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Cite this article as:

Che Kun-Ming, Zhang Ming-Zu, He Jin-Lin, Ni Pei-Hong. Polyphosphoester-modified Cellulose Nanocrystals for Stabilizing Pickering Emulsion Polymerization of Styrene[J]. *Chinese J. Polym. Sci.*, 2020, 38(9): 921-931. doi: 10.1007/s10118-020-2404-z

View online: <https://doi.org/10.1007/s10118-020-2404-z>

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Polyphosphoester-modified Cellulose Nanocrystals for Stabilizing Pickering Emulsion Polymerization of Styrene

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Electronic Supplementary Information

Abstract The structure and properties of functional nanoparticles are important for stabilizing Pickering emulsion polymerization. Recently, cellulose nanocrystals (CNCs) are increasingly favored as a bio-based stabilizer for Pickering emulsions. In this study, we reported a novel functionalized polyphosphoester-grafted CNCs for the stabilization of oil-in-water Pickering emulsions and the emulsion polymerization of styrene. First, polyphosphoester containing an amino group at one end of the chain, abbreviated as PBYP-NH₂, was prepared by ring-opening polymerization (ROP) and hydrolysis reaction, wherein PBYP represents poly[2-(but-3-yn-1-yloxy)-2-oxo-1,3,2-dioxaphospholane]. Subsequently, CNC-COOH was obtained via 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation of CNCs. The functionalized nanocrystals CNC-PBYP-COOH with carboxyl groups and polyphosphoester on the surface were obtained by the amidation reaction of PBYP-NH₂ with CNC-COOH. Finally, we used CNC-PBYP-COOH as sole particle emulsifiers to stabilize styrene-in-water Pickering emulsions and studied its effects on the emulsions in details by using dynamic light scattering (DLS). The results indicated that the properties of these emulsions depended on the concentration of hydrophobically modified CNCs, volume ratios of oil to water, and pH values. The modified CNCs had higher ability to stabilize the styrene-in-water emulsions relative to the unmodified CNCs, and a stable oil-in-water (o/w) Pickering emulsion with diameter of hundreds of nanometers could be obtained. The resulting emulsions could be polymerized to yield nanosized latexes. The polyphosphoester-modified CNCs as green particle emulsifiers can efficiently stabilize nanoemulsions and latexes, which would promote the development of novel environmentally friendly materials.

Keywords Cellulose nanocrystals (CNCs); Polyphosphoesters (PPEs); Pickering emulsion; Emulsion polymerization

Citation: Che, K. M.; Zhang, M. Z.; He, J. L.; Ni, P. H. Polyphosphoester-modified cellulose nanocrystals for stabilizing pickering emulsion polymerization of styrene. *Chinese J. Polym. Sci.* 2020, 38, 921–931.

INTRODUCTION

An emulsion is a mixture of two or more normally immiscible liquids that need to be stabilized by an emulsifier. The role of the emulsifier is to increase the kinetic stability of the emulsion. Conventional surfactants are small molecules or polymers that contain both hydrophobic segments and hydrophilic groups. In the early 20th century, Ramsden and Pickering found that solid particles could be adsorbed at oil/water interfaces as surface-active stabilizer to form so-called Pickering emulsion.^[1,2] This is because the solid nanoparticles have partial wettability and strong interfacial adsorption energy in both phases.^[3] Unlike adsorption and desorption of small molecule surfactants in a fast dynamic equilibrium, solid nanoparticles tend to adsorb irreversibly at the oil-water interface.^[4,5] Thus, the resulting Pickering emulsion can exhibit better stability and reduce the

amount of stabilizers.^[6–8] Particulate emulsifiers have many potential advantages compared to conventional emulsifiers, for example, higher robustness, lower toxicity, and lower cost.^[9,10]

Pickering emulsion did not attract enough attention when it was first discovered in 1907. However, it has aroused a renewed attention in recent years, mainly because it has many unique properties such as low toxicity, low emulsifier content, and adjustable droplet size. According to literature reports, both inorganic and organic particles can stabilize Pickering emulsions, such as silica,^[11] graphene oxide,^[12] calcium carbonate,^[13] montmorillonite,^[14] Janus particles,^[15] polymeric particles,^[16] starch nanocrystals,^[17] and cellulose nanoparticles.^[18] From the perspective of environmental protection, researchers are more inclined to formulate strategies for environmental sustainable development by using low-cost, low-energy-consumption, low-toxicity, and highly biodegradable materials.^[19] Based on this, biomass materials are good candidates for stable emulsions, which are of great interest. Therefore, cellulose-based materials are favored for their non-toxic, sustainable, and biodegradable properties.^[20,21]

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Received December 28, 2019; Accepted February 17, 2020; Published online April 20, 2020

Cellulose materials are available from a wide range of plants and animals, and are green renewable resources. Some different types of cellulose particle including microcrystalline cellulose, microfibrillated cellulose, cellulose nanofibers, and cellulose nanocrystals can be obtained by mechanical treatment and acid hydrolysis.^[22] Cellulose is a linear homopolymer of β -(1,4)-D-glucose residues and has a flat ribbon-like conformation.^[23] Due to the inherent hydrophilicity of cellulose materials, unmodified cellulose materials can only stabilize oil-in-water emulsions. The first investigation on using solid cellulose particle as stabilizer was reported by Oza and Frank, whose research showed that microcrystalline cellulose could be used to stabilize the oil-in-water emulsion.^[24] Since then, many emulsions stabilized by various kinds of nanocellulose particles have been investigated, for example, regenerated cellulose nanoparticles,^[25] cellulose nanocrystals,^[26,27] cellulose nanofibers,^[28,29] and bacterial cellulose nanocrystals.^[18] In addition, water-in-oil (w/o) emulsion can be obtained by hydrophobic modification of the cellulose materials. Researches involved water-in-oil emulsions stabilized solely by esterification with organic acids of bacteria cellulose nanofibrils,^[30] and nanofibrillated cellulose tailored by chemical modification with lauroyl chloride.^[31] One feature of these cellulose materials is that they are long fibers and tend to aggregate. This limits their ability to effectively adsorb at the interface of the two phases, making it difficult to adjust drop sizes and easy to form large emulsion droplets (in the range from 10 μm to 500 μm), as well as affecting their application in some fields.^[32,33]

In order to adjust the characteristics of emulsion, the size of cellulose particles should be small and uniform. CNCs can meet the above requirement because they are hard, rod-shaped nanoparticles with a cross-section of 5–30 nm and different lengths from 100 nm to microns (depending on their source), which can be obtained by acid hydrolysis.^[22,34] Capron's group has researched on oil-in-water emulsions stabilized by non-chemically modified cellulose nanoparticles. They reported that bacterial cellulose nanocrystals (BCNs) could prompt the monodispersity of oil-in-water droplets, and the stability of Pickering emulsions lasted for months.^[18] The effect of amphiphilic properties of CNCs and various aspect ratios of cellulosic nanorods on the stability of emulsion droplets was investigated.^[32,35] It has been found that CNCs with low surface charge density, below 0.03 e/nm², could efficiently stabilize emulsion. And cellulosic nanorods with different aspect ratios had a direct influence on the coverage ratio, *i.e.* lower aspect ratio had a higher coverage. Capron's group also studied high internal phase emulsions^[36] and water-in-water emulsions^[37] stabilized with CNCs. Furthermore, they studied the packing characteristics of cotton CNCs at the interface of Pickering emulsion, which promoted the postulate that the hydrophobic (2 0 0) crystalline plane of the CNCs directly interacts with interface.^[38]

