

## Electronic Supplementary Information

### Hydrophilic Ultrafiltration Membranes with Surface-Bound Eosin Y for an Integrated Synthesis-Separation System of Aqueous RAFT Photopolymerization

Yujie Zhao<sup>a,§</sup>, Senlin Shao<sup>b,§</sup>, Jiangbin Xia<sup>c</sup>, Ya Huang<sup>a,d</sup>, Yu Chi Zhang<sup>a,d</sup>,  
Xue Li<sup>a,d,\*</sup> and Tao Cai<sup>a,d,\*</sup>

<sup>a</sup>Key Laboratory of Biomedical Polymers of Ministry of Education, College of Chemistry and Molecular Science, Wuhan University, Wuhan, Hubei 430072, P. R. China

<sup>b</sup>School of Civil Engineering, Wuhan University, Wuhan, Hubei 430072, P. R. China

<sup>c</sup>Hubei Key Laboratory on Organic and Polymeric Optoelectronic Materials, College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, P. R. China

<sup>d</sup>Wuhan University Suzhou Research Institute, Suzhou, Jiangsu 215123, P. R. China

<sup>§</sup>These authors contribute equally to this work.

\*Corresponding authors.

Email address: [chemcaitao@whu.edu.cn](mailto:chemcaitao@whu.edu.cn)

[li.x@whu.edu.cn](mailto:li.x@whu.edu.cn)

## Experiment Section

### Materials

Eosin Y disodium salt (EY,  $\geq 85\%$ ), 3-bromopropylamine hydrobromide (98%), *N*-Boc-1,4-diaminobutane (Boc-DAB, 96%), poly(ethylene glycol) diglycidyl ether (PGE, molecular weight (MW) 500 g/mol), *N,N*-dimethylaminoethylamine (DAEA, 99%), 1,3-propanesultone (PS, 98%), tris(hydroxymethyl)aminomethane (Tris,  $\geq 99.8\%$ ), copper(II) sulfate ( $\text{CuSO}_4$ ,  $\geq 99\%$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt%), dopamine hydrochloride (DA, 99%), triethylamine (TEA,  $\geq 99\%$ ) and poly(ethylene glycol) (PEG400, MW 400 g/mol; PEG4000, MW 4000 g/mol; PEG6000, MW 6000 g/mol) were purchased from Sigma-Aldrich or Alfa-Aesar and used as received unless otherwise indicated. The flat-sheet polyethersulfone (PES) membrane used in this study was an FM UP005 membrane (Microdyn-Nadir GmbH) characterized by a 5000 Da MWCO (molecular weight cutoff). According to the manufacturer, the recommended maximum temperature is 95 °C, and the suggested pH range is 0-14 for the FM UP005 membrane. Prior to experiments, the membranes were pretreated with deionized water by compacting them for 5 h at the operating transmembrane pressure to remove preservatives and to obtain a stable membrane structure. All water-soluble monomers including *N,N*-dimethylacrylamide (DMA, 99%), *N,N*-diethylacrylamide (DEA, 99%), 4-acryloylmorpholine (AMP, 98%) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, MW 500 g/mol) were purchased from Sigma-Aldrich Chem. Co. and purified by percolating over an inhibitor-removal column prior to use. *N*-isopropylacrylamide (NIPAM, 97%) was recrystallized twice from toluene/hexane (7:3, v/v). 2-(Butyltrithiocarbonothioylthio)propionic acid (BTPA) were prepared according to procedures described in the literature.<sup>1,2</sup>

## Instrumentation

Nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) were used to characterize the molecular weights and chemical structures of the synthesized polymers.  $^1\text{H}$  NMR spectroscopy were recorded on a Bruker ARX operating at 400 MHz for  $^1\text{H}$  using deuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ ) and deuterated chloroform ( $\text{CDCl}_3$ ) as the solvents and an internal reference with chemical shifts ( $\delta$ ) reported in ppm. GPC analyses 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 ( $M_{n,\text{GPC}}$ ) and polydispersity index ( $D = M_{w,\text{GPC}}/M_{n,\text{GPC}}$ ) were measured with narrow molecular weight distribution poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMMA) as the standards, coupled with water, tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL/min.

The absorbance spectra of different samples were measured by UV-vis photospectrometer (Lambda Bio40, PerkinElmer, USA) equipped with a temperature controller. Surface chemistry of the membranes was analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra DLD spectrometer sourcing with a monochromatized Al  $K\alpha$  X-ray source (1468.71 eV photons). The morphology of the membranes was observed by field-emission scanning electron microscopy (FESEM, SIGMA, Carl Zeiss AG, Germany). Water contact angle was measured by a goniometer (Dataphysics OCA20, Germany) in static mode. Three  $\mu\text{L}$  of water was dropped on the membrane surface by an automatic piston syringe and photographed by a video capture.

### Synthesis of ZPEY Random Copolymer<sup>3</sup>

EY (2.08 g, 3.0 mmol), 3-bromopropylamine hydrobromide (985 mg, 4.5 mmol) and DMF (15 mL) were successively added to a Schlenk tube. The reaction mixture was deoxygenated by sparging argon for 20 min. The reaction was allowed to proceed at 80 °C for 8 h under vigorous stirring. After that, the reaction was quenched by immersing the Schlenk tube into an icy water bath, followed by precipitating in a mixed solution of diethyl ether and deionized water (v/v, 1:1) to eliminate any nonreacted reactants. The purification protocol was repeated twice. Finally, EY-NH<sub>2</sub> was dried under vacuum at 60 °C overnight and obtained as a red solid. Yield: ~70%.

