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RPPR Final Report
as of 25-Apr-2019

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Agreement Number: W911NF-15-1-0190

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Title: One-Component Composites based on Nanorods: From fundamental studies to multifunctional materials

Begin Performance Period: 01-Jun-2015

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Report Term: 0-Other

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STEM Degrees: 0

STEM Participants: 5

Major Goals: Create one-component nanocomposites (OCNs) based on polymer-grafted cellulose nanocrystals and investigate their properties,

Specifically:

Develop robust chemistries and procedures for the synthesis of Hairy NanoRods (HNRs) based on CNCs

Demonstrate that homopolymer-CNC based OCNs can overcome the limitations of conventional CNC nanocomposites (aggregation, embrittlement)

Investigate structure-property relationship of polymer-functionalized OCNs. Demonstrate structure-specific functions such as shape-memory behavior, toughening, selective transport, healing, adhesion.

Accomplishments: See uploaded PDF

Training Opportunities: Graduate: Sandra Wohlhauser (formerly Graterol) attended three conferences. 34th Surface Science and Thin Films Community of Switzerland (SAOG) Meeting; February 1st, 2018, Fribourg, Switzerland; International Symposium Frontiers in Polymer Science; May 17th to 19th, 2017; Seville, Spain and Trends in Nanotechnology International Conference, September 5th - 9th, 2016; Fribourg, Switzerland.

RPPR Final Report

as of 25-Apr-2019

Results Dissemination: Papers

Wohlhauser, S.; Delepierre, G.; Labet, M.; Morandi, G.; Thielemans, W.; Weder, C.; Zoppe, J.; Grafting Polymers from Cellulose Nanocrystals: Synthesis, Properties and Applications. *Macromolecules* 2018, 51, 16, 6157-6189. Editor's choice. Cover Artwork. Most accessed manuscript when first published.

Risteen, B.; Delepierre, G.; Srinivasarao, M.; Weder, C.; Russo, P.; Reichmanis, E.; Zoppe, J.; Thermally switchable liquid crystals based on cellulose nanocrystals with patchy polymer grafts. *Small* 2018. In Press. DOI: 10.1002/smll.201802060

Cudjoe, E.; Rowan, S.J. Strong, Rebondable, Dynamic Cross-linked Cellulose Nanocrystal Polymer Nanocomposite Adhesives. *Appl. Mater. Inter.* 2018, in press DOI: 10.1021/acsami.8b10520.

Wohlhauser, S.; Kuhnt, T.; Meesorn, W.; Montero de Espinosa, L.; Zoppe, J. O.; Weder, C.; One-component nanocomposites based on homopolymer-grafted cellulose nanocrystals. *Macromolecules* 2018. In preparation.

Natarajan, B.; Krishnamurthy, A.; Emiroglu, C.D.; Forster, A.; Foster, E.J.; Weder, C.; Fox, D.; Obrzut, J.; Gilman, J.; Hierarchical Cellulose Nanocrystal Blends for Bioinspired Damage Tolerant Photonic Films; *Adv. Funct. Mater.* 2018 28, 1800032. DOI: 10.1002/adfm.201800032.

Zoppe, J.; Dupire, A.; Lachat, T.; Lemal, P.; Rodriguez-Lorenzo, L.; Petri-Fink, A.; Weder, C.; Klok, H.A.; Cellulose nanocrystals with tethered polymer chains: chemically patchy versus uniform decoration *ACS Macro Letters* 2017, 6, 892-897.

Cudjoe, E.; Khani, S.; Way, A.E.; Hore, M.J.A.; Maia, J.; Rowan, S.J. Biomimetic Reversible Heat-Stiffening Polymer Nanocomposites *ACS Central Sci.* 2017, 3, 886-894.

Herbert, K.M.; Schrettl, S.; Rowan, S.J.; Weder, C.; Solid-state Multi-stimuli, Multi-responsive Polymeric Materials; *Macromolecules*, 2017, 50, 8845-8870. (50th Anniversary Perspective Invited Review). Cover Artwork.

Posters

Sandra Wohlhauser; One-component nanocomposites based on "hairy" cellulose nanocrystals; 34th Surface Science and Thin Films Community of Switzerland (SAOG) Meeting, February 1st, 2018, Fribourg, Switzerland.