Besides the study on emulsion system stabilized with pristine cellulose nanoparticles, various modification strategies have also been used to modify the surface of CNCs to regulate the properties of Pickering emulsions. Capron and co-workers used CNCs modified with lauroyl chloride to stabilize water-in-oil emulsions.^[31] Cranston and co-workers had two cationic charged surfactants, didecyltrimethyl-ammoni-

um bromide (DMAB) and cetyltrimethylammonium bromide (CTAB), adsorb on the CNCs surface to enhance their hydrophobicity.^[39] They found that adding surfactant could improve emulsion stability and reduce droplet size. Special was a double transitional phase inversion, from o/w to w/o and then back to o/w, which was stabilized by CNCs with increasing amounts of DMAB. Capron and co-workers reported another work about carboxylic acid functionalized CNCs modified by adsorbing quaternary ammonium salts, and the CNCs with physical adsorption, which were capable of stabilizing inverse water-in-oil emulsions.^[40] Zoppe *et al.* grafted thermo-responsive poly(*N*-isopropylacrylamine) (PNIPAM) brushes onto CNCs surface. They observed that the emulsions could be stabilized for 4 months and exhibited a temperature responsive behavior.^[41] Tang *et al.* studied pH/temperature-responsive Pickering emulsion stabilized by CNCs grafted poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA).^[42] However, to the best of our knowledge, biodegradable polymers were less used for hydrophobic modification of cellulose nanocrystals.

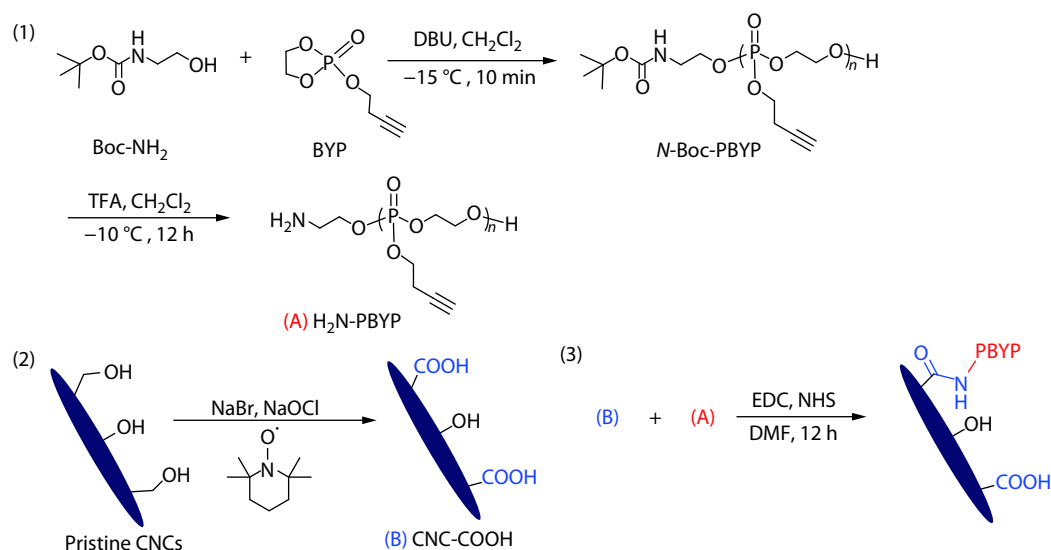
A key factor in many applications of emulsions and latexes is the resulting particle size. Researchers have shown that emulsions with droplet size in the range of 20–500 nm tend to have good properties and thus many different applications compared to microemulsions.^[43,44] The o/w nanoemulsions have been utilized in the food industry, which has been shown to enhance the bioavailability of the encapsulated flavor/ingredients during digestion.^[45] Furthermore, nanoemulsions can serve as a carrier for oral hydrophobic drugs. Nanoemulsions with ability to carry drugs provide a vehicle for keeping drugs from environmental conditions, such as harsh pH and hydrolytic enzymes.^[46] In cosmetic products, Sonnevile-Aubrun and co-workers showed that nanosized emulsion droplets could facilitate absorption through the skin.^[47]

Polyphosphoesters-based materials have good biocompatibility and biodegradability.^[48] Our group used poly(ethylene phosphate) (PEEP) to modify CNCs and as a drug carrier to load Doxorubicin (DOX). We found that the drug delivery system showed a desirable antitumor activity against HeLa cells.^[49] Based on the concept of green and sustainable development, in this work, we introduced a hydrophobic polyphosphoester, poly[2-(but-3-yn-1-yloxy)-2-oxo-1,3,2-dioxaphospholane] (PBYP), containing alkynyl on the side chain of CNCs to improve surface-active and amphipathic of CNCs, as shown in Scheme 1. The synthesis of CNC-PBYP-COOH and their application as emulsifiers for stabilizing Pickering emulsions were investigated. This study first proposed using CNCs modified by PBYP as the sole particle stabilizer to prepare the styrene emulsion, and final nanocomposite latex particles with size around 500 nm were synthesized by polymerization in aqueous dispersed media. The effects of the stabilizer concentration, volume ratios of oil to water, and pH of the media on the emulsion stability and particle size were also studied in details.

EXPERIMENTAL

Materials

The following agents were purchased and used as received without further purification: sodium hypochlorite (NaOCl, with



Scheme 1 Synthesis routes to polyphosphoester-modified CNCs *via* a combination of ROP and amidation reaction.

14.5% available chlorine, Energy Chemical), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 97%, Accela), sodium bromide (NaBr, 99%, Energy Chemical), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, 98%, TCI), *N*-Boc-ethanolamine (98%, Adamas), *N*-hydroxy-succinimide (NHS, 98%, Sigma-Aldrich), 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide hydrochloride (EDC, 99%, Energy Chemical), trifluoroacetic acid (TFA, 99.5%, Aladdin), cellulose nanocrystals (CNCs) with diameter of 5–20 nm and length of 100–200 nm (ScienceK, <http://sciencek.com/>), *N,N*-dimethyl-formamide (DMF, A.R., Sinopharm Chemical Reagent). Styrene monomer (Sigma-Aldrich) was purified by passing through a basic alumina packed column to remove the 4-*tert*-butylcat-echol inhibitor prior to usage. Dichloromethane (CH_2Cl_2 , A.R., Sinopharm Chemical Reagent) was refluxed with CaH_2 and distilled before use. 2-(But-3-yn-1-yloxy)-2-oxo-1,3,2-dioxaphospholane (BYP) was prepared and purified according to the literature method.^[50] Azodiisobutyronitrile (AIBN, A.R., Enox) was purified by recrystallization from ethanol. Milli-Q water (18.2 M Ω ·cm at 25 °C) was generated using a water purification system (Simplicity UV, Millipore).

