Electronic Supplementary Information

Construction of Membrane Reactors Coupled with Conjugated Network Hollow Microspheres for Cascade Production of Block Copolymers

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Experiment Section

Materials

All chemicals were obtained from commercial sources and used as received unless otherwise noted. 5,10,15,20-Tetra(4-ethynylphenyl)-21*H*,23*H*-porphyrin (TEPP, ≥97%) and 3-azidopropanoic acid (97%) were purchased from Jilin Chinese Academy of Sciences Yanshen Technology. Tetraethyl orthosilicate (TEOS, 98%), ammonium hydroxide solution (28.0~30.0 wt% NH_3 basis), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 99%), 1,4-diiodobenzene (IB, 98%), triethylamine (TEA, ≥99.5%), triethanolamine (TEOA, 97%), 4-(dimethylamino)pyridine (DMAP, ≥99%), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC, ≥98%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), glycidol (96%), phthalimide (≥99%), potassium phthalimide (98%), hydrazine monomhydrate (98%), pentafluorophenyl acrylate (PFA, 98%), 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoic acid (CDSPA, 97%), poly(ethylene glycol) (PEG400, molecular weight (MW) 400 $g \cdot mol^{-1}$; PEG800, MW 800 $g \cdot mol^{-1}$; PEG1000, MW 1000 g mol^{-1}; PEG2000, MW 2000 $g \cdot mol^{-1}$; PEG6000, MW 6000 $g \cdot mol^{-1}$; PEG11000, MW 11000 $g \cdot mol^{-1}$; PEG20000, MW 20000 $g \cdot mol^{-1}$), poly(ethylene glycol) methyl ether (MPEG, MW 2000 $g \cdot mol^{-1}$), sodium ascorbate (NaAsc, ≥99%) and *N*-[tris(hydroxymethyl)methyl] acrylamide (NAT, 93%) were purchased from Sigma Aldrich. The flat-sheet polyethersulfone (PES) membrane used in this study was a FM UP020 membrane (Microdyn-Nadir GmbH) characterized by a 20000 Da molecular weight cutoff (MWCO). According to the manufacturer, the recommended maximum temperature is 95 ºC, and the suggested pH range is 0-14 for the FM UP020 membrane. Prior to experiments, the membranes were soaked in a mixture of ultrapure water and ethanol (1:1, v/v) for 5 h to remove preservatives and obtain a stable

membrane structure. The monomers including *N,N*-dimethylacrylamide (DMA, 99%), *N,N*-diethylacrylamide (DEA, 98%), 4-acryloylmorpholine (AMP, 98%) and *N*-hydroxyethyl acrylamide (HEAA, 97%) were purchased from Sigma Aldrich and purified by percolating over an inhibitor-removal column prior to polymerization. *N*-isopropylacrylamide (NIPAM, 97%, Sigma Aldrich) was recrystallized twice from toluene/hexane (7:3, v/v) prior to polymerization. Copper(I) bromide (CuBr, 99%, Sigma Aldrich) was purified by stirring in acetic acid for 4 h, followed by washing thoroughly with ethanol and diethyl ether before being stored under an argon atmosphere.

Instrumentation

Nuclear Magnetic Resonance (NMR): NMR spectroscopy was carried out with a Bruker ARX operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C with a tetramethylsilane (TMS) as an internal reference. The data obtained was reported as chemical shifts (δ) measured in ppm downfield from TMS.

Gel Permeation Chromatography (GPC): GPC were performed on a Waters GPC system equipped with an isocratic pump model 1515, a differential refractometer model 2414, a dual-wavelength UV detector model 2487 and Styragel columns. The number-average molecular weight ($M_{n,GPC}$) and polydispersity index (Đ = $M_{w,GPC}/M_{n,GPC}$) were measured with narrow molecular weight distribution poly(methyl methacrylate) (PMMA) as the standards, coupled with tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL·min^{-1}.

Field-Emission Scanning Electron Microscopy (FESEM): The morphology of the samples was observed by FESEM (JEOL-6700F, JEOL Ltd., Japan).

Transmission Electron Microscope (TEM): The morphology and size of the samples were analyzed by TEM (JEOL-2010, JEOL Ltd., Japan) at an accelerating voltage of 100 kV.

X-Ray Diffraction (XRD): The powder XRD (X'pert Pro, PAN analytical) was used confirmed the structural integrity of the samples.

Thermogravimetric Analysis (TGA): The thermal stability was investigated by TGA. The samples were heated from 30 ºC to around 800 ºC with a heating rate of 10 ºC·min^{-1} under a dry nitrogen atmosphere in a thermal analyzer (TGS-II, Perkin-Elmer).

Brunauer-Emmett-Teller (BET): The N_2 absorption-desorption isotherms were collected by AUTOSORB-1 Analyzer from Quantachrome Instruments and the specific surface area was acquired by the BET method, while the pore size distribution was calculated from the desorption branch according to the BJH model.

X-Ray Photoelectron Spectroscopy (XPS): Surface composition of the samples was investigated by XPS on a Kratos AXIS Ultra DLD spectrometer sourcing with a monochromatized Al Kα X-ray source (1468.71 eV photons).

Ultraviolet-visible (UV-vis) Spectrophotometer: UV-vis spectrophotometer (Mini 1240, Shimadzu) was utilized to characterize the absorption properties at 25 ºC.

Cyclic Voltammetry (CV): CV was performed on a CHI 650E electrochemical analyzer in anhydrous CH_3CN containing recrystallized tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as supporting electrolyte at 298 K. A conventional three electrode cell was used with a glassy carbon working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The glassy carbon working electrode was routinely polished with a polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to Ag/AgCl reference electrode. The sample was wet-transferred onto the surface of a glassy carbon working electrode and let the solvent evaporate at room temperature for 30 min.

Synthesis of MPEG-N_3

MPEG (12 g, 6 mmol), EDC (1.38 g, 7.2 mmol) and DMAP (175.7 mg, 1.44 mmol) was dissolved in dichloromethane (DCM, 150 mL). The flask was immersed in an ice bath, and 3-azidopropoic acid (828.6 mg, 7.2 mmol) in DCM (5 mL) was added dropwise. Upon completion of the addition, the reaction mixture was kept in the ice-water bath for 1 h and then at room temperature for 24 h. The precipitated salt was filtered off and the solvent was evaporated. After that, the reaction mixture was precipitated in a 10-fold excess of *n*-hexane to remove any leftover reactants. The above dissolution-precipitation cycle was repeated twice. Finally, the MPEG-N_3 polymer was dried under vacuum at room temperature overnight and obtained as a white solid. Yield: ~92%. ^1H NMR ($CDCl_3$,

δ, ppm, TMS): 4.2 (2H, -CH_2OC(=O)-), 3.54-3.67 (H×4m, -OCH_2CH_2O-, -CH_2N$_3$), 3.37 (3H, -OCH_3), 2.83 (2H, -C(=O)CH_2-).

Synthesis of MPEG-CDSP

Poly(ethylene glycol) methyl ether 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoate (MPEG-CDSP) was synthesized according to the procedure described in the literature.[1,2] MPEG (6 g, 3 mmol), EDC (0.69 g, 3.6 mmol) and DMAP (87.9 mg, 0.72 mmol) was dissolved in DCM (100 mL). The flask was immersed in an ice bath, and CDSPA (1.45 g, 3.6 mmol) in DCM (10 mL) was added dropwise. Upon completion of the addition, the reaction mixture was kept in the ice-water bath for 1 h and then at room temperature for 24 h. The precipitated salt was filtered off and the solvent was evaporated. After that, the reaction mixture was precipitated in a 10-fold excess of *n*-hexane to remove any leftover reactants. The above dissolution-precipitation cycle was repeated twice. Finally, the water-soluble MPEG-CDSP chain transfer agent (CTA) was dried under vacuum at room temperature overnight and obtained as a yellow solid. Yield: ~90%. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 4.25 (2H, -CH_2OC(=O)-), 3.61-3.68 (H×(4m-2), -OCH_2CH_2O-), 3.37 (3H, -OCH_3), 2.83 (2H, -C(=O)CH_2CH_2-), 2.63 (2H, -C(=O)CH_2-), 1.88 (3H, -C(CN)CH_3), 1.25 (20H, -(CH_2)$_{10}$CH_3), 0.88 (3H, -CH_2CH_3).

Synthesis of HPGA

Acrylamide-monofunctionalized hyperbranched polyglycerol (HPGA) was synthesized according to the procedure described in the literature.[3] The synthesis of phthalimide-monofunctionalized hyperbranched polyglycerol (PhIm-HPG) was achieved in a straightforward bulk ring-opening multibranching polymerization of glycidol, using

phthalimide and potassium phthalimide as the initiators. Briefly, phthalimide (1.99 g, 13.6 mmol) and potassium phthalimide (0.28 g, 1.5 mmol) were placed into a dry 100 mL round-bottom flask. The flask was flushed with argon for 15 min. The flask was then sealed with a rubber stopper and the reaction was allowed to proceed under continuous stirring at 95 ºC. A freshly distilled, argon-purged glycidol (20.00 mL, 300.8 mmol) was slowly syringed to the reaction mixture over a period of 6 h. After dosing, the polymerization was conducted for another 3 h for thorough reaction. Afterwards, the reaction flask was quenched in an icy water bath and ethanol was added to protonate the active chain ends. Unreacted monomers and solvents were removed by distillation and the crude product was purified by repeated precipitation from ethanol into a 10-fold excess of cold *n*-hexane and finally dried *in vacuo*, to afford PhIm-HPG as a highly viscous liquid. Yield: ~75%.

PhIm-HPG (10.0 g, 8 mmol) was dissolved in ethanol (200 mL), followed by the addition of hydrazine monohydrate (3.86 mL, 80 mmol) to the polymer solution. The reaction mixture was stirred at room temperature for 24 h. Afterwards, the reaction flask was quenched in an icy water bath and the resulting solution was filtered. The crude product was purified by repeated precipitation from ethanol into a 10-fold excess of cold *n*-hexane and finally dried *in vacuo*, to afford HPG-NH_2 as a highly viscous liquid. Yield: ~80%.

