Synergetic effect of water-soluble PEG-based macromonomers and cellulose nanocrystals for the stabilization of PMMA latexes by surfactant-free emulsion polymerization

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ABSTRACT. The combination of cellulose nanocrystals (CNCs) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) was evaluated to synthesize stable latexes by surfactant-free emulsion polymerization of methyl methacrylate (MMA). Cellulose-particle interaction was provided due to the dual role of PEGMA, acting as water-soluble comonomer with MMA under emulsion polymerization conditions and able to interact with CNCs – recovered from sulfuric acid hydrolysis (H_2SO_4 -CNCs). After preliminary experiments designed to validate the affinity between CNCs and PEG-stabilized PMMA particles obtained by MMA/PEGMA emulsion copolymerization, the effect of the PEGMA content and molar mass, and also of the content of CNCs on the kinetics of the polymerization and the stability of the latexes were investigated. The use of PEGMA₃₀₀ ($M_n = 300 \text{ g mol}^{-1}$, 2 to 10 wt%) allowed the formation of a stable latex, however with a broad particle size distribution and the presence of both small (*ca.* 25 - 50 nm) and large (*ca.* 425 - 650 nm) particles (at 10 wt%, $D_n = 278 \text{ nm}$ and $D_w/D_n = 1.34$). Increasing the molar mass of PEGMA (PEGMA₉₅₀ or PEGMA₂₀₈₀) significantly increased the fraction of small particles. This was explained by the nucleation and growth of small polymer particles adsorbed at the CNCs' surface, resulting in a particular organization where the CNCs were covered by several polymer particles. The influence of the initial amount of CNC in these systems was finally evidenced, the polymerization being faster as the content of CNCs increased, but only the latexes prepared with 2 and 5 wt% of CNCs were stable.

Introduction

Pickering stabilization relies on the use of colloidal particles located at the surface of droplets (or bubbles) to ensure their stability.^{1, 2} This concept was presented as an alternative to the use of low molar mass surfactants as stabilizers of liquid-liquid emulsions (*i.e.* oil-in-water or water-in-oil). Different colloids have been used, especially inorganic solid nanoparticles.³ With a growing need for materials with improved properties, the concept of Pickering stabilization has been extended to the stabilization of polymer particles synthesized *via* polymerization in dispersed media.⁴ This allows the formation of hybrid latexes *in situ* which can combine the properties of both polymer particles and stabilizer.⁵ The obtained nanocomposite might have superior properties than the polymer alone or the same composite formed *ex situ*.⁶ In addition, once at the polymer/water interface, the solid particles can be considered as irreversibly adsorbed, unlike low molar mass surfactants, which adsorb and desorb on a relatively fast timescale.⁷ Indeed, in films/coatings obtained from surfactant-stabilized latexes, such hydrophilic species can migrate over time and accumulate at film interfaces, negatively impacting the film properties (*e.g.* transparency, gloss, barrier to gas and adhesion to a substrate).⁸⁻¹³ Various inorganic solid nanoparticles have thus been used for polymerization in dispersed media, including silica nanoparticles as filler for coatings,¹⁴ Laponite clay platelets as mechanical reinforcement as well as for their barrier properties,^{15, 16} cerium oxide as anti-UV agent for coatings,¹⁷ or iron oxide to produce magnetic particles for the biomedical field.¹⁸

Due to their intrinsic properties, cellulose nanocrystals (CNCs)¹⁹ constitute another very interesting class of Pickering stabilizer, possible to produce from renewable resources. Indeed, their low density and high aspect ratio combined with a high axial elastic modulus (*ca.* 140 GPa, comparable to steel) make them very attractive candidates for the preparation of nanocomposite

materials with improved mechanical performances.^{20, 21} CNCs are extracted from cellulose, the most abundant of the polysaccharides. The well-known production^{19, 22} uses concentrated sulfuric acid or hydrochloric acid, or weaker acids²³ to hydrolyze the amorphous or less ordered regions of cellulose leading to rod-like objects, having at least one dimension in the nanometer range. The most widely used process is the “sulfuric acid hydrolysis”, which has been successfully applied to various sources of cellulose, especially wood pulp and cotton linter,^{24, 25} producing H₂SO₄-CNCs. This step generally results in substantially charged surfaces that enhance the hydrophilicity of the H₂SO₄-CNCs.^{26, 27} Charge density measurements have revealed that the surface of H₂SO₄-treated cellulose is highly charged (80-350 mmol kg⁻¹)²⁸ ascribed to sulfate half-ester groups (OSO₃⁻) that may functionalize up to 6 mol% of the glucose units of cellulose polymer chains.¹⁹

CNCs have recently been evaluated as potential Pickering stabilizers in polymerization in dispersed media. Even if it is now generally admitted that CNCs can display hydrophobic regions and thus amphiphilic properties,²⁹ they are dominantly hydrophilic. Thus, similarly to other Pickering stabilizers, the success of the process relies on the use of a (macro-)molecule able to favor interaction between the CNCs and the polymer particles, and different strategies have been reported in the literature. Some of the published works rely on the concomitant use of CNCs and conventional low molar mass surfactants³⁰⁻³² and will not be detailed here, as one of the aims of this study is to avoid the use of such molecules by performing surfactant-free emulsion polymerization. In the work of Kedzior *et al.*,³³ methyl cellulose-coated CNCs were used as stabilizers in the microemulsion polymerization of methyl methacrylate (MMA) using benzoyl peroxide as oil soluble radical initiator. Micron-sized droplets were first formed by a sonication step. After polymerization, bipopulated latexes were systematically obtained with the concomitant formation of both microparticles (15 ± 3 μm) and nanoparticles (100 to 200 nm), most of the