Characterization

^1H -NMR spectra were recorded on the 400 MHz spectrometer (INOVA-400, Varian) using deuterated chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as the internal standard. The morphologies of all the CNCs samples were observed by TEM instrument (HT7700, Hitachi) operated at an accelerating voltage of 120 kV. All the CNCs samples for TEM measurement were dispersed in water at a concentration of 1 mg/mL. About 10 μL of the aqueous suspensions was added onto the freshly carbon-coated copper grid and partly stained with 2 wt% phosphotungstic acid solution. The excess solution was removed by blotting. The dimension of CNC-PBYP-COOH was measured by an atomic force microscope (AFM, Multimode 8, Bruker) equipped with a Nanoscope 5 controller. Briefly, CNCs were dispersed in deionized water and diluted to 0.1 mg/mL. Then 20 μL of the CNC aqueous dispersion was dropped onto the previously processed silicon wafer. The images were acquired using scan assist mode, and the length and thickness

of the CNCs were analyzed using the height image by NanoScope Analysis software. Crystalline structures of all the CNCs samples were studied by X-ray diffraction (XRD, X' Pert-Pro MPD, Holland Panalytical) at the voltage of 40 kV and the 40 mA power from $2\theta = 5^\circ$ – 40° at the scan rate of 4 ($^\circ$)/min. Elemental changes of modified CNCs compared to the original CNCs were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI, Thermo Fisher Scientific). Water contact angle measurements of the pristine CNCs and modified CNCs were carried out with distilled water using a contact angle meter (JC2000D, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd.) at room temperature. The films with smooth surfaces were obtained by compressing the powder under 2 MPa of pressure using an IR press. A digital image of each water droplet was recorded using a Canon Power shot SX260 HS digital camera. Zeta potential of CNCs samples was measured by using a dynamic light scattering instrument (Zetasizer Nano ZS, Malvern) at 25 °C.

The number of carboxylic groups on the surface of CNCs was determined *via* conductometric titrations (JENWAY 4520, Bibby Scientific Ltd.). CNC-COOH (30 mg) was dispersed in 80 mL of deionized water *via* sonication for 3 h, and then stirred for 12 h. Hydrochloric acid was added in 10 μL increments under stirring until pH of the dispersion was below 3, and the titration was performed using 0.01 mol/L NaOH solution. The results can be calculated using the equation as fol-low:

$$\text{Carboxylic acid density (mmol/kg)} = \frac{\Delta V c_{\text{NaOH}}}{m}$$

where ΔV is the difference in NaOH volume for the plateau region, c_{NaOH} is the concentration of NaOH, and m represents the mass of the CNCs used in the titration.

The average droplet size of resulting Pickering emulsion was measured by using a dynamic light scattering instrument (Zetasizer Nano ZS, Malvern) at 25 °C. Briefly, the emulsion was diluted 100 times to measure by DLS. 30 μL of emul-sions sample was diluted in 3 mL of 0.1 wt% SDS aqueous solution to prevent agglomeration. It has been reported that SDS solution facilitates the measurement of individual par-

ticles without changing their particle size.^[32] The resulting Pickering emulsions were visualized by light microscopy (BX51, Olympus) and polarization microscopy (CPV-900C, Shanghai Yuming Optical Instrument Company). Confocal microscopy was used to observe emulsions. CNC-PBYP-COOH was dispersed in water at 5 mg/mL with 1 wt% (compared to CNCs) of Calcofluor white fluorescence dye prior to preparing the emulsion. The resulting emulsion was characterized using a confocal microscope (TCS SP5 II, Leica).

The morphologies of polystyrene particles were visualized using scanning electron microscopy (SEM, SU8010, Hitachi) at 5 kV acceleration voltage and transmission electron microscopy (TEM, HT7700, Hitachi) at 120 kV acceleration voltage.

Synthesis of Polyphosphoester-modified CNCs

Synthesis of H_2N -PBYP

First, *N*-Boc-PBYP was prepared by the ROP reaction of BYP monomer using *N*-Boc-ethanolamine as the initiator and DBU as the catalyst under a nitrogen atmosphere. Briefly, DBU (0.5190 g, 3.41 mmol) and 5 mL of anhydrous CH_2Cl_2 were added to a 50 mL round-bottomed flask under a nitrogen atmosphere. After three cycles of exhausting-refilling nitrogen, BYP (1.5090 g, 8.25 mmol) and *N*-Boc-ethanolamine (0.2751 g, 1.71 mmol) were added to the flask by using a syringe under a nitrogen atmosphere, and the reaction mixture was kept under stirring at $-15\text{ }^\circ\text{C}$ for 10 min. The solvent was removed by rotary evaporation. The product was precipitated in 100 mL of cold methanol-diethyl ether (1/10, V/V) three times. The precipitate was dried under vacuum at $25\text{ }^\circ\text{C}$ for 48 h (*N*-Boc-PBYP, 1.4482 g, yield: 82.0%).

H_2N -PBYP was prepared by the removal of Boc group from *N*-Boc-PBYP. Typically, *N*-Boc-PBYP (1.0417 g, 1.00 mmol) was first dissolved in 10 mL of CH_2Cl_2 , and then 3 mL of TFA was added dropwise at $-5\text{ }^\circ\text{C}$ for 12 h under stirring. The solvent was removed by rotary evaporation. The product was precipitated in 100 mL of *n*-hexane three times. The product was obtained by drying in vacuum at $25\text{ }^\circ\text{C}$ for 48 h (H_2N -PBYP, 0.7965 g, yield: 76.46%).

Synthesis of CNC-COOH

TEMPO oxidation was carried out following the previous published literature procedures with minor modification.^[51] CNCs (3 g) was stirred in 300 mL of deionized water and ultrasonicated. TEMPO (60.0 mg, 0.38 mmol) and NaBr (1.2000 g, 11.67 mmol) were added into the solution with stirring, and then the pH was adjusted to 5.6 by 0.5 mol/L NaOH. The oxidation was initiated by slowly adding NaClO (33.0980 g, 443.00 mmol) over 30 min under gentle agitation. Then the pH was kept constant at 10 by continuous adding 0.5 mol/L NaOH. The reaction was finished when the pH did not change within 15 min. After stirring for 12 h, the excess oxidant was quenched using 30 mL methanol and then the solution was stirred for 1 h. The pH was adjusted to 1 by 1 mol/L HCl, and the color of solution changed from yellow to pale after stirring for 24 h. The final CNCs aqueous dispersion was centrifuged, and the supernatant containing the water-soluble oxidized CNCs was precipitated by adding an excess of ethanol and centrifuged again to yield CNC-COOH. The product was further washed alternately three times by methanol and deionized water. Finally, the product was dialyzed (MWCO 12000) against deionized water for three days. CNC-COOH was obtained

through lyophilization for three days.

