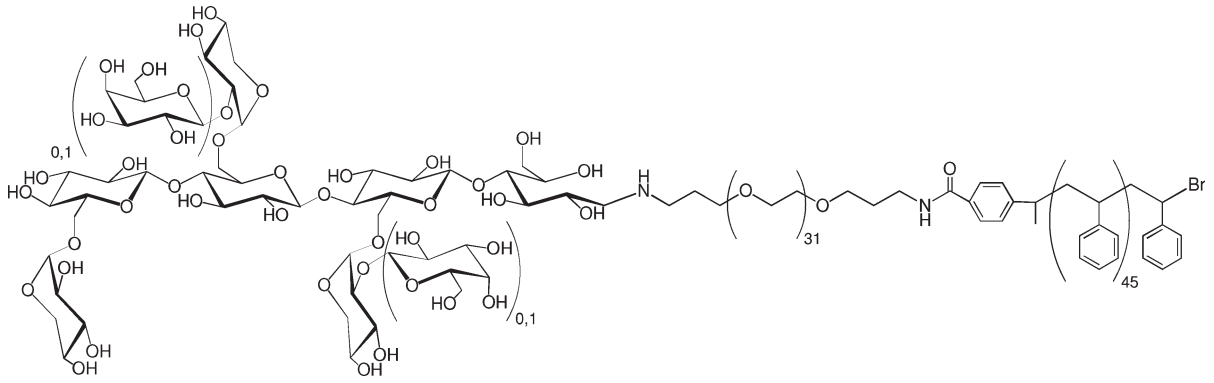

Figure 1. Chemical structure of the xyloglucan oligosaccharide−poly(ethylene glycol)−polystyrene triblock copolymer.

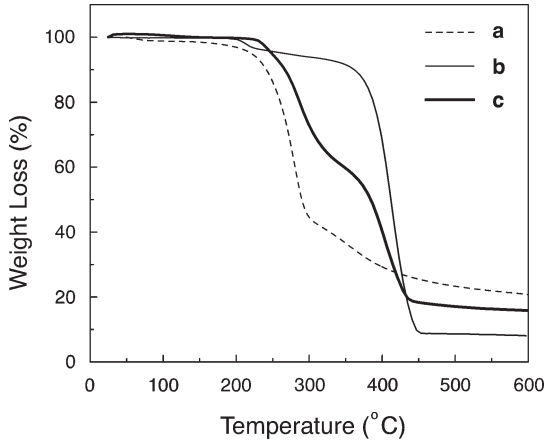

Figure 2. Thermogravimetric curves of (a) the pure cellulose nanocrystals, (b) the XGO−PEG−PS triblock copolymer, and (c) the cellulose nanocrystals adsorbed with the triblock copolymer.

the ^{1}H NMR spectra that the synthesis of the triblock copolymer was successful.

The cellulose nanocrystals suspension was prepared from cotton cellulose by sulfuric acid hydrolysis.[30] In brief, 20 g of Whatman No. 1 cellulose filter paper was stirred with 175 mL of 64 wt % sulfuric acid at 45 °C for 1 h. The suspension was diluted 10-fold with deionized water and then centrifuged at 4300 rpm for 10 min to concentrate the cellulose and to remove excess aqueous acid. The resultant precipitate was rinsed, recentrifuged, and dialyzed against water for 7 days until constant neutral pH was achieved. Mixed bed ion-exchange resin (Dowex Marathon MR-3 hydrogen and hydroxide form) was added to the cellulose suspension for 48 h and then removed by filtration. The suspension was sonicated repeatedly (Branson Sonifier Model 250 ultrasonic cell disruptor/homogenizer) at 80% output (with cooling in an ice bath) to create cellulose crystals of colloidal dimensions.

The triblock copolymer (100 mg) was first dissolved in 0.5 mL of DMF. Then 50 mL of water was added, and the solution was vigorous stirred for 24 h at room temperature (22 °C). The resulting solution was translucent, and no precipitation was observed even after centrifugation at 2000*g* for 30 min. This copolymer solution was then mixed with 0.2 mL of 10 wt % aqueous suspension of cellulose nanocrystals and stirred for 4 h at room temperature. The final suspension was freeze-dried and redispersed in 1 mL of toluene using the ultrasonic cell disruptor/homogenizer at 40% output for 1 min. The suspension was then centrifuged at 12 000*g* for 10 min at 4 °C to remove the excess of copolymer. The resulting pellet, i.e., cellulose nanocrystals adsorbed with the copolymer, was easily redispersed in the desired amount of toluene with an ultrasonic treatment of a few tens of seconds.

The amount of the triblock copolymer adsorbed on the cellulose nanocrystals was obtained from the decomposition behavior in thermogravimetry (Figure 2). The thermal degradation of original cellulose nanocrystals proceeded in two separate pyrolysis processes in the range of 200−290 and 300−400 °C, similar to spherical cellulose nanocrystals with sulfate groups.[31] The triblock copolymer decomposed rapidly at 360−450 °C, with a residue of 9% at 550 °C. The degradation profile of cellulose nanocrystals adsorbed with the copolymer clearly showed a two-step decrease, i.e., a superposition of the features of cellulose nanocrystals and the copolymer. The decrease in copolymer weight was determined as ca. 41% from curve c, by extrapolation of the copolymer component. Therefore, the weight fraction of the adsorbed triblock copolymer was 45%, assuming that the adsorbed copolymer decomposes in the same way as the free one.

