CO₂-responsive low molecular weight polymer with high osmotic pressure as a draw solute for forward osmosis

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Figure S1. Glassware apparatus used to measure the flux of PDMAAm solutions.



Figure S2. Conductivity of a 35 wt% low-molecular-weight PDMAAm/water mixture during CO₂ addition.



Figure S3. (A) Molecular weight distributions of linear and branched poly(N,N-dimethylacrylamide), (B) Cumulative percentage of the slice Mw height from the total of all Mw slice heights for the low molecular weight polymer.

Polymers	LCST (°C)	Ref.
PEOx ^a	65	1
PNnPAM ^b	37	2
PNIPAM-SA ^c	20	3
PiBuCPMAd	13	4
PiPA ^e	32	5
$PnPA^{\rm f}$	34	5
PEG ^g	150	6
PDEAEMA ^h	35	7
nBu-TAEA ⁱ	37	8
PNMm ^j	22	9
PNAGA ^k	36	10
PNIPAM ¹	32	11
PNIPAM-SSS ^m	33	12
PNVCL ⁿ	33	13

Table S1 : LCST of the thermoresponsive polymers/polyelectrolytes in water.

^a PEOx= poly(ethylene oxide).

^bPNnPAM = poly(N-n-propylacrylamide).

[°] PNIPAM-SA= poly(N-isopropylacrylamide-sodium acrylate).

^d PiBuCPMA=poly(N-(N'-isobutylcarbamido)propyl methacrylamide).

^ePiPA = poly(isopropylacrylamide).

^f PnPA= poly(N-n-propylacrylamide).

^g PEG= polyethylene glycol.

^h PDEAEMA= poly(2-(diethylamino)ethyl methacrylate).

ⁱ nBu-TAEA= poly(n-butyl tetra(ethylene glycol) acrylate-co-2-aminoethyl methacrylate).

^jPNMm= poly(N-(2-methoxy-1,3-dioxan-5-yl) methacrylamide.

^kPNAGA= poly(N-acryloyl glycinamide).

¹PNIPAM = poly(N-isopropylacrylamide.

^mPNIPAM-SSS = poly(sodium styrene-4-sulfonate-co-n-isopropylacrylamide).

ⁿPNVCL = poly(N-vinylcaprolactam).



Figure S4: Conductivity as a function of time during the FO test after 3 h of (A) 0.2 wt% (B) 1.75 wt%, (C) 3.5 wt% of NaCl feed solution and (D) 3.5 wt% after 21 h.



Figure S5: Volume of water passed through the membrane during the FO process with different initial feed NaCl concentrations using the small scale apparatus. After 3 h, 9.0 mL, 5.0 ml and 2.5 mL of water permeated from 0.2 wt%, 1.75 wt% and 3.5 wt% NaCl feed solutions into the draw solution.



Figure S6: Water flux (LMH) over the time using different scale FO apparatus (large scale: 45 g polymer and small scale: 7.5 g polymer). In all cases, the draw solution was 50 wt% PDMAAm (low Mw) in carbonated water.



Figure S7. (A) IR spectrum of the draw agent solution before and after FO test and (B) ¹H NMR spectrum of the feed solution of 3.5 wt% after the FO test (all three feed solutions showed only the water peak in NMR and IR spectrum after the FO process).



Figure S8. (A) Diluted draw solution after the FO test, (B) phase separation after removing CO₂ from the mixture, (C) recovered 1-PDMAAm.



Figure S9. (A) FTIR spectra and (B) ¹H NMR spectra of the polymer-rich phase (i.e. the separate polymer phase) and the water-rich phase after the removal of the CO_2 from the diluted draw solution.



Figure S10. FTIR and ¹H NMR of the water-rich phase after the removal of the CO₂ and precipitated polymer from the diluted draw solution.

References:

[1] Weber, C., Hoogenboom, R., & Schubert, U. S. Temperature responsive bio-compatible polymers based on poly (ethylene oxide) and poly (2-oxazoline) s. *Progress in Polymer Science*, 37, 2012, 686-714.

[2] de Oliveira, T. E., Marques, C. M., & Netz, P. A. Molecular dynamics study of the LCST transition in aqueous poly (Nn-propylacrylamide). *Physical Chemistry Chemical Physics*, 20, 2018, 10100-10107.

[3] Ou, R., Wang, Y., Wang, H., & Xu, T. Thermo-sensitive polyelectrolytes as draw solutions in forward osmosis process. *Desalination*, 318, 2013, 48-55.

[4] Akiyama, Y., Shinohara, Y., Hasegawa, Y., Kikuchi, A., & Okano, T. Preparation of novel acrylamide-based thermoresponsive polymer analogues and their application as thermoresponsive chromatographic matrices. *Journal of Polymer Science Part A: Polymer Chemistry*, 46, 2008, 5471-5482.

[5] Maeda, Y., Nakamura, T., Ikeda, I. Changes in the hydration states of poly (N-alkylacrylamide)s during their phase transitions in water observed by FTIR spectroscopy. Macromolecules, 34, 2001, 1391-1399.

[6] Saeki, S., Kuwahara, N., Nakata, M., & Kaneko, M. Upper and lower critical solution temperatures in poly (ethylene glycol) solutions. *Polymer*, 17, 1976, 685-689.

[7] Plamper, F. A., Ballauff, M., & Müller, A. H. Tuning the thermoresponsiveness of weak polyelectrolytes by pH and light: lower and upper critical-solution temperature of poly (N, N-dimethylaminoethyl methacrylate). *Journal of the American Chemical Society*, 129, 2007, 14538-14539.

[8] Noh, M., Mok, Y., Lee, S., Kim, H., Lee, S. H., Jin, G. W., Lee, Y. Novel lower critical solution temperature phase transition materials effectively control osmosis by mild temperature changes. *Chemical Communications*, 48, 2012, 3845-3847.

[9] Huang, X., Du, F., Ju, R., & Li, Z. Novel acid-labile, Thermoresponsive poly (methacrylamide) s with pendent Ortho Ester moieties. *Macromolecular rapid communications*, 28, 2007, 597-603.

[10] Seuring, J., Bayer, F. M., Huber, K., & Agarwal, S. Upper critical solution temperature of poly (N-acryloyl glycinamide) in water: a concealed property. *Macromolecules*, 45, 2012, 374-384.

[11] Pelton, R. Poly (N-isopropylacrylamide)(PNIPAM) is never hydrophobic. *Journal of colloid and interface science*, 348, 2010, 673-674.

[12] Zhao, D., Wang, P., Zhao, Q., Chen, N., Lu, X. Thermoresponsive copolymer-based draw solution for seawater desalination in a combined process of forward osmosis and membrane distillation. Desalination. 348, 2014, 26-32.

[13] Doberenz, F., Zeng, K., Willems, C., Zhang, K. and Groth, T., 2020. Thermoresponsive polymers and their biomedical application in tissue engineering–a review. *Journal of Materials Chemistry B*, 8, 2020, 607-628.