HPG-NH_2 (5.5 g, 5 mmol) and TEA (0.77 mL, 5.5 mmol) was dissolved in ethanol (100 mL), followed by the addition of PFA (0.91 mL, 5.5 mmol) to the polymer solution. The reaction flask was flushed with argon for 15 min. The reaction mixture was stirred at

room temperature for 24 h. Afterwards, the reaction flask was quenched in an icy water bath and the resulting solution was filtered. The crude product was purified by repeated precipitation from ethanol into a 10-fold excess of cold *n*-hexane and finally dried *in vacuo*, to afford HPGA as a highly viscous liquid. Yield: ~85%. $M_{n,NMR}$ = 1200 g·mol^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm, TMS): 6.58 (1H, -C*H*=CH$_2$), 6.09 (1H, -CH=C*H*$_2$), 5.60 (1H, -CH=C*H*$_2$), 5.19 (2H, -(C=O)NHC*H*$_2$), 4.35-4.84 (H×(*l*+1), -O*H*), 3.25-3.85 (H×(5*l*-2), -OC*H*-, -OC*H*$_2$-), where the note *l* refers to the degree of polymerization of glycidol in HPGA.

Synthesis of H-PPrIB-M Microspheres

Typically, TEOS (14.0 mL) was added dropwise to a mixture of ethanol (144 mL), ultrapure water (18 mL) and ammonium hydroxide solution (7.0 mL, 28-30 wt% NH_3 basis). The mixture was stirred vigorously at room temperature for 2 h. Finally, the raw product was purified by five cycles of centrifugation/redispersion/washing in excessive ethanol and ultrapure water. The SiO_2 microspheres (MSs) were centrifuged and stored in ethanol prior to use.

The SiO_2 MSs (300 mg) were dispersed in a mixture of toluene (15 mL) and TEA (15 mL). TEPP (0.12 mmol, 85.3 mg), IB (0.24 mmol, 79.2 mg), Pd(PPh$_3$)$_4$ (13.9 mg) and CuI (2.3 mg) were successively introduced. The reaction mixture was deoxygenated by sparging argon for 20 min. The reaction was allowed to proceed at 90 ºC for 72 h. After that, the reaction was quenched by immersing the Schlenk tube into an icy water bath. The raw product was collected by filtration and washed with ethanol, acetone and THF

thrice. After extracted in a Soxhlet extractor with THF for 48 h, SiO_2@PPrIB MSs were dried under vacuum at 80 ºC for 24 h and obtained as a dark brown powder.

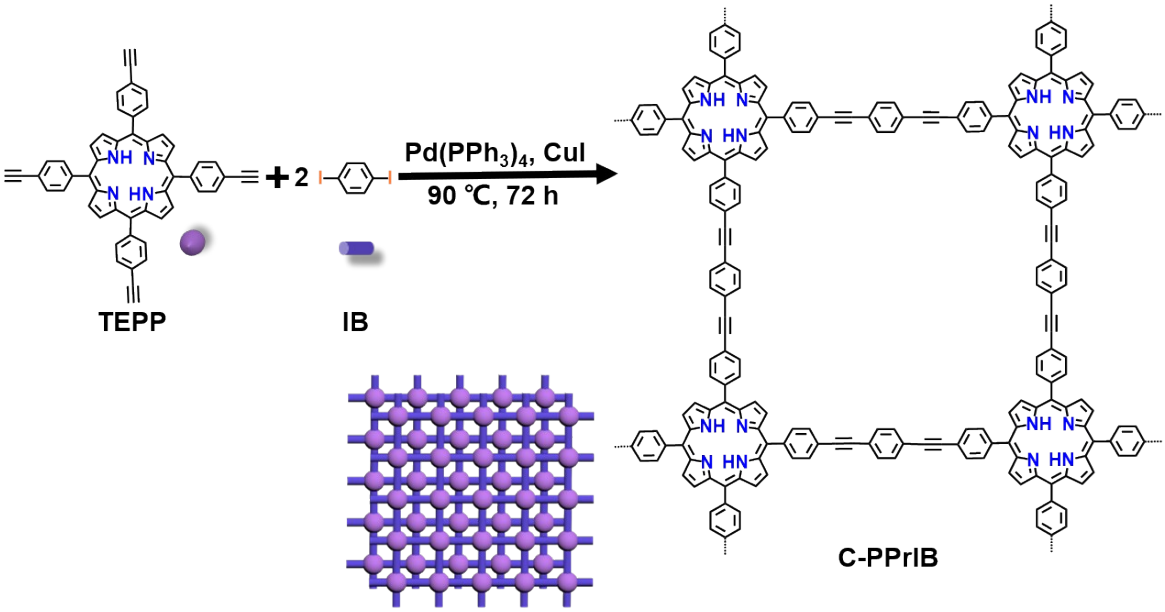
SiO_2@PPrIB MSs (120 mg) were added to an aqueous HF solution (5 mL, 20 wt%). The etching process was performed at ambient temperature overnight. Afterward, the crude products were purified by four thorough centrifugation-redispersion cycles in water/ethanol mixed solutions to eliminate the excessive HF and SiF_4. Furthermore, the H-PPrIB MSs were recovered by centrifugation and redispersed in 10 mL of ethanol prior to use.

The H-PPrIB MSs (40 mg) were dispersed in DMF (20 mL). MPEG-N_3 (110 mg, 0.1 mmol), PMDETA (10.5 μL, 0.05 mmol) and CuBr (7.2 mg, 0.05 mmol) were successively introduced. After deoxygenated by sparging argon for 20 min, the glass vial was sealed and the reaction was allowed to proceed at 50 ºC for 24 h. After that, the reaction was quenched by immersing the glass vial into an icy water bath. The raw product was collected by filtration and washed with ethanol, acetone and THF thrice. Furthermore, the H-PPrIB-M MSs were recovered by centrifugation and redispersed in 10 mL of ethanol prior to use.

Synthesis of C-PPrIB-M Conjugated Microporous Polymers

TEPP (0.5 mmol, 387.1 mg), IB (1.0 mmol, 329.9 mg), $Pd(PPh_3)_4$ (20.0 mg), CuI (10.0 mg) were dissolved in a mixed solution of DMF (4 mL) and THEA (4 mL). The reaction mixture was deoxygenated by sparging argon for 20 min. The reaction was allowed to proceed at 90 ºC for 72 h. After that, the reaction was quenched by immersing the

Schlenk tube into an icy water bath. The raw product was collected by filtration and washed with ethanol, acetone and THF thrice. After extracted in a Soxhlet extractor with THF for 48 h, C-PPrIB conjugated microporous polymers (CMPs) were dried under vacuum at 80 ºC for 24 h and obtained as a dark brown powder in ~80% yield.

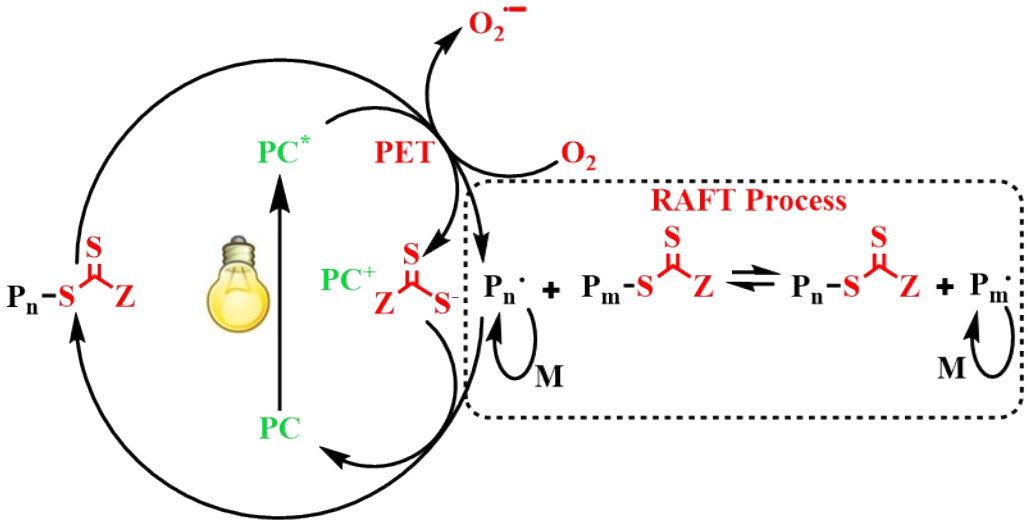


Scheme S1. Synthetic routes for C-PPrIB CMPs.

The C-PPrIB CMPs (40 mg) were dispersed in DMF (20 mL). MPEG-N_3 (110 mg, 0.1 mmol), PMDETA (10.5 μL, 0.05 mmol) and CuBr (7.2 mg, 0.05 mmol) were successively introduced. After deoxygenated by sparging argon for 20 min, the glass vial was sealed and the reaction was allowed to proceed at 50 ºC for 24 h. After that, the reaction was quenched by immersing the glass vial into an icy water bath. The raw product was collected by filtration and washed with ethanol, acetone and THF thrice. Furthermore, the C-PPrIB-M CMPs were recovered by centrifugation and redispersed in 10 mL of ethanol prior to use.

General Procedure for PET-RAFT Polymerization Mediated by H-PPrIB-M MSs under White or Red Light Irradiation in Batch

A typical PET-RAFT polymerization of DMA was performed using a reaction formulation of $[DMA]_0$:$[MPEG\text{-}CDSP]_0$:[H-PPrIB-M] = 200:1:0.04. The reaction mixture was placed in a glass vial and sonicated for 15 min. Afterwards, the glass vial was exposed under white light (1.2 mW·cm^{-2}) or red light (λ_{max} = 680 nm, 4.0 mW·cm^{-2}) irradiation with or without the coverage of rubber septum. After a certain period, the polymerization was terminated by ceasing the light irradiation. The residual reaction mixture was purified by dialysis against ultrapure water, collected by lyophilization. To investigate the polymerization kinetics, aliquots of reaction mixtures were withdrawn at specific time points by argon-purged syringe and analyzed by ^{1}H NMR to calculate the monomer conversions and GPC to measure number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (Đ).



Scheme S2. Proposed reaction pathway for PET-RAFT polymerization mediated by H-PPrIB-M MSs in this study.

