Electronic Supplementary Information (ESI) Nanocomposite hydrogels of laponite mixed with polymers bearing dopamine and cholic acid pendants

Yong-Guang Jia, X. X. Zhu*

Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, QC, H3C 3J7, Canada

Experimental Section

Acryloyl chloride, *p*-nitrophenol, cholic acid, dopamine hydrochloride and β -cyclodextrin were purchased from Aldrich and used without further purification unless otherwise stated. 2,2'-Azoisobutyronitrile (AIBN) was recrystallized twice from methanol. *N*,*N*'-Dimethylacrylamide (DMA) was distilled before use. Laponite XLG (Laponite) was a gift from Southern Clay Products, Inc. (Austin, TX). Cholic acid-based methacrylate monomer (CA) was prepared as reported previously.¹ *p*-Nitrophenyl acrylate (NPA) was synthesized according to the literature.² P(DMA-CA2%) and P(DMA-NPA2%) were synthesized as our previous report.³



Figure S1. Synthetic scheme of P(DMA-DOP-CA). Catechols are well-known polymerization inhibitor by reacting with radicals to form aryloxy free radicals.⁴ In order to obtain polymers with the linear structures, precursor polymers P(DMA-NPA-CA) consisting of 4-nitrophenyl ester and cholic acid pendants were synthesized firstly via a straightforward free radical polymerization. Excess dopamine substituting the NPA moieties on the precursors results in P(DMA-DOP-CA).

Synthesis of P(DMA-NPA-CA). A mixture of DMA (2.97 g, 30.0 mmol), NPA (116 mg, 0.6 mmol), CA (346 mg, 0.6 mmol), AIBN (11 mg, 0.067 mmol) and DMF (5 mL) was added to a 50 mL round-bottom flask. The mixture was purged with N_2 for 20 min prior to its immersion in a preheated oil bath. The reaction was allowed to proceed for 18 h at 70 °C

before being quenched by immersion into ice-water. Polymer P(DMA-NPA2%-CA2%) was precipitated from diethyl ether and 3.02 g (88%) white powder was obtained after drying *in vacuo*.

Synthesis of P(DMA-DOP-CA). P(DMA-NPA2%-CA2%) (488 mg, equals to 0.085 mmol NPA units), dopamine hydrochloride (66 mg, 0.35 mmol) and triethylamine (35 mg, 0.35 mmol) were dissolved in DMF (5 mL) at 22 °C. The substitution reaction was carried out at 50 °C for a period of 24 h. Polymer was precipitated from diethyl ether and the other impurities were removed through dialysis for 3 days in water (pH < 3). Pure P(DMA-DOP2%-CA2%) (379 mg) was obtained by drying the dialyzed solution. The other polymers with different molar ratios of DOP and CA units were synthesized similarly.

Preparation of nanocomposite hydrogels. All the nanocomposite hydrogels are prepared similarly. For example, an equal volume of aqueous dispersion of laponite at 2 wt% was added into the aqueous solution of P(DMA-DOP2%-CA2%) at 4 wt%. After a mixing on vibration machine for 1 minute, P(DMA-DOP2%-CA2%)/laponite hydrogel was obtained with a weight ratio of 2:1 wt%. Milli-Q water was used throughout the experiments without pH control.

Polymer characterization. Size exclusion chromatography (SEC) was performed on a Breeze system from Waters equipped with a 717 plus autosampler, a 1525 Binary HPLC pump, and a 2410 refractive index detector using two consecutive Waters columns (Phenomenex, 5 μ m, 300 mm \times 7.8 mm; Styragel HR4, 5 μ m, 300 mm \times 7.8 mm). The eluent DMF containing 0.05 M LiBr was filtered through 0.20 µm Nylon Millipore filters. The flow rate was 1 mL/min. Poly(methyl methacrylate) standards (2500-296 000 g/mol) were used for calibration. ¹H and ¹³C NMR spectra in CDCl₃ or D₂O were recorded on a Bruker AV400 spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C. UV-vis spectra of the samples in aqueous solution were determined on a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent) equipped with a Cary temperature controller. Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer NanoZS instrument (Malvern CGS-2 apparatus) equipped with a He-Ne Laser with a wavelength of 633 nm and the scattering angle was fixed at 173°. Intensity-average hydrodynamic diameters of the dispersions were obtained by DLS through the use of non-negative least-squares (NNLS) algorithm. Disposable cuvettes were used and the suspensions were filtered through 0.45 µm Millipore filters to remove dust. The measurements were taken after 2 minutes of equilibration time. Transmission electron microscopy (TEM) was done on a FEI Tecnai 12 TEM equipped with a Gatan 792 Bioscan $1k \times 1k$ wideangle multiscan CCD camera with an accelerating voltage of 120 kV. The samples were prepared by placing a drop of polymer or laponite solution (1 g/L in water) on 300 mesh carbon-coated copper grids (Carbon Type B with Formvar, from Ted Pella, Inc.). The solution was dried via slow evaporation under air. Fourier transform infrared (FTIR) spectra were recorded on a NICOLET 6700 spectrometer using the attenuated total