Presentations

Wohlhauser, S.; Natterodt, J.; Zoppe, J. O.; Weder, C.; Polymer nanocomposites with cellulose nanocrystals: Effects of polymer grafting and processing methods on thermomechanical properties; 255th American Chemical Society, Functional Structures from Wood-Based Materials, Designed Structures & Processing; March 18th to 22nd, New Orleans, USA.

Zoppe, J. O.; Rojas, O. J.; Klok, H.-A.; Surface engineering of cellulose nanocrystals via controlled radical polymerization. 10th World Congress of Chemical Engineering, Joint Event – Nanocelluloses, October 1-5, 2017, Barcelona, Spain.

Zoppe, J. O.; Polymer grafting from cellulose nanocrystals: new synthetic pathways, properties and applications. 5th EPNOE International Polysaccharide Conference 2017, August 20-24, 2017, Jena, Germany

Christoph Weder; Bio-inspired stimuli-responsive materials; Swiss Society for Biomaterials and Regenerative Medicine, Annual Meeting, June 6, 2018; Fribourg, Switzerland.

Christoph Weder; Polymer nanocomposites with cellulose nanocrystals; 254th American Chemical Society National Meeting, August 22, 2017; Washington DC, USA.

Stuart Rowan ; Invited Lecture: Design and Synthesis of Adaptive Polymeric Materials, Department of Chemistry, Penn State University May 2018

Stuart Rowan ; Invited Lecture: Cellulose Nanocrystals as Sustainable Nanomaterials Center for Sustainable Polymers, University of Minnesota Apr 2018

Stuart Rowan ; Invited Lecture: Cellulose Nanocrystals as Sustainable Nanomaterials and their Nanocomposites ACS Workshop on Nano-, Meso-, and Microstructured Materials for Energy, Electronics and Biotechnology, SUSTECH, Shenzhen, China Apr 2018

Stuart Rowan ; Cheetham Lecture: Design and Synthesis of Adaptive Polymeric Materials Materials Research Laboratory, University of California, Santa Barbara Feb 2018

Stuart Rowan ; Dow Lecture Series: Design and Synthesis of Adaptive Polymeric Materials Department of Chemistry, University of Minnesota Nov 2017

Stuart Rowan ; Invited Lecture: Cellulose Nanocrystals and their Composites NIST, Washington DC Sept 2017

Stuart Rowan ; Keynote Lecture: Using Dynamic Chemistry to Access Stimuli-responsive and Adaptive Materials ACS Chicago Section, Loyola University, Chicago Sept 2017

Honors and Awards: Stuart Rowan, named Fellow of the American Chemical Society (2018)

Christoph Weder named Fellow of the Polymer Division of the American Chemical Society (2017) Christoph Weder elected Member of the Swiss Academy of Engineering Sciences (SATW) (2017)

RPPR Final Report
as of 25-Apr-2019

Protocol Activity Status:

Technology Transfer: Patent Application:

Rowan, S.J.; Cudjoe, E. Strong, Rebondable, Dynamic Cross-Linked Cellulose Nanocrystal Polymer Nanocomposite Adhesives Provisional Application Number: 62/502,959 filled 05/08/17.

PARTICIPANTS:

Participant Type: PD/PI

Participant: Stuart J Rowan

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: PD/PI

Participant: Christoph Weder

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Nanetta Pon

Person Months Worked: 4.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Sandra Wohlhauser

Person Months Worked: 8.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Katie M Herbert

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

RPPR Final Report
as of 25-Apr-2019

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Han Yang

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: James Lettow

Person Months Worked: 4.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Richard Kaplan

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

PATENTS:

Intellectual Property Type: Patent

Date Received: **06-Sep-2018**

Patent Title: Strong, Rebondable, Dynamic Cross-Linked Cellulose Nanocrystal Polymer Nanocomposite Adhesives

Patent Abstract: A dynamic cross-linked polymer nanocomposite adhesive has been developed by the oxidation

Patent Number: 62/502,959

Patent Country: USA

Application Date: 08-May-2017

Application Status: 1

Date Issued:

Contract Number: W911NF1510190

Title: One-Component Composites based on Nanorods: From fundamental studies to multifunctional materials

Accomplished

Section 1: Synthetic Methods to CNC-Hairy Nanorods and CNC-OCNs

Section 1: Synthetic Methods to CNC-Hairy Nanorods and CNC-OCNs

We have focused on two different routes to accessing hairy nanorods, which can then be processed into OCNs films and materials by standard solution or melt processing. That is the “grafting-to” and “grafting-from” approaches (Figure 1a).