Briefly, EY-NH<sub>2</sub> (705 mg, 1.0 mmol), PGE (1.50 g, 3.0 mmol), DAEA (109 μL, 1.0 mmol), Boc-DAB (191 μL, 1.0 mmol) and DMSO (15 mL) were successively added to a Schlenk tube. The reaction mixture was deoxygenated by sparging argon for 20 min. The polymerization was allowed to proceed at 80 °C for 24 h under vigorous stirring. For the complete reaction of the unmodified epoxy groups, excess DAEA (109 μL, 1.0 mmol) was injected into the mixtures and the system was kept at 60 °C for another 1 h. After that, the polymerization was terminated by immersing the Schlenk tube into an icy water bath, followed by precipitating in a 10-fold excess of diethyl ether to eliminate any unreacted monomers. The crude product was dialyzed against ultrapure water (4 × 200 mL) with a dialysis membrane (MWCO 3500 Da) at room temperature for 48 h. Finally, P[PGE-EY-DAEA-(Boc-DAB)] was collected via lyophilization as a mauve solid. Yield: ~84%.

In the next step, P[PGE-EY-DAEA-(Boc-DAB)] (0.62 g) and PS (0.61 g, 5.0 mmol) were successively dissolved in DMSO (10 mL). The reaction mixture was deoxygenated by

sparging argon for 20 min. Then, the reaction was allowed to proceed at room temperature for 24 h after being sealed with a rubber septum. Afterwards, the reaction was terminated by pouring into a large amount of acetone to eliminate any leftover reactants. This purification protocol was repeated thrice. Finally, the copolymer was dried under vacuum at 60 °C overnight and obtained as a tangerine solid. Yield: ~95%.

In a typical procedure, ZP[PGE-EY-DAEA-(Boc-DAB)] (0.74 g) was dissolved in DMSO (10 mL). Subsequently, trifluoroacetic acid (0.50 mL) was added dropwise to the solution. Upon completion of the addition, the reaction was performed at room temperature for 12 h. After that, the reaction was terminated by immersing the flask into an icy water bath, followed by precipitating in a 10-fold excess of acetone to remove any leftover reactants. The above dissolution-precipitation cycle was repeated twice. Finally, the ZP[PGE-EY-DAEA-DAB] (abbreviated as ZPEY) copolymer was dried under vacuum at 60 °C overnight and obtained as a tangerine solid. Yield: ~94%. GPC (water as eluent, PEO standard):  $M_{n, GPC} = 12000$  g/mol,  $D = 1.92$ .

### **Deposition of ZPEY Coatings on the PDA Pretreated Ultrafiltration Membranes**

A typical protocol for the polydopamine (PDA) deposition was developed according to our previous work.<sup>4-8</sup> The PDA coating solution was prepared by dissolution of DA (2.0 mg/mL), CuSO<sub>4</sub> (0.85 mg/mL) and H<sub>2</sub>O<sub>2</sub> (0.9 mg/mL) in a Tris-HCl buffer solution (0.05 mol/L, pH 8.5). The obtained homogeneous solution was poured into a reaction cell consisting of UP005 ultrafiltration membranes, which were then incubated at ambient temperature for 3 h under gentle shaking to immobilize sufficient coupling anchors for

the subsequent polymer conjugation. The resultant PDA pretreated UP005 ultrafiltration membranes were rinsed thoroughly with deionized water thrice.

The as-prepared PDA-UP membranes were soaked in a ZPEY solution (10 g/L) containing TEA (0.1 mol/L), and the Schiff base reaction was allowed to proceed for 12 h. The resultant membranes, denoted as ZPEY-UP membranes, were then extracted thoroughly and stored in deionized water to eliminate any bound polymers before further tests.

#### **General Procedure for the Kinetic Studies of PET-RAFT Polymerization in an Integrated Synthesis-Separation System**

A typical PET-RAFT polymerization of DMA in ultrapure water was performed using varied molar feed ratio of [DMA]:[BTPA] in an integrated synthesis-separation system.<sup>7,8</sup> After the reaction mixture was placed in synthesis-separation cell with a mechanical stirrer and deoxygenated by sparging argon for 20 min, the cell was sealed and irradiated to green LED light (9.6 W,  $\lambda_{\text{max}} = 520 \text{ nm}$ , 2.4 mW/cm<sup>2</sup>) at room temperature. After a certain period, the polymerization was terminated by ceasing the LED light irradiation. The total volume of reaction mixture was topped up to 100 mL by dilution with ultrapure water. Then monomers and residual reactants were separated out from the cell. The product polymers were collected after thorough membrane separation and recovered by lyophilization. To investigate the polymerization kinetics, aliquots of reaction mixtures were withdrawn periodically by argon-purged syringe and analyzed by <sup>1</sup>H NMR and GPC measurements. After separation, the ZPEY-UP membrane was extracted thoroughly with ultrapure water for regeneration.

