

Cite this: *Chem. Commun.*, 2011, **47**, 1710–1712

www.rsc.org/chemcomm

## COMMUNICATION

## Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination†

Dan Li,<sup>a</sup> Xinyi Zhang,<sup>a</sup> Jianfeng Yao,<sup>a</sup> George P. Simon<sup>b</sup> and Huanting Wang<sup>\*a</sup>

Received 30th October 2010, Accepted 10th December 2010

DOI: 10.1039/c0cc04701e

**Ionic polymer hydrogels with thermal responsive units are found to induce higher water permeation rates in the osmosis process, and higher water release rates under a combination of pressure and thermal stimuli. These hydrogels have the potential for use as draw agent in forward osmosis desalination.**

Forward osmosis (FO) desalination processes have become a growing area of research because of the great potential for much lower energy desalination as compared with reverse osmosis (RO) desalination processes.<sup>1–4</sup> In the FO process, a draw solute of high osmotic pressure (compared to that of the saline water) passes across one side of the membrane, and saline water passes across the other side. Water permeates through the membrane from the saline water to the draw solute side due to the naturally-driven osmotic flow.<sup>2</sup> It is then necessary to regenerate the draw solute and remove the water transferred by the FO process. In principle, the FO process does not require high pressures for separation, and should be able to reduce energy for desalination towards the thermodynamic minimum.

In the FO process, draw agents must have a high osmotic pressure, but should also be able to release their water at a modest energy cost. A number of draw agents (chemicals) have been studied, such as ammonium carbonate (CO<sub>2</sub> and ammonia), sugar, and ethanol.<sup>2</sup> Ammonium carbonate has been considered to be a most promising draw agent for FO desalination because it has high osmotic pressure and can be regenerated by distillation at low temperature such as 60 °C.<sup>3</sup> However, it is desirable to explore other draw agents which enable us to win back the pure water at even lower temperatures, and thus at a lower energy cost.

Here we report our work on the development of polymer hydrogel particles as a new class of draw media. Hydrogels are

three-dimensional networks of polymer chains that are cross-linked by either physical or chemical bonds, and are able to entrap large volumes of water attracted by the high concentration of hydrophilic groups. In particular, hydrogels with ionic groups on the comonomer unit are able to attract even greater amounts of water, this increased osmotic pressure arising because the covalently-incorporated ionic groups are balanced by mobile counter ions, and these counter ions provide a positive osmotic pressure inside the hydrogel which drives greater water sorption. When a dehydrated or deswollen hydrogel uptakes water, its polymer chains extend, creating a swelling pressure. For example, weakly crosslinked poly(acrylic acid)/poly(sodium acrylate) copolymers with polymer volume fractions between 0.03 and 0.30 exhibit a swelling pressure ranging from 0.20–4.23 MPa.<sup>5</sup> In principle, the swelling pressure of polymer hydrogels can be even higher if strategically-designed polymer structures are employed. Therefore, polymer hydrogels have the potential to provide a sufficient driving force to draw saline water, including high-salinity seawater through the membrane (its osmotic pressure being 2.7 MPa or 27 bar at 27 °C).

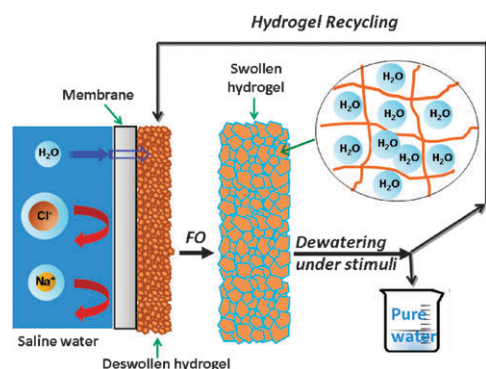
An important, advantageous aspect of such polymer hydrogels is that they can undergo reversible volume change or solution–gel phase transitions in response to environmental stimuli (this behavior causing them to be labeled ‘intelligent’ or ‘smart’ hydrogels). Many physical and chemical stimuli have been applied to induce various responses of such smart hydrogel systems, in particular to change them from hydrophilic to hydrophobic, thereby releasing water. These stimuli include: temperature, electric fields, solvent composition, light, pressure, sound and magnetic field, whilst the chemical or biochemical stimuli include pH, ions and specific molecular recognition events.<sup>6–9</sup> Such stimuli-responsive hydrogels have found many applications as biomaterials, drug delivery systems, porous materials, sensing materials and super water absorbents and size selective separation agents,<sup>10</sup> and as additives in controlling growth inorganic materials.<sup>11–13</sup>