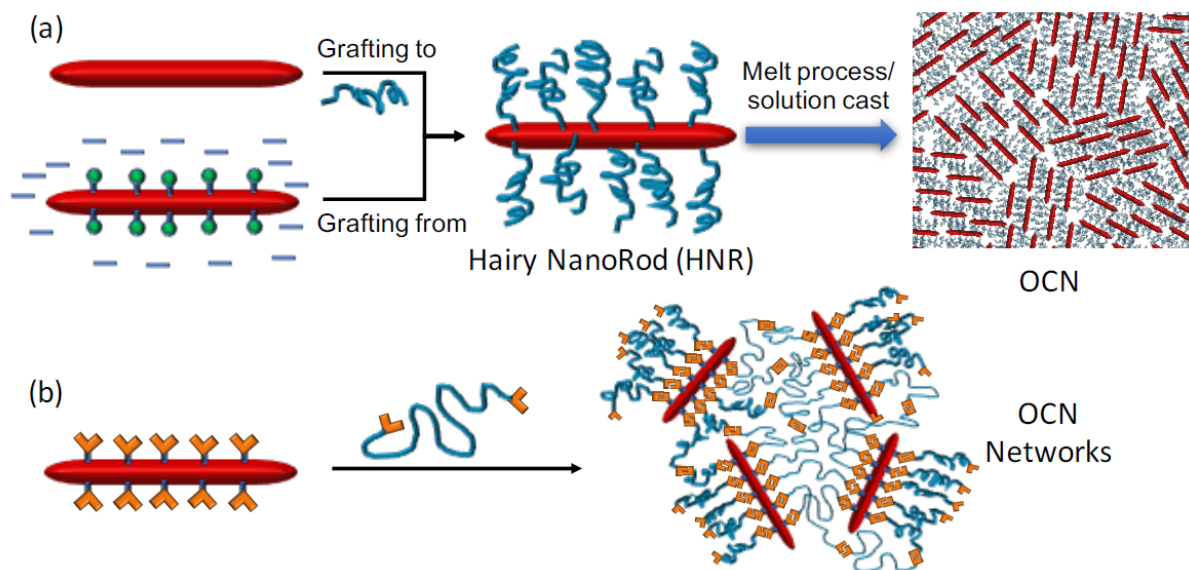


Figure 1. Schematic showing the three routes used by the PIs to access CNC one-component nanocomposites (OCNs). (a) The “grafting-to and -from” routes to access HNRs which can be processed into OCNs and (b) Reacting a functionalized CNC with telechelic polymers to access OCN networks.

In the “grafting-from” approach, the CNCs are functionalized with an initiating group and the polymer is grown from that site. Our initial investigation in this approach focused on attaching the photo-initiator benzophenone onto the CNC surface via isocyanate chemistry, resulting in CNC-Bp (Figure 2a). While this photo-initiated free radical polymerization provides little control over the resulting products, the synthetic pathway is straightforward and high molecular weight grafts can be easily obtained. As the utilization of this approach to access modified CNC-HNRs in scenarios where a high level of control is not required. This basic approach was used to access materials outlined in sections 2 and 3 in PDF attachment.

The “grafting-to” approach involves the synthesis of a polymer with a reactive chain-end followed by coupling onto the CNC. Primarily for this approach we have synthesized amine-end capped polymers using either RAFT or ATRP chemistries and carried out an amide coupling reaction to attach the polymers onto carboxylic acid functionalized CNCs (Figure 2b), see section 4 in PDF attachment.

The different approach to OCNs is different from the above two routes in that the OCN is accessed directly by reacting functionalized CNCs with telechelic polymers (Figure 1b). In this approach, the functionalized CNCs are effectively used as a crosslinking moiety for the polymer and as such the OCN has a network architecture. To do this we have particularly focused on exploring the use of either dynamic covalent chemistry (section 5 in PDF attachment) or supramolecular chemistry (section 6 in PDF attachment) to access the adaptive and responsive OCNs as the use of these chemistries allows the melt (re)processing of the OCN films.