General Procedure for Kinetic Studies of PET-RAFT Polymerization in SCBMR

A typical PET-RAFT polymerization ($[DMA]_0$:$[MPEG\text{-}CDSP]_0$:[H-PPrIB-M] = 800:1:0.16) in ultrapure water was performed in suspended-catalysts-based membrane reactor (SCBMR).[5,6] MPEG-CDSP (300 mg, 0.125 mmol), DMA (10.3 mL, 100 mmol), NaAsc (24.8 mg, 0.125 mmol) and H-PPrIB-M (25.6 mg) were placed in synthesis-separation cell with a mechanical stirrer. The monomer concentration was fixed at 10 vol% in ultrapure water. The cell was sealed and irradiated to white light (2.4 $mW \cdot cm^{-2}$) or red light (λ_{max} = 680 nm, 8.0 $mW \cdot cm^{-2}$) at room temperature. To investigate the polymerization kinetics, aliquots of reaction mixtures were withdrawn periodically by argon-purged syringe. After a certain period, the polymerization was terminated by ceasing the LED light irradiation. The total volume of reaction mixture was topped up to 200 mL by dilution with ultrapure water. Then monomers and residual reactants were separated out from the cell. The resultant polymers were collected after thorough membrane separation and recovered by lyophilization. After certain cycles of separation, the ultrafiltration membrane was extracted thoroughly with ultrapure water for regeneration.

Membrane Separation after PET-RAFT Polymerization

All filtration experiments are carried out using a membrane reactor. A stirrer is placed above the membrane, which was stirred at 500 rpm to minimize the concentration polarization effect. The effective membrane area is 13.8 cm^2. Permeate samples for flux measurements are collected at predetermined time intervals, and samples for rejection evaluations are taken after steady permeate flux is achieved. The solute rejections of membrane are measured by the solute transport method a hydraulic pressure difference of 3 ± 0.2 bar. The concentrations of the solutes are measured by a total organic carbon

analyzer (TOC ASI-5000A, Shimadzu, Japan). After each testing cycle, deionized water (DI water, ELGA MicroMEG) is pumped into the filtration cell immediately at 20 ºC for 10 min to wash the fouled membranes. The measured feed (C_f) and permeate (C_p) concentrations are used for the calculation of the effective solute rejection coefficient R_s (%):

$$R_s = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (1)$$

The water permeation flux, J_w ($L \cdot m^{-2} \cdot h^{-1}$, LMH), is calculated from Eq. 2 based on the effective membrane area, A_m (m^2):

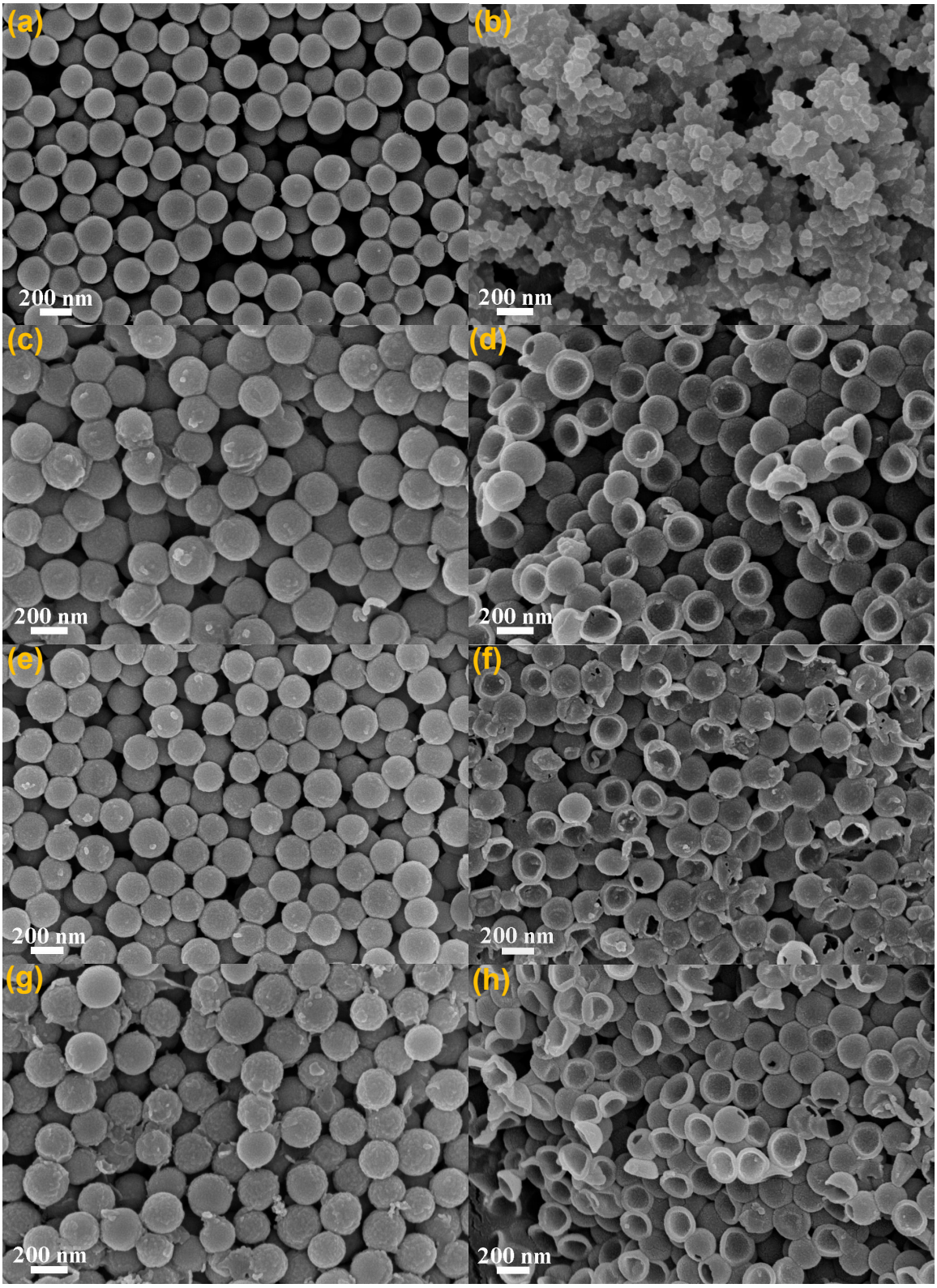
$$J_w = \frac{\Delta\omega}{\Delta t} \frac{1}{A_m} \quad (2)$$

where $\Delta\omega$ (L) is the volume of water permeated through the membrane over a predetermined time Δt (h). The robustness of the process is expressed in normalized concentration of impurities and number of diavolumes required to achieve the purity of the polymer products >99%. Number of diavolumes is a parameter to describe the progress of filtration which is defined in Eq. 3:

$$\text{Number of diavolumes} = \omega_a/\omega_0 \quad (3)$$

The measured amount of polymer products (W_P) and residual impurity (W_I) are used for the calculation of purity of the polymer products P (%):

$$P = (W_P - W_I)/W_P \times 100\% \quad (4)$$


(a)
200 nm
(b)
200 nm
(c)
200 nm
(d)
200 nm
(e)
200 nm
(f)
200 nm
(g)
200 nm
(h)
200 nm

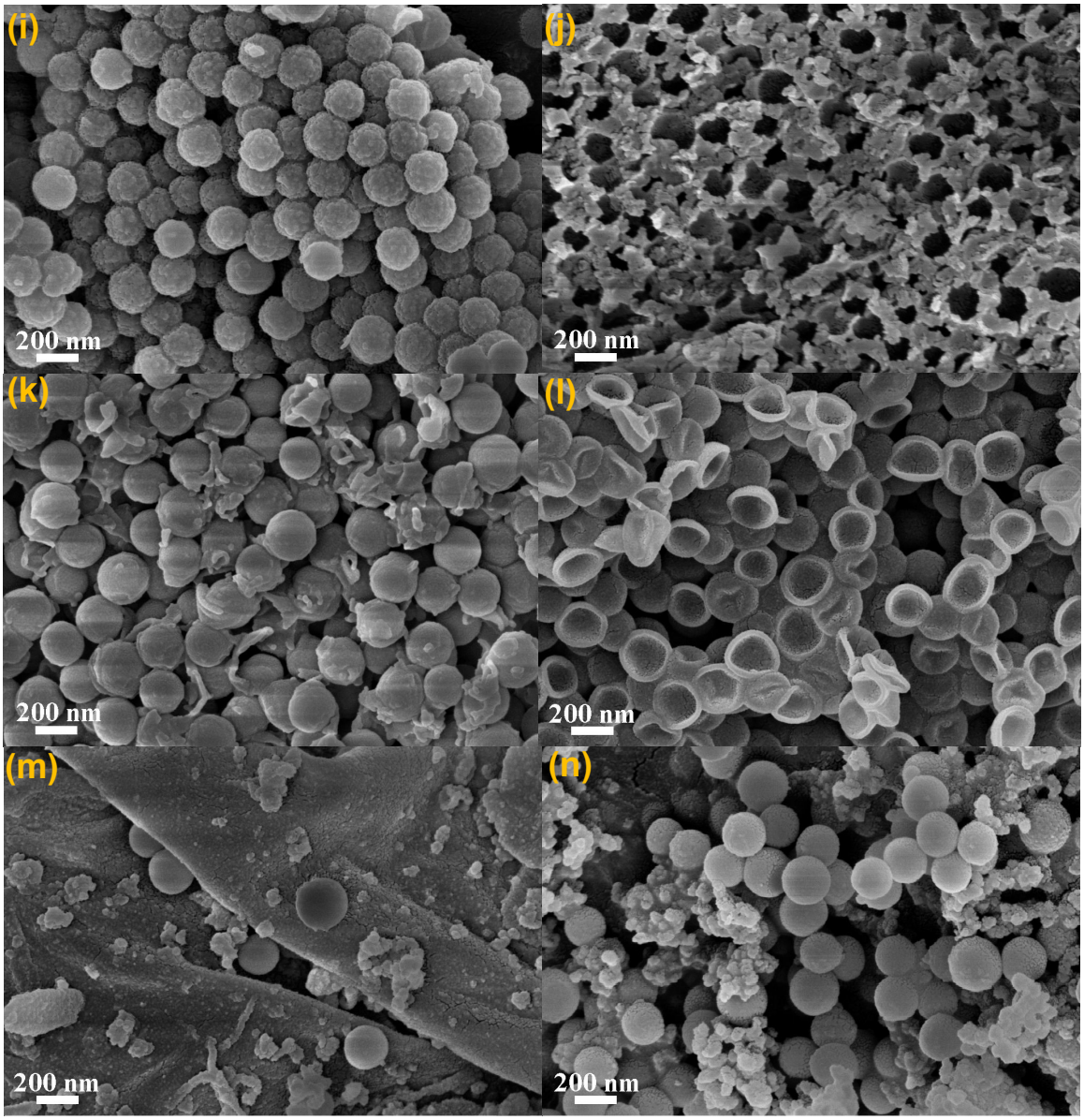


Figure S1. FESEM images of (a) SiO_2, (b) C-PPrIB, (c) SiO_2@PPrIB-1, (d) H-PPrIB-1, (e) SiO_2@PPrIB-3, (f) H-PPrIB-3, (g) SiO_2@PPrIB-4, (h) H-PPrIB-4, (i) SiO_2@PPrIB-5, (j) H-PPrIB-5, (k) SiO_2@PPrIB-6, (l) H-PPrIB-6, (m) SiO_2@PPrIB-7 and (n) SiO_2@PPrIB-8.

