

# Thermoresponsive copolymer-based draw solution for seawater desalination in a combined process of forward osmosis and membrane distillation



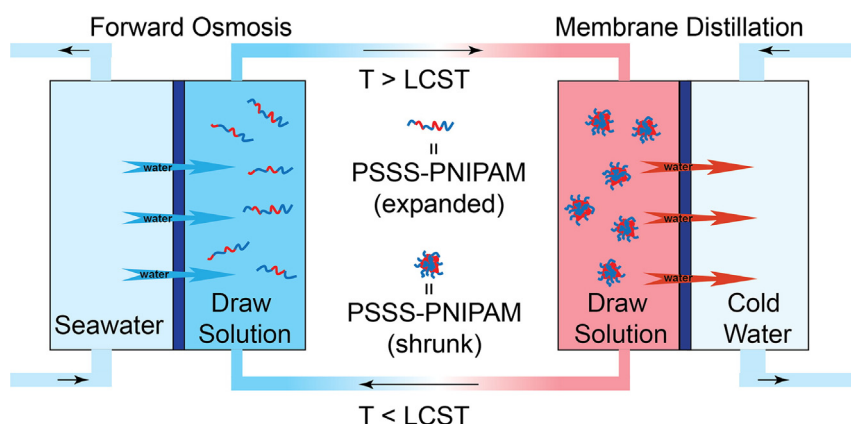
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## HIGHLIGHTS

- Thermoresponsive PSSS-PNIPAM is employed as FO draw solute for seawater desalination.
- The osmotic pressure of PSSS-PNIPAM solution can be thermally controlled.
- A water flux of 4 LMH is achieved in FO when seawater is used as the feed solution.
- The thermoresponsive behavior facilitates draw solution regeneration via MD.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A thermoresponsive copolymer, poly(sodium styrene-4-sulfonate-co-*n*-isopropylacrylamide) (PSSS-PNIPAM), is employed as a draw solute in forward osmosis (FO) for seawater desalination. When PSSS-PNIPAM is dissolved in water to form a draw solution, PSSS as a strong polyelectrolyte generates a high osmotic pressure and extracts water from seawater in an FO process. A water flux of 4 LMH has been attained with simulated seawater as the feed solution. The draw solution is then regenerated with membrane distillation (MD) at a temperature above the low critical solution temperature (LCST) of PNIPAM, which agglomerates and leads to decreased osmotic pressure of the solution and thus higher water vapor pressure. The combined FO-MD process with PSSS-PNIPAM as the draw solute should be promising not only for seawater desalination, but also for other membrane-involved separation processes in wastewater treatment and protein or medicine enrichment.

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## 1. Introduction

Clean water scarcity has long been a serious concern for many communities, and it will be aggravated due to the rapid growth of population. The desalination of seawater has been proposed as a solution to

this worldwide problem since seawater accounts more than 97% of the total water resource on earth. For decades, researchers have been looking for low-energy and highly efficient desalination techniques [1–8]. Among existing desalination methods, forward osmosis (FO, also known as direct osmosis) is an attractive and promising one [1–7, 9,10]. In an FO process, water in the feed solution at a lower osmotic pressure can pass spontaneously through a semipermeable membrane

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to the draw solution at a higher osmotic pressure. A subsequent regeneration process extracts water from the draw solution and re-concentrates the draw solution for reuse. Unlike reverse osmosis (RO), which requires a high hydraulic pressure to desalinate seawater, FO is driven by the difference in osmotic pressure between the feed and the draw solutions and eliminates the need for high hydraulic pressure. As an emerging membrane technology with low-energy consumption, FO is promising for wastewater treatment [11,12], desalination [13–18], protein concentration [19–21], power regeneration [22–24], and many other applications [25–29].

Research in FO has been mainly focused on both the fabrication of high-performance FO membranes [23,30–39] and the development of efficient draw solutions [40,41]. An ideal FO draw solution should meet three general requirements, namely, high osmotic pressure for high water flux, facile regeneration method for low-energy consumption, and minimum reverse solute flux for low replenishment cost [40, 41]. Conventional draw solutions based on inorganic salts such as NaCl, MgCl<sub>2</sub>, and NH<sub>4</sub>HCO<sub>3</sub> can generate high water flux, but the corresponding reserve flux of solute is also high, thus affecting the product quality and increasing the replenishment cost [17,42]. In addition, there is a lack of an efficient method to produce clean water from these draw solutions. Most recently, a number of novel draw solutions have been proposed [12–15,43–51]. Polyelectrolytes such as sodium polyacrylate (PAA-Na) have been investigated as FO draw solutes by Ge and coworkers [43]. This type of draw solute with relatively high molecular weight can reduce reverse flux. Ultrafiltration (UF) and membrane distillation (MD) are promising for the regeneration of polyelectrolyte-based draw solutions [11,43]. Draw solutes based on thermoresponsive compounds have also attracted increasing attention because of their unique response to temperature [45,46,52]. For instance, *n*-acylated polyethylenimine derivatives are soluble in water below their lower critical solution temperature (LCST), but phase separation occurs when the temperature is increased above the LCST [46]. Using this type of thermoresponsive draw solute, Lee et al. demonstrated temperature-induced reversible water flux between the draw and the feed solutions. Ling et al. [45] employed thermoresponsive poly(*n*-isopropylacrylamide) (PNIPAM) to functionalize magnetic nanoparticles (MNPs). The resultant PNIPAM-capped MNPs may agglomerate to larger sizes when heated up to the LCST of PNIPAM. Therefore, when the thermoresponsive MNPs are used as the draw solute, the regeneration of draw solution can be achieved efficiently by applying a magnetic field. As another example, Wang et al. [15,53] also evaluated stimuli-responsive polymer hydrogels as FO draw solutes and investigated the effects of hydrogel size on the performance of FO and dewatering process.