### Membrane Separation after PET-RAFT Polymerization

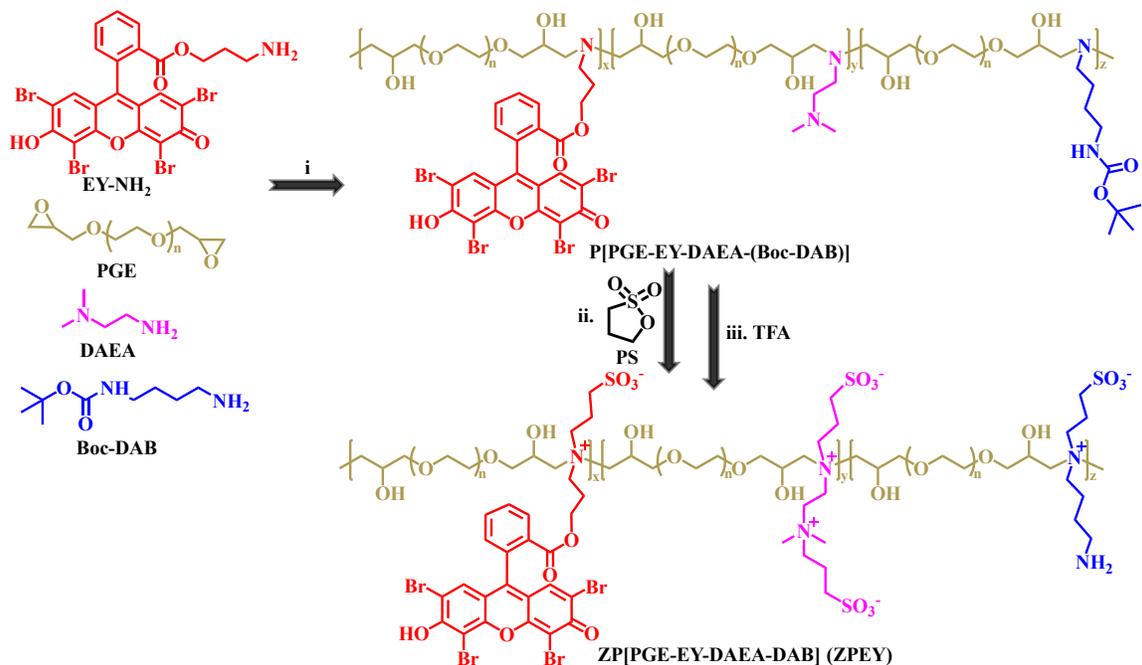
Membrane performance was evaluated according to flux and rejection. All filtration experiments were carried out using an integrated synthesis-separation system. A stirrer was placed above the membrane, which was stirred at 500 rpm to minimize the concentration polarization effect. The effective membrane area was 14.52 cm<sup>2</sup>. Permeate samples for flux measurements were collected at intervals of 1 h or 0.5 h, and samples for rejection evaluations were taken after steady permeate flux was achieved. The solute rejections of membrane were measured by the solute transport method a hydraulic pressure difference of 4 ± 0.2 bar. The concentrations of the solutes were measured by a total organic carbon analyzer (TOC ASI-5000A, Shimadzu, Japan). The measured feed ( $C_f$ ) and permeate ( $C_p$ ) concentrations were used for the calculation of the effective solute rejection coefficient  $R_s$  (%):

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

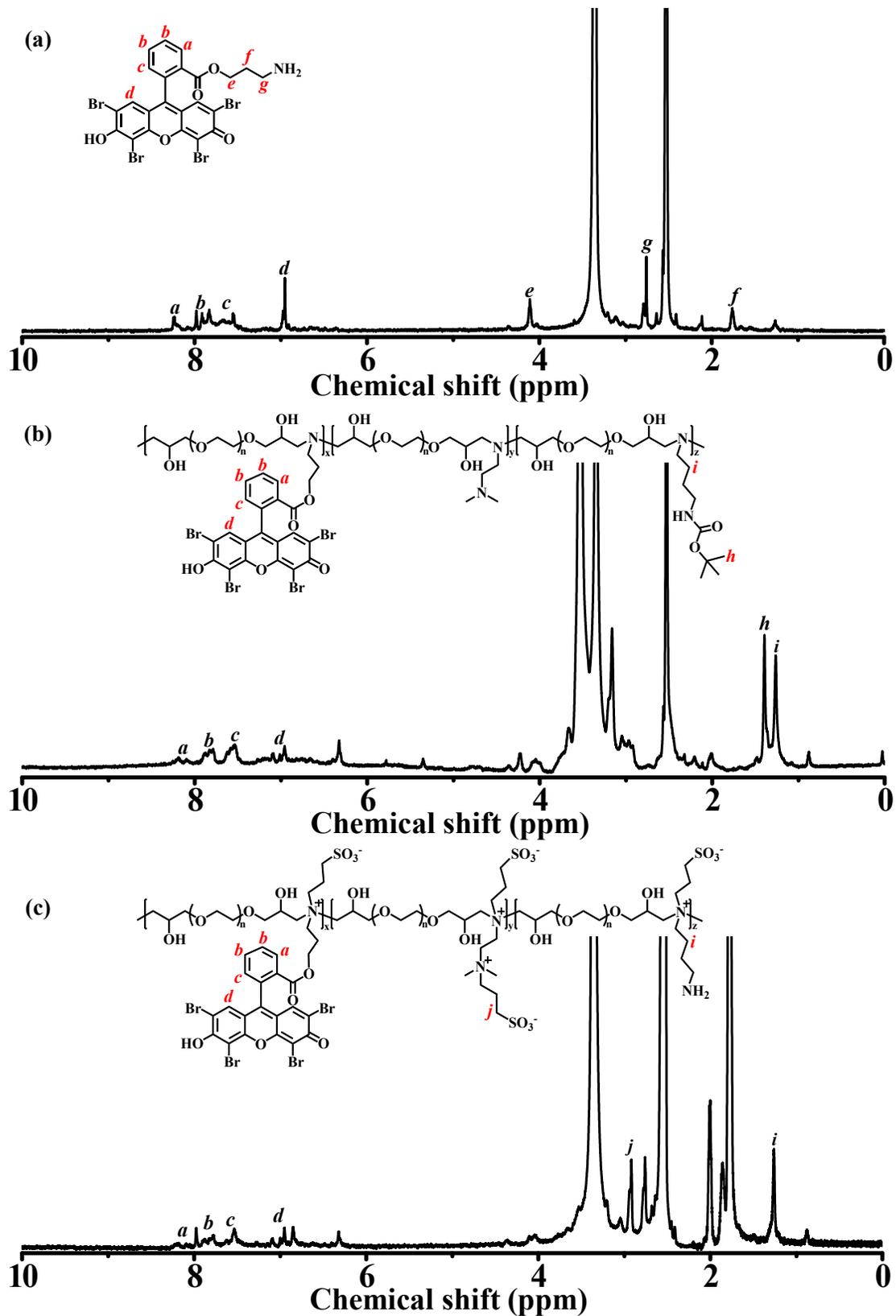
The water permeation flux,  $J_w$  (L m<sup>-2</sup> h<sup>-1</sup>, LMH), is calculated from Eq. 2 based on the effective membrane area,  $A_m$  (m<sup>2</sup>):