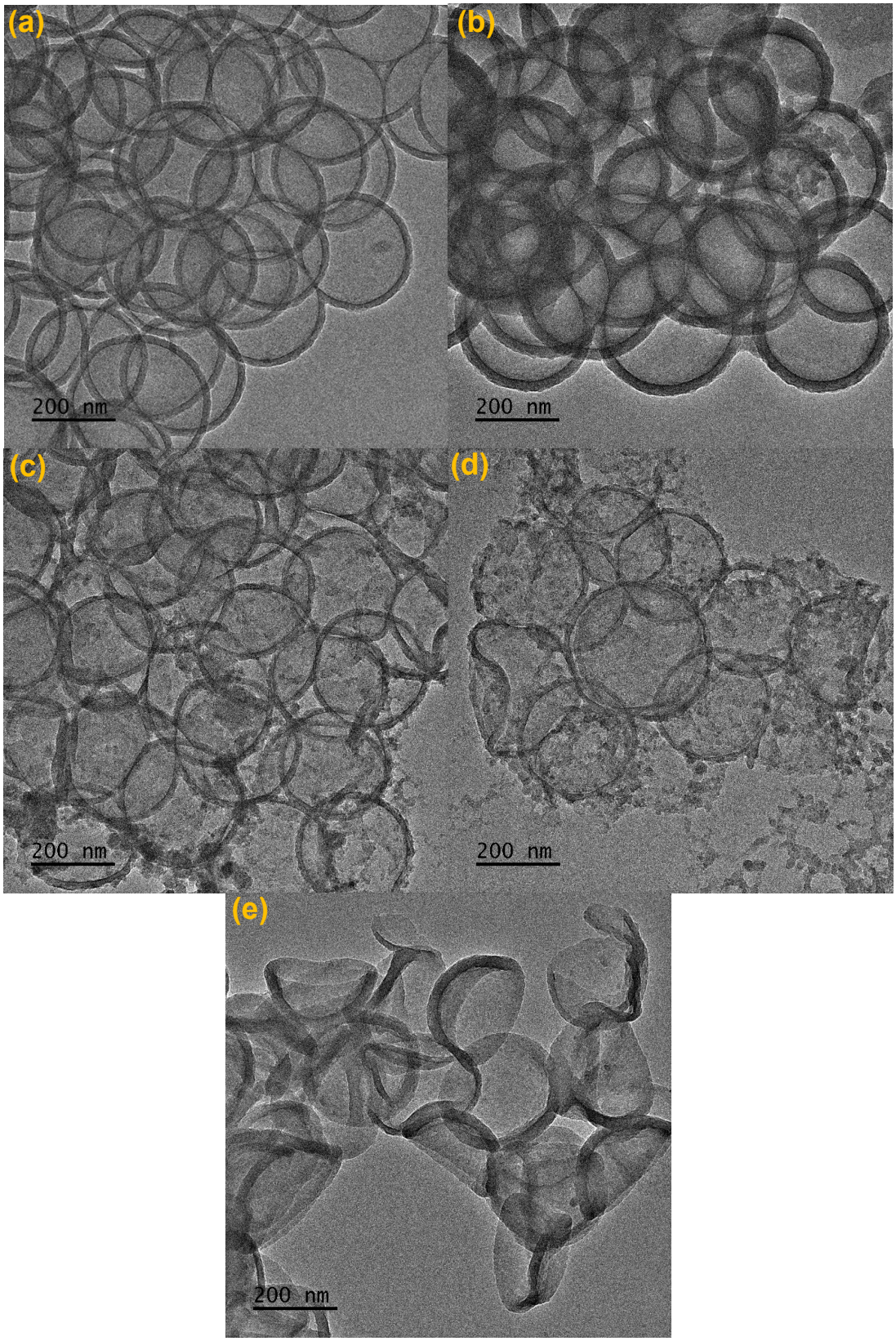
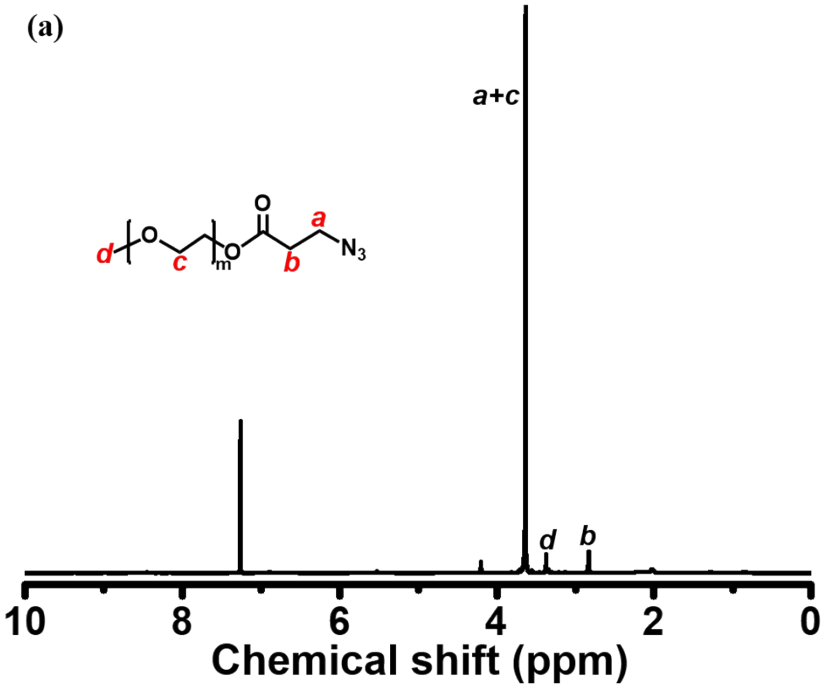
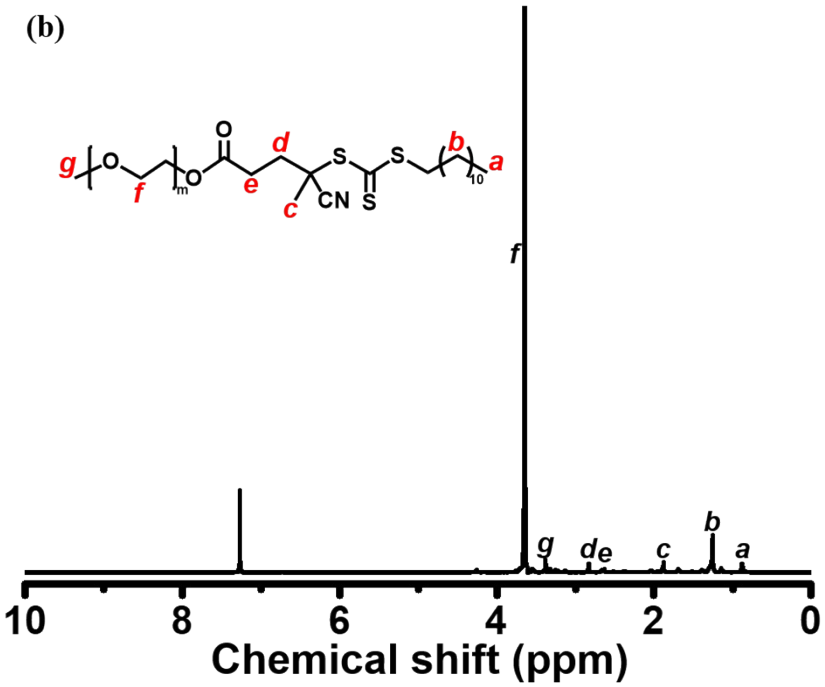


Figure S2. TEM images of (a) H-PPrIB-1, (b) H-PPrIB-3, (c) H-PPrIB-4, (d) H-PPrIB-5 and (e) H-PPrIB-6 MSs.


(a)
a+c
d
c
b
a
N3
d
b
10
8
6
4
2
0
Chemical shift (ppm)


(b)
g
f
d
e
c
CN
S
b
a
f
g
d
e
c
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a
10
8
6
4
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Chemical shift (ppm)

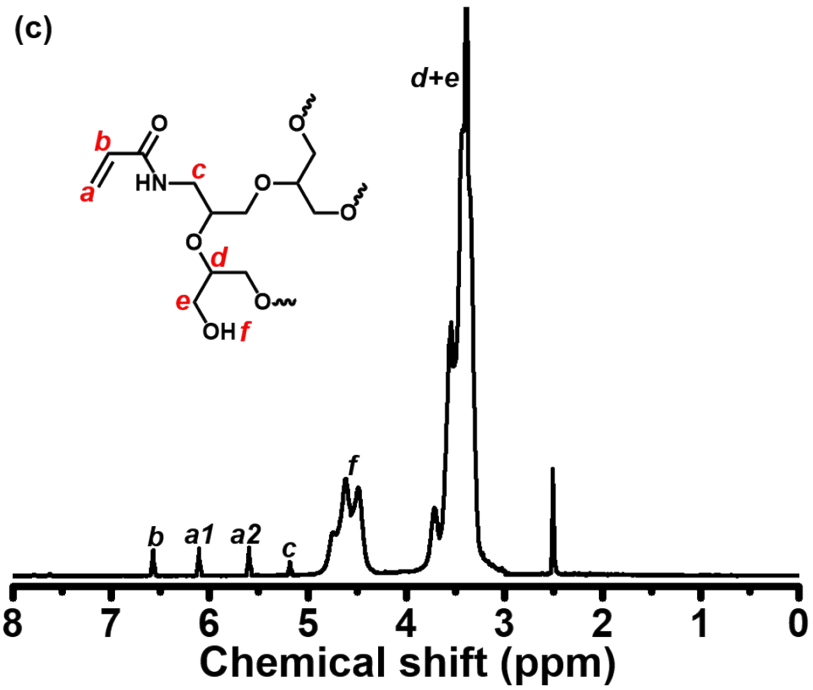


Figure S3. ^{1}H NMR spectra of (a) MPEG-N_3, (b) MPEG-CDSP and (c) HPGA.