The dispersion quality of cellulose nanocrystals was confirmed by visualization of the individualized nanocrystals using transmission electron microscopy (Figure 3). A good dispersion was observed for the toluene suspension of the cellulose nanocrystals adsorbed with the copolymer. The nanocrystals were of typical dimensions ranging mostly from 200 to 300 nm in length and around 15 nm in width. A coating layer was clearly observed on the surface of the cellulose nanocrystals (Figure 3b), and the width of the nanocrystals increased with an average of 10 nm compared to the unmodified ones (Figure 3a). The level of dispersion of cellulose nanocrystals in toluene is better than previously reported surfactant-assisted dispersion, in which bundles of nanocrystals aggregates were observed.[9]

To study the self-organization behavior of cellulose nanocrystals in liquid crystalline structures, a 20 wt % toluene suspension of the cellulose nanocrystals adsorbed with the triblock copolymer was prepared. Thus, the concentration of cellulose in the suspension was 11 wt %. The suspension was sealed in flat-sided capillary and observed with optical microscopy between crossed polars. The equilibrium between an upper disordered isotropic phase and a lower anisotropic phase was achieved after standing at room temperature for 24 h (Figure 4a). Small birefringent droplets nucleated within the isotropic phase as shown in Figure 4b, corresponding to a class of spherulites of an anisotropic chiral−nematic phase in an isotropic phase. These droplets, usually described as "tactoids", are similar to those observed in the case of an aqueous suspension of cellulose crystallites that were prepared by acid hydrolysis of bleached kraft wood pulp from black spruce.[1] The anisotropic phase exhibited fingerprint patterns with alternating black and white lines, a typical chiral−nematic structure (Figure 4c). The distance between two adjacent black or white lines is equivalent to one-half the full pitch. We found a pitch size of 17 μm, a typical value that has been reported for the aqueous suspension with similar

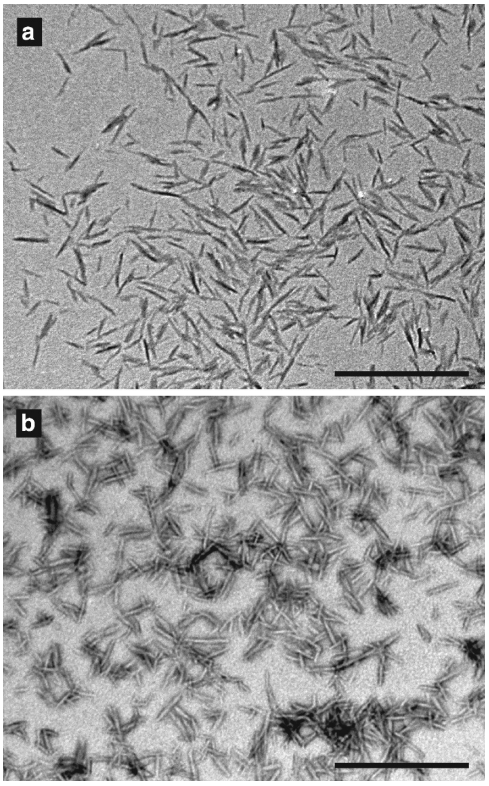

Figure 3. Transmission electron micrographs of (a) the cotton nanocrystals from dilute water suspension and (b) the cotton nanocrystals adsorbed with the triblock copolymer from dilute toluene suspension (scale bar: 1 μm).

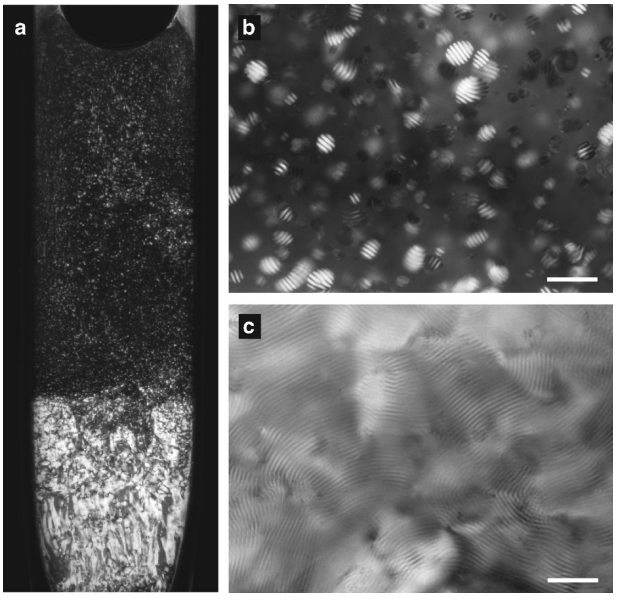

Figure 4. Equilibrium (a) between ordered and disordered phases of a toluene dispersion of the triblock copolymer coated cotton nanocrystals (20 wt %) and optical micrographs of (b) the upper isotropic and (c) the lower anisotropic phases, viewed between crossed polars (scale bar: 100 μm).

cellulose concentration.[5] This supports the idea that a chiral interaction arises from the global shape of the rods, not from the chirality of the cellulose chain or the surface charges on the rods.

We believe this is the first time a saccharide-based amphiphilic block copolymer has been used for the surface modification of cellulose. This method opens the opportunity for designing new cellulose nanocrystal-based biocomposite materials that were previously impossible to produce. The results that we presented here are preliminary, and work is in progress to characterize the system in detail.

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Supporting Information Available: Characterization methods and ^{1}H NMR spectra monitoring the synthesis of the triblock copolymer XGO−PEG−PS. This material is available free of charge via the Internet at http://pubs.acs.org.

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