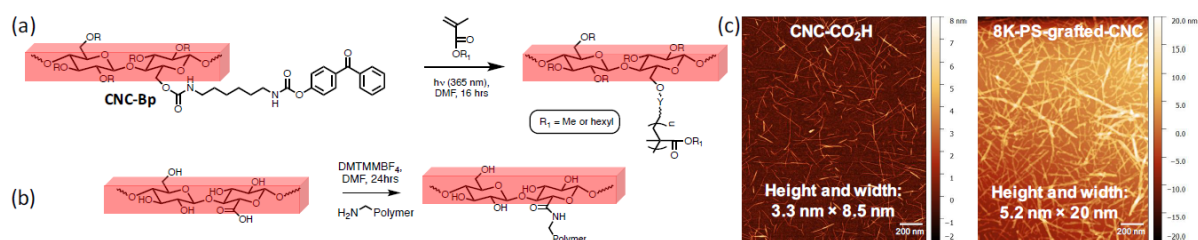


Figure 2. The (a) grafting-from and (b) grafting-to approaches used to access CNC-HNRs.

Section 2. Comparison of the Mechanical Properties of one and two-component CNC composites

In initial steps towards the development of novel one-component nanocomposites (OCNs) poly(hexyl methacrylate), a non-crystallizing, low- T_g polymer, and glassy poly(methyl methacrylate) were grafted from CNCs via surface-initiated free radical polymerization from an immobilized benzophenone photoinitiator (**Figure 2a**), to yield CNC-PHMA and CNC-PMMA, respectively. The amount of CNC in the hairy nanorods was controlled to be 10 or 20% w/w via the monomer concentration during the grafting-from step. The M_n of the grafted polymers on the CNC using this approach was ca. 200,000 g/mol (for the PMMA-OCN with 10 wt% CNC). All OCNs formed transparent, self-supporting films (**Figure 3 a,b**). Their mechanical properties were investigated and compared to those of the corresponding two-component composites, which were prepared by solvent casting. Shown in **Figure 3c** are dynamic mechanical analyses traces that show the storage modulus (E') of the CNC-PMMA-OCNs, two-component nanocomposites, and the neat PMMA. Neat PMMA displayed the typical behavior of high E' in the glassy state before reaching a T_g of ca. 100 °C, followed by a rapid decrease in E' upon increasing temperature. The two-component nanocomposites containing 10 and 20 wt% CNCs exhibited similar behavior, albeit with a slightly higher E' , especially in the rubbery region. By contrast, both PMMA-OCNs -showed a marked increase in T_g of >20 °C, and a significantly higher E' in the temperature range of 80-200 °C, arguably on account of pronounced chain entanglements between the CNC-grafted macromolecules. These effects are even more pronounced in the case of the PHMA-OCNs, where the OCN structure leads to a new rubbery plateau that extends from ca. 40 to 160 °C (**Figure 3c**). Significant changes were also observed in tensile tests (**Figure 3d**), which for PHMA-OCNs containing 10 and 20 wt% CNCs show an increase of the tensile strength by a factor of 4 and 6,

respectively (which is ca. 3 and 4 times higher than in the case of the conventional PHMA/CNC composites), while the strain at break remains appreciable (Figure 3d). Thus, these results demonstrate strikingly that OCNs offer much improved mechanical properties in comparison to classical nanocomposites, arguably, because do not suffer from mixing and phase separation problems that common to two-component composites systems. In addition, the stress-transfer mechanisms in these materials appear to differ significantly.