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

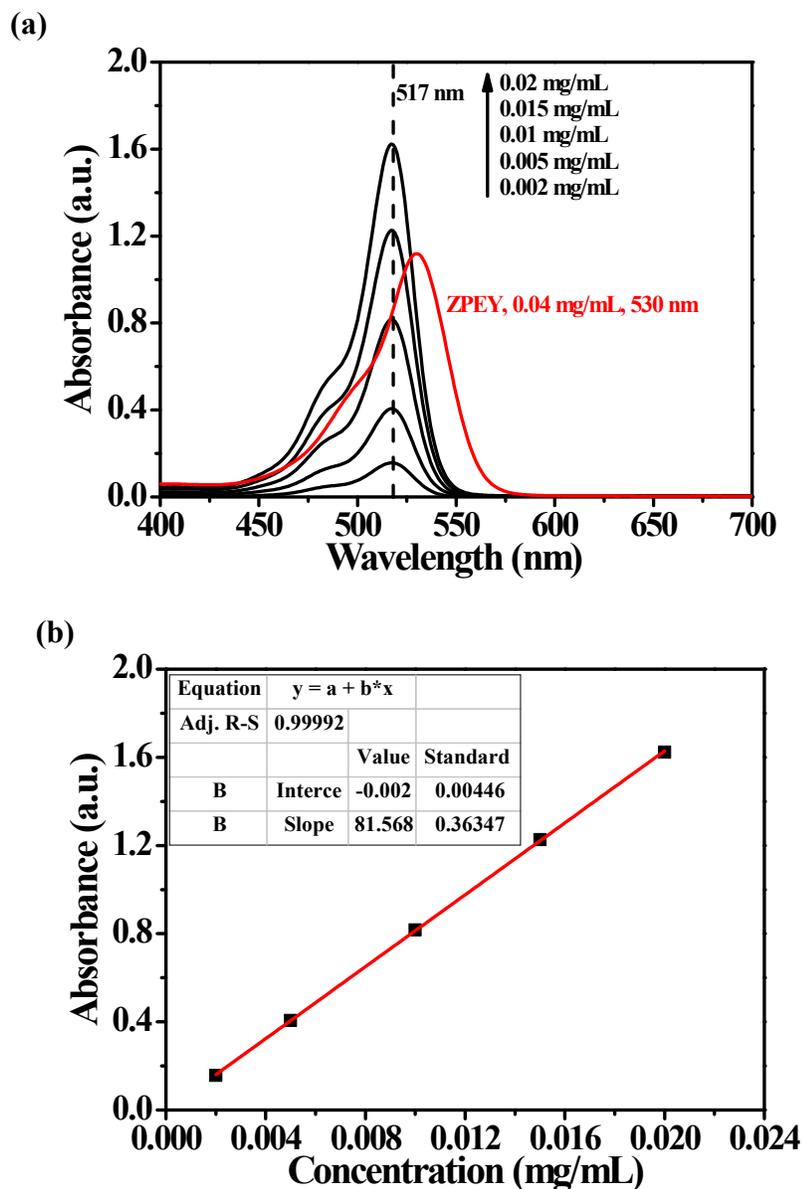
where  $\Delta\omega$  (L) is the volume of water permeated through the membrane over a predetermined time  $\Delta t$  (h).



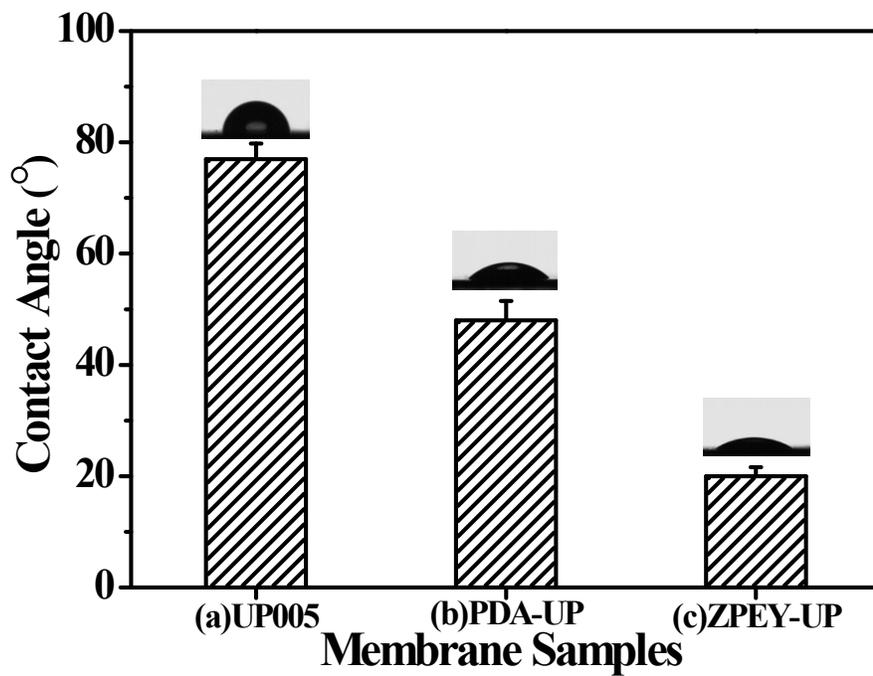
**Scheme S1.** Synthesis of ZP[PGE-EY-DAEA-DAB] (ZPEY) copolymers. Reagents and conditions: (i) amino-terminated eosin Y (EY-NH<sub>2</sub>), poly(ethylene glycol) diglycidyl ether (PGE), *N,N*-dimethylaminoethylamine (DAEA), *N*-Boc-1,4-diaminobutane (Boc-DAB), DMSO, 80 °C, 24 h; (ii) 1,3-propanesultone (PS), DMSO, RT, 24 h; (iii) trifluoroacetic acid (TFA), DMSO, RT, 12 h.