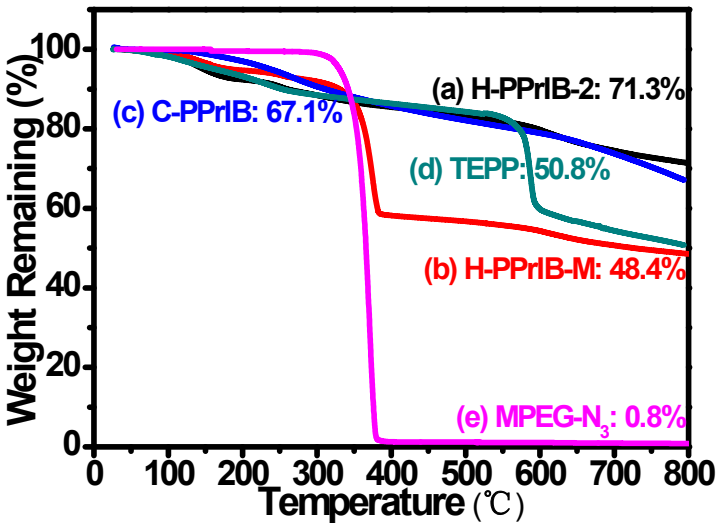


Figure S4. TGA curves of (a) H-PPrIB-2 MSs, (b) H-PPrIB-M MSs, (c) C-PPrIB CMPs, (d) TEPP and (e) MPEG-N_3.

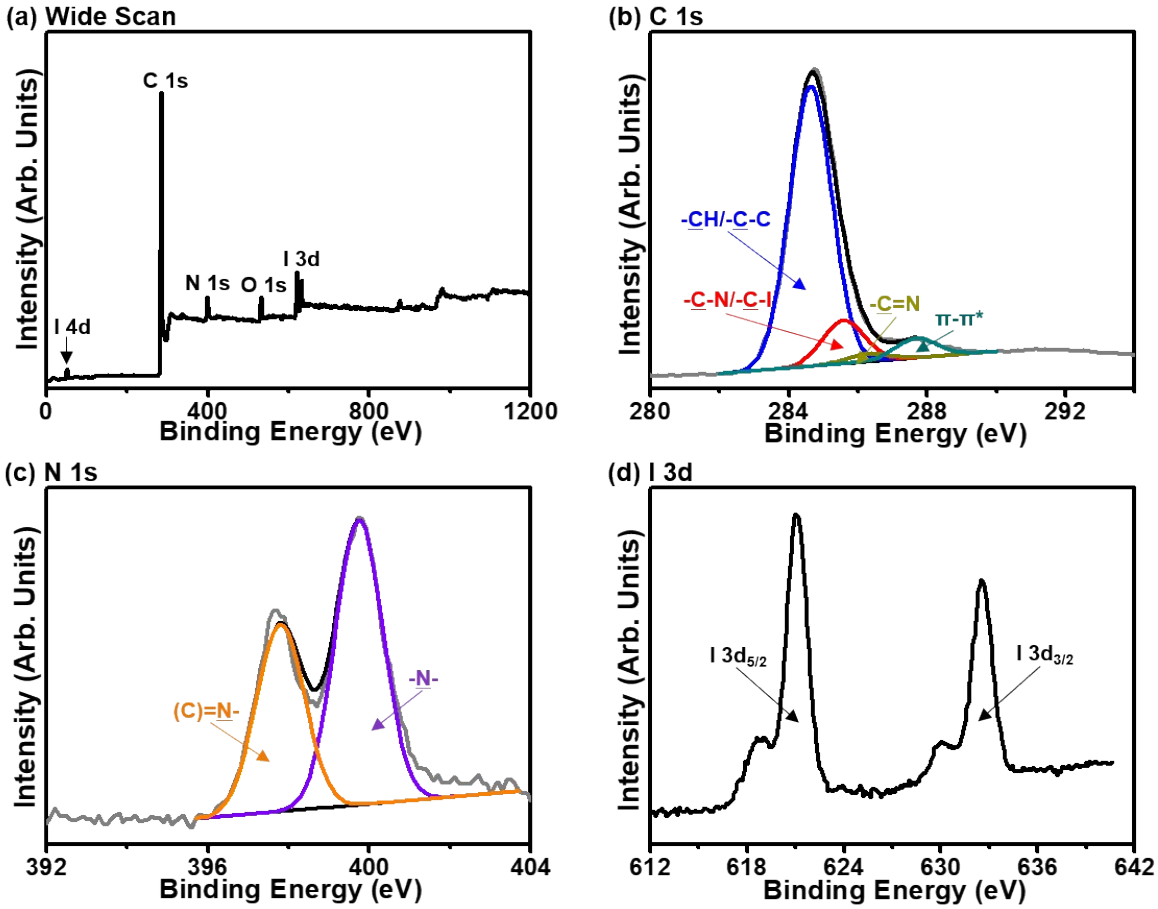
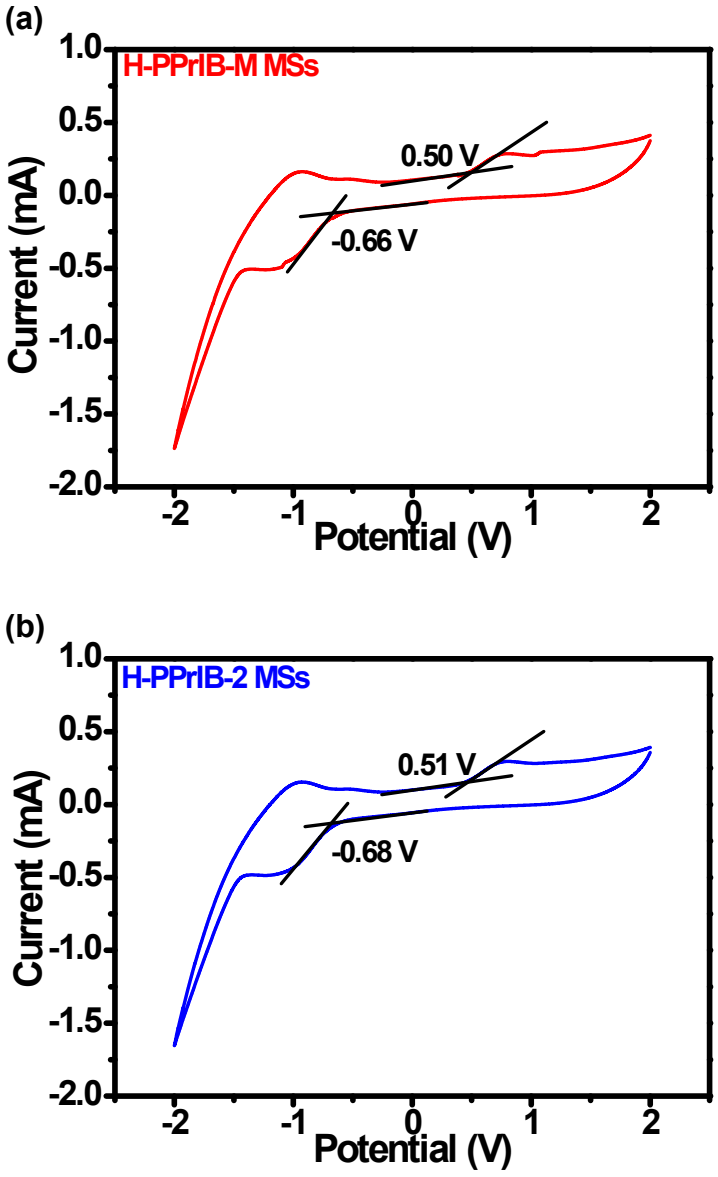


Figure S5. XPS (a) wide scan, (b) C 1s, (c) N 1s and (d) I 3d core-level spectra of H-PPrIB-2 MSs.


(a)
H-PPrIB-M MSs
0.50 V
-0.66 V
Current (mA)
Potential (V)
(b)
H-PPrIB-2 MSs
0.51 V
-0.68 V
Current (mA)
Potential (V)