nanoparticles being attached to the micrometric ones. The respective amounts of micro- and nanoparticles could be tuned by the CNCs to methyl cellulose weight ratio; the excess of methyl cellulose ensuring the stabilization of the nanoparticles. In the work of Du and coworkers,³⁴ octadecyl groups were selectively introduced at the reducing ends of CNCs. These CNC-C₁₈ were then used as stabilizers of styrene/divinyl benzene/azobisisobutyronitrile (AIBN) droplets (~18 μm) and upon polymerization cross-linked polystyrene (PS) microspheres (~16 μm) densely covered with CNCs were formed. Zhang *et al.*³⁵ used carboxylic acid CNCs partially functionalized with different alkylamines to stabilize styrene-in-water emulsions (average diameter after sonication between 250 and 700 nm, depending on the type of CNCs and length of the alkyl chain), using either microcrystalline cellulose (MCC) or Miscanthus x. Giganteus (MxG) as natural source of cellulose. Polymerization of the nanosized emulsions obtained with *n*-hexyl-functionalized CNCs, initiated by ammonium persulfate (APS), provided stable PS latexes (*ca.* 250 nm). Approximately at the same time, Werner *et al.*³⁶ reported the use of acetylated CNCs (CNCAs) as Pickering stabilizer of styrene-in-water emulsions obtained after sonication. Polymerization of the emulsion formed with 5 g of CNCAs per liter of styrene (10.6 ± 1.4 μm) was performed in presence of different initiators (AIBN and lauroyl peroxide (LPO) at 65 °C, and 2,2-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) at 35 °C). In all cases, stable latexes were obtained, composed of a mixture of PS microbeads (*ca.* 2 to 20 μm depending on the initiator) and unexpected PS nanobeads (*ca.* 200-250 nm). Polymerization should mainly occur inside the monomer droplets, and the procedure is thus similar to a suspension polymerization. According to the authors, the microbeads resulted from the polymerization inside the styrene micrometric droplets formed after the sonication step. On the other hand, the production of the nanolatex could be ascribed to two simultaneous mechanisms: (1) the expulsion of styrene from the micrometric

Sty droplets (inside which polymerization takes place) that results from partial surface coverage by the CNCAs (this may occur only when a gas is produced during initiator decomposition), and (2) the polymerization of styrene and/or PS oligoradicals released to the water phase, stabilized by free CNCAs, through a nucleation and growth process. The presence of sodium chloride however suppressed the formation of the nanolatexes by increasing the CNCAs coverage of the PS particles. The authors then investigated the impact of the water solubility of different monomers (*i.e.* styrene, *tert*-butyl acrylate, *n*-butyl methacrylate (BMA), MMA, vinyl acetate and methyl acrylate (MA)) on the preparation of CNCs or CNCAs-stabilized O-in-W emulsions, in the presence of NaCl.³⁷ The obtained micrometric droplets (*ca.* 4 to 16 μm , depending on the CNCs and the monomer used) were then polymerized at 35 °C using V70. The acetylation step revealed to be key: the emulsions stabilized with the CNCAs were the only ones allowing high conversions to be reached, whatever the monomer, with no significant amount of coagulum. The particle sizes were between 4 and 10 μm , and quite similar to that of the corresponding droplets, except for MA (twice as large) which was ascribed to its very high solubility in water. The weight fraction of CNCs was about 0.5 % with respect to the polymer.

Finally, Glasing *et al.* recently reported a very interesting mechanistic study on styrene polymerization in microsuspension, utilizing either bare H_2SO_4 -CNCs or CNCs grafted with poly(styrene-*co*-*N*-3-(dimethylamino)propyl methacrylamide) or poly(styrene-*co*-*N,N*-(diethylamino)ethyl methacrylate), respectively, as stabilizers.³⁸ Both types of CNCs led to stable emulsions of styrene (droplet diameter of 18-20 and 5-9 μm , respectively). These emulsions were then polymerized using different initiators: water-soluble APS, slightly water-soluble AIBN and 2-2'-azobis(2,4-dimethylvaleronitrile) (Vazo-52), and very poorly water-soluble LPO. The authors demonstrated that the nature of the initiator and CNCs impacted the polymerization kinetics,

particle size, and molar mass distribution. When Vazo-52 or AIBN were used, nanometric latexes (*ca.* 160 to 320 nm) were obtained together with the targeted micrometric CNC-armored particles (3 to 20 μm). The authors also showed that without sonication (*i.e.* performing the polymerization under emulsion conditions, using APS, AIBN or LPO), the obtained particles were not stabilized by the CNCs.

To simplify the procedure, some works have focused on the use of the neat H_2SO_4 -CNCs only. Jiménez Saelices *et al.* recently performed polymerization of Pickering emulsions stabilized by H_2SO_4 -CNCs, using a range of monomers having different water solubility to investigate the mechanism of nucleation and particle growth.³⁹ First using styrene, two populations of droplets were observed for the initial emulsions, leading to bipopulated latexes after polymerization initiated by AIBN. Micrometric (6 to 18 μm , according to CNCs amount) and nanometric (*ca.* 300 nm) particles were formed according to two concomitant mechanisms, suspension and emulsion polymerization, respectively. Then, hydrophobic monomers with various water solubility were investigated, either lower than styrene, *i.e.* lauryl methacrylate (LMA, completely insoluble in water) and isobornyl acrylate (iBoA), or higher, *i.e.* BMA and MMA. The study demonstrated the impact of the water solubility of the monomer on both droplet and particle formation (with either suspension polymerization or combination of suspension and emulsion processes). Indeed, the respective fractions of micro- and nanoparticles in the final latex is directly linked to the ease of monomer diffusion across the aqueous phase. It is worth mentioning that no stable emulsion could be formed with MMA. CNC-armored PMMA particles were, however, recently obtained by emulsion polymerization by Limousin *et al.*⁴⁰ In this work, a cationic initiator, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA), was employed to induce electrostatic interactions between the latex particles and the negatively charged H_2SO_4 -CNCs. The authors

demonstrated that with a good balance between the cationic and anionic species, stable latexes with high conversion and small particle size (*ca.* 160 nm, with nevertheless a quite broad particle size distribution) could be formed. An optimum CNC/AIBA charge ratio around 1 was necessary so that a majority of CNCs could be adsorbed on the polymer surface. Whereas the film cast from the CNC-armored latex at 23 °C was brittle, homogeneous and transparent films could be obtained at 65 °C, film which showed enhanced mechanical properties – Young’s modulus above 1 GPa compared to 10 – 100 MPa for emulsion polymers typically used in coatings. Besides, room temperature film-formation could be achieved when blending the CNC-armored latex with conventional cationically-stabilized PMMA particles. Finally, Ben Mabrouk *et al.* recently demonstrated that H₂SO₄-CNCs could partially contribute to the stability of poly(vinyl acetate) particles obtained by emulsion polymerization (sizes ranging from 300 to 500 nm).⁴¹ The addition of poly(ethylene glycol) methyl ether methacrylate (PEGMA) as comonomer was demonstrated to impact both latex stability and particle size, favoring the binding of CNCs to the particle surface. Indeed, DLS effectively indicated the formation of smaller particles (200-300 nm), which however look polydisperse by electron microscopy with also the presence of micrometric particles (2-3 µm) and very small particles (20-100 nm) free of CNCs adhering to larger polymer particles coated with CNCs. Transparent to translucent films were obtained after casting of the dispersions. When the latter were added as binder in a PVAc matrix, the CNCs were shown to bring a strong reinforcing effect clearly demonstrating the importance of controlling the interfacial properties.