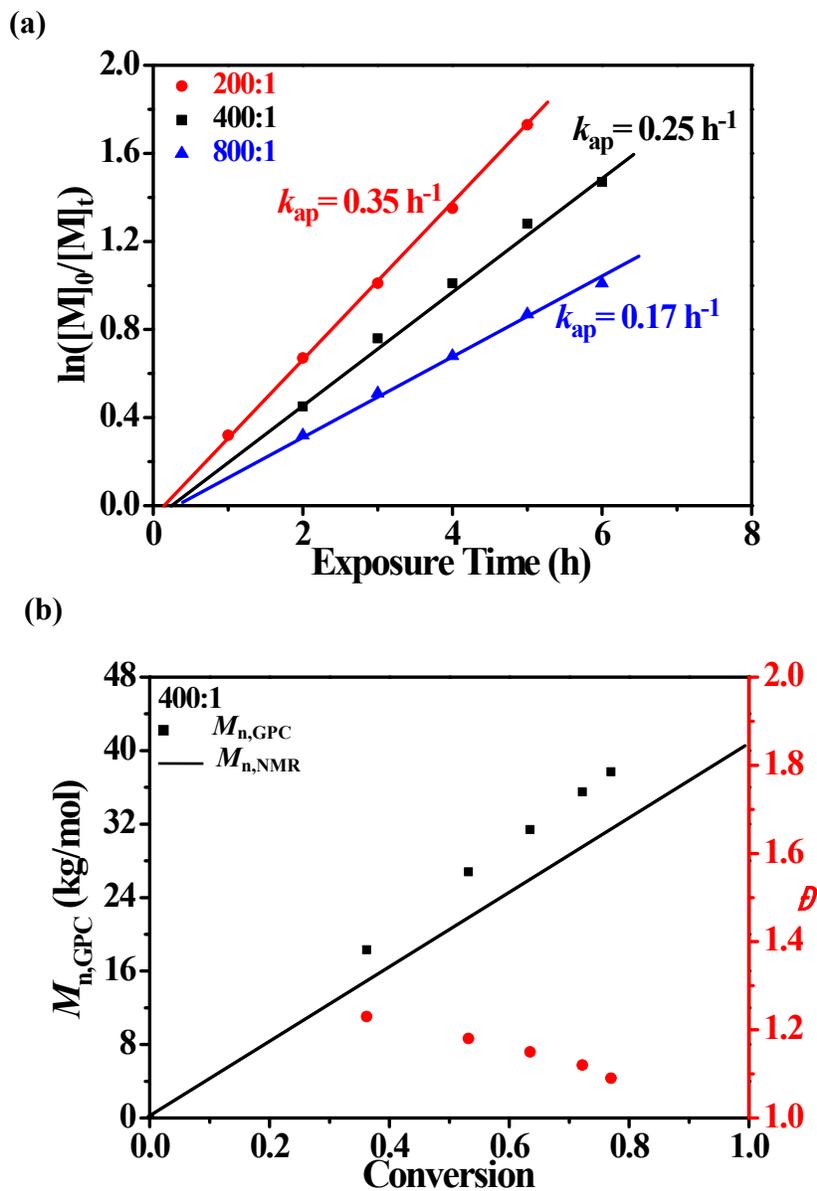
**Figure S1.**  $^1\text{H}$  NMR spectra of (a)  $\text{EY-NH}_2$ , (b)  $\text{P}[\text{PGE-EY-DAEA-(Boc-DAB)}]$  and (c)  $\text{ZP}[\text{PGE-EY-DAEA-DAB}]$  (ZPEY) in  $\text{DMSO-}d_6$ .



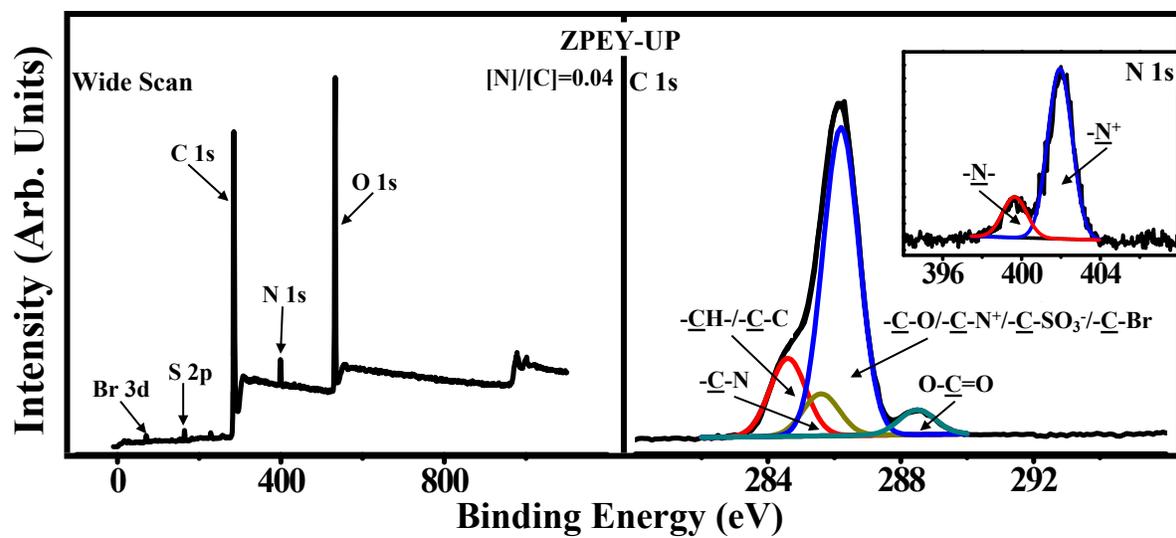
**Figure S2.** (a) UV-vis absorption spectra of various concentration of eosin Y and ZPEY (0.04 mg/mL) dissolve in ultrapure water; (b) plot of absorbance in the maximum wavelength ( $\lambda_{\max} = 517$  nm) as a function of eosin Y concentration. Considering the UV-Vis absorption and assuming that the number of eosin Y is proportional to the absorbance, the molar ratio of eosin Y in the ZPEY polymer was estimated to be  $5.3 \times 10^{-7}$  mol per mg of ZPEY polymer.