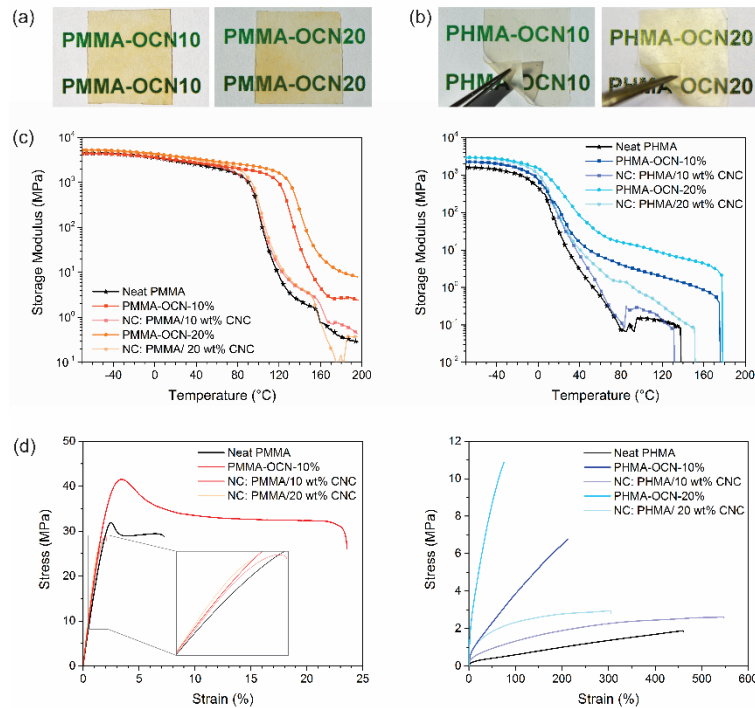


Figure 3. Pictures of (a) PMMA-OCNs and (b) PHMA-OCNs containing 10 and 20 wt% CNCs. (c) Storage modulus vs. temperature and (d) stress-strain curves of the neat PMMA (left) and PHMA (right), conventional two-component nanocomposites based on these polymers and unmodified CNCs, and the corresponding OCNs.

Section 3. Investigating Polymer Grafting-to Chemistry with CNCs

We have investigated different methods to graft polymers to CNCs. Using DIC/NHS as the coupling reagents we investigated the attachment of amine endcapped polystyrene (8K) onto carboxylic acid functionalized MxG-CNCs (Figure 4a) which were either directly dispersed in DMF or dispersed using a solvent exchange procedure (water then DMF). The results were strikingly different, 2% and 10% of carboxylic acid groups were reacted respective, which resulting in material with 12 and 40wt.% of PS in grafted CNC, respectively (as determined by TGA). It is proposed that the solvent exchange method allows for better dispersing CNC, which increases the available surface of CNC and thus increases the grafting density. As such all grafting to experiments used CNC using the solvent exchange method. Using DIC/HOBt, EDC/NHS, and DMTMMBF₄ as coupling reagents, 17%, 7.4%, 34% of carboxylic acid groups were reacted with PS, (resulting in materials with 52%, 32%, 68% weight percentage of PS in the grafted CNC, respectively). Among all the coupling reagents, DMTMMBF₄ shows the highest efficiency in the CNC grafting reaction in DMF. FITR spectra show that comparing to the starting material

CNC and PS (8 k PS), the CNC-graft-PS shows a new peak at 1650 cm^{-1} is for the amide groups formed between amine group on PS and carboxylic acid groups on CNC. DSC results (Figure 4b) also conformed the PS was grafted onto CNC surface. Free PS has a glass transition temperature peak at $96.3\text{ }^{\circ}\text{C}$, for PS and CNC mixture (which has similar PS to CNC ratio as PS-grafted-CNC) is $99.3\text{ }^{\circ}\text{C}$, PS grafted CNC has the highest T_g among them, $104.1\text{ }^{\circ}\text{C}$. AFM images (Figure 4c) of MxG-CNC and PS-grafted-CNC show the height and width of MxG-CNC (3.3 nm and 8.5 nm) is increased to 5.2 nm and 16 nm after grafting. Films prepared from PS-grafted-CNC and PS/CNC two component composite (at a similar PS to CNC ratio as PS-grafted-CNC) show that the film of PS-grafted-CNC do not show phase separation. In addition, the cross section of the PS-grafted-CNC film show they have uniform periodic layered structures. Two more PS with different molecular weight (5k and 30k) were investigated in the coupling reaction with DMTMMBF₄. Results showed that 38% and 26% of carboxylic acid groups were reacted with PS (c.f. 34% for 8k PS), to yield materials with 60% and $86\text{wt.}\%$ of PS, respectively (c.f. 68% for 8k PS). The results show that the percentage of carboxylic acid groups engaged in the coupling reaction will decrease with increasing the molecular weight of polymer, presumably due to the increasing of steric hindrance but that the overall wt.% can be increased through the use of longer polystyrene grafts.