The present work investigates the potential of H₂SO₄-CNCs to be used as Pickering stabilizers during surfactant-free emulsion polymerization of MMA. In most of the works depicted above, a sonication step was applied before the polymerization to form stable droplets. The strategy we develop in the present paper does not require any kind of pretreatment. To favor the interaction

between H₂SO₄-CNCs and the forming latex particles during the polymerization, a mixture of MMA and PEGMA was employed. PEGMA was chosen not only because of a possible interaction between PEG moieties and CNCs,⁴¹⁻⁴⁵ but also because this hydrophilic monomer should copolymerize with methacrylate-based hydrophobic monomers such as MMA, inducing a compatibilizing effect between the H₂SO₄-CNCs and the particles. Therefore, if successful, this approach will allow interactions between PEGMA chains and CNCs at the early stages of the polymerization, ensuring Pickering stabilization of the final particles throughout emulsion copolymerization. Considering the simplicity of the proposed protocol, the resulting surfactant-free CNCs/polymer hybrid latexes may be employed in a large range of applications depending on the latex particle size and size distribution.

Materials and Methods

Materials. Methyl methacrylate (MMA, 99 %, Sigma-Aldrich) and poly(ethylene glycol) methyl ether methacrylates (PEGMA₃₀₀, $M_n = 300 \text{ g mol}^{-1}$, *i.e.* 3-4 ethylene glycol (EG) units; PEGMA₉₅₀, $M_n = 950 \text{ g mol}^{-1}$, *i.e.* 18-19 EG units; PEGMA₂₀₈₀, $M_n = 2080 \text{ g mol}^{-1}$, *i.e.* 44 EG units; 50 % by weight in H₂O - all from Sigma-Aldrich - see Scheme S1) were used as received without treatment. Potassium persulfate (KPS, $\geq 99 \%$, Sigma-Aldrich) was stored at -21 °C and set back at ambient temperature before use. Sodium hydroxide solution (NaOH, 0.1 N, Sigma-Aldrich) and sulphuric acid (H₂SO₄, >95%, Sigma-Aldrich) were used as received. Water was deionized before use (Purelab Classic UV, Elga lab Water).

Sulfuric acid hydrolysis. Hydrolysis of cellulose fibers from cotton was performed according to a procedure described previously for pulp hydrolysis.⁴⁶ Roughly cut and grinded pieces of a

Whatman filter paper (*ca.* 40 g) was added into a sulfuric acid solution at 64 wt% concentration (700 mL) in a 1 L round bottom flask. The flask was immersed in a pre-heated oil bath at 45 °C and left to react for 45 min. The suspension was quenched by dilution with cold MilliQ-water (7 L). The resulting suspension was then centrifuged at 4800 rpm for 10 min and washed with MilliQ-water to remove excess acid until no pellet was created, *i.e.* a stable colloidal dispersion was formed due to pH increase. The dispersion was placed in regenerated cellulose dialysis membranes (Spectrum Spectra/Por) having a molecular weight cut-off of 12 000 – 14 000 and dialyzed against water until the water pH remained constant. Finally, the H₂SO₄-CNCs dispersion was sonicated using a probe sonicator (Vibracell sonicator, Sonics & Materials Inc., Danbury, CT) at 30 % amplitude for 15 min three times in an ice bath and filtered over a glass filter (Whatman GF/B, GE Healthcare) to remove metal particles from the probe. The final dispersion (at 1 wt% in water) was analyzed by DLS and TEM, corroborating previously published protocols on average size²⁸ (DLS: $90 < D_h < 110$ nm and $0.20 < \text{PdI} < 0.25$; TEM: average length: 130 ± 34 nm and average width = 12 ± 4 nm).

Preparation of dried H₂SO₄-CNCs in sodium form. Dried H₂SO₄-CNCs were produced *via* freeze-drying after counterion exchange of the aqueous H₂SO₄-CNC dispersion as described in the literature.⁴⁷ Briefly, NaOH was added dropwise into a pre-sonicated volume of the aqueous dispersion of H₂SO₄-CNCs while monitoring pH at ambient temperature. Once pH reached a value close to 7, the neutralized dispersion was freeze-dried for 24 h under low pressure (0.010 mbar) and low temperature (-100 °C). The final neutral H₂SO₄-CNCs (now in sodium form) were recovered and later re-dispersed in water with respect to the monomer content before starting the emulsion polymerization. The freeze-drying procedure was performed shortly before the particle synthesis to minimize water adsorption on the dried H₂SO₄-CNCs.

Synthesis of latex particles *via* surfactant-free emulsion polymerization. In a typical experiment including MMA, PEGMA and CNCs, the desired amount of H₂SO₄-CNCs (from 0.06 up to 0.3 g, equivalent to 2–10 % of the monomer content) was first dispersed in water (30 g) by sonication for 15 min at 40 % amplitude (Sonics Vibracel Model CV33). This dispersion was then added into a round-bottom flask containing the monomers, MMA (3 g) and PEGMA (from 0.06 up to 0.3 g, equivalent to 2 up to 10 % of the monomer content), immersed in an ice/water bath. The resulting mixture was stirred under argon for 15 to 20 min. Finally, the round-bottom flask was immersed in an oil bath set at 80 °C, and KPS (0.12 g) was added into this initial emulsion to start the polymerization. Polymerization was quenched after 2 h for each experiment and Table 1 summarizes the experimental conditions and results for all the experiments.

Table 1. Reactions conditions and main features of the latexes obtained from emulsion polymerization of MMA performed in the presence of H₂SO₄-CNCs as stabilizer and PEGMA as comonomer.