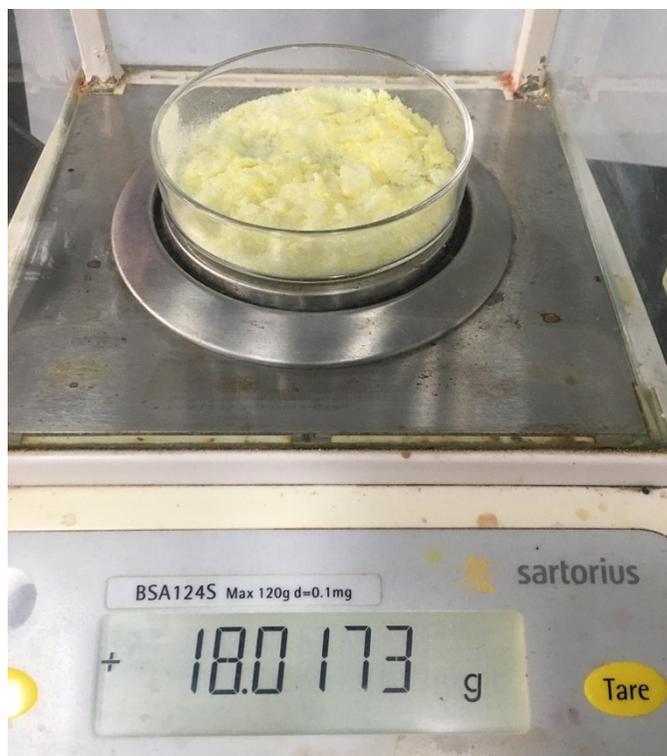
**Figure S3.** Photographs of water contact angles of (a) UP005, (b) PDA-UP and (c) ZPEY-UP membranes.



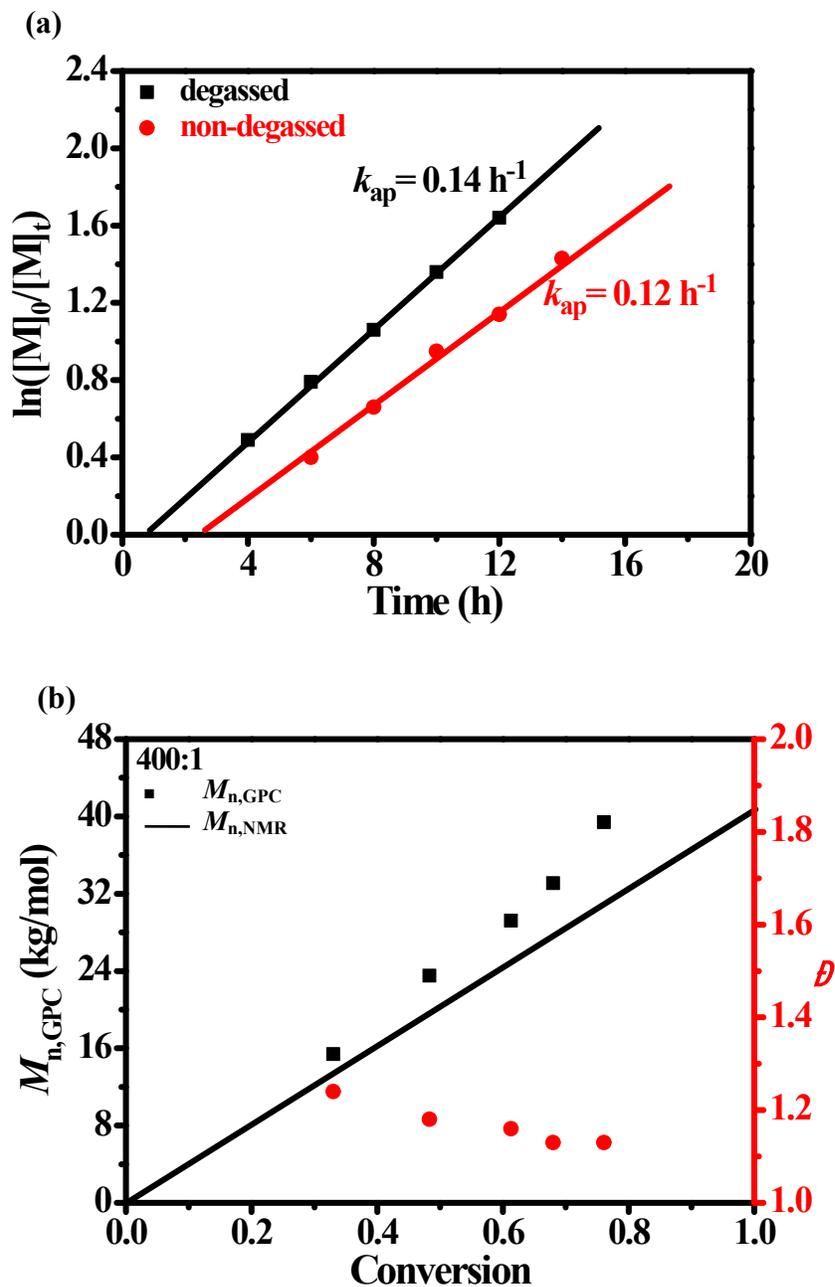
**Figure S4.** Kinetic analyses of PET-RAFT polymerization of DMA with constant concentration of unbound eosin Y photocatalysts in ultrapure water. (a) Plot of  $\ln([M]_0/[M]_t)$  versus exposure time  $t$  with varied molar feed ratio of  $[DMA]/[BTPA]$  in the absence of oxygen at room temperature under green LED light (9.6 W,  $\lambda_{\max} = 520$  nm,  $2.4$  mW/cm<sup>2</sup>) with BTPA as the CTA and (b)  $M_{n,NMR}$ ,  $M_{n,GPC}$  and  $\bar{D}$  versus monomer conversion.



