Supporting information

Dual responsive polymers as draw solutes for forward osmosis desalination

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Experimental procedures

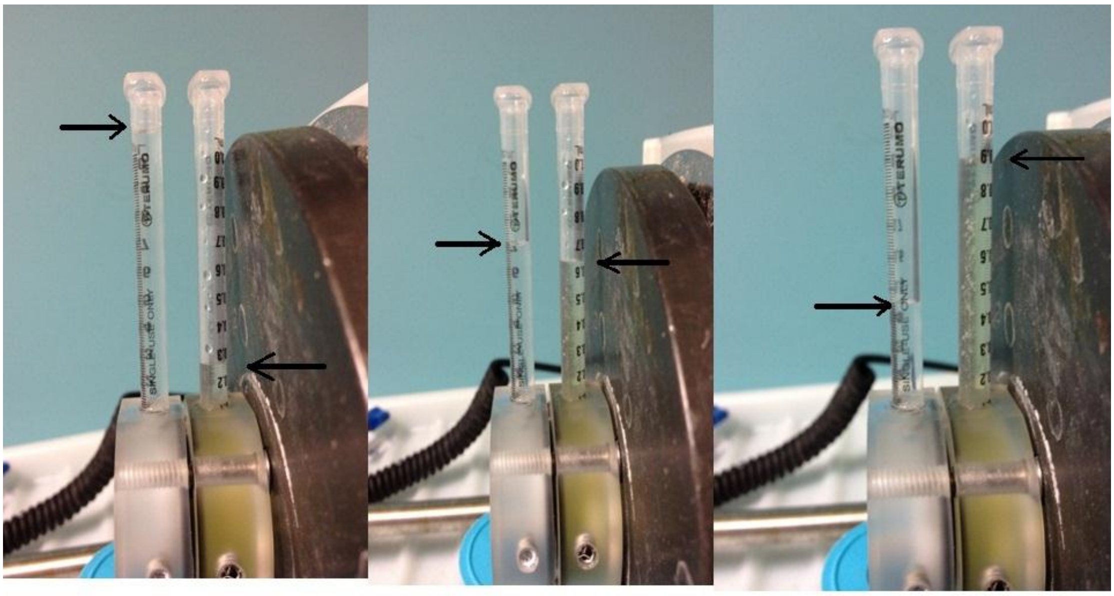
Polymer synthesis: All the chemicals were purchased from Aldrich, Singapore. Atom transfer radical polymerization of DMAEMA was carried out in the solvent THF using 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the ligand, CuBr as the catalyst and ethyl α-bromoisobutyrate (EBiB) as the initiator. The expected molecular weight is tuned by the molar ratio of monomer to initiator. In a typical synthesis 5 mL THF was purged with pure nitrogen for 15 minutes before 85 mg (0.59 mmol) CuBr, 323 μL (1.18 mmol) HMTETA and 5 mL (29.6 mmol) DMAEMA were charged. 87 μL (0.59 mmol) EBib was injected into the system at 50°C to initiate the polymerization. The polymerization was terminated by immersing into liquid nitrogen. The ligand-catalyst complex was removed by passing the diluted polymer solution through a neutral aluminum oxide column. The polymer was precipitated in hexane and dried in a vacuum oven at 60°C after the supernatant was decanted. The polymers used for the back diffusion measurements, membrane salt rejection and produced water quality analyses were further precipitated once from aqueous solution and then freeze-dried to remove trace amounts of the ligand. The average molecular weight (Mn and Mw), and polymer dispersity index (PDI) of the three PDMAEMA polymers synthesized in this study are summarized in Table S1. The molecular weights were determined by size exclusion chromatography (SEC) relative to polystyrene calibration in chloroform with 1% triethylamine at 35°C.

Table S1. Summary of number average molecular weight (M_n), weight average molecular weight (M_w) and polymer dispersity index (PDI) of the three PDMAEMA polymers synthesized in this study.

Code	M_n (g/mol)	M_w (g/mol)	PDI
P4000	3921	5254	1.34
P9000	8876	11620	1.31
P13000	12946	16426	1.27

Water flux measurement: the water flux in the FO process was measured by the in-house apparatus shown in Fig. S1. Two chambers were separated by the FO membrane from Hydration Technologies Inc. (HTI) with the orientation of the active layer towards the draw solution (PRO mode). Magnetic stirring was used to reduce concentration polarization. The water flux was calculated as $\Delta m/(A\cdot t)$, where Δm is the weight increase of draw solution (kg), A is the membrane area (m^2) and t is the FO duration(h). In this study we set the FO duration at 15 minutes. Although a smaller FO duration time would be better for practical operation, the associated small incremental mass collected during the FO is problematic to measure accurately. However, an excessively long FO duration time dilutes the draw solution so that the value would be largely underestimated given that the chamber volume is about 7 ml.