Entry ^a	CNCs ^b (wt %)	PEGMA comonomer ^b	X ^c (%)	D _h (nm)/ PDI ^d	D _n (nm)/ D _w /D _n ^e	τ _c ^f (%)	Aspect ^g
1	-	-	100	596/0.17	569/1.01*	-	stable
2	2	-	75	767/0.25	218/1.75	12.6	unstable
3	5	-	49	697/0.35	228/1.73	23.3	unstable
4	10	-	89	1060/0.57	-	8.1	unstable
5	-	2 wt% PEGMA ₉₅₀	100	691/0.13	580/1.01*	-	stable
6	-	2 wt% PEGMA ₃₀₀	100	708/0.16	-	-	stable
7	-	2 wt% PEGMA ₂₀₈₀	100	876/0.08	-	-	stable
8	2	2 wt% PEGMA ₃₀₀	100	692/0.27	228/1.94	8.1	stable

9	2	5 wt% PEGMA ₃₀₀	100	754/0.34	-	-	stable
10	2	10 wt% PEGMA ₃₀₀	100	969/0.49	278/1.34	-	stable
11	2	10 wt% PEGMA ₉₅₀	100	363/0.47	78/3.57	-	stable
12	2	10 wt% PEGMA ₂₀₈₀	100	444/0.63	88/3.21	-	stable
13	5	10 wt% PEGMA ₉₅₀	100	655/0.39	123/2.31	-	stable
14	10	10 wt% PEGMA ₉₅₀	67	398/0.32	-	8.9	stable
15	5	10 wt% PEGMA ₂₀₈₀	100	579/0.36	162/1.82	-	stable
16	10	10 wt% PEGMA ₂₀₈₀	40	385/0.37	-	48.8	unstable

^a All polymerizations were performed during 2 h at 80 °C and 500 rpm with water: 30 g, KPS: 0.12 g, MMA: 3 g. ^b Weight content according to MMA content. ^c Monomer conversion determined by gravimetric analysis after 2 h of polymerization. ^d Hydrodynamic diameter and polydispersity index determined by DLS performed on a diluted sample of the final latex. ^e Number-average diameter and diameter dispersity index obtained by statistical analysis of 110 to 1250 particles from cryo-TEM micrographs (*from FE-SEM micrographs). ^f Experimental coagulum content based on the initial mass of MMA. ^g Macroscopically observed during the polymerization.

Characterization techniques

Gravimetric analysis. To follow monomer conversion during the emulsion polymerization, small aliquots were withdrawn at different reaction times. For each sample, a known amount was put in an aluminum pan, evaporated at ambient temperature in the fume hood overnight. Weighing of the remaining solid and comparison with the initial weight allowed to determine the conversion.

Dynamic light scattering (DLS). The hydrodynamic diameter (D_h) and polydispersity index (PDI) were determined using a Malvern Zetasizer NanoZS at 25 °C. Typically, one drop of latex was placed in a conventional plastic cuvette and diluted with 1 mL of water. The data were collected at 173° scattering angle over 3 runs, using the fully automatic mode of the Zetasizer system, and fitted with the cumulants analysis.

Transmission electron microscopy in cryogenic mode (cryo-TEM). One drop of diluted latex was deposited onto 300 Mesh holey carbon grid (Quantifoil R2/1) and quench-frozen in liquid

ethane. The sample was then transferred in the microscope (Phillips CM120) using a precooled Gatan 626 specimen holder. All observations were made at -180 °C using a Philips CM120 microscope operating at an accelerating voltage of 120 kV (Centre Technologique des Microstructures (CTμ), platform of the Claude Bernard Lyon 1 University, Villeurbanne, France). The number-average diameter (D_n), the weight-average diameter (D_w) and the diameter dispersity (D_w/D_n) were determined by statistical analyses of micrographs using ImageJ software.

Scanning electron microscopy (SEM). One drop of diluted latex was deposited on a 200-mesh formvar-carbon grid. The latter was dried at ambient temperature overnight. Before observation, the grid was covered by a thin copper layer (10 nm thickness, sputtering Cu with Baltec MED-020). All observations were made at ambient temperature in a FEI Quanta 250 FEG microscope at an acceleration voltage of 5 kV (at the CTμ).

Field emission-scanning electron microscopy (FE-SEM). Diluted latexes were drop casted onto silica wafers cleaned by successive addition of Milli-Q water, acetone, and Milli-Q water. The wafers were placed onto a metal stub with carbon tape and coated with a 5 nm layer of Pt/Pd with a Cressington 208HR sputter coater. FE-SEM performed with a Hitachi S-4800 microscope (KTH, Stockholm, Sweden) was conducted at 1.0 kV or 3.0 kV acceleration voltage if nothing else was stated. ImageJ software was also used to determine D_n and D_w/D_n by statistical analysis of a specific number of particles.

Results and discussion

Influence of H₂SO₄-CNCs content in MMA emulsion polymerization

MMA emulsion polymerization was first performed in presence of H₂SO₄-CNCs (herein used in the sodium form after counterion exchange) re-dispersed in water at 2, 5 and 10 wt% with

respect to the amount of MMA (Entries 2, 3 and 4, respectively). A reference experiment was also conducted without CNCs (Entry 1). In all cases, KPS was used as initiator and the MMA amount was fixed to target a solids content of 10 wt%. Table 1 summarizes the results obtained after 2 h of polymerization in terms of monomer conversion (X), particle diameter (D_h), polydispersity index (PdI), and experimental coagulum content (τ_c).

In the absence of CNCs, complete conversion was attained in about 60 min (Figure 1). The particle diameter varied between *ca.* 330 and 500 nm during the polymerization, before a sharp increase at high conversions ($X > 93\%$) (Figure S1), ascribed to limited particle aggregation, the stabilization being only ensured by the charged initiator fragments. Field emission-scanning electron microscopy (FE-SEM) was used to obtain additional information on the particle size and size distribution of the final latex (Figure S2). The resulting micrographs show exclusively spherical particles (diameter between 500 and 600 nm) with a quite narrow particle size distribution. Statistical analysis allowed determining a number-average diameter (D_n) of 569 nm and diameter dispersity (D_w/D_n) of 1.01. The observed discrepancies between FE-SEM and DLS results ($D_h = 596$ nm / PdI = 0.17) could be explained by the limited stability of the latex, as the presence of small aggregates of a few particles during DLS analysis, contributing to a larger average particle size, cannot be excluded (see Figure S1). In addition, the FE-SEM micrograph also shows very few cases of particle coalescence, but it is hard to determine whether this phenomenon occurred during the polymerization or upon SEM observation.

The polymerization was significantly slower when H_2SO_4 -CNCs were added, with the presence of an induction period, which increases with the CNC content (5 min for Entry 2, 10 min for Entries 3 and 4). The use of H_2SO_4 -CNCs ($D_h = 90 - 100$ nm) systematically led to a destabilization of the system, with the formation of macroscopic aggregates. A closer look at the evolution of MMA

conversion (Figure 1) revealed that the destabilization occurred more rapidly when the H_2SO_4 -CNCs content increased, at 45 min in presence of 2 wt% of stabilizer ($X = 70\%$) and after 30 min in presence of 5 or 10 wt % of H_2SO_4 -CNCs ($X = 38$ and 23% , respectively). As a direct consequence of coagulum formation, the monomer conversion values determined when the latex started to destabilize were obviously underestimated and plateaued. Considering these stability issues, combined with the presence of the anisotropic rod-shape CNCs, the particle sizes measured by DLS (Figure S1) are difficult to evaluate for these experiments.