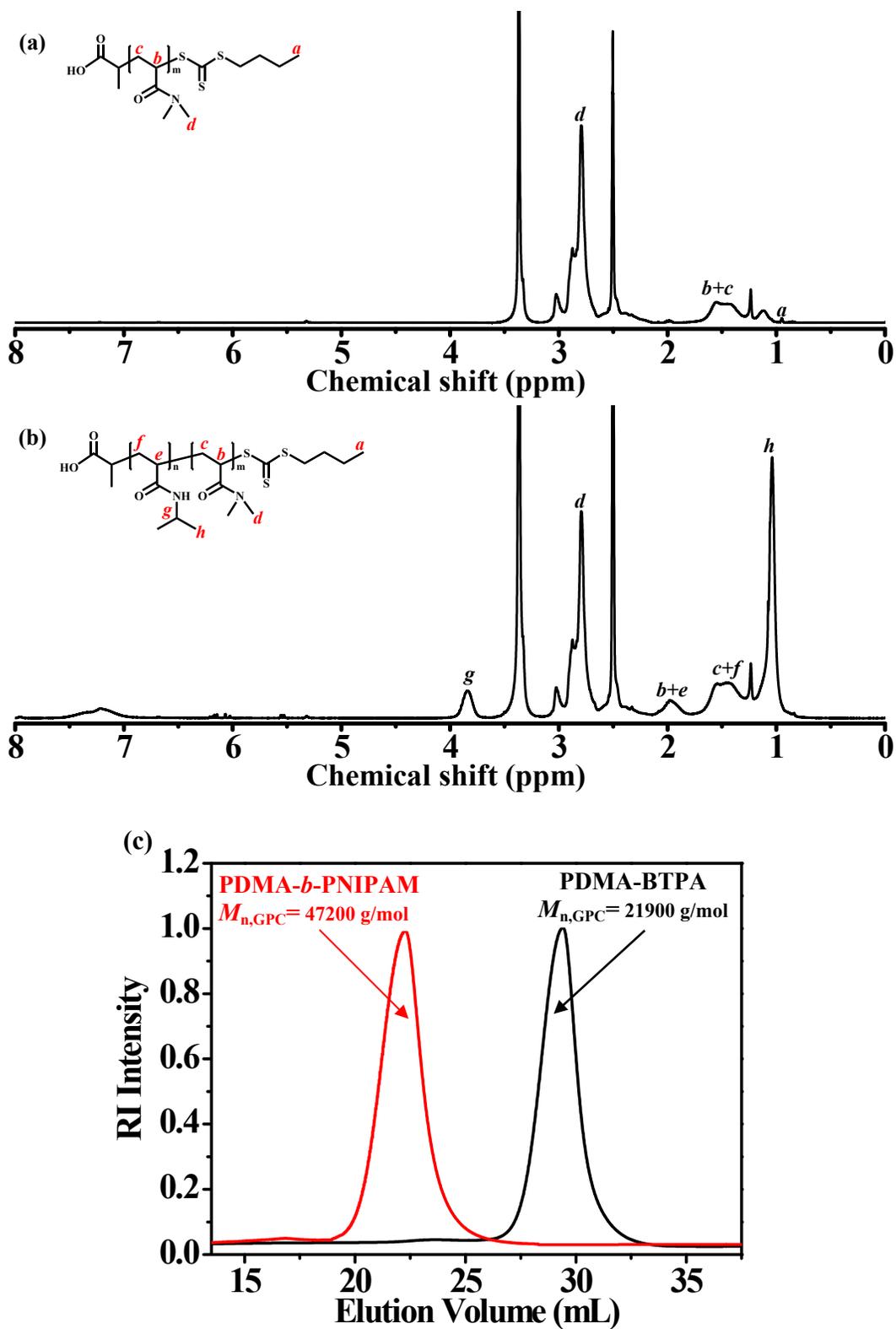
**Figure S5.** XPS wide-scan, C 1s and N 1s core-level spectra of the ZPEY-UP membranes after extracting with ultrapure water.



**Figure S6.** A photograph of batch-wise polymerization producing PDMA polymers on a balance.



**Figure S7.** Kinetic analyses of PET-RAFT polymerization of DMA with ZPEY-UP membrane in ultrapure water. (a) Plot of  $\ln([M]_0/[M]_t)$  versus exposure time  $t$  with and without prior deoxygenation at room temperature under green LED light irradiation (9.6 W,  $\lambda_{max} = 520 \text{ nm}$ ,  $2.4 \text{ mW/cm}^2$ ) with BTPA as the CTA ( $[DMA]/[BTPA] = 400:1$ ) and (b)  $M_{n,NMR}$ ,  $M_{n,GPC}$  and  $\bar{D}$  versus monomer conversion.



**Figure S8.**  $^1\text{H}$  NMR spectra of (a) PDMA-BTPA and (b) PDMA-*b*-PNIPAM in DMSO and (c) GPC profiles for evolution of molecular weight of PDMA-BTPA and PDMA-*b*-PNIPAM.

**Table S1.** Permeation Flux of PDA-UP and ZPEY-UP Membranes<sup>a</sup>

Membrane	Permeation Flux in Pure Water (L m <sup>-2</sup> h <sup>-1</sup> )	Flux Recovery after 1 <sup>st</sup> Run (%)	Flux Recovery after 2 <sup>nd</sup> Run (%)	Flux Recovery after 3 <sup>rd</sup> Run (%)
PDA-UP	29.1 ± 2.9			
ZPEY-UP	19.9 ± 3.4	96.0	87.8	90.3

<sup>a</sup> Testing condition: 4.0 bar at 25 °C.