Synthesis of CNC-PBYP-COOH

CNC-COOH was decorated with H_2N -PBYP using the amidation reaction with a few slight modifications.^[52] CNC-COOH₁₅₁₀ (100.1 mg, 0.15 mmol of carboxylic acid moieties) was dispersed in 150 mL of DMF via sonication. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (433.3 mg, 2.26 mmol, 15 equiv.) was added, and the reaction was further stirred for 30 min. Then *N*-hydroxysuccinimide (NHS) (260.7 mg, 2.26 mmol, 15 equiv.) was added, and the reaction was stirred for another 12 h. H_2N -PBYP5 (1.4217 g, 1.51 mmol, 10 equiv.) was then added dropwise, and the reaction system was stirred at room temperature for 24 h. The reaction mixture was precipitated in excess methanol and then centrifuged. The residual was further washed alternately three times by methanol and deionized water under successive centrifuge. The products were dialyzed (MWCO 12000) against deionized water, and finally lyophilized to yield CNC-PBYP5-COOH. Similarly, CNC-PBYP10-COOH was also prepared using this method. Among them, PBYP5 and PBYP10 mean that the number of structural units of BYP is 5 and 10, respectively.

Preparation of Pickering Emulsion

The samples of modified CNCs were dispersed in water (pH 5.75) at the desired concentrations via ultrasonication prior to making the emulsions and used as the aqueous phase. All the emulsions were prepared using an oil/water ratio of 30/70 (V/V). Practically, 0.9 mL of styrene monomer was added as the oil phase to 2.1 mL of the CNCs samples aqueous dispersion in a glass vial and then emulsified by using JYD-650 ultrasonic cell crusher under pulse mode by alternating 3 s sonication with a 3 s standby for 90 s.

Preparation of Latex Particles

The oil-soluble initiator AIBN was added to the styrene monomer phase before emulsification (ratio: 1/100 W/W). Then, 5 mL of styrene-in-water emulsion with 30/70 ratio (V/V) was prepared by ultrasonication and purged with nitrogen for 10 min and then polymerized at $65\text{ }^\circ\text{C}$ without stirring for 24 h. After the end of polymerization, the reaction was cooled to room temperature. The resulting beads were washed by repeated centrifugation, which were defined as PS particles.

RESULTS AND DISCUSSION

Functionalization and Characterization of CNCs

The chemical structures of *N*-Boc-PBYP and H_2N -PBYP were verified by ^1H -NMR analysis, which are shown in Fig. 1. Comparing Figs. 1(A) and 1(B), it can be seen that the chemical shift of $-CH_3$ at δ 1.45 ppm (signal a) of Fig. 1(B) disappears and a new signal of $-NH_2$ at δ 8.50 ppm (signal b) appears in Fig. 1(A), indicating that H_2N -PBYP has been prepared.

According to the ^1H -NMR spectrum of *N*-Boc-PBYP in Fig. 1(B), the number of repeat units (*n*) was calculated by the Eq. (1), where A_g and A_a represent the integral values of the signal g and signal a, respectively. Each repeat unit is composed of BYP monomer, and *n* is 5 or 10 according to the calculation result.

$$n = \frac{9A_g}{A_a} \quad (1)$$

For improving the hydrophobicity of CNCs, hydrophobic PBYP chains were grafted onto the surface of CNCs as shown in Scheme 1. Briefly, charged carboxylic acid moieties were first introduced to the surface of CNCs by TEMPO oxidation, and then CNC-COOH was obtained. The results of conductometric titrations with sodium hydroxide showed that surface carboxylic acid density of these CNC-COOH was about 1510 mmol/kg (Fig. S1a, in the electronic supplementary information, ESI), abbreviated as CNC-COOH₁₅₁₀.

Then PBYP chains were introduced to the surface of CNCs via amidation reaction between CNC-COOH and H₂N-PBYP. The amount of hydrophobic PBYP chains was calculated by the difference in the amount of carboxylic acid groups before and after functionalization, as measured via conductometric titration. As shown in Figs. S1(b) and S1(c) (in ESI), the amounts of PBYP5 and PBYP10 were 804 mmol/kg for CNC-PBYP5₈₀₄-COOH₇₀₆ and 683 mmol/kg for CNC-PBYP10₆₈₃-COOH₈₂₇, respectively. Table 1 summarizes CNC-COOH₁₅₁₀ and the hydrophobic modified CNCs, which were prepared using PBYP with different repeat units.

The morphologies of CNC-PBYP5₈₀₄-COOH₇₀₆ and CNC-PBYP10₆₈₃-COOH₈₂₇ nanoparticles were estimated from AFM images (Fig. 2) to be around 6.3 and 8.1 nm in height, respectively. TEM characterizations of the functionalized nanocrystals CNC-PBYP-COOH (Figs. 3c and 3d) also show that the length of CNCs had no significant change compared to pristine CNCs (Fig. 3a) and CNC-COOH₁₅₁₀ (Fig. 3b). However, some of the modified CNCs appeared to have a slight increase in thickness and were more prone to aggregation, which may be related to the decrease of dispersity of the nanoparticles. So, the chemical modification did not significantly change the dimensions of the CNCs.

We studied the dispersion stability of CNCs in water phase

before and after modification, and the results are shown in Fig. S2 (in ESI). From Fig. S2(a) (in ESI), we can see that pristine CNCs nanoparticles stably dispersed in water on account of electrostatic repulsions. After the introduction of PBYP chains on the surface of CNCs, the dispersity of CNC-PBYP5₈₀₄-COOH₇₀₆ and CNC-PBYP10₆₈₃-COOH₈₂₇ was remarkably decreased and opaque was displayed (Figs. S2b and S2c, in ESI), indicating the formation of aggregates with larger size. Both modified CNCs aqueous dispersions had obvious precipitation at the bottle bottom. The poor dispersity of modified CNCs resulted from the increased hydrophobicity due to the introduction of PBYP chains. The dispersity of CNC-PBYP10₆₈₃-COOH₈₂₇ sample in water was better than that of CNC-PBYP5₈₀₄-COOH₇₀₆, which was consistent with the zeta potential test results (Table 2). Particles with lower zeta potential had a stronger electrostatic repulsion effect in aqueous dispersion.

The crystalline structures of pristine CNCs and the two CNC-PBYP-COOH samples were investigated by X-ray diffraction. The XRD patterns are shown in Fig. 4. Three groups of diffraction peaks at 2θ around 16.6°, 22.8°, and 34.6°, corresponding to (110), (200), and (004) crystalline planes, respectively, appeared in the XRD pattern of pristine CNCs (Fig. 4a). These characteristic diffraction peaks did not exhibit any shift change after the introduction of PBYP chains (Figs. 4b and 4c), indicating that the hydrophobic modification of CNCs with PBYP did not significantly change the crystalline structure of the materials.