Figure 1. Evolution of conversion *versus* time during MMA emulsion polymerizations performed in the presence of various amounts of H_2SO_4 -CNCs (Entries 1 to 4, Table 1) – the dotted lines indicate when the systems starts to destabilize.

The stable fractions of the latexes prepared with 2 or 5 wt% of H_2SO_4 -CNCs were further analyzed by cryo-TEM (Figure 2b and c, respectively). PMMA particles and H_2SO_4 -CNCs seem to interact to some extent. Indeed, the CNCs are exclusively located around PMMA particles, but this interaction is likely very limited as no deformation of the particles is locally observed near the CNC, unlike what was reported for Pickering stabilization of polymer particles using inorganic

particles with high surface area such as Laponite¹⁶ or Montmorillonite clay.⁴⁸ The CNCs are indeed localized in the particle vicinity, with no free CNCs detected. Whereas these rod-shaped CNCs covered the grid dispersed individually when the neat aqueous dispersion containing 1 wt% of H₂SO₄-CNCs was observed (Figure 2a).

The use of CNCs strongly impacts the particle sizes, with a particle diameter varying between 25 nm and 640 nm. Indeed, statistical analysis revealed that in both latexes the particles are both smaller ($D_n = 218$ and 228 nm, for Entries 2 and 3, respectively) and more polydisperse in size ($D_w/D_n = 1.75$ and 1.73 , respectively) than those of the stabilizer-free latex (Figure S2, $D_n = 569$ nm, $D_w/D_n = 1.01$). These observations, combined with the fact that there was no coagulum in absence of H₂SO₄-CNCs and that the kinetics was different, indicate that even if their interaction is not strong, H₂SO₄-CNCs definitively have an impact on the nucleation step and the growth of the PMMA particles during emulsion polymerization. Similar observations were made in the work of Limousin and coworkers.⁴⁰

Figure 2. Cryo-TEM micrographs of a) H₂SO₄-CNCs from aqueous dispersion as received, and the stable fraction of the latex particles obtained after emulsion polymerization of MMA in presence of b) 2 wt% (Entry 2) and c) 5 wt% (Entry 3) of H₂SO₄-CNCs – the red arrows point out some of the H₂SO₄-CNCs.

All these observations show that the H₂SO₄-CNCs likely participate in the particle formation and growth, but also that their interaction with the particles is weak. Both PMMA oligomers generated in water and the surface of the PMMA particles are negatively charged (sulfate groups coming from the initiator), and so are the H₂SO₄-CNCs. Efficient adsorption of the growing oligoradicals to create nucleation sites on the H₂SO₄-CNCs, or the adsorption of H₂SO₄-CNCs on growing PMMA particles are thus not favored, which may explain their poor adsorption to the particle surface. One could, however, consider that some chains could be initiated by hydroxyl radicals. Indeed, SO₄[•] radicals can hydrolyze in aqueous solutions via a reaction favored by acidic conditions to form such HO[•] radicals, which are able to initiate the polymerization.^{49, 50} In that case, electrostatic repulsion would no longer be an issue and uncharged growing PMMA chains could precipitate onto the CNCs, creating nucleation sites at their surface, which can further grow (by precipitation of PMMA chains and/or nuclei), or allowing the PMMA-modified CNCs to adsorb onto growing PMMA particles. At one point, the system may however not be able to accommodate the stabilization of the total surface area created, and destabilization would occur. Nevertheless, the H₂SO₄-CNCs are dominantly hydrophilic, which also does not favor any interaction with hydrophobic polymer chains. Therefore, the hydrophilic nature of the H₂SO₄-CNCs and their negative surface charge prevent their efficient adsorption onto the nucleated PMMA particles. Similar behavior has been reported by Bel Haaj *et al.* when negatively charged starch nanocrystals (H₂SO₄-SNCs) were used as stabilizer during BMA emulsion polymerization, also using KPS as initiator.⁵¹ In this particular case, an alternative strategy was then tested by the authors, consisting in the tuning of the hydrophilic/hydrophobic character of the Pickering stabilizer by using a poly(ethylene glycol)-based macromonomer, namely poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 375 \text{ g mol}^{-1}$), to facilitate interactions with H₂SO₄-

SNCs. During the writing of this paper, the same team extended this strategy to the use of H₂SO₄-CNCs (around 250 ± 20 nm and average width of 10 ± 2 nm) for the emulsion polymerization of vinyl acetate in the presence of PEGMA,⁴¹ showing the positive impact of PEGMA to favor CNC/polymer particles interaction. There are, however, conflicting results in the literature whether linear PEG-based macromolecules can or cannot interact and adsorb onto H₂SO₄-CNCs.⁵² Nevertheless, we decided to investigate the use of PEGMA of different molar masses as comonomer during MMA emulsion polymerization.

As previously described in the literature, copolymerization of PEGMA ($M_n = 475 \text{ g mol}^{-1}$) with an excess of MMA (1 mol% PEGMA) has been studied and reactivity ratios were determined ($r_{\text{MMA}} = 0.75 \pm 0.07$, and $r_{\text{PEGMA}} \approx 1.33$, in toluene at 80 °C), indicating that PEGMA units will react more rapidly than MMA ones.⁵³ To the best of our knowledge, no study reports the determination of the same reactivity ratios under emulsion conditions, but we can reasonably assume that PEGMA, more soluble in water, will most likely be consumed more rapidly than MMA at the early stages of the polymerization, potentially favoring early interaction with the CNCs.

PEGMA-mediated MMA emulsion polymerization in the presence of H₂SO₄-CNCs

Preliminary interaction tests between CNCs and PEG-stabilized particles.

To investigate the interaction of H₂SO₄-CNCs with PEG-stabilized particles, a preliminary study was undertaken. A PEG-stabilized latex was prepared by stabilizer-free emulsion copolymerizations of MMA with 2 wt% of PEGMA₉₅₀ ($M_n = 950 \text{ g mol}^{-1}$) in the absence of CNCs (Table 1, Entry 5). Full conversion was reached in 1 h (Figure S3) and a stable latex was obtained. FE-SEM observation of this latex shows monodisperse particles with $D_n = 580 \text{ nm}$, $D_w/D_n = 1.01$

(Figure S4). The interaction between the CNCs and PEG was then investigated by mixing free H_2SO_4 -CNCs (2 wt%) with either the reference latex (Entry 1) or the latex prepared with PEGMA₉₅₀ (Entry 5). The similar size obtained for these two experiments indeed allows for a consistent comparison behavior against CNC adsorption. The resulting mixtures were analyzed by FE-SEM (Figure 3). The PEG-stabilized PMMA particles (Figure 3c-d) show a stronger interaction with the CNCs than the PMMA ones (Figure 3a-b). This was a promising result suggesting that the use of PEGMA as a comonomer leads to particles with polymer chains at their surface showing better interaction with H_2SO_4 -CNCs than pure PMMA ones. However, such improved interaction, as shown by SEM imaging here, could also be an effect of drying, where PEG-based structures are expected to interact with CNCs.⁵² Nonetheless, this preliminary test prompted us to evaluate the combined use of PEGMA and H_2SO_4 -CNCs in MMA emulsion polymerization.