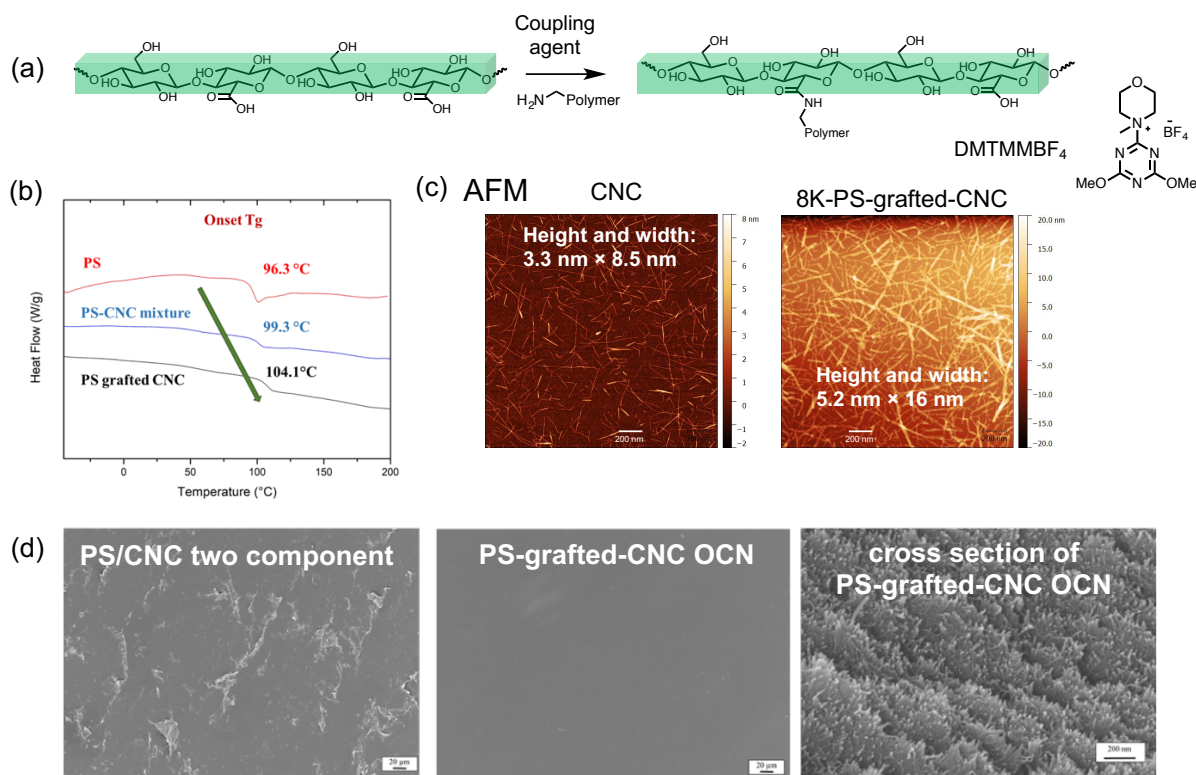


Figure 4. (a) synthetic approach used to graft polystyrene to the cellulose nanocrystals. (b) DSC heating curves for free PS, PS-grafted-CNC and PS-CNC mixture. (c) AFM images of MxG-CNC, and PS-grafted-CNC and (d) SEM images of PS/CNC mixture film, PS-grafted-CNC OCN film, and cross section of the PS-grafted-CNC OCN film.