The draw solution is injected and taken out by a syringe and needle to ensure that no draw solution is lost before and during weight measurement. When the concentration of the P4000 rises over 0.6 g/g, the viscosity is too high for the draw solution to pass through the needle with the pressure that can be applied via the syringe; however, this would not be a problem if a pump were used in a larger scale FO process.



0 min 7 min 15 min

Fig. S1 The water flux measurement by an in-house apparatus. The right chamber contains the P4000 with an initial concentration of 0.4 g/g and the left chamber contains the brackish solution with an initial concentration of 0.15 M NaCl. The magnetic stirring rate is 600 rpm.

Back diffusion measurement: Protonated P4000 and P9000 aqueous solutions at concentrations of 0.2 g/g and 0.3 g/g, respectively, were used as the draw solution and DI water was used as the feed solution. The amount of draw solute diffusing into the feed solution was determined from the concentration of draw solute in the feed solution and the volume of feed solution after the FO process. The draw solute concentration was determined from total organic carbon (TOC) measurement. Traditional method of measuring by conductivity is not accurate here, because the contribution of permeated CO_2 and draw solute to conductivity is not known.

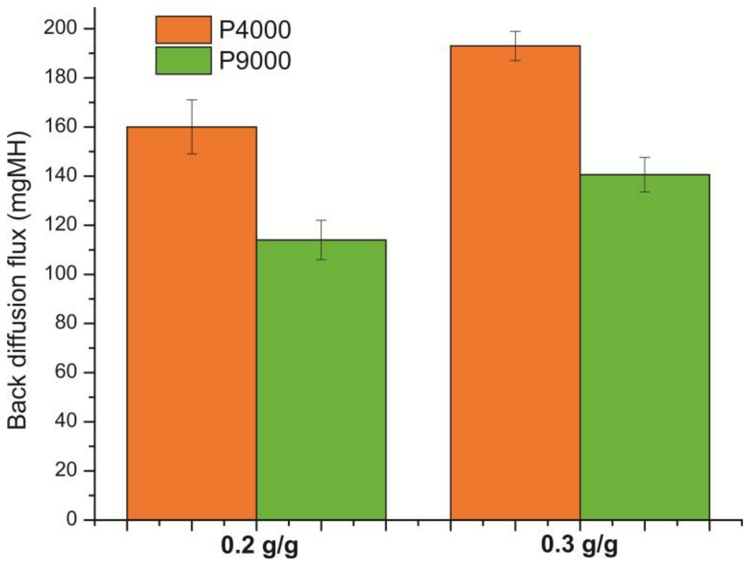


Fig. S2 Draw solute back diffusion flux as a function of molecular weight and concentration.

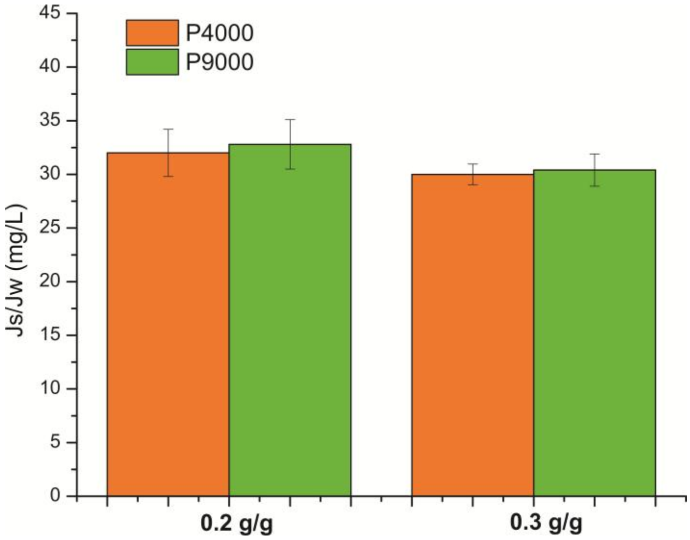
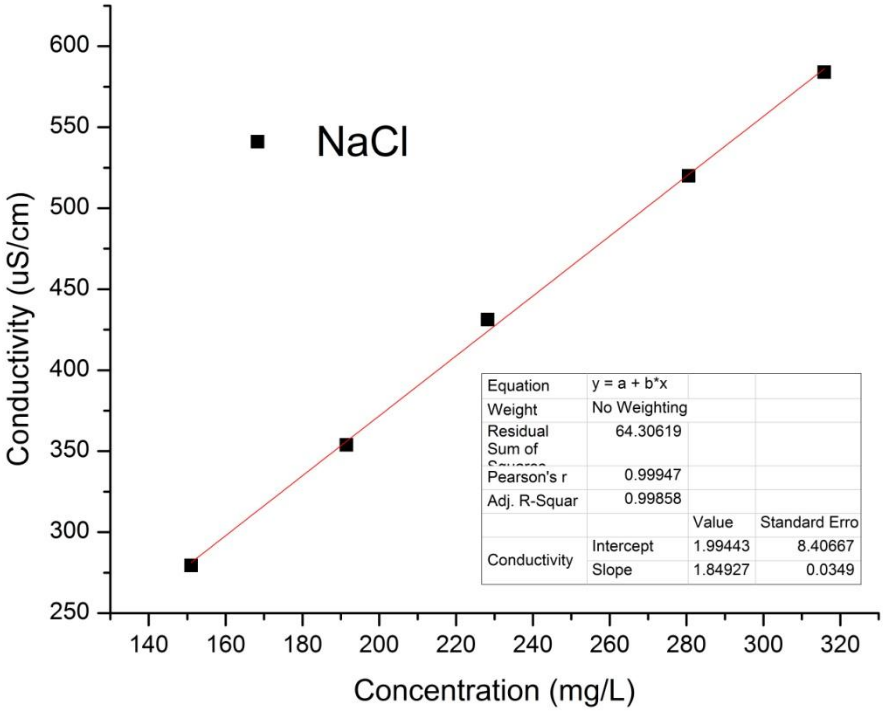