Figure 3. FE-SEM micrographs of the mixtures obtained after addition of H_2SO_4 -CNCs (2 wt%) into (a-b) the reference PMMA latex (Entry 1), and (c-d) the PMMA latex prepared in the presence of 2 wt% of PEGMA₉₅₀ (Entry 5).

Emulsion copolymerization of MMA and PEGMA in the presence of CNCs.

In order to investigate the impact of the PEGMA molar mass in the following experiments, two additional CNC-free latexes were first prepared using 2 wt% of PEGMA₃₀₀ (Entry 6) or PEGMA₂₀₈₀ (Entry 7) (Table 1 and Figure S5). The number of ethylene glycol (EG) units was globally the same in the experiments performed with the three different comonomers, while the number of PEGMA macromolecules decreased as its molar mass increased. The addition of PEGMA comonomer shows no significant impact neither on the kinetics (Figure S5a) nor on the particle size (Figure S5b). Whatever the comonomer molar mass, stable latexes were obtained, and thus the three types of PEGMA were used in the next experiments.

First, PEGMA₃₀₀ was selected to investigate the impact of the comonomer content in the presence of H_2SO_4 -CNCs. Emulsion copolymerizations of MMA and PEGMA₃₀₀ were thus conducted in presence of increasing comonomer content (2, 5 and 10 wt%, Table 1, Entries 8, 9 and 10, respectively), but with the same low amount of H_2SO_4 -CNCs (*i.e.* 2 wt%) to avoid rapid destabilization of the system as previously observed in absence of comonomer (Table 1, Entry 2).

Independently of PEGMA₃₀₀ content, full conversion was reached within 1 h (Figure 4a) and the latexes obtained were stable during the emulsion copolymerization. Such enhancement in colloidal stabilization can very likely be attributed to the interaction between PEGMA₃₀₀ units and H₂SO₄-CNCs, prior to or during the polymerization. 8.1 % coagulum was still obtained with 2 wt% of PEGMA₃₀₀, but could be eliminated when the comonomer amount was increased to 5 and 10 wt%.

Irrespectively of the PEGMA amount, the particle size increases during the polymerization (Figure 4b), indicating a limited stability of the latexes, which is also indicated by the high PDI values (from 0.27 to 0.49 as the concentration increases). Nevertheless, for a similar conversion, the higher the PEGMA amount, the lower the particle size. It is worth mentioning that the average diameters determined by DLS assume a spherical shape for the particles, and the presence of rod-shape CNCs will obviously skew the results. Nevertheless, in a first approximation, DLS remains a useful tool for sample comparison. A closer look at the distributions of particle size in intensity (Figure S6a) and in number (Figure S6b) at the end of the emulsion copolymerizations showed that a second population of smaller particles (D_h between 150 and 250 nm, Figure S6b) emerges when the content of PEGMA₃₀₀ comonomer increased from 2 to 5 and 10 wt%, explaining the broadening of particle size distribution with increasing PEGMA₃₀₀ content. The size of this population also seems to decrease as the amount of comonomer increases.

Figure 4. Evolutions of a) conversion *versus* time and b) D_h *versus* conversion during MMA emulsion copolymerizations with 2 wt% (Entry 8), 5 wt% (Entry 9) and 10 wt% of PEGMA₃₀₀ (Entry 10) in presence of 2 wt% of H₂SO₄-CNCs – the black symbols correspond to MMA emulsion polymerization in presence of 2 wt% of H₂SO₄-CNCs (Entry 2), which did not lead to a stable latex (the dotted line indicates when the system started to destabilize).

To get further insight into the particle size distribution, the latexes obtained *via* emulsion copolymerization performed with 2 and 10 wt% of PEGMA₃₀₀ were observed by cryo-TEM (Figure 5). In good agreement with the PDI values from DLS analysis, both samples show broad particle size distribution and confirm the presence of small particles. Statistical analyses (Figure 5c and 5f) indicate that the number-average diameter decreases with the content of PEGMA₃₀₀ (D_n = 278 nm à 10 wt% *vs.* 228 nm at 2 wt%, Table 1). On the other hand, the size dispersity is lower when adding PEGMA₃₀₀ at 10 wt% (1.34 *vs.* 1.94). Indeed, particles are overall smaller at 2 wt% (some being smaller than 70 nm), with a few big particles (> 300 nm), which contribute to the increase of the dispersity value. One can also notice that there are few or no free H₂SO₄-CNCs in

these micrographs, all being located around the particles (red arrows) as already observed when only H₂SO₄-CNCs are added during MMA emulsion polymerizations (Figure 2).

Figure 5. Cryo-TEM micrographs of the latex obtained *via* emulsion copolymerization of MMA with 2 wt% (a and b, Entry 8) or 10 wt% of PEGMA₃₀₀ (d and e, Entry 10) in presence of 2 wt% H₂SO₄-CNCs – the red arrows point out some of the H₂SO₄-CNCs. Histograms of the diameter distributions determined by statistical analysis of 227 particles (c, Entry 8) or 760 particles (f, Entry 10) from cryo-TEM micrographs.