**Table S2.** PET-RAFT Polymerization of Varied Water-Soluble Monomers Using a ZPEY-UP Membrane in an Integrated Synthesis-Separation System

Entry	Photocatalyst	Monomer	CTA	Solvent	[M]/[CTA]	Time (h)	$\alpha^b$ (%)	$M_{n,NMR}^b$ (kg/mol)	$M_{n,GPC}^c$ (kg/mol)	$\mathcal{D}^c$
1 <sup>d</sup>	ZPEY-UP	DEA	BTPA	water	400:1	6	49	25.2	33.6	1.16
2	ZPEY-UP	DEA	BTPA	water	400:1	12	75	38.4	46.4	1.12
3	ZPEY-UP	AMP	BTPA	water	400:1	6	53	29.8	36.9	1.18
4	ZPEY-UP	AMP	BTPA	water	400:1	12	79	44.8	59.2	1.15
5	ZPEY-UP	NIPAM	BTPA	water	400:1	6	56	25.6	29.3	1.12
6	ZPEY-UP	NIPAM	BTPA	water	400:1	12	82	37.3	42.7	1.10
7	ZPEY-UP	PEGMA	BTPA	water	200:1	12	36	36.3	48.5	1.28
8	ZPEY-UP	PEGMA	BTPA	water	200:1	24	61	61.6	79.8	1.25
9	ZPEY-UP	DMA	BTPA	water	200:1	12	94	18.9	21.9	1.12
10 <sup>e</sup>	ZPEY-UP	NIAPM	PDMA-BTPA	water	200:1	12	95	40.4	47.2	1.13
11 <sup>e</sup>	ZPEY-UP	DEA	PDMA-BTPA	water	200:1	12	88	41.3	48.5	1.16

<sup>a</sup> The polymerizations were performed under green LED light irradiation (9.6 W,  $\lambda_{max} = 520$  nm, 2.4 mW/cm<sup>2</sup>) with prior deoxygenation at room temperature.

<sup>b</sup> The molecular weight was calculated using the following equation:  $M_{n,NMR} = [M]_0/[CTA] \times MW^M \times \alpha + MW^{CTA}$ , where  $[M]_0$ ,  $[CTA]$ ,  $MW^M$ ,  $\alpha$  and  $MW^{CTA}$  correspond to initial monomer concentration, initial CTA concentration, molecular weight of monomer, monomer conversion derived from <sup>1</sup>H NMR spectroscopy, and molecular weight of CTA.

<sup>c</sup> Derived from GPC profiles (calibration with PMMA molecular weight standards), polydispersity index ( $\mathcal{D}$ ) =  $M_{w,GPC}/M_{n,GPC}$ .

<sup>d</sup> Abbreviations: ZPEY-UP, ZPEY copolymer modified UP005 ultrafiltration membrane; DMA, *N,N*-dimethylacrylamide (MW 99.1 g/mol); DEA, *N,N*-diethylacrylamide (MW 127.2 g/mol); AMP, 4-acryloylmorpholine (MW 141.2 g/mol); NIPAM, *N*-isopropylacrylamide (MW 113.2 g/mol); PEGMA, poly(ethylene glycol) methyl ether methacrylate (MW 500 g/mol); CTA, chain transfer agent; BTPA, 2-(butyltrithiocarbonothioylthio)propionic acid (MW 238 g/mol).

<sup>e</sup> The block copolymers were synthesized using PDMA-BTPA in Entry 9 as macro-CTA.

**Table S3.** Differences between Our Work and Previous Reports on PET-RAFT Polymerization upon Visible Light Harvesting

	Our work EY modified on UP005 ultrafiltration membranes	Previous report 1 TPP modified on cotton thread <sup>9</sup>	Previous report 2 ZnTPP modified on cellulose <sup>10</sup>
Reaction Type	PET-RAFT polymerization	PET-RAFT polymerization	PET-RAFT polymerization
Solvent	Water	Organic solvents	Organic solvents and water
Monomer Scope	Water soluble (meth)acrylates and (meth)acrylamide	DMA	(Meth)acrylates and (meth)acrylamide
Catalyst Model	EY	TPP	ZnTPP
Monomer and Reaction Condition	DMA in water with a molar feed ratio of 200:1	DMA in water with a molar feed ratio of 200:1	MA in DMSO with a molar feed ratio of 200:1
$k_{ap}$ <sup>a</sup>	0.20 h <sup>-1</sup>	0.34 h <sup>-1</sup>	0.78 h <sup>-1</sup>
$\alpha$	88% over 4 consecutive runs	77% over 4 consecutive runs	~55% over 5 consecutive runs
$\bar{D}$	Excellent: $\bar{D} < 1.15$	Excellent: $\bar{D} < 1.10$	Excellent: $\bar{D} < 1.15$

<sup>a</sup> Abbreviations:  $k_{ap}$ , apparent propagation rate coefficients;  $\alpha$ , average monomer conversion;  $\bar{D}$ , polydispersity; EY, eosin Y; TPP, tetraphenylporphyrin; ZnTPP, zinc tetraphenylporphyrin; DMA, *N,N*-dimethylacrylamide; MA, methyl acrylate.

## References

- [1] D. J. Keddie, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2012, **45**, 5321-5342.
- [2] J. Xu, K. Jung and C. Boyer, *Macromolecules*, 2014, **47**, 4217-4229.
- [3] Y. Zhu, C. Xu, N. Zhang, X. Ding, B. Yu and F. J. Xu, *Adv. Funct. Mater.*, 2018, **28**, 1706709.
- [4] Y. Zhang, J. L. Li, T. Cai, Z. L. Cheng, X. Li and T. S. Chung, *J. Membr. Sci.*, 2018, **563**, 521-530.
- [5] J. L. Li, Y. Zhang, S. Zhang, M. Liu, X. Li and T. Cai, *J. Mater. Chem. A*, 2019, **7**, 8167-8176.
- [6] J. L. Li, C. P. Wang, Z. Xiang, Y. Zhao, Y. Zhang, X. Li and T. Cai, *ACS Appl. Mater. Interfaces*, 2019, **11**, 42322-42329.
- [7] Y. Liu, K. Ai and L. Lu, *Chem. Rev.*, 2014, **114**, 5057-5115.
- [8] C. Zhang, Y. Lv, W. Z. Qiu, A. He and Z. K. Xu, *ACS Appl. Mater. Interface*, 2017, **9**, 14437-14444.
- [9] Y. Chu, N. Corrigan, C. Wu, C. Boyer and J. Xu, *ACS Sustainable Chem. Eng.*, 2018, **6**, 15245-15253.
- [10] Y. Chu, Z. Huang, K. Liang, J. Guo, C. Boyer and J. Xu, *Polym. Chem.*, 2018, **9**, 1666-1673.