Table 2 shows the results of element content of pristine CNCs, CNC-PBYP5₈₀₄-COOH₇₀₆, and CNC-PBYP10₆₈₃-COOH₈₂₇ measured by XPS. In contrast to pristine CNCs, the element contents of nitrogen and phosphorus of modified CNCs increased significantly. The result of sample CNC-PBYP5₈₀₄-COOH₇₀₆ indicated that the contents of nitrogen and phos-

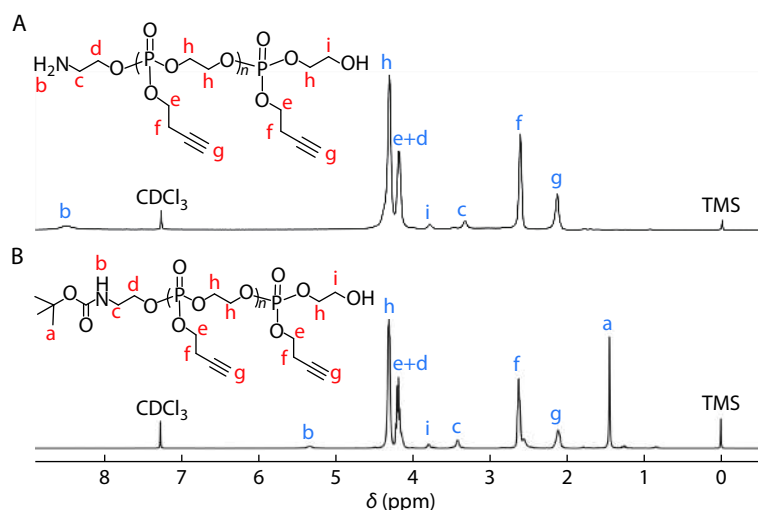


Fig. 1 ¹H-NMR spectra of (A) H₂N-PBYP and (B) N-Boc-PBYP.

Table 1 Summary of the modified CNCs samples.

Sample	Repeat units of BYP	COOH density (mmol/kg)	PBYP group density (mmol/kg)
CNC-COOH ₁₅₁₀	—	1510	—
CNC-PBYP5 ₈₀₄ -COOH ₇₀₆	5	706	804
CNC-PBYP10 ₆₈₃ -COOH ₈₂₇	10	827	683

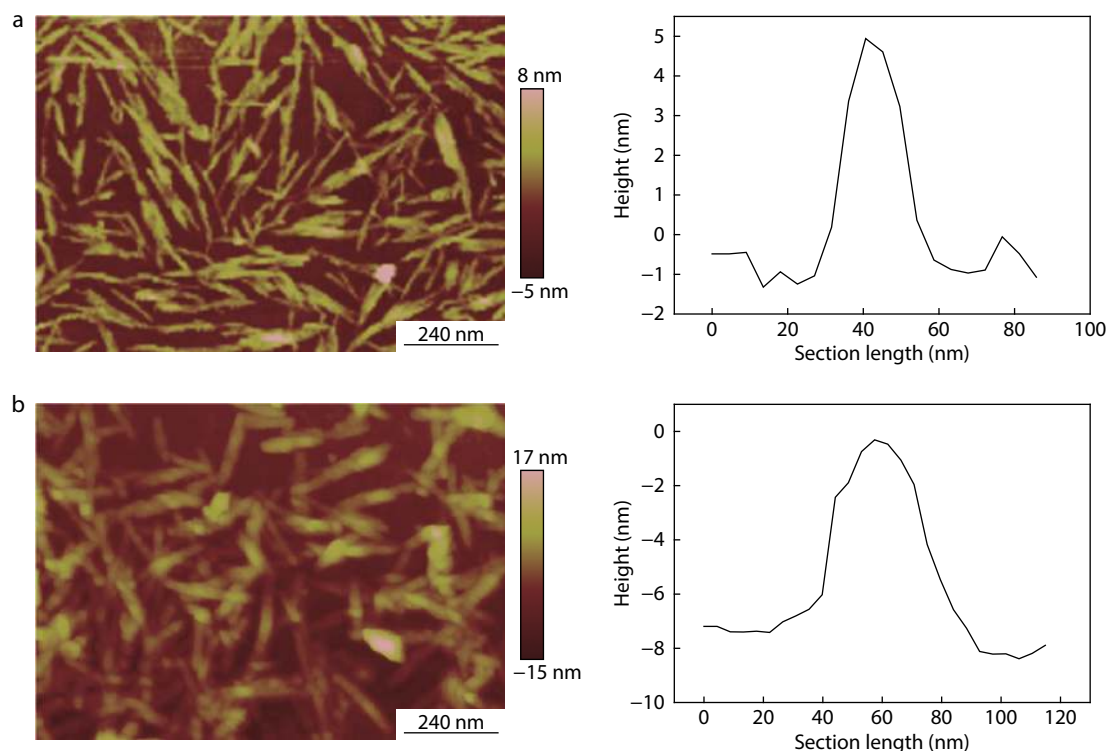


Fig. 2 AFM images as well as height profiles of the cross section of (a) CNC-PBYP5₈₀₄-COOH₇₀₆ and (b) CNC-PBYP10₆₈₃-COOH₈₂₇.

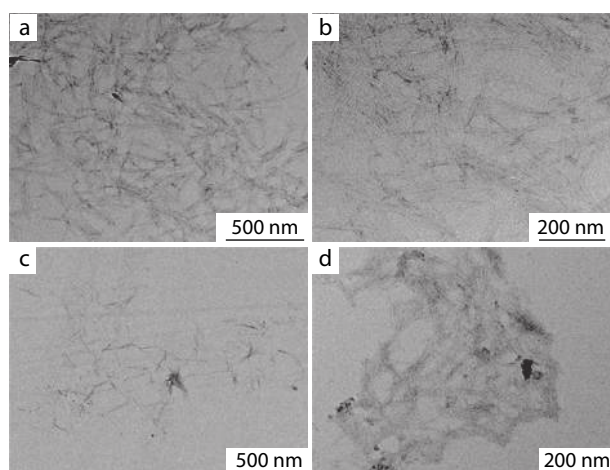


Fig. 3 TEM images of (a) pristine CNCs, (b) CNC-COOH₁₅₁₀, (c) CNC-PBYP5₈₀₄-COOH₇₀₆, and (d) CNC-PBYP10₆₈₃-COOH₈₂₇.

phorus were 3.66% and 0.22%, respectively. CNC-PBYP10₆₈₃-COOH₈₂₇ showed nitrogen content and phosphorus content of 3.52% and 0.45%, respectively. This further indicated the successful modification of pristine CNCs with hydrophobic polyphosphoester chains.

In addition, we tried to demonstrate the successful modification of CNCs by static contact angle measurements. We believe that the introduction of hydrophobic polyphosphoester chains would increase hydrophobicity of CNCs and further improve the emulsion stability. Using contact angle measurements, we observed that the contact angle of pristine CNCs was 19.5° (Fig. S3b, in ESI), while those of modified CNCs in-

Table 2 Element contents measured by XPS for pristine CNCs, CNC-PBYP5₈₀₄-COOH₇₀₆, and CNC-PBYP10₆₈₃-COOH₈₂₇ and zeta potential results.