Our strategy relies on the adsorption of PEG moieties onto the CNCs, either as PEGMA macromonomer or as copolymer chains incorporating PEGMA units, or both. As mentioned above, there are conflicting opinions in the literature regarding whether the more simple structure of a

linear PEG chain can⁴²⁻⁴⁴ or cannot^{52, 54, 55} adsorb on cellulosic surfaces. It is however important to distinguish between such linear PEG chains and the herein used methacrylate PEGMA macromonomers, with PEG side chains of different lengths and a methacrylate function which will allow their incorporation in a polymethacrylate backbone. Indeed, the structure of the PEG-based macromolecules is very likely to play a critical role. Holappa *et al.* studied the adsorption of PEG chains end-capped with hydrophobic octadecenylsuccinic anhydride (OSA-PEG₆₀₀₀-OSA) on an ultrathin film of cellulose.⁵⁴ They demonstrated that the telechelic hydrophobic modification promoted adsorption through decreased flexibility and solubility of this polymer compared to the PEG₆₀₀₀-OH homopolymer, combined with hydrophobic interactions between the OSA chains and the pyranose backbone of cellulose. Once located on the surface, attachment of OSA-PEG₆₀₀₀-OSA becomes possible thanks to hydrophobic interaction and hydrogen bonding. The presence of a hydrophobic group at the end of a PEG chain can thus boost its adsorption on cellulose. It seems reasonable to assume that the methacrylate function of PEGMA could similarly promote its adsorption as a macromonomer. Adsorption could also be favored once PEGMA units are incorporated into a polymeric backbone, via the gain in entropy achieved by adsorption onto the CNCs. In addition, the very recent work from Ben Mabrouk *et al.* also seems to support the beneficial role of PEGMA to favor interaction of H₂SO₄-CNCs with poly(vinyl acetate) particles.⁴¹

Considering that PEGMA₃₀₀ could be initially adsorbed onto H₂SO₄-CNCs and/or be present as a free macromolecule in water, particle formation could occur as follows. When the polymerization starts, i) radicals coming from the initiator will react with MMA molecules in water creating oligomers, which will then be captured by the H₂SO₄-CNCs through copolymerization with adsorbed PEGMA, and/or ii) oligomers incorporating PEGMA units will adsorb onto the CNCs. These adsorbed polymer chains will be swollen with MMA and will become a preferential

adsorption site for new oligomers or oligoradicals, leading to surface nuclei. Depending on their stability these primary particles will either continue to grow individually or agglomerate to form larger particles. This scenario does not exclude the generation of polymer particles *via* homogeneous nucleation, onto which polymer-modified H₂SO₄-CNCs can adsorb to lower the surface energy. Even if the mechanisms operating in these systems are still to investigate, and in particular the nature of the interactions between PEGMA and CNCs, the concomitant use of these compounds definitively leads to a significant improvement in latex stability (*versus* Entry 2, 2 wt% CNC, without PEGMA).

Influence of PEGMA molar mass (10 wt% PEGMA)

Relying on the improved colloidal stability achieved in presence of PEGMA₃₀₀ as comonomer, the effect of PEGMA molar mass during emulsion copolymerizations with MMA was investigated, replacing PEGMA₃₀₀ by either PEGMA₉₅₀ or PEGMA₂₀₈₀ (Table 1, Entry 11 and 12, respectively). The PEGMA weight content was the same in each experiment (*i.e.* 10 wt%), which means that the higher the PEGMA molar mass, the lower the number of PEGMA macromolecules, thus the lower the number of methacrylate functions. Nevertheless, the number of EG units able to interact with H₂SO₄-CNCs is approximately the same in each reaction.

As shown in Figure 6, varying PEGMA molar mass did not impact the kinetics of the polymerization, and stable, aggregate-free, latexes were obtained. However, replacing PEGMA₃₀₀ by either PEGMA₉₅₀ or PEGMA₂₀₈₀ led to significantly lower particle size ($D_h \sim 400 \pm 40$ nm), suggesting that these macromonomers and/or the copolymer chains in which they are incorporated, are more efficient to interact with H₂SO₄-CNCs. Nevertheless, DLS still indicates broad distribution ($PdI \geq 0.47$) and at least two populations of particles could be detected (intensity

distribution, Figure S7a). The number distributions (Figure S7b) show that nanometric particles ($D_h \sim 110 \pm 20$ nm) are almost exclusively detected when PEGMA₉₅₀ or PEGMA₂₀₈₀ are used as comonomer, while some large particles and/or aggregates (*ca.* 1 μ m) are also present together with small particles ($D_h \sim 210 \pm 15$ nm) at the end of the copolymerization with PEGMA₃₀₀.

Figure 6. Evolution of a) conversion *versus* time and b) D_h *versus* conversion during MMA emulsion copolymerizations with 10 wt% of PEGMA₃₀₀ (Entry 10), PEGMA₉₅₀ (Entry 11) or PEGMA₂₀₈₀ (Entry 12) performed in presence of 2 wt% of H₂SO₄-CNCs – the black symbols correspond to MMA emulsion polymerization in presence of 2 wt% of H₂SO₄-CNCs (Entry 2), which did not lead to a stable latex (the dotted line indicates when the system starts to destabilize).

The small particles are not detected before 30 min of polymerization (data not shown), corresponding to 55, 46 and 47 % conversion in presence of PEGMA₃₀₀, PEGMA₉₅₀, and PEGMA₂₀₈₀, respectively. This suggests that homogeneous nucleation occurs rapidly (due to the water solubility and reactivity of MMA and PEGMA) while the growth of small particles, more likely from the surface of H₂SO₄-CNCs, is a slower event which needs i) the copolymerization to

occur with PEGMA adsorbed on CNC and/or ii) the formation of (co)oligomers incorporating PEGMA units followed by their adsorption onto the CNC surface. Judging from the increased number of small particles observed when using an increasing number of EG units in the PEGMA macromonomer (cryo-TEM images in Figure 7), the interaction between the particles and the H₂SO₄-CNCs is improved in these experiments, as compared to the one performed with PEGMA₃₀₀. These results are likely driven by a stronger adsorption of PEGMA₉₅₀ and PEGMA₂₀₈₀ (and/or of their copolymers) compared to PEGMA₃₀₀.

Determining the adsorption isotherms of PEGMA₉₅₀ and PEGMA₂₀₈₀ onto H₂SO₄-CNCs could provide additional information regarding the optimum protocol to perform emulsion copolymerization in these conditions, but these analyses were not undertaken in the frame of this study. In agreement with DLS measurement, a great number of nanometric particles ($D_n \sim 50$ to 80 nm) is observed in TEM micrographs – the larger particles having an average diameter from 170 to 410 nm – and these particles are found in proximity to a large amount of H₂SO₄-CNCs (red arrows). Statistical analyses indicate significantly lower D_n values (Figure 7c and 7f), even if the dispersities are quite high owing to the presence of a few big particles (> 130 nm).

Figure 7. Cryo-TEM micrographs of the latexes obtained *via* MMA emulsion copolymerization with PEGMA₉₅₀ (a and b, Entry 11) and PEGMA₂₀₈₀ (d and e, Entry 12) added at 10 wt% and in presence of 2 wt% of H₂SO₄-CNCs – the red arrows point out some of the H₂SO₄-CNCs. Histograms of the diameter distributions determined by statistical analysis of 450 particles (c, Entry 10) or 700 particles (f, Entry 12) from cryo-TEM micrographs.