Section 4. Synthesis of Patchy Polymer Functionalized CNCs

During the course of this project, the PIs' discovered a simple water-tolerant synthetic approach toward asymmetric, i.e. end-group modified, hairy CNCs shown in Figure 5. The inherent directionality of cellulose chains, which feature a non-reducing and a reducing end, within individual cellulose nanocrystals (CNCs) renders such site-selective end group functionalization. At first, CNC reducing end groups were oxidized and modified with ethylenediamine, followed by attachment of 2-bromoisobutanoic acid N-hydroxysuccinimide ester. Subsequently, various monomers were polymerized from initiator-modified CNCs via surface-initiated atom transfer radical polymerization. In order to directly visualize reducing end group-selective chemical modification of CNCs, sub-5 nm Au nanoparticles stabilized by anionic surface charges were synthesized and electrostatically adsorbed to patchy CNC-cationic polymer hybrids. Shown in the right of Figure 5 is a typical cryo-electron micrograph of AuNP-labeled patchy CNC/PMETAC hybrids. The image reveals slightly aggregated CNC hybrid structures in which the AuNPs appear to be concentrated at the end groups. In comparison to CNCs uniformly modified with tethered polymers, such end-modified CNCs may allow the formation of solid-state anisotropic phases, maintain CNC inherent mechanical strength, thus a novel platform for OCNs based on "patchy" nanorods.

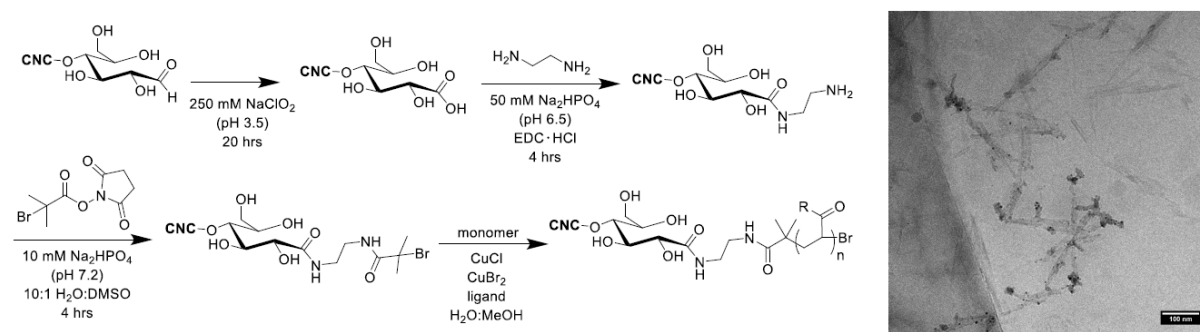


Figure 5. Synthetic protocols for conducting SI-ATRP from reducing end groups of CNCs (left) and cryo-EM micrograph of patchy CNC/PMETAC hybrids (CNC-RE-g-PMETAC) labeled with AuNPs (right).

A thermally "switchable" liquid-crystalline (LC) phase was observed in aqueous suspensions of CNCs featuring patchy grafts of the thermoresponsive polymer poly(*N*-isopropylacrylamide) (PNIPAM). "Patchy" polymer decoration of the CNCs was achieved by preferential attachment of an ATRP initiator to the ends of the rods and subsequent surface-initiated atom transfer radical polymerization (SI-ATRP). The patchy PNIPAM-grafted CNCs display a higher colloidal stability above the lower critical solution temperature (LCST) of PNIPAM than CNCs that are decorated with PNIPAM in a brush-like manner. A 10 wt% aqueous suspension of the "patchy" PNIPAM-modified CNCs displays birefringence at room temperature, indicating the presence of a LC phase. When heated above the LCST of PNIPAM (~32 °C), the birefringence disappears, indicating the transition to an isotropic phase. This switching process is fully reversible and appears to be driven by the collapse of the PNIPAM chains above the LCST,

causing a reduction of the rods' packing density and thus an increase in translational and rotational freedom. Aqueous suspensions of the "brush" PNIPAM-modified CNCs display a very different behavior. In this case, heating above the LCST causes phase separation while the mesophase is maintained, likely because the chain collapse renders the particles more hydrophobic. The thermal switching observed for the "patchy" PNIPAM-modified CNCs is unprecedented and possibly useful for sensing and smart packaging applications.