Sample	Content of element (wt%)				Zeta potential (mV)
	N	P	C	O	
Pristine CNCs	—	—	60.82	39.18	−40.6
CNC-PBYP5 ₈₀₄ -COOH ₇₀₆	3.66	0.22	60.16	35.96	−18.8
CNC-PBYP10 ₆₈₃ -COOH ₈₂₇	3.52	0.45	61.51	34.51	−24.0

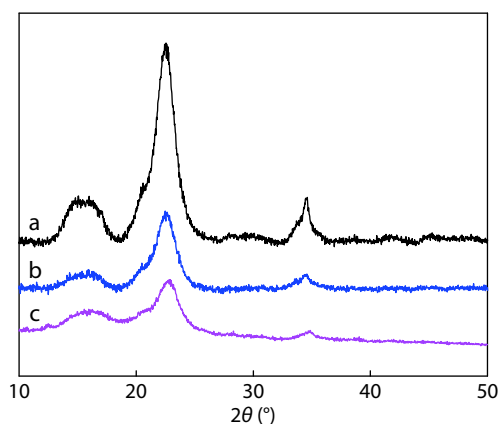


Fig. 4 X-ray diffraction patterns of (a) pristine CNCs, (b) CNC-PBYP5₈₀₄-COOH₇₀₆, and (c) CNC-PBYP10₆₈₃-COOH₈₂₇.

cluding CNC-PBYP5₈₀₄-COOH₇₀₆ and CNC-PBYP10₆₈₃-COOH₈₂₇ were 69.0° and 53.5° (Figs. S3c and S3d in ESI), respectively. These results further indicate that the hydrophobicity of modified CNCs was higher than that of pristine CNCs.

Oil-in-water Emulsions Stabilized by CNC-PBYP-COOH

For all emulsions in the present study, styrene monomer was used as the oil-phase component and the aqueous component consisted of either CNC-PBYP₅₈₀₄-COOH₇₀₆ or CNC-PBYP₁₀₆₈₃-COOH₈₂₇ dispersed in deionized water at the desired concentrations. The preparation process of the styrene-in-water emulsion could be simply described as mixing the styrene monomer and CNC-PBYP-COOH aqueous dispersion at a 30/70 ratio (V/V), and then ultrasonicated (Scheme 2).

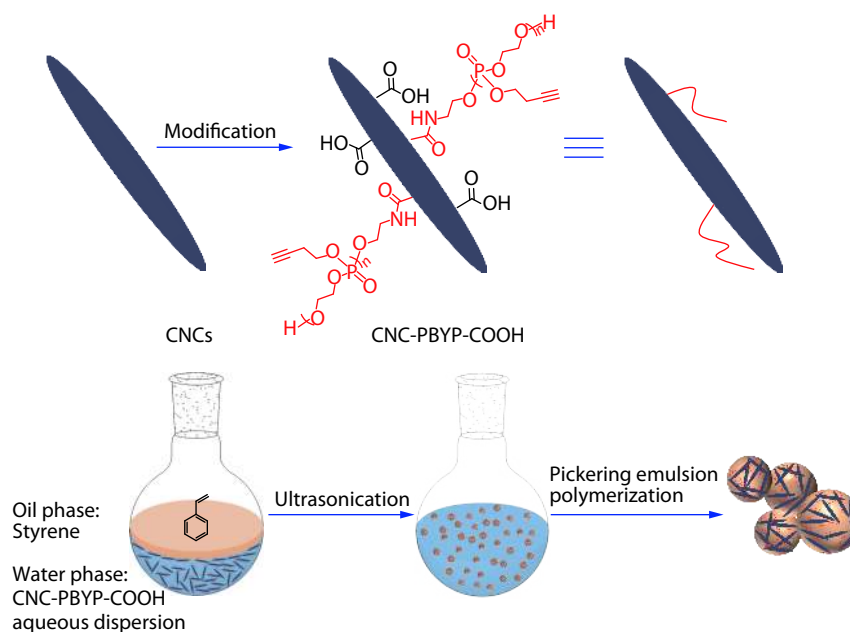
As shown in Fig. S3(a) (in ESI), the type of emulsions that we prepared in this study was oil-in-water emulsions. We investigated the stability of a series of styrene-in-water emulsions. The original nanocrystals and the modified nanocrystals were used to stabilize the styrene/water emulsion, respectively. Figs. 5(a) and 5(c) show the styrene-in-water emulsions, which were separately stabilized by pristine CNCs and CNC-PBYP₅₈₀₄-COOH₇₀₆ at different CNC/aqueous concentrations ranging from 0.5 mg/mL to 10 mg/mL. The phenomenon of no phase separation in the emulsion indicated stable o/w emulsions were formed by modified CNCs at the concentrations above 5 mg/mL, but pristine CNCs did not completely stabilize o/w emulsions at all the concentrations.

In order to test the stability of the emulsions stabilized by pristine CNCs and modified CNCs, samples were subjected to centrifugation at 4000 g for 10 min, and the optical images of the delamination of these emulsions are shown in Figs. 5(b) and 5(d). The state of the emulsion after centrifugation was directly observed by the naked eye. Under such strong centrifugation force, the creaming process would be accelerated. If the stability of the emulsion was poor, coalescence would occur. As shown in Fig. 5(d), the emulsions stabilized by 0.5, 1.0, 2.0, 3.0, or 4.0 mg/mL of CNC-PBYP₅₈₀₄-COOH₇₀₆ showed separation of the oil phase and water layer. However, when the concentration of the crystals exceeded 5.0 mg/mL, the emulsion layer above the top of the water layer still remained stable.

Similar phenomenon could also be observed from emulsions stabilized by CNC-PBYP₁₀₆₈₃-COOH₈₂₇ (Figs. S4c and S4d in ESI). The results indicate that stable oil-in-water emulsion could be obtained only if concentration of modified CNCs in the aqueous phase was above 5.0 mg/mL. Moreover, we could simply see that pristine CNCs had almost no ability to stabilize the emulsion, because of the complete phase separation of the oil and the water layer after centrifugation (Fig. 5b and Fig. S4b in ESI).

The optical micrographs of Pickering emulsion droplets stabilized by modified CNCs at various concentrations are shown in Fig. 6. The average size of the emulsion droplets gradually decreased with the increasing concentration of the modified CNCs. As shown in Figs. 6(a) and 6(d), the emulsion droplets stabilized by modified CNCs at the concentration of 1.0 mg/mL were so obvious that they could be observed directly with the naked eye. However, the emulsion droplet sizes were significantly decreased when the concentration of the modified CNCs increased from 1.0 mg/mL to 5.0 mg/mL (Fig. 6). At the same time, we also could find that the emulsion droplet size was more uniform as the concentration of modified CNCs increased.

Then the average diameter of the emulsion droplets was measured by dynamic light scattering (DLS), and the results are shown in Fig. 7. For all o/w Pickering emulsions stabilized by the modified CNCs, the average diameters gradually decreased as the concentration of the modified CNCs increased in the aqueous phase until it reached a plateau value. The value for CNC-PBYP₅₈₀₄-COOH₇₀₆ at 5.0 mg/mL was about 450 nm and for CNC-PBYP₁₀₆₈₃-COOH₈₂₇ at 5.0 mg/mL was around 550 nm. Another noteworthy phenomenon is that the size of the emulsion droplets stabilized by CNC-PBYP₅₈₀₄-COOH₇₀₆ was larger than that of the droplets stabilized by CNC-PBYP₁₀₆₈₃-COOH₈₂₇ at the same concentration. This may be attributed to the stronger electrostatic repulsion caused by the higher carboxyl density of CNC-PBYP₁₀₆₈₃-COOH₈₂₇,



Scheme 2 Schematic representation of the styrene-in-water emulsion process using modified CNCs as the surfactant.