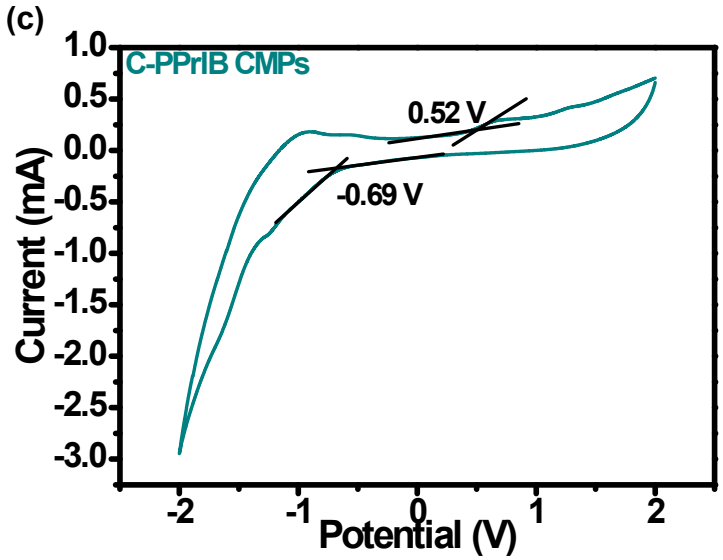
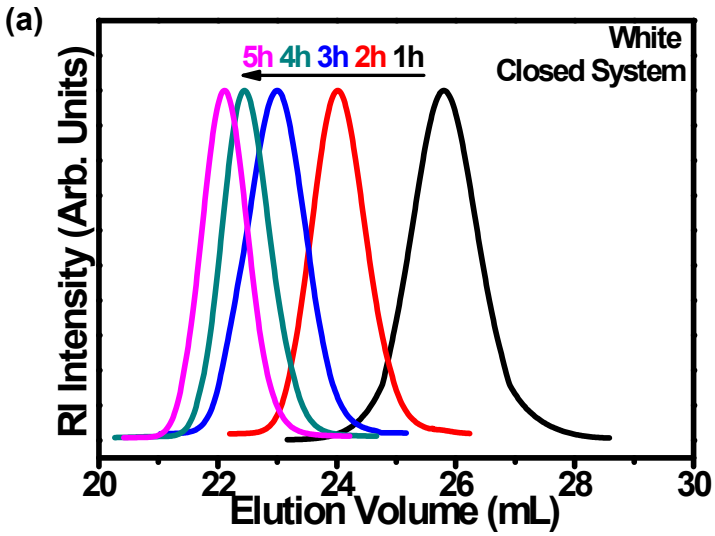
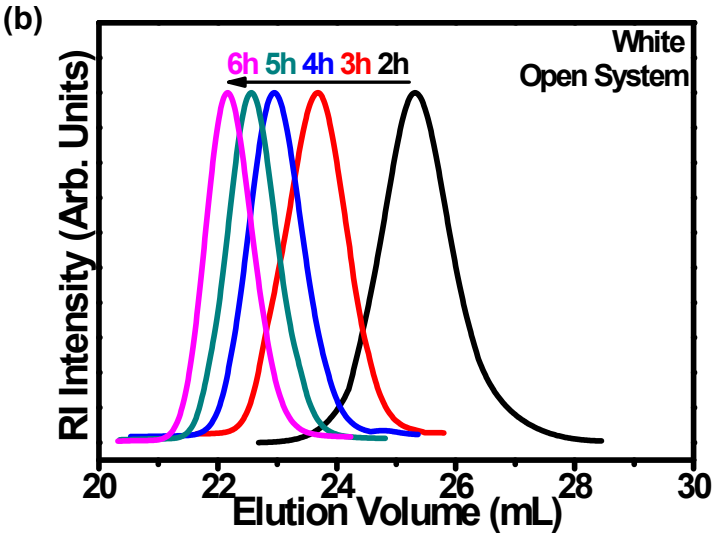


Figure S6. Cyclic voltammogram of (a) H-PPrIB-M MSs, (b) H-HPPrIB-2 MSs and (c) C-PPrIB CMPs. Scan rate: 100 $mV \cdot s^{-1}$. Reference electrode: Ag/AgCl. Electrolyte: Bu_4NPF_6 (0.1 M) in deaerated acetonitrile. The HOMO or LUMO levels of the sample can be electrochemically estimated from the equation: E_{HOMO}/E_{LUMO} = -(Eonset – Eox(ferrocene)) - 4.8 eV using the onset potentials (vs. Ag/Ag^+) of the samples. Here, the reference energy level of ferrocene was considered as 4.8 eV. The onset oxidation potential of ferrocene was observed to be 0.38 eV. The energy band gaps of the samples can be estimated from the equation: $E_g = E_{LUMO}-E_{HOMO}$. E_g = 1.16 eV (H-PPrIB-M MSs); E_g = 1.19 eV (H-PPrIB-2 MSs); E_g = 1.21 eV (C-PPrIB CMPs).


(a)
White
Closed System
5h 4h 3h 2h 1h
RI Intensity (Arb. Units)
20
22
24
26
28
30
Elution Volume (mL)


(b)
White
Open System
6h 5h 4h 3h 2h
RI Intensity (Arb. Units)
20
22
24
26
28
30
Elution Volume (mL)

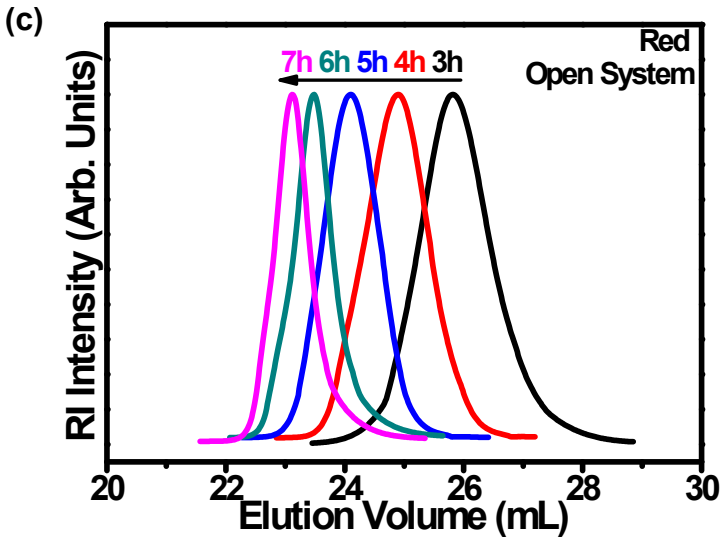
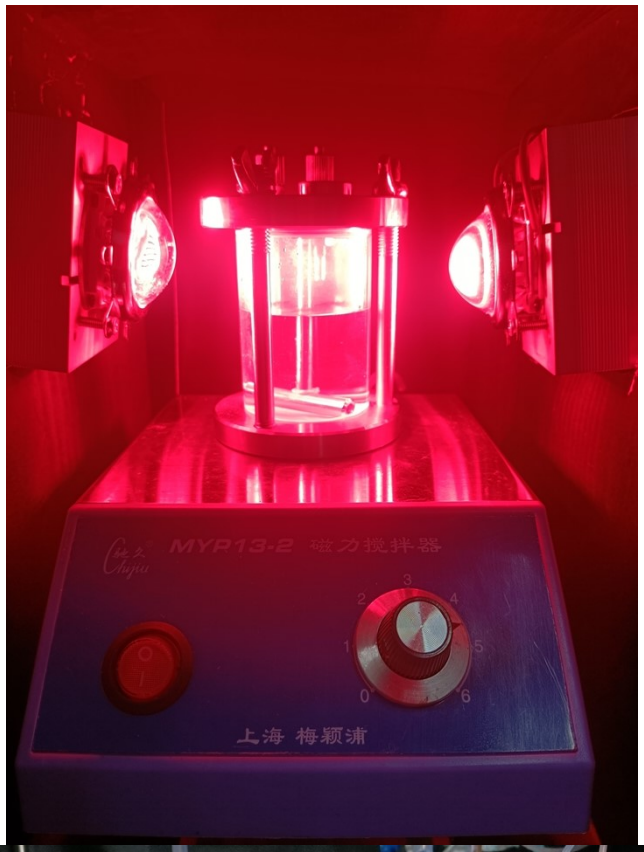


Figure S7. Kinetic analyses of H-PPrIB-M MSs mediated PET-RAFT polymerization of DMA using a reaction stoichiometry of $[DMA]_0$:$[MPEG\text{-}CDSP]_0$:[H-PPrIB-M] = 200:1:0.04 in a closed or open vessel under white light (1.2 mW·cm^{-2}) or red light (λ_{max} = 680 nm, 4.0 mW·cm^{-2}) irradiation. (a) GPC traces of the purified PDMA polymers in different time points under white light (1.2 mW·cm^{-2}) irradiation in a closed vessel; (b) GPC traces of the purified PDMA polymers in different time points under white light (1.2 mW·cm^{-2}) irradiation in an open vessel; (c) GPC traces of the purified PDMA polymers in different time points under red light (λ_{max} = 680 nm, 4.0 mW·cm^{-2}) irradiation in an open vessel.

(a)



(b)

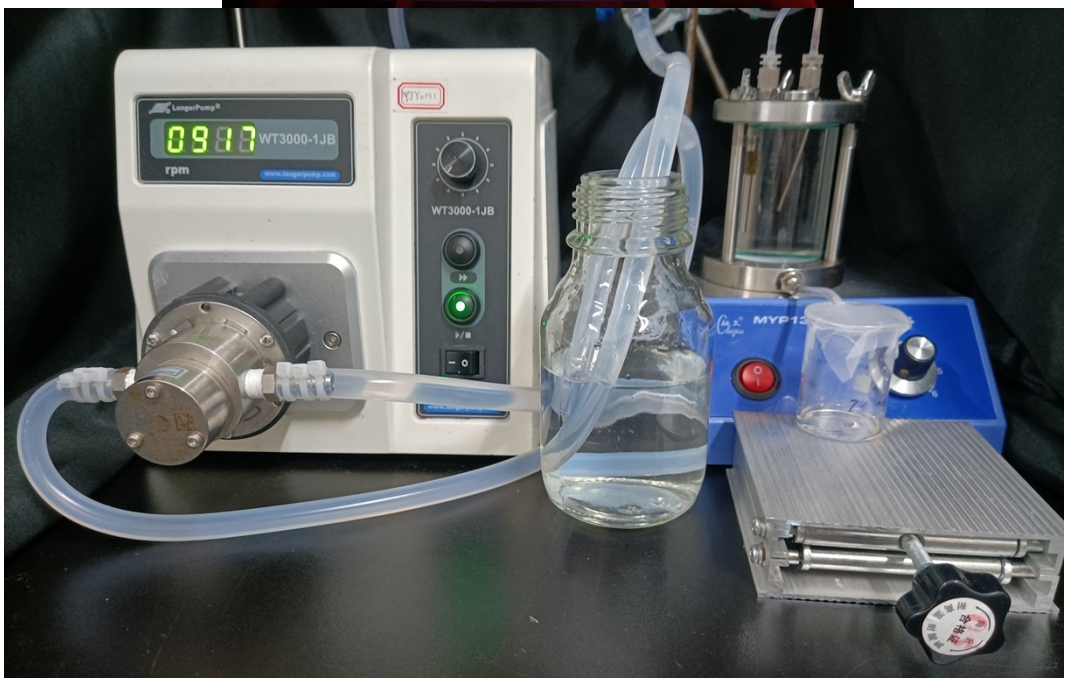


Figure S8. Photographs of (a) aqueous PET-RAFT polymerization and (b) membrane separation process in a succession of stages.