Fig. S3 The ratio of draw solute back diffusion flux to the water flux as a function of molecular weight and concentration.

Salt rejection measurement: The draw and feed solution concentrations were 0.3 g/g P9000 and 0.1M NaCl, respectively. After the FO process the draw solution was purged with argon at a temperature of 60°C to deprotonate and precipitate the draw solute. The supernatant was filtrated isothermally with a syringe filter (450nm) before passing through an ultrafiltration (UF) membrane with a molecular weight cutoff (MWCO) of 3 KDa. Theoretically all the draw solute should be removed from the draw solution since only NaCl and water can pass through the UF membrane (actually conductivity contribution from trace amount of draw solute is negligible). The concentration was determined from its conductivity and the salt rejection was calculated from $R=1-(C_d/C_f)\cdot 100\%$, where C_d is the NaCl concentration in the draw solution, and C_f is the NaCl concentration in the feed solution.

For the FO process with the new membrane, the conductivity was 452.9 μS/cm and the NaCl concentration determined from Fig. S4 was 243.8 mg/l. For the membrane after 24 hours of immersion in a concentrated protonated draw solution, the conductivity was 431.1 μS/cm and the NaCl concentration was 232.1 mg/l. The small difference of ~10 mg/L might be measurement error. The salt rejection for both membranes was $R=1-(0.238/5.936)\cdot 100\%=96\%$, which is close to the 93%~95% salt rejection provided by the manufacturer of the membrane (HTI).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of	64.30619		
Pearson's r	0.99947		
Adj. R-Squar	0.99858		
		Value	Standard Erro
Conductivity	Intercept	1.99443	8.40667
	Slope	1.84927	0.0349

Fig. S4 Conductivity-concentration calibration curve for aqueous NaCl solutions.