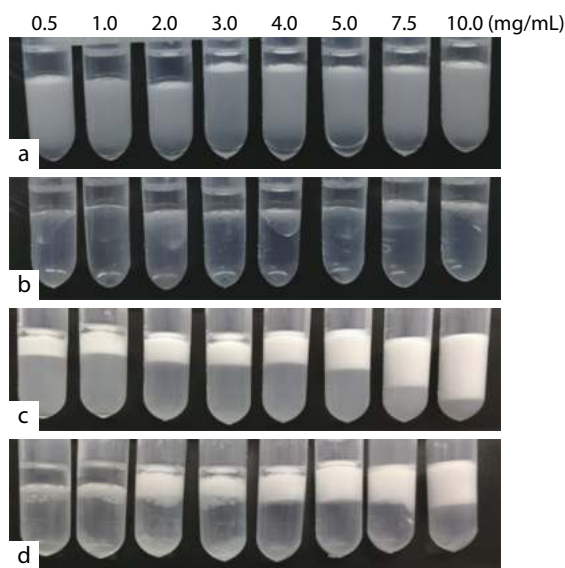


Fig. 5 Styrene-in-water emulsions stabilized by (a, b) pristine CNCs, (c, d) CNC-PBYP5₈₀₄-COOH₇₀₆ at different CNC/aqueous concentrations (from left to right: 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 7.5 and 10.0 mg/mL) (a, c) before and (b, d) after centrifugation.

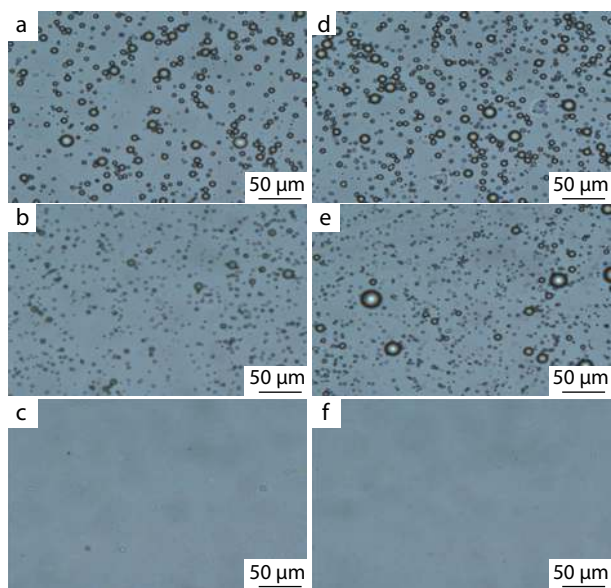


Fig. 6 Optical micrographs of styrene-in-water Pickering emulsion droplets stabilized by (a–c) CNC-PBYP5₈₀₄-COOH₇₀₆ or (d–f) CNC-PBYP10₆₈₃-COOH₈₂₇ at different aqueous dispersion concentrations: (a, d) 1.0 mg/mL, (b, e) 3.0 mg/mL, (c, f) 5.0 mg/mL.

thereby the better water solubility. All of these made it difficult for these crystals to efficiently pack at the droplet surface. The effect of different volume ratios of oil-water on the droplet size of emulsion stabilized by CNC-PBYP5₈₀₄-COOH₇₀₆ at 5.0 mg/mL was also studied and the results are shown in Fig. S5 (in ESI). When the volume ratios of oil-water were changed from 0.2 to 0.5, the average diameters of the emulsion droplets gradually increased from 500 nm to 1.3 μ m.

Since carboxylate groups are sensitive to pH values of the surrounding environment, we investigated the effect of dif-

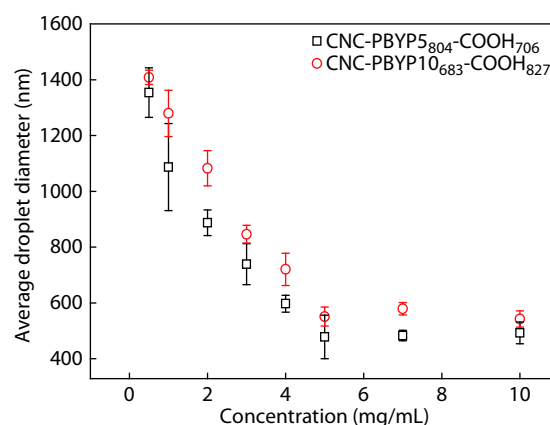


Fig. 7 DLS results of the average diameters of the o/w emulsion droplets stabilized by CNC-PBYP5₈₀₄-COOH₇₀₆ and CNC-PBYP10₆₈₃-COOH₈₂₇ at different concentrations.

ferent pH media on the particle size of the emulsion. CNC-PBYP10₆₈₃-COOH₈₂₇ was dispersed in phosphate buffer solutions at 5.0 mg/mL with different pH 3, 4, 5, 6, and 7, and the phosphate buffer solutions were used as aqueous phases to prepare styrene-in-water Pickering emulsions with oil/water ratio of 30/70 (V/V). DLS results (Fig. 8) show that average diameters of the emulsions droplets increased slowly from 451 nm at pH 3 to 457 nm at pH 4, but then began to increase significantly to 663 nm as the pH value was changed from 4 to 7. This is because the total negative charges of modified CNCs decreased by the protonation effect of carboxylate groups at lower pH, and increased at higher pH when the carboxylic acid moieties were deprotonated. These results were in good agreement with the data of average diameters of the emulsions droplets. The later was stabilized by CNC-PBYP5₈₀₄-COOH₇₀₆ and had smaller diameter than that of CNC-PBYP10₆₈₃-COOH₈₂₇ at the same concentrations. This indicated that droplet size could be affected by the surface charge of the CNCs, and the less charge was more conducive to forming smaller size droplet. Thus, it is possible to control the droplet size of the emulsion stabilized by CNC-PBYP-COOH *via* adjusting the pH values of the environment.

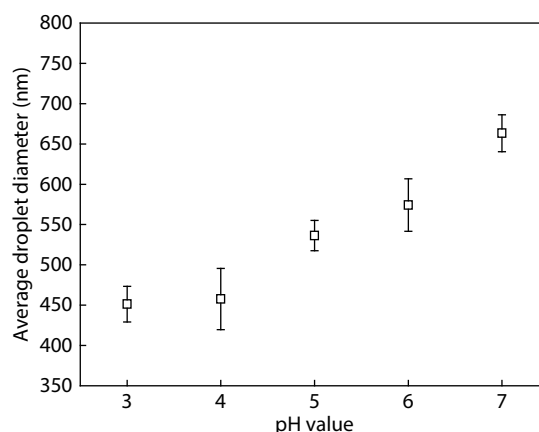


Fig. 8 DLS results of the average diameters of the o/w emulsions stabilized by CNC-PBYP10₆₈₃-COOH₈₂₇ dispersed in phosphate buffer at different pH values.