reflection (ATR) method. All the samples, including hydrogels were measured in the dry state. Rheological characterization of the hydrogels was done with a AR 2000 rheometer (TA Instruments) equipped with a 2° steel cone geometry of 20 mm diameter and solvent trap. Rheological gel characteristics were monitored by oscillatory time sweep, frequency sweep, strain sweep and temperature sweep experiments. During time sweep experiments, the *G*' (storage modulus) and *G*''(loss modulus) were measured at 20 °C for a period of 5 min. Temperature sweep experiments were done with a heating rate of 1 °C/min. After each temperature increment (1 °C) and 30 s equilibration, *G*' and *G*'' were measured. In both time and temperature sweep experiments, a constant strain of 10% and frequency of 1 Hz was used.



Figure S2. ¹H NMR spectra of (A) P(DMA-NPA2%-CA2%) and (B) P(DMA-DOP2%-CA2%) in CDCl₃ (25 °C) show the peaks of the dopamine moieties at 6.9-6.5 ppm with the disappearance of the peaks of the active ester at 8.4 and 7.6 ppm. The characteristic peaks of cholic acid moieties at 0.63, 0.83 and 0.94 ppm remained unchanged. The extent of dopamine substitution is estimated to be almost quantitative from the integration of the ¹H NMR peaks.



Figure S3. SEC curves of the polymers P(DMA-CA), P(DMA-NPA) and P(DMA-NPA-CA). DMF was used as the mobile phase with a flow rate of 1.0 mL/min and with PMMA standards.

Polymers ^[a]	Feed Ratio ^[b]	Yield ^[c]	$M_{n,SEC}^{[d]}$	$M_{\rm w}/M_{\rm n}^{\rm [d]}$
P(DMA-NPA2%-CA2%)	100:2:2	88	166.4×10^{3}	2.60
P(DMA-NPA2%-CA1%)	100:2:1	93	145.4×10^{3}	2.87
P(DMA-NPA1%-CA2%)	100:1:2	85	160.3×10^{3}	2.93
P(DMA-NPA2%)	100:2	91	88.7×10^3	2.78
P(DMA-CA2%)	100:2	93	49.2×10^{3}	2.46

Table S1. Characteristics of the P(DMA-CA) and precursor polymers P(DMA-NPA) and P(DMA-NPA-CA).

^[a]NPA unit was substituted by dopamine and corresponding polymers P(DMA-DOP-CA) are obtained.^[b]Molar ratio of DMA to the second and third monomers in the feed. ^[c]Yield calculated from the insoluble portion in ethyl ether. ^[d] Determined by SEC



Figure S4. Inverted vial tests: (A) 1 wt% of laponite; (B) 1 wt% of P(DMA-DOP2%-CA2%); (C) 1 wt% of P(DMA-DOP2%-CA2%) mixed with 1 wt% of laponite and (D) mixture in image C after the addition of 1 molar equivalent of β -cyclodextrin to cholic acid units and (E) after the addition of 5 molar equivalents of Fe³⁺ to dopamine units.



Figure S5. Storage (*G*', solid symbols) and loss moduli (*G*'', open symbols): (A) Hydrogels of 1 wt% of P(DMA-DOP2%-CA2%) with 0.5, 1 and 2 wt% of laponite under time sweep at 20 °C, respectively. (B) P(DMA-DOP-CA)/laponite hydrogels under frequency sweep at 20 °C (2 wt% of polymers and 1 wt% of laponite). (C) P(DMA-DOP2%-CA2%)/laponite hydrogel under a heating and cooling cycle (temperature sweep, 2 wt% of polymer and 1 wt% of laponite). *G*' reached its original value after cooling, demonstrating almost perfect thermoreversibility of the hydrogel in the temperature range.



Figure S6. UV/vis absorbance spectra of laponite, P(DMA-DOP2%-CA2%) and mixture of P(DMA-DOP2%-CA2%) and laponite in water at 25 °C, all at a concentration of 1 g/L.



Figure S7. ¹H NMR spectra (25 °C, polymer concentration 10 g/L equivalent to 1.7 mmol/L cholic acid units) of P(DMA-DOP2%-CA2%) in the absence and presence of β -CD in D₂O ([β -CD]/[CA] = 3:1). The signals of the three methyl protons on the cholic acid moieties all shift downfield and become sharper in the presence of β -CD. The signals of the methyl protons on position 18 and 21 are downfield-shifted more significantly (18-18' and 21-21', respectively).

Reference:

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