Despite the recent progress, it remains a challenging task to employ thermoresponsive materials as draw solutes to desalinate seawater. This is because the osmotic pressure of a thermoresponsive polymer solution is generally not high enough to counteract that of seawater. Here, we present a study on a thermoresponsive copolymer, poly(sodium styrene-4-sulfonate-co-*n*-isopropylacrylamide) (PSSS-PNIPAM), as an FO draw solute for seawater desalination in a process combined with forward osmosis and membrane distillation (FO-MD). The purpose of using PSSS-PNIPAM as the draw solute is twofold: (i) PSSS is a strong polyelectrolyte which can provide a large number of ions in aqueous solution and thus a high osmotic pressure, and (ii) PNIPAM may facilitate the regeneration of the draw solution based on its thermoresponsive property. In our study, FO desalination is performed at room temperature, which is below the LCST of the polymer. Therefore, the polymer chains are fully expanded in the FO draw solution to provide maximum osmotic pressure. After drawing water from seawater, the polymer solution is re-concentrated by MD to produce clean water and to regenerate the draw solution. Because MD is performed at a temperature (50 °C) above the LCST of the copolymer, the osmotic pressure of the draw solution drops due to the agglomeration of the polymer chains. Lower osmotic pressure leads to a higher effective water vapor pressure, which facilitates the separation

of water from the solution [54]. Although MD may be applied for the desalination of seawater directly, NaCl crystals and liquid water can penetrate into the membrane pores and cause serious membrane fouling and pore wetting problems. Therefore, the FO-MD hybrid seawater desalination process with thermoresponsive PSSS-PNIPAM as the draw solute has the potential to achieve high product quality, long operational time and low cost.

## 2. Materials and methods

### 2.1. Materials

*n*-Isopropylacrylamide (NIPAM, >97%), sodium-4-styrenesulfonate (SSS, >90%), 4,4'-azobis(4-cyanovaleric acid) (ACVA, >98%), dimethyl sulfoxide (DMSO), and sodium chloride (>99.5%) were purchased from Sigma-Aldrich and used as received. Deionized (DI) water with a resistivity of 18 MΩ·cm was obtained with a Milli-Q unit (Millipore, USA). Thin film composite (TFC) forward osmosis membrane was provided by Hydration Technologies Inc. (HTI Albany, OR).

### 2.2. Preparation and characterization of PSSS-PNIPAM

The copolymer PSSS-PNIPAM was synthesized based on an adaptation of the approach reported by Grebosz et al. [55] (Fig. 1). Briefly, SSS and NIPAM with designated feeding ratio (Table 1) were charged into a three-neck flask loaded with 120 mL of DMSO. The mixture was degassed for 20 min by bubbling N<sub>2</sub> to remove O<sub>2</sub>. After degassing, it was heated up to 80 °C, followed by the injection of ACVA. The reaction was allowed to proceed at 80 °C for 24 h under the protection of N<sub>2</sub>. After cooling down to room temperature, the copolymer was precipitated by adding acetone and washed with acetone for three times. The resulting product was dissolved in water and purified by dialysis membranes with a molecular weight cutoff of 3500 (slide-A-lyzer dialysis cassette G2, Thermo Fisher). Finally, the copolymer was dried under vacuum. PSSS-PNIPAM copolymers with 5, 10, 15, and 20 wt% of SSS were prepared and denoted as 5SN, 10SN, 15SN, and 20SN, respectively. The relative viscosities ( $\eta_r$ , compared to DI water) of the copolymer solutions at different concentrations were calculated with the following equation:

$$\eta_r = \eta/\eta_0 = (t\rho)/(t_0\rho_0)$$

where  $t$  and  $t_0$  (s) are the respective elution times of 15SN solution and DI water measured by an AVS 360 inherent viscosity meter, and  $\rho$  and  $\rho_0$  (g mL<sup>-1</sup>) are the densities of 15SN solution and DI water, respectively.

Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad spectrometer (Excalibur series, FTS3500). The molecular weight of the copolymer was measured by gel permeation chromatography (Waters GPC system) equipped with a Waters 1515 isocratic HPLC pump, a Waters 717 plus Autosampler injector, a Waters 2414 refractive index detector, and an Agilent PLgel 5 μm mixed-D column (Cat. No. 79911GP-MXD), using DMF as the eluent at 30 °C and at a flow rate of 1.0 mL min<sup>-1</sup>.

### 2.3. Characterization of thermoresponsive property

The low critical solution temperatures (LCSTs) of the solutions containing 33.3 wt% of 5SN, 10SN, 15SN, and 20SN, respectively, were measured by a UV-Vis spectrophotometer (SHIMADZU, UV-3600). Transmittance at a wavelength of 500 nm was measured as the temperature was increased and stabilized for 5 min for each data point. The LCST is defined as the temperature at which the transmittance is below 5%. The osmolality of the copolymer solution was measured with an osmometer (Wescor, VAPRO vapor pressure osmometer). Typically, 10 μL of the solution was dropped on a small piece of filter paper (6.5 mm in diameter). By measuring the vapor pressure at room temperature in natural equilibrium, the osmolality of the solution was determined.

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