It is anticipated that the use of fast stimuli-responsive polymer hydrogels as draw media would have a number of advantages during the water regain cycle. Using the type of stimuli mentioned above, it should be possible to release high-purity water, without degradation products such as currently occurs when thermally breaking down existing FO draw solutes, potentially allowing recovery of the draw agent at a

<sup>a</sup> Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia. E-mail: huanting.wang@monash.edu; Tel: +61 3 9908 3449

<sup>b</sup> Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia

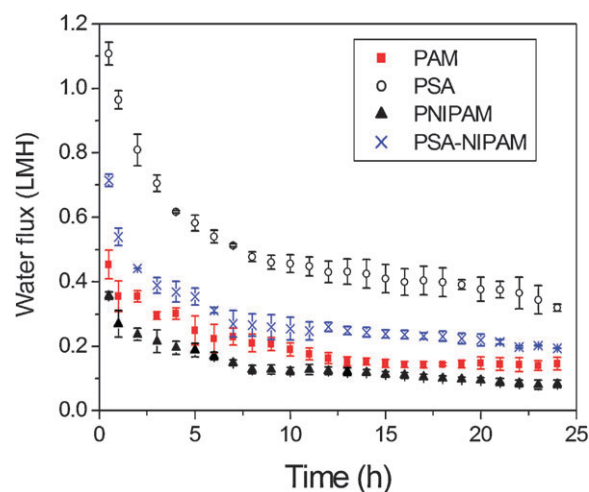
† Electronic supplementary information (ESI) available: Experimental (synthesis and characterization of hydrogels, testing of polymer hydrogels as draw agents in FO process, dewatering of deswollen polymer hydrogels), SEM images and FT-IR spectra of PAM, PSA, PNIPAN and PSA–NIPAM, and water recovery for swollen hydrogels (PAM, PSA, PNIPAM and PSA–NIPAM) with different water loadings at ambient temperature. See DOI: 10.1039/c0cc04701e



**Fig. 1** Schematic representation of the polymer hydrogel-forward osmosis desalination process. This process involves water permeation through a selective membrane driven by swelling pressure of deswollen polymer hydrogel (forward osmosis process) and dewatering of swollen polymer hydrogel under various stimuli conditions.

low energy cost. The use of polymer hydrogels as a draw agent in FO desalination is schematically illustrated in Fig. 1. Polymer hydrogels with a high swelling pressure drive water molecules to permeate through a selective membrane, whilst salt is rejected. These hydrogel particles can be designed to be amenable to rapid deswelling and water release under a range of stimuli. In this report, we demonstrate the dewatering of polymer hydrogels using hydraulic pressure alone, and a combination of hydraulic pressure and low temperature thermal processing.