By using polarized optical microscopy (POM) and confocal microscopy with Calcofluor White fluorescence dye as a staining agent for modified CNCs, we further demonstrated the behavior that the modified CNCs were adsorbed at the emulsion droplets interface. A birefringence pattern could be seen around droplets under POM (Fig. 9a), and the modified CNCs stained with Calcofluor White fluorescence dye were adsorbed at the o/w interface (Fig. 9b).

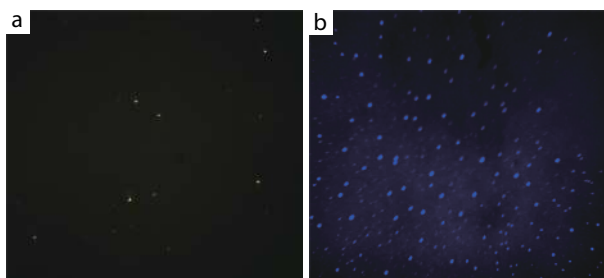


Fig. 9 (a) Polarized optical microscopy (POM) image and (b) confocal microscopy image (with Calcofluor White fluorescence dye as a staining agent) of the styrene-in-water emulsion stabilized by CNC-PBYP5₈₀₄-COOH₇₀₆ (5.0 mg/mL).

Solidifying Emulsion Droplets via the Polymerization of Styrene

As mentioned in the introduction, a key factor for the application of emulsions and latexes is the final particle size. In particular, nanoemulsions with the size in range of 20–500 nm have more unique applications, such as food, cosmetics, and coatings. Here, what we want to see is whether the nanoemulsions stabilized by CNC-PBYP5₈₀₄-COOH₇₀₆ or CNC-PBYP10₆₈₃-COOH₈₂₇ at 5.0 mg/mL could be converted into nanosized latexes. For this purpose, the stable styrene-in-water emulsions were polymerized using AIBN as initiator. The morphologies of resulting PS latex particles could be clearly observed under SEM (Fig. 10), and the average sizes of PS latex particles stabilized by CNC-PBYP5₈₀₄-COOH₇₀₆ and CNC-PBYP10₆₈₃-COOH₈₂₇ were 418 and 496 nm, respectively, as measured by DLS (Fig. 11). The droplet sizes of the emulsion before polymerization were also compared with the size of latex

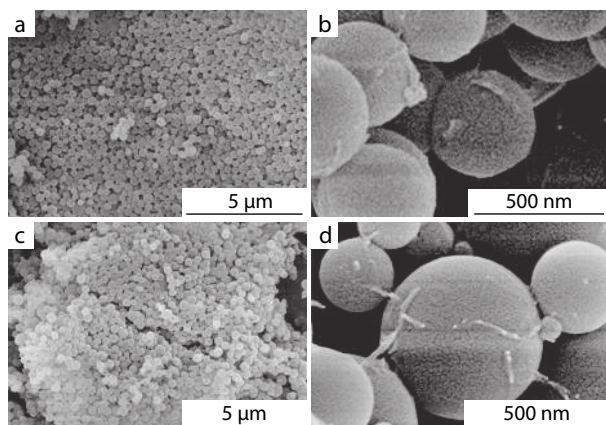


Fig. 10 SEM images of the polystyrene latex particles stabilized by (a, b) CNC-PBYP5₈₀₄-COOH₇₀₆ and (c, d) CNC-PBYP10₆₈₃-COOH₈₂₇ at different magnifications.

particles after polymerization, and the DLS results showed that the emulsion remained stable during polymerization without obvious coalescence (Fig. 11). The CNCs could be clearly seen on the surface of the PS latex particles by combining SEM and TEM (Fig. 10 and Fig. S6 in ESI), indicating that they were adsorbed at the interface as a stabilizer.

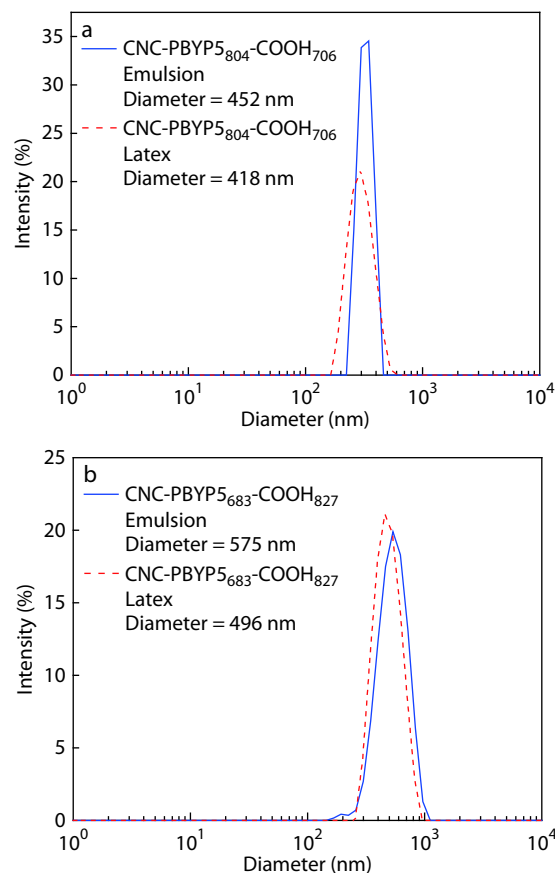


Fig. 11 DLS results of the average diameters of the o/w emulsions after sonication and the average diameters of the latex particles after polymerization for (a) CNC-PBYP5₈₀₄-COOH₇₀₆ and (b) CNC-PBYP10₆₈₃-COOH₈₂₇.

CONCLUSIONS

In this study, we have developed polyphosphoester-modified cellulose nanocrystals (CNCs) by introducing hydrophobic PBYP chains onto the surface of CNCs. CNC-PBYP-COOH was obtained via combining the TEMPO oxidation of CNCs, ROP of BYP monomer, and amidation reaction. The polyphosphoester-modified CNCs (CNC-PBYP5₈₀₄-COOH₇₀₆ and CNC-PBYP10₆₈₃-COOH₈₂₇) showed higher emulsifying performance by comparison with the pristine CNCs. Styrene-in-water emulsions stabilized by modified CNCs were stable when the concentration of the crystals aqueous solution was above 5.0 mg/mL, and the resulting droplet sizes of formed Pickering emulsions were about 500 nm. Nanosized latex particles were successfully prepared by Pickering emulsion polymerization stabilized by modified CNCs, and the emulsions displayed good stability in the polymerization. Furthermore, the size of the latex particles

after polymerization was consistent with those emulsion droplets before the polymerization. This kind of polyphospho-ester-modified CNCs could be used as novel green stabilizers to access nanosized emulsions and latexes, which can be applied in many fields such as cosmetic products and coatings products.

E Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2404-z>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21975169 and 21374066), the Major Program of the Natural Science Project of Jiangsu Higher Education Institutions (No. 15KJA150007), the Natural Science Foundation of Jiangsu Province (No. BK20171212), a Project Funded by the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions, and Soochow-Waterloo University Joint Project for Nanotechnology from Suzhou Industrial Park.

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