Section 5. Moisture-responsive nanocomposites

Further research has been focused on the synthesis of OCNs in which poly(vinyl alcohol) was grafted from the CNC surfaces (CNC-g-PVA). This was accomplished by grafting poly(vinyl acetate) from CNC surface (using again surface-initiated free radical polymerization from an immobilized benzophenone photoinitiator, Figures 6) followed by controlled hydrolysis of acetyl groups to alcohols. The main challenge in the polymerization of vinyl acetate is the high radical, which promotes fast termination of growing chains and makes the control of the polymerization reaction very difficult. By using the benzophenone-functionalized CNCs in the presence of methyl(ethoxycarbonothioyl) sulfanyl acetate, CNC-g-PVAc was obtained via xanthate mediated reversible addition fragmentation polymerization with 33 wt% of grafted polymer. By contrast, the synthesis of a similar OCN via surface-initiated free radical polymerization using benzophenone-functionalized CNC, resulted only in ca. 10 wt% of grafted polymer on the surface. The investigation of the mechanical properties of these materials are in progress.

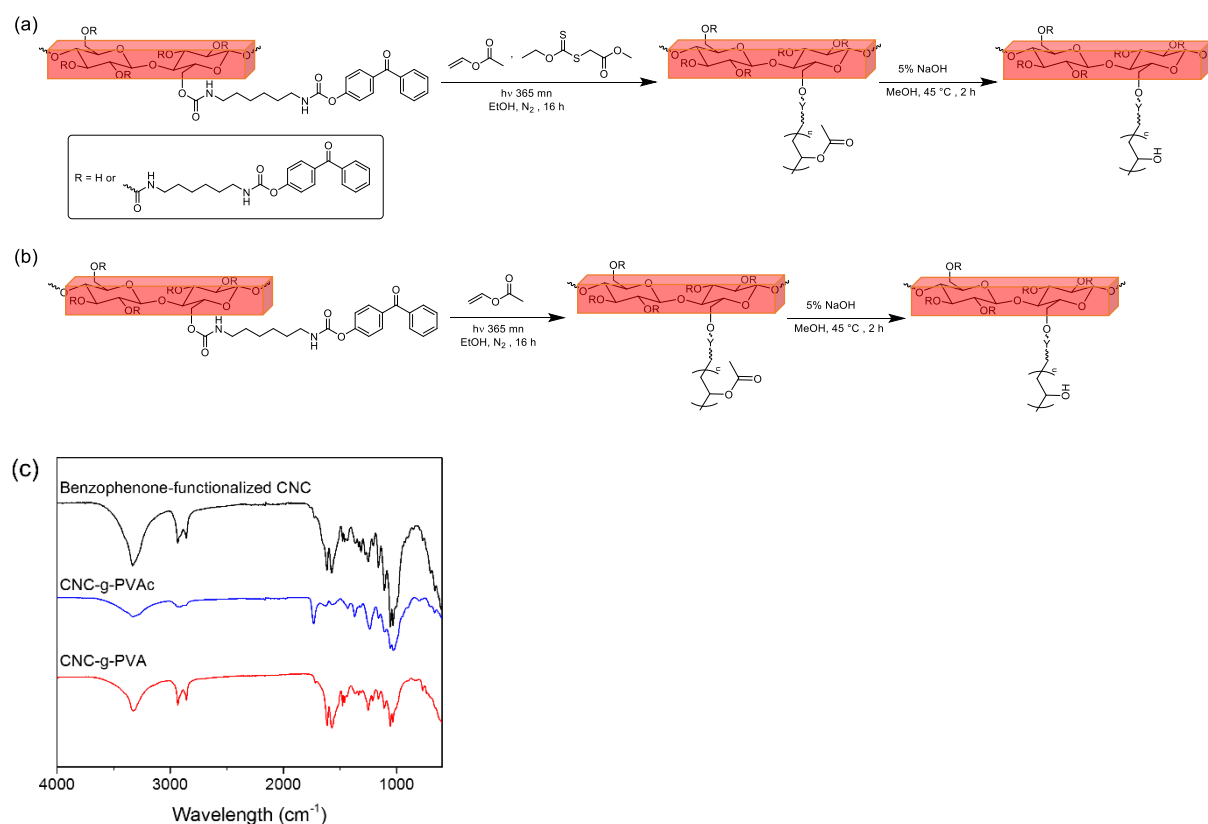


Figure 6. Synthetic protocols for grafting PVA on CNC surface via (a) xanthate mediated reversible addition fragmentation polymerization and (b) surface-initiated free radical polymerization. (c) FT-IR spectra of modified CNCs.