In this work, four different types of polymer hydrogels were synthesized, including two ionic polymer hydrogels: poly(sodium acrylate, PSA) and (poly(sodium acrylate)-*co*-poly(*N*-isopropylacrylamide) with an equimolar NIPAM and SA, PSA–NIPAM); and two non-ionic hydrogels: poly(acrylamide), PAM) and poly(*N*-isopropylacrylamide), PNIPAM (see Experimental details in the ESI†). The purpose of choosing these four types of polymers is to study the effect of the charge density on the swelling pressure (*i.e.*, ability to withdraw water through the membrane) of polymer hydrogels, and the effect of thermal process on the dewatering of swollen polymer hydrogels. In particular, PNIPAM is a thermo-sensitive polymer, with its hydrogel showing a volume phase transition in water at its lower critical solution temperature (LCST), which occurs around 34 °C. At a temperature below its LCST, PNIPAM hydrogels absorb water and exist in a swollen state. Conversely, it experiences a dramatic shrinkage as the environmental temperature is raised to a temperature above LCST.<sup>14</sup> The chemical structures of as-synthesized polymers were confirmed by FT-IR, and their particles sizes are in the range of 50–150 μm (see SEM and FT-IR results in ESI†, Fig. S1 and S2). The forward osmosis permeation process was carried out at room temperature and used 2000 ppm NaCl as the feed saline water. It was found that hydrogels were able to cause the drawing of water through the membrane. The water flux induced by swelling of dry polymer hydrogels as a function of time is shown in Fig. 2. It can be seen that the PSA hydrogel with the highest charge density produced the highest water flux, whilst PSA–NIPAM hydrogel with a 50 mol% reduced charge induced a much lower flux (0.55 L m<sup>-2</sup> h<sup>-1</sup>). Non-ionic PAM and PNIPAM hydrogels produced yet lower fluxes than

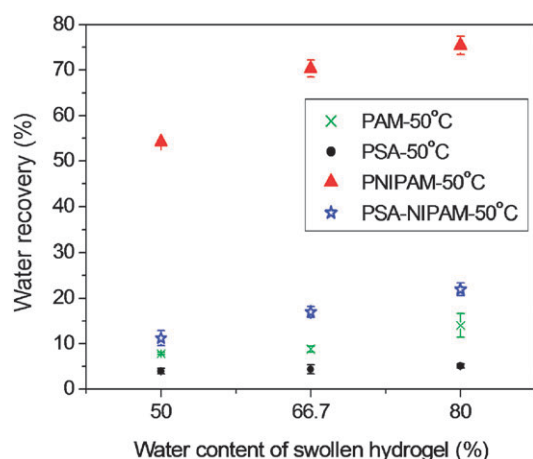


**Fig. 2** Water fluxes in the 24 h FO process using polymer hydrogels and 2000 ppm NaCl solution as feed.

PSA and PSA–NIPAM hydrogels. The water flux for all four types of hydrogels decreases with time. The average flux in the first hour was recorded at 0.96, 0.55, 0.36 and 0.30 L m<sup>-2</sup> h<sup>-1</sup> for PSA, PSA–NIPAM, PAM, and PNIPAM, respectively. After 24 h, the water content of swollen hydrogels reaches 73.1 ± 1.5%, 62.4 ± 1.2%, 53.4 ± 4.5%, and 42.2 ± 3.4% for PSA, PNIPAM–SA, PAM, and PNIPAM, respectively. The water absorption of polymer hydrogels largely depends on their swelling pressure (osmotic pressure), which is the key driving force in the FO process. As stated above, charged polymer hydrogels usually produce higher osmotic pressures (or higher degrees of swelling) than neutral hydrogels<sup>15</sup> and thus polymer hydrogels with the higher charged density provide a higher driving force in FO process. As the FO process proceeds, the swelling pressure of polymer hydrogels decreases with increasing their degree of swelling, resulting in the observed decrease in water flux.

The dewatering process is achieved *via* deswelling of polymer hydrogels, with release of water. The water recovery rate for swollen polymer hydrogels with different water contents after dewatering was determined based on hydrostatic pressure at different temperatures. When the dewatering was carried out at ambient temperature (see ESI†, Fig. S3), the water recovery rate slightly increased with increasing the water content of the hydrogels. For example, PSA sample with 50% water content releases 2.3% liquid after pressure dewatering, whilst the PSA sample with 80% water loading yielded 2.9% water. The overall water recovery rates appear to be quite low (less than 5%) for all four types of polymer hydrogels, and significant proportions of water remain within the hydrogel structure after the physical compression process. This may be because of strong molecular interaction between water and polymer chains, especially when there is a low water content (*e.g.* 50%) in hydrogels. This result indicates that short-time (2 minutes) room temperature pressure dewatering is not effective.