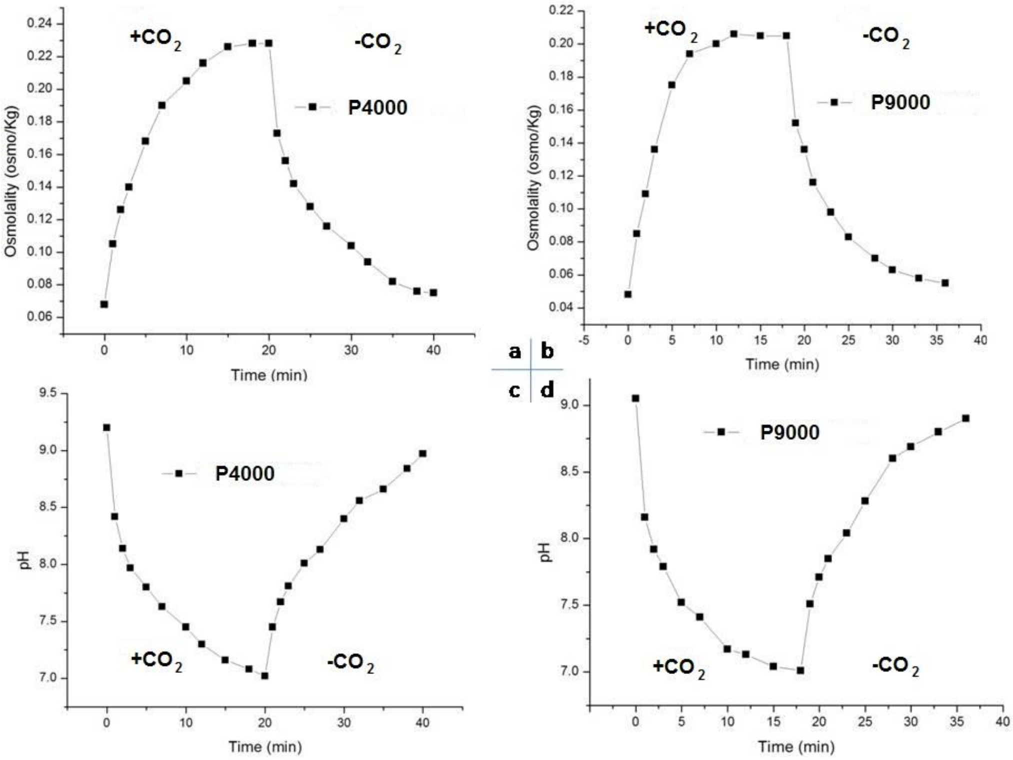


Fig. S5 Membrane protonation reversibility achieved by purging with carbon dioxide at 25°C and then by Ar at 60°C shown by osmolality (a,b) and pH (c,d) measurements. The gas flow rate was ~300 ml/min and the draw solution volume was 10ml with a concentration of 0.1 g/g.

Draw solute recovery and final water quality assessment: After the draw solutes were precipitated, the draw solute concentration in the supernatant (Fig.S6) was determined by conductivity measurement to be about 6 g/l and 9 g/l for P4000 and P9000, respectively. This means that more than 90% of the draw solute was precipitated. We further decreased the concentration by isothermally filtering the supernatant through a microfiltration (MF) membrane with a pore size of 450 nm in order to remove the agglomerated but unprecipitated clusters. The final water quality after UF was estimated by total organic carbon (TOC) measurement. The UF setup is shown in Fig. S7. Visual comparison of the diluted draw solution, supernatant and final water product is shown in Fig. S8.

