



Highly Hydrophobic, Homogeneous Suspension and Resin by Graft Copolymerization Modification of Cellulose Nanocrystal (CNC)

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1. Materials and Methods

The hardwood pulp was purchased from Zhongshan NFC Bio-materials Co. 4-(trifluoromethyl) aniline (98%), phenol (99%), 9-bromo-1-nonanol (98%), NaNO_2 (99%) and N-N-dimethylacetamide (DMAc, 99.8%) were purchased from Macklin used as received. Acryloyl chloride (97%), CuBr (98%), 4-(dimethylamino) pyridine (DMAP, 99%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), α -bromoisobutyl bromide (BiBB, 98%) and ethyl α -bromoisobutyrate (98%) was purchased from Sigma-Aldrich used as received. Sulfuric acid and other reagents were purchased from Damao Chemical Reagent Factory. All reagents were analytically pure and used directly.

1.1. Preparation of Cellulose Nanocrystals

The hardwood pulp (10 g) was thoroughly mixed with sulfuric acid (100 mL, 64%) in the prepared ice bath and stirred at 45 °C for 1 hour. Immediately following hydrolysis, the suspension was diluted 10-times to stop the reaction. Through centrifuging to remove the acid and retain the precipitated part. Using semipermeable membrane (cutoff molar mass, 14,000 Da) and deionized water dialysis for several days was applied until the aqueous solution was neutral so that the residual sulfuric acid can be removed entirely. The suspension was recovered by freeze-drying. After dried, the fluffy CNC was collected, which was dried in a vacuum for 48 hours at 45 °C until the weight is constant.

1.2. Synthesis of 4-(4-trifluoromethylphenylazo) phenol (FAZOH)

4-(Trifluoromethyl) aniline (2.41 g, 15 mmol) was dissolved in 1 mol/L HCl (40 mL) and cooled to 0 °C. Then, NaNO_2 aqueous solution (1.56 g, 22.5 mmol) was added dropwise with stirring at 0~5 °C. Subsequently, the diazonium salt solution was slowly added to a phenol (2.1 g, 22.5 mmol) in 1 mol/L NaOH (40 mL) at 0~5 °C and adjust the pH of the reaction solution to 7~10 with a saturated solution of sodium bicarbonate. The obtained reaction mixture was stirred for another 2 h. The resulting orange precipitate was filtered, dried in a vacuum oven at 50 °C and recrystallized with n-hexane (yield: 79.4%).

1.3. Synthesis of 9-[4-[2-[4-(trifluoromethyl) phenyl] diazenyl] phenoxy]-1- nonanol(FAZ9OH)

At room temperature, K_2CO_3 (5.52 g, 40 mmol) was added to a solution of FAZOH (2.66 g, 10 mmol) in DMAc (40 mL) and stirred for 30 min under the argon protection. Subsequently, the solution was added with KI (0.015 g, 90 mmol), 9-bromo-1-nonanol (5.335 g, 39 mmol) was added dropwise and then heated to 100 °C with vigorous stirring for 24 h. The resulting mixture was poured into 1 L ice water, and the resulting red-brown precipitate was filtered, dried in a vacuum oven, and crystallized from n-hexane (yield: 80.5%).

1.4. Synthesis of 9-[4-[2-[4-(trifluoromethyl) phenyl] diazenyl] phenoxy] nonayl acrylate (FAZO)

A solution of acryloyl chloride (3.064 g, 8 mmol) in CH_2Cl_2 (10 mL) was dropped slowly into a solution containing FAZ9OH (1.672 g, 16 mmol), triethylamine (1.624 g, 16 mmol) and CH_2Cl_2 (40 mL) at 0~5 °C. The reaction mixture was stirred vigorously for 20 h at room temperature. Then, the reaction mixture was washed with diluted HCl solution (20 wt.%) (10 mL), NaHCO_3 solution (10 mL), and NaCl solution (10 mL), respectively. The colored organic layer was collected, and the solvent was removed with a rotary

evaporator. The crude product was purified by neutral alumina column chromatography using CH_2Cl_2 as eluent. After removing the solvent, the product was recrystallized from n-hexane as a yellow solid (yield: 42.2%).

1.5. Binding of the brominated initiators on cellulose nanocrystals Surface (CNC-Br)

Cellulose nanocrystals (1.0 g) were mixed with triethylamine (1.82 mL, 16 mmol), DMAP (0.4 g) and DMAc (80 mL) under a nitrogen atmosphere. 20 mL DMAc mixed BIBB (2.6 mL, 20 mmol) were added dropwise under stirring. The reaction proceeded under argon at an ice bath ($\sim 2\text{--}5\text{ }^\circ\text{C}$) for two h and then at room temperature for 24 h and then filtered through an extraction thimble. Purification of the modified nanocrystals was realized by successive Soxhlet extractions with CH_2Cl_2 to remove any small residual molecules, then freeze-dried to a constant weight.

1.6. Grafting poly-FAZO Brushes on cellulose nanocrystals

The CNC-Br (0.2 g), CuBr (143.5 mg, 0.1 mmol), DMAc (15.0 mL), Ebib (146 μL , 0.1 mmol) PMDETA (208.7 μL , 0.1 mmol) and FAZO (1.02 g, 2.18 mmol) were added into a dry glass tube. The glass tube was degassed with three freeze–pump–thaw cycles and then sealed under vacuum. The tube was then placed in a thermostatic oil bath and left at $90\text{ }^\circ\text{C}$ for 24 h. These suspensions were then centrifuged for 15 min at 10,000 rpm, the non-bound polymer (PFAZO, unreacted monomer) were removed from the PFAZO-grafted CNC by Soxhlet extraction with CH_2Cl_2 . The product was dried at $50\text{ }^\circ\text{C}$ under a vacuum environment for 24 h.

2. Characterizations

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectra of the raw and modified CNC in KBr pellets were obtained with a Vertex 70 spectrometer.

Nuclear magnetic resonance spectroscopy (NMR)

^1H NMR was recorded with a superconducting Fourier digital NMR spectrometer (Bruker, AVANCE NEO 600 MHz). CDCl_3 was used as solvent, and TMS was used as a reference.

X-ray diffraction (XRD)

For the X-ray diffraction (XRD) measurements, CNCs, CNCs-Br, and CNCs-PFAZO were formed into small pellets with a laboratory press. XRD was carried out using a Bruker D8 Advance (Bruker Co., Germany). The diffracted intensity of Cu $\text{K}\alpha$ radiation (wavelength 0.1542 nm, at 50 kV and 40 mA) was measured in the 2θ range of $5\text{--}50^\circ$.

Dynamic Light Scattering (DLS)

The size distribution was measured for native and surface-modified CNCs in water and DMSO using Zetasizer Nano ZS90 (Malvern). Triplicate samples were measured 11 times each, and the average hydrodynamic size is reported. The standard deviation from the triplicate samples is reported as the error for the measurements.

Contact angle measurements

Contact angle measurement was carried out with a data physics OCA15 pro contact angle measuring instrument, Germany.