In contrast, as shown in Fig. 3, when the swollen hydrogel was dewatered under thermal (50 °C)-pressure condition, the water recovery rates were significantly increased. In addition, the water recovery rate of each type of hydrogel increased with increasing the water content, as was observed at room temperature.



**Fig. 3** Water recovery for swollen hydrogels (PAM, PSA, PNIPAM and PSA-NIPAM) with different water loadings after 2 min dewatering process at 50 °C.

Note that different temperature effects were observed for different types of polymer hydrogels. The water recovery rate of thermo-sensitive PNIPAM hydrogels increased from only 3–5% at room temperature to 54–75% at 50 °C. PSA–NIPAM swollen gel with 66.7% water releases no more than 3% of water at room temperature, whereas its water recovery rate is increased to over 17% at 50 °C. The increase of dewatering rate of PSA–NIPAM is higher than that of PSA and PAM, however, it remains less than that of PNIPAM.

The swollen hydrogels obtained after 24 h FO process were used to measure the water fluxes in the thermal-pressure dewatering process. The water fluxes were determined to be 74.2 LMH, 40.0 LMH, 36.8 LMH, and 27.7 LMH for PNIPAM–SA, PSA, PNIPAM, and PAM, respectively. By taking into account the water fluxes in the FO and dewatering processes, as well as the recovery rate, PSA–NIPAM appears to be the best choice compared with the other polymer hydrogels.

The dewatering process with a combination of hydraulic pressure and heating stimulates much greater water loss in the polymer hydrogels with NIPAM units, than those non-NIPAM polymer systems. This is because the NIPAM-containing hydrogels (*i.e.*, PSA–PNIPAM and PNIPAM) undergo significant physical structure change in response to temperature change. The thermoresponsiveness of PNIPAM in aqueous solution originates from the amphiphilic nature of the monomer unit itself,<sup>16–19</sup> which consists of hydrophilic  $-\text{C}=\text{O}$  and  $-\text{N}-\text{H}$  groups and hydrophobic hydrocarbon backbone and pendent isopropyl groups.<sup>20</sup> The H-bonding ability of  $-\text{C}=\text{O}$  and  $-\text{N}-\text{H}$  groups is instrumental in stabilizing a chain conformation of PNIPAM at a temperature below LCST, in which polymer–water interactions predominate over polymer–polymer interactions.<sup>16</sup> The destabilization of hydrogen bonds occurs between water molecules and amide groups with increasing temperature, likely induced by the presence of the hydrophobic isopropyl group and backbone.<sup>17–19</sup> This onset of the coil–globule transition with its attendant sudden deswelling occurs in close proximity to the LCST.<sup>21</sup> Note that that pure NIPAM gel containing no ionic SA groups undergoes a continuous volume change around 34.3 °C, whereas gels with ionic groups show discontinuous transitions.<sup>14</sup> The gel with a high ionic

concentration (*e.g.*, the ratio of NIPAM to SA < 4.5) may not shrink at less than 80 °C due to the presence of high ionic-based, osmotic pressure.<sup>14,22</sup> However, the exposed hydrophobic groups would tend to aggregate, forcing the polymer chains into a conformation in which polymer–polymer interactions dominate, despite no abruptness of the phase transition. Therefore our study demonstrates that the thermoresponsive NIPAM portion plays a significant role in promoting water release from swollen PSA–NIPAM hydrogels that are synthesized from equimolar amount of SA and NIPAM under the external pressure.