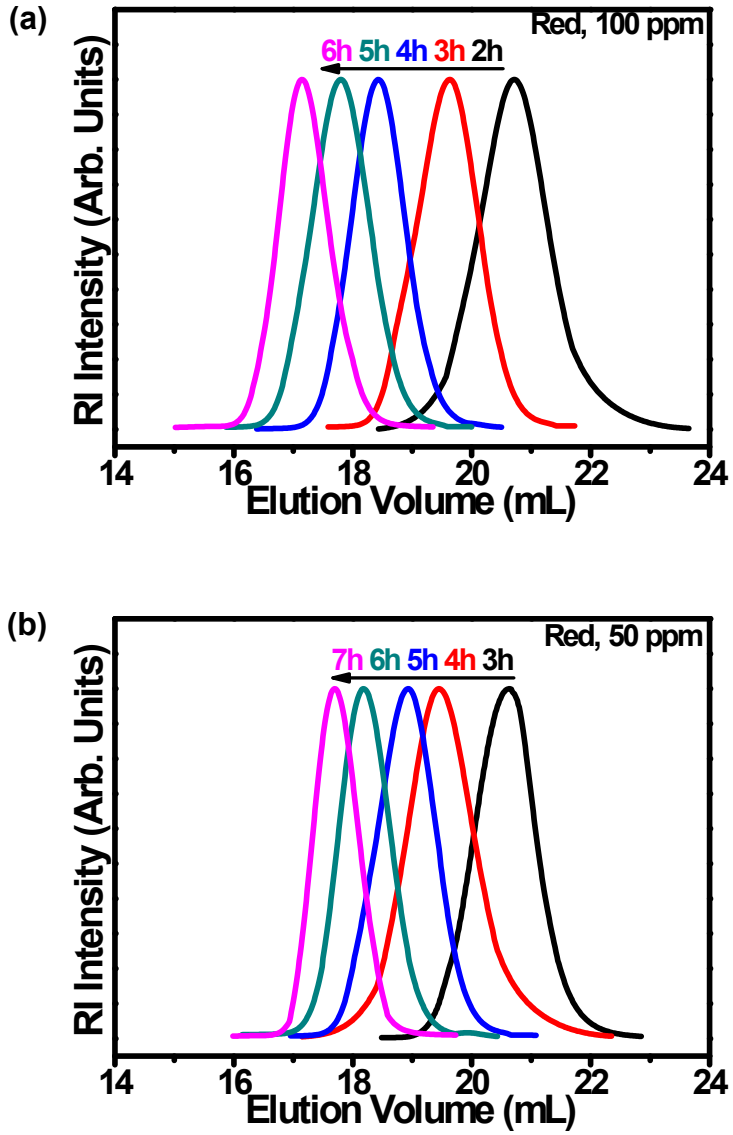


Figure S9. Kinetic analyses of H-PPrIB-M mediated PET-RAFT polymerization of DMA conducted in ultrapure water under red light (λ_{max} = 680 nm, 8.0 mW·cm^{-2}) irradiation using a reaction stoichiometry of $[DMA]_0$:$[MPEG\text{-}CDSP]_0$ = 800:1 without prior deoxygenation in SCBMR. (a) GPC profiles at different time points with 100 ppm catalyst under red light (λ_{max} = 680 nm, 8.0 mW·cm^{-2}) irradiation and (b) GPC profiles at different time points with 50 ppm catalyst under red light (λ_{max} = 680 nm, 8.0 mW·cm^{-2}) irradiation.

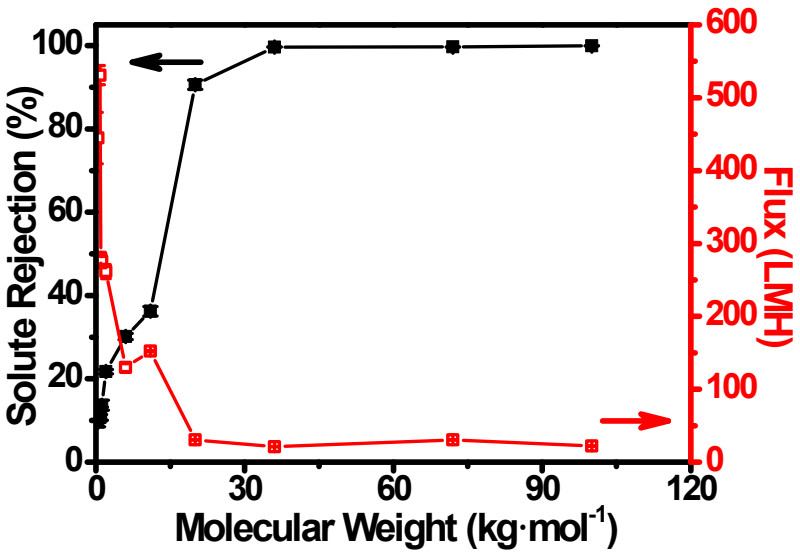


Figure S10. Solute rejection and water flux for the UP020 ultrafiltration membrane.

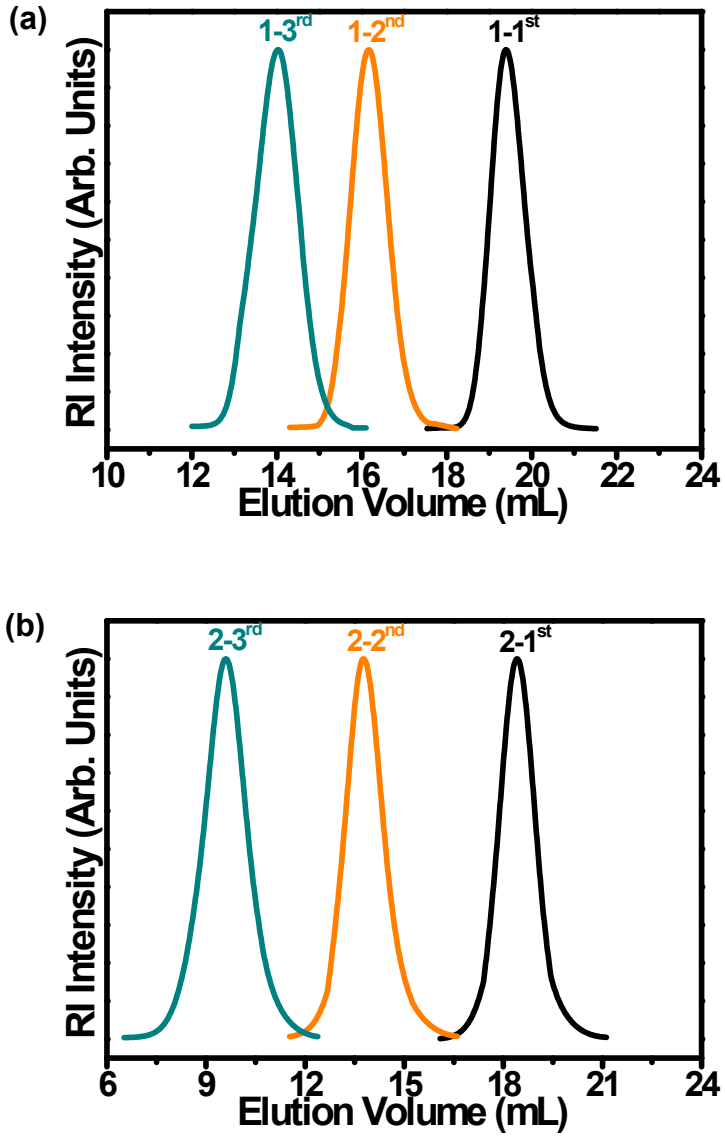


Figure S11. PET-RAFT polymerization was performed in ultrapure water by using a single initial loading of H-PPrIB-M as catalysts without prior deoxygenation under red light (λ_{max} = 680 nm, 8.0 mW·cm^{-2}) irradiation in SCBMR. (a) GPC profiles for evolution of molecular weight of PDMA-CDSP polymers in the first three cycles of polymerization and (b) GPC profiles for evolution of molecular weight of PHEAA-*b*-PNAT-*b*-PHPGA-CDSP polymers in the second three cycles of polymerization.

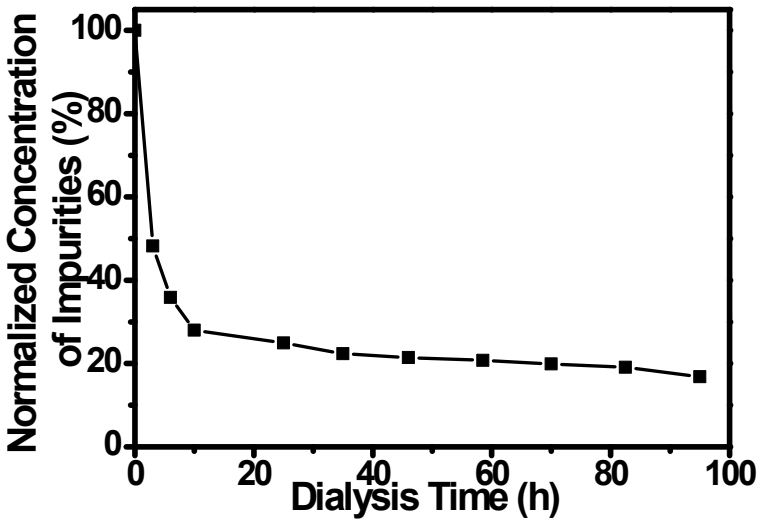


Figure S12. Normalized concentration of impurities in the retentate of purification process as a function of dialysis time for the aqueous solutions of PHEAA-*b*-PNAT-*b*-PHPGA-CDSP triblock copolymers. The crude reaction mixture containing PHEAA-*b*-PNAT-*b*-PHPGA-CDSP triblock copolymers synthesized in the 2-3rd cycle in SCBMR was took out and dialyzed against ultrapure water with 1 L ultrapure water (MWCO 10000 Da). The dialysate was changed with fresh ultrapure water and analyzed by TOC at specific time intervals.