Nevertheless, these cryo-TEM micrographs do not allow distinguishing a specific organization between particles and the CNCs (most likely due to sample preparation). On the contrary, SEM and FE-SEM micrographs in Figure 8 show an interesting organization where several particles seem to grow from one nanocrystal, with several particles covering one H₂SO₄-CNC (some of them are highlighted by red circles). The SEM images confirm the presence of two populations of different particle diameter, large particles between 200 nm and 550 nm, and small particles

between 50 nm and 100 nm. It is difficult to visualize the surface of the small particles, but the larger ones show a rough surface (wrinkled particles). For these large particles, which have similar aspect ratio and size as those of the surfactant-free system (Figure S2), H_2SO_4 -CNCs do not contribute (or to a very little extent, and in some cases) to particle stabilization.

Figure 8. SEM (a and b) and FE-SEM micrographs (c and d) of the latex synthesized by emulsion copolymerization of MMA with PEGMA₉₅₀ in presence of 2 wt% of H_2SO_4 -CNCs (Entry 11) – the red circles point out to the organization between particle(s) and H_2SO_4 -CNCs.

Influence of H₂SO₄-CNCs content.

In an attempt to induce the stabilization of a greater number of particles and avoid the growth of large PMMA particles which results in a broadening of the particle size distribution, H₂SO₄-CNCs content was increased from 2 wt% to 5 and 10 wt% for emulsion copolymerization of MMA in the presence of 10 wt% of PEGMA₉₅₀ (Table 1, Entry 13 and 14). Increasing H₂SO₄-CNCs content to 10 wt% led to rapid destabilization of the systems after 15 min of polymerization (Figure 9a), preventing sample withdrawal after 45 min of reaction. With 5 wt% of PEGMA, the system remained stable throughout the polymerization. A careful look at the conversions reached after 15 min (*i.e.* just before destabilization occurs for the system with 10 wt% of PEGMA) indicates that the higher the H₂SO₄-CNCs content, the higher the conversion (16, 19, and 24 %, for 2, 5 and 10 wt% CNCs, respectively). Thus, increasing the amount of CNCs leads to an increase of the polymerization rate. This again suggest that CNCs contribute to particle nucleation, a greater number of particles being formed at the early stages of the polymerization as the CNCs amount increases, but also that too many nuclei were formed with 10 wt% CNCs and that their stability could not be ensured, leading to partial latex destabilization (see coagulum content, Table 1 and Figure 9b). Besides, since the comonomer content remained the same in these experiments (10 wt%), there is likely less PEGMA units (either as the monomer or in copolymer chains) to efficiently interact with the CNCs when their content increases to 10 wt%. The absence of small particles (number distribution from DLS, Figure S8b) seems to indicate that those lead to coagulum after destabilization due to their too high number. No large particles were detected by DLS for 2 wt% of CNC, and only a small amount with 5 wt%. The average size of the small particles was similar ($D_h = 110 \pm 20$ nm).

Figure 9. Evolution of a) conversion *versus* time and b) D_h *versus* conversion during MMA emulsion copolymerization with PEGMA₉₅₀ (10 wt%), performed in the presence of 2 wt% (Entry 11), 5 wt% (Entry 13) or 10 wt% (Entry 14) of H₂SO₄-CNCs – the dotted lines indicate when the systems start to destabilize.

The stable latex obtained in the presence of 5 wt% of H₂SO₄-CNCs was analyzed by cryo-TEM to visualize the mutual organization of the particles and the H₂SO₄-CNCs (Figure 10). In good agreement with the DLS analyses, a broad range of particle sizes, from 20 to 320 nm, can be observed with a great number of small particles having an average diameter of 55 nm. Furthermore, the specific organization of one H₂SO₄-CNC covered with several particles can again be spotted in Figure 10b (red circle), indicating the production of small particles forming *via* favorable interactions between PEGMA units and H₂SO₄-CNCs, possibly through adsorption either prior to their copolymerization with MMA or as monomer units incorporated in growing oligomers.

A similar study was conducted with PEGMA₂₀₈₀ (Entries 12, 15 and 16, Table 1 and Figures S9 and S10), leading to the overall same trends and conclusions.

Figure 10. Cryo-TEM micrographs of the latex obtained *via* MMA emulsion copolymerization with PEGMA₉₅₀ (10 wt%) in the presence of 5 wt% of H₂SO₄-CNCs (a and b, Entry 13) – the red arrows point out some of the H₂SO₄-CNCs, the red circle shows one specific organization between particles and stabilizer. Histogram of the diameter distributions determined by statistical analysis of 370 particles (c) from cryo-TEM micrographs.

Conclusions

PMMA polymer particles were obtained *via* surfactant-free emulsion polymerization in the presence of cellulose nanocrystals, H₂SO₄-CNCs, evaluated as Pickering-type stabilizer to form hybrid latexes of CNCs and PMMA. A synergetic effect between H₂SO₄-CNCs and PEGMA was found to stabilize hydrophobic PMMA particles by *in situ* modification of the hydrophilic H₂SO₄-CNCs (before and/or during the polymerization) by favorable interactions between CNCs and PEGMA-based macromolecules. Adding the H₂SO₄-CNCs in MMA emulsion polymerization led to limited monomer conversion, suggesting that the H₂SO₄-CNCs were involved in the nucleation step, but aggregation occurred and was attributed to particle coalescence and/or coagulation events due to poor stabilization. To promote particle stabilization, PEGMA was added to the emulsion to act as a compatibilizer between the particles and the CNCs. Three PEGMAs of different molar

mass were evaluated (300, 950 and 2080 g mol⁻¹), leading to an enhancement of the colloidal stability in the presence of H₂SO₄-CNCs. Small particles were also observed (diameter between 50 and 80 nm), the fraction of which increased with the molar mass of PEGMA, even though a few large particles were still formed. Eventually, using the same amount of PEGMA monomer (10 wt%), the amount of CNCs loaded in the synthesis (2, 5 and 10 wt%) was evaluated. It was shown that particle stabilization was very dependent on the mass ratio between PEGMA and CNCs, small particles being mostly observed for 2 wt% CNCs at 10 wt% PEGMA loading. Observation of such stable latexes by cryo-TEM highlighted an interesting morphology, where one nanocrystal is covered by several small polymer particles. Even if the final morphologies were not the ones initially targeted (*i.e.* PMMA particles decorated with CNCs), they however remain interesting as potential additives for the preparation of CNC-based materials.⁵⁶

ASSOCIATED CONTENT

Supporting Information. Structures of PEGMA macromonomers, Polymerization kinetics, DLS, FE-SEM and TEM characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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