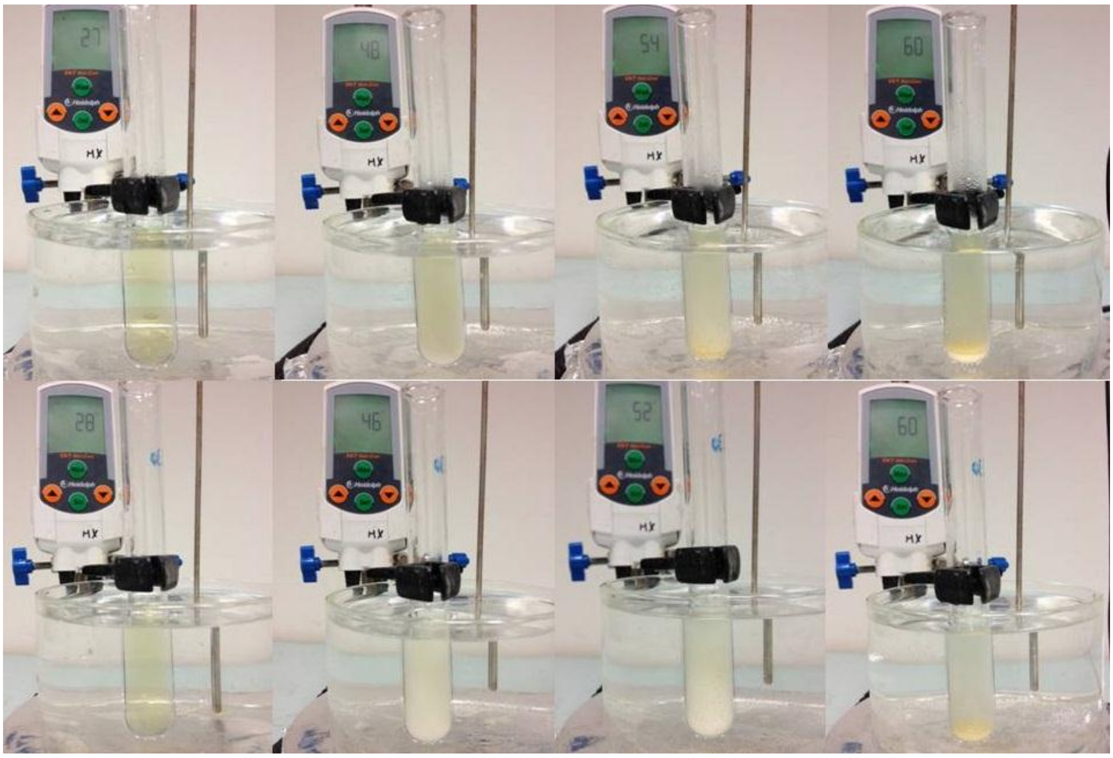


Fig. S6 Effect of increasing the temperature on the precipitation of the draw solutes. The temperature is increasing from left to right. The upper row is the P9000 and the bottom row is the P4000.

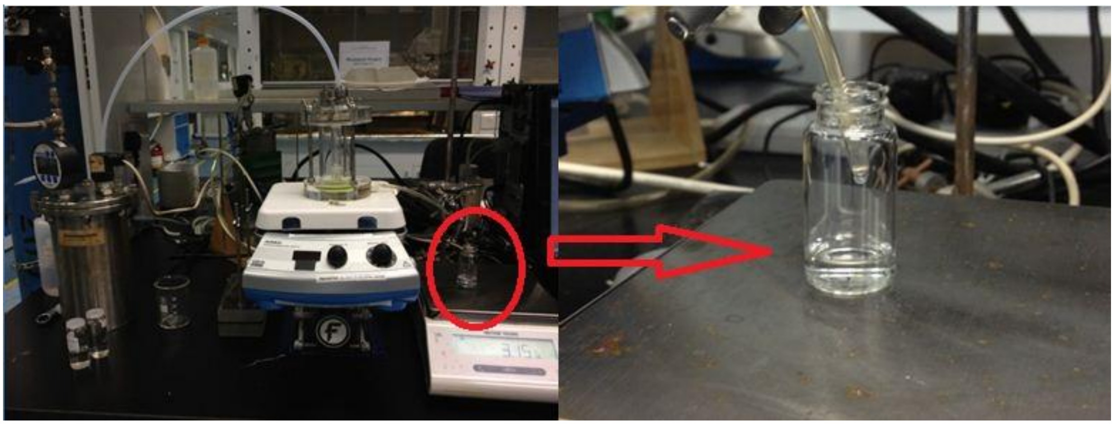


Fig. S7 The ultrafiltration setup

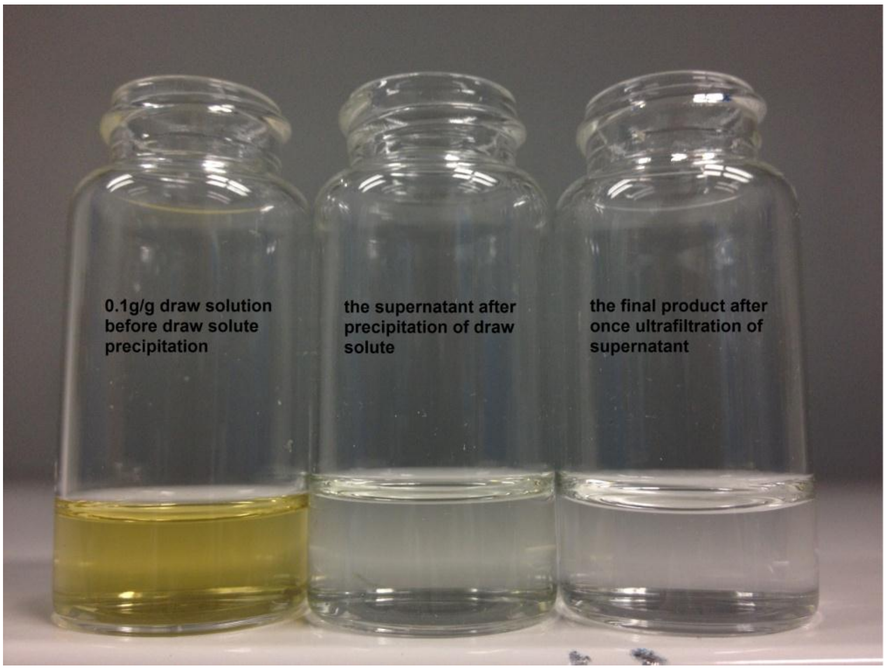


Fig. S8 (left) The draw solution of 0.1 g/g PDMAEMA(4000), (middle) the supernatant before microfiltration, and (right) the final product water.