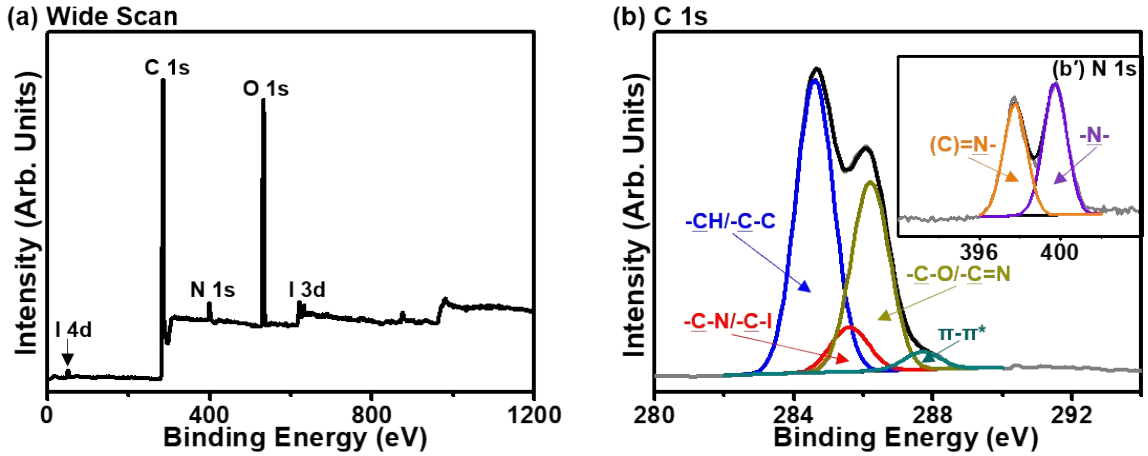


Figure S13. XPS (a) wide scan, (b) C 1s and (b') N 1s core-level spectra of H-PPrIB-MMSs after six cycles of polymerization.

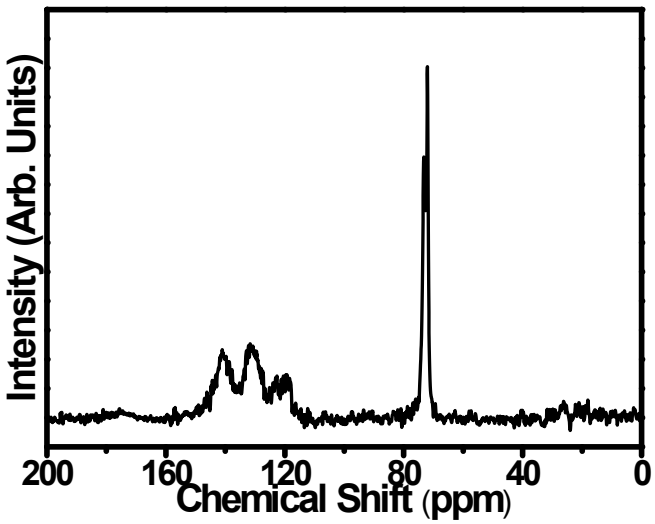


Figure S14. Solid-state ^{13}C NMR spectrum of H-PPrIB-M MSs after six cycles of polymerization.

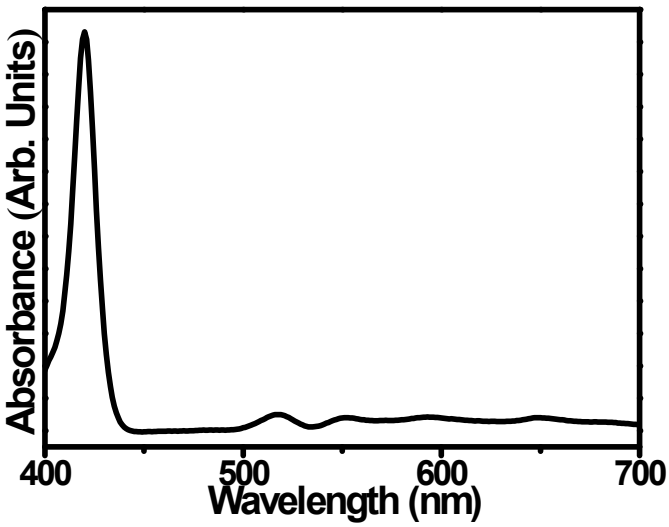


Figure S15. UV-visible spectrum of H-PPrIB-M MSs after six cycles of polymerization.

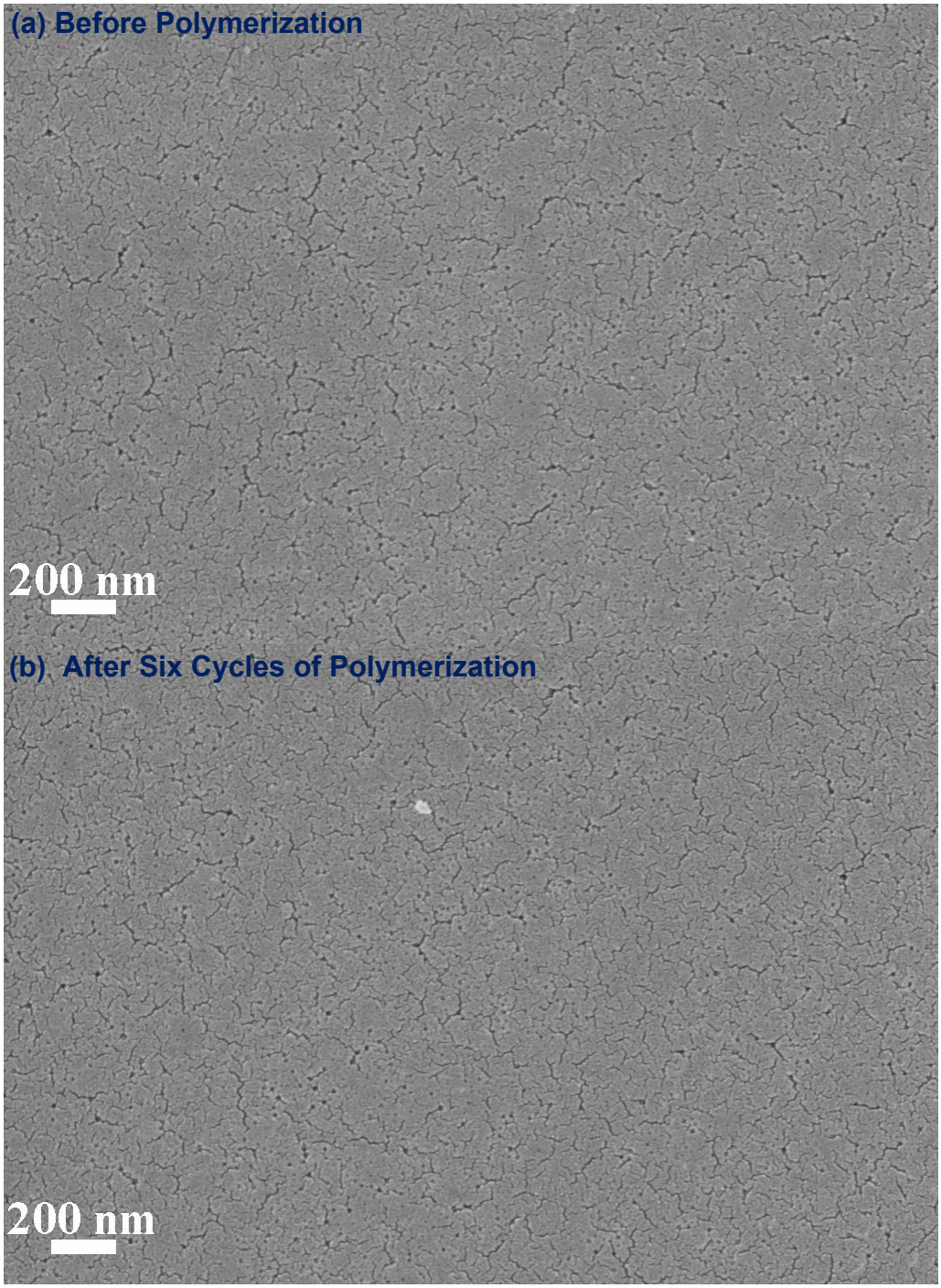


Figure S16. FESEM images of UP020 ultrafiltration membranes (a) before and (b) after six cycles of polymerization.

Table S1. PET-RAFT Polymerization of DMA in Batch[a]

#	Monomer	Light Source	PC[a]	$[Monomer]_0$:$[MPEG\text{-}CDSP]_0$:[PC]	Time (h)	α[b] (%)	$M_{n,th}$[c] (kg·mol^{-1})	$M_{n,GPC}$[c] (kg·mol^{-1})	Đ[c]
1[d]	DMA	White	H-PPrIB-M	200:0:0.04	6	-	-	-	-
2	DMA	680 nm	H-PPrIB-M	200:0:0.04	6	-	-	-	-
3	DMA	White	H-PPrIB-M	200:1:0	6	13.7	-	-	-
4	DMA	680 nm	H-PPrIB-M	200:1:0	6	6.3	-	-	-
5	DMA	-	H-PPrIB-M	200:1:0.04	6	-	-	-	-
6	DMA	white	C-PPrIB-M	200:1:0.04	6	90.8	20.4	22.6	1.07
7	DMA	680 nm	C-PPrIB-M	200:1:0.04	6	82.6	18.8	20.1	1.05

[a] Abbreviations: PC, photocatalysts; MPEG-CDSP, poly(ethylene glycol) methyl ether 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoate; DMA, *N,N*-dimethylacrylamide.

[b] Monomer conversion (α) derived from ^{1}H NMR spectroscopy.

[c] Derived from GPC profiles (calibration with PMMA molecular weight standards), polydispersity index (Đ) = $M_{w,GPC}/M_{n,GPC}$.

[d] The polymerizations were performed under white light (1.2 mW·cm^{-2}) or red light (λ_{max} = 680 nm, 4.0 mW·cm^{-2}) irradiation in a sealed vessel.

Table S2. XPS Results of Nanocomposites in This Study

Sample	C(%)	N(%)	O(%)	I(%)	N/C
H-PPrIB-2 (Original)	89.02	6.39	3.85	0.74	0.072
H-PPrIB-M (Original)	72.21	3.12	24.46	0.21	0.043
H-PPrIB-M (After six cycles of polymerization)	72.68	3.08	24.06	0.18	0.042

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