In summary we have demonstrated a new strategy of using polymer hydrogels as a draw agent in the forward osmosis process, and also shown that we can extract significant water from such a swollen hydrogel draw agent under optimized thermal-pressure conditions. Our results show that considering both the FO and dewatering processes, polymer hydrogels with ionic groups (such as PSA–NIPAM) are preferred for this new FO desalination application. It is believed that this work holds promise for further development as the swelling pressure and stimuli-responsive property of polymer hydrogels can be improved by optimizing polymer structures. Only thermal-pressure dewatering is shown here, however other methods may be explored to further improve dewatering efficiency through further functionalization of the hydrogel matrix, for example, using solar energy to initiate heating *via* light responsive moieties.

This work was supported by the Australian Research Council through discovery grants. J.Y. thanks Monash University for the Monash Fellowship.

## Notes and references

- 1 A. A. Burbano, S. S. Adham and W. R. Pearce, *J. Am. Water Works Assoc.*, 2007, **99**, 116.
- 2 T. Y. Cath, A. E. Childress and M. Elimelech, *J. Membr. Sci.*, 2006, **281**, 70.
- 3 R. L. McGinnis and M. Elimelech, *Desalination*, 2007, **207**, 370.
- 4 D. Li and H. T. Wang, *J. Mater. Chem.*, 2010, **20**, 4551.
- 5 H. Wack and M. Ulbricht, *Polymer*, 2009, **50**, 2075.
- 6 T. Tanaka, I. Nishio, S. T. Sun and S. Uenonishio, *Science*, 1982, **218**, 467.
- 7 T. Serizawa, K. Wakita and M. Akashi, *Macromolecules*, 2002, **35**, 10.
- 8 J. J. Litor-Santos, B. Sierra-Martin, R. Vavrin, Z. B. Hu, U. Gasser and A. Fernandez-Nieves, *Macromolecules*, 2009, **42**, 6225.
- 9 Y. Qiu and K. Park, *Adv. Drug Delivery Rev.*, 2001, **53**, 321.
- 10 K. L. Wang, J. H. Burban and E. L. Cussler, *Adv. Polym. Sci.*, 1993, **110**, 67.
- 11 H. T. Wang, B. A. Holmberg and Y. S. Yan, *J. Am. Chem. Soc.*, 2003, **125**, 9928.
- 12 J. F. Yao, D. Li, X. Y. Zhang, C. H. Kong, W. B. Yue, W. Z. Zhou and H. T. Wang, *Angew. Chem., Int. Ed.*, 2008, **47**, 8397.
- 13 L. Han, J. F. Yao, D. Li, J. Ho, X. Y. Zhang, C. H. Kong, Z. M. Zong, X. Y. Wei and H. T. Wang, *J. Mater. Chem.*, 2008, **18**, 3337.
- 14 S. Hirotsu, Y. Hirokawa and T. Tanaka, *J. Chem. Phys.*, 1987, **87**, 1392.
- 15 N. Kayaman, O. Okay and B. M. Baysal, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 1313.
- 16 D. Dhara and P. R. Chatterji, *Polymer*, 2000, **41**, 6133.
- 17 R. O. R. Costa and R. F. S. Freitas, *Polymer*, 2002, **43**, 5879.
- 18 F. Ilmain, T. Tanaka and E. Kokufuta, *Nature*, 1991, **349**, 400.
- 19 S. M. Cho and B. K. Kim, *J. Biomater. Sci., Polym. Ed.*, 2010, **21**, 1051.
- 20 H. Feil, Y. H. Bae, J. Feijen and S. W. Kim, *Macromolecules*, 1993, **26**, 2496.
- 21 Y. Hirose, T. Amiya, Y. Hirokawa and T. Tanaka, *Macromolecules*, 1987, **20**, 1342.
- 22 E. S. Matsuo and T. Tanaka, *J. Chem. Phys.*, 1988, **89**, 1695.