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Thermo-responsive oligomeric poly(tetrabutylphosphonium styrenesulfonate)s as draw solutes for forward osmosis (FO) applications

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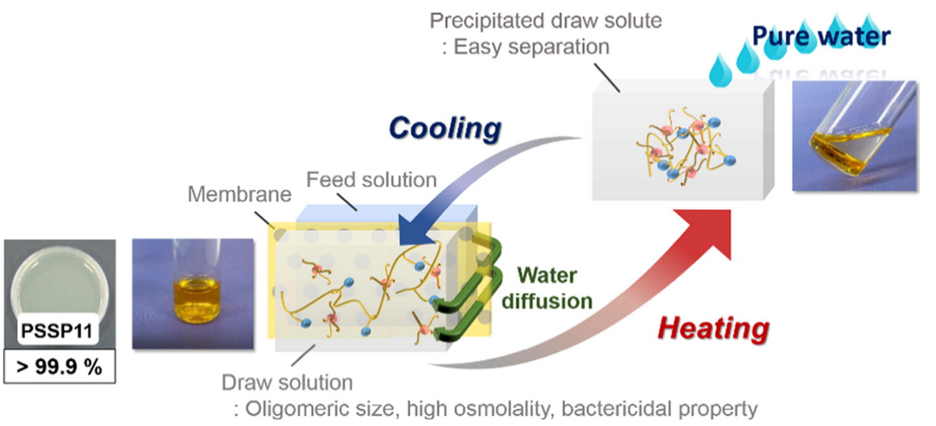
HIGHLIGHTS

- A PSSP# series was prepared as oligomeric draw solutes for forward osmosis (FO).
- The effect of molecular weight on FO properties was studied systematically.
- PSSP# was separated from the solution with the formation of a hydrated gel.
- Water permeation flux was maintained after recycling the draw solute.
- The PSSP# efficiently inhibit the bacterial growth.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of oligomeric poly(tetrabutylphosphonium styrenesulfonate)s (PSSP#, where # is the number of monomer units in the oligomer) were prepared from tetrabutylphosphonium styrenesulfonate (SSP) as a monomer for application as a draw solute in a forward osmosis (FO) system. Although the water permeation flux values in the FO system using the oligomeric PSSP as a draw solute were slightly smaller than those using the monomeric SSP, the reverse solute flux values using the PSSPs were found to be much smaller than those using the SSP, indicating that the oligomers are more efficient draw solute materials in the FO system than the low molecular weight monomer. For example, when 20 wt.% of the PSSP5 aqueous solution is used as the draw solution, the water permeation flux and reverse solute flux values are 14.50 LMH and 0.14 gMH, respectively, and when 20 wt.% of the SSP aqueous solution is used, they are 16.28 LMH and 0.53 gMH, respectively. Since PSSPs have a lower critical solution temperature (LCST), the PSSP in water could be simply separated by heating to above the LCST without any other separation process. Moreover, it was found that the PSSPs have excellent bactericidal property above 99.9% against *Escherichia coli* (ATCC 8739).

1. Introduction

Water scarcity has emerged recently as a global problem due to the increasing demand for fresh water as a result of the increasing global population, water pollution, and climate change [1,2]. A number of studies have focused on water treatment technologies to alleviate the water shortage problem and also to improve the quality of treated [3–6].

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Among the water treatment technologies, the forward osmosis (FO) system has drawn much attention due to the advantages in energy consumption. In the FO system, the high osmotic pressure between the feed and draw solutions is used to induce the diffusion of water molecule through a semi-permeable membrane from the feed to the draw solution [7]. Therefore, the FO system has been studied intensively in various applications such as desalination [8], wastewater treatment [9], food processing [10], protein concentration [11,12], energy production [13], and so on [1]. However, the practical application of the FO system has been limited because of the remaining obstacles such as the absence of both adequate draw solute systems and efficient membranes [14]. Many studies have focused on the exploration of proper draw solutes that demonstrate several characteristics such as high water solubility, high osmotic pressure, high water permeation flux, low reverse solute flux, and efficient recovery [15]. For example, sugars [16,17], organic and inorganic salts [18,19], hydrogels [20,21], polyelectrolytes [22–25], magnetic nanoparticles [26–28], metal–acid complexes [29,30], and carbon quantum dots [31] were studied as draw solutes, while the task of the development of draw solute systems that have both high FO performances and recovery efficiency still needs to be carried out [2,14].

Recently, thermal treatment for recovery in the FO system has received growing attentions as an effective recovery method for draw solutes because the waste heat and/or geothermal heat can be used as the heat source [32]. If polymers having lower critical solution temperature (LCST) are used as the draw solute, the polymers in the draw solution could be separated easily by heating them to above their LCST followed by a membrane filtration process [33–37]. These polymers could be prepared by the copolymerization of thermo-responsive monomers, such as *N*-isopropylacrylamide and di(ethylene glycol)methyl methacrylate, with ionic monomers such as sodium styrene-4-sulfonate, sodium acrylate, and [2-(methacryloyloxy)ethyl]-trimethylammonium chloride. The draw solutions of the resulting polymers obtained with the copolymerization showed reasonable water permeation flux and the purified water and the polymers could be separated using the membrane filtration method as reported by the authors and by others [24,32,33,37]. Still the FO water permeation flux values of these systems are not high enough for practical application because of the presence of nonionic thermo-responsive moieties and high molecular weights of the copolymers [24,33].

As a continuous effort to develop the thermo-responsive polymers for the draw solute, thermo-responsive oligomeric poly(tetrabutylphosphonium styrenesulfonate) (PSSP#) was prepared in this study because other poly(styrenesulfonate) derivatives were known to have the LCST in a very narrow range as reported by Kohno et al. [38–40]. The effect of molecular weight of the PSSP on the osmotic pressure, water permeation flux, reverse solute flux, and LCST behavior was systematically observed here. Recovery of the draw solute from the solution could be simply achieved by mild heating at 60 °C followed by separating the supernatant liquid from the precipitated polymer without any membrane process. In addition, the PSSP solutions showed a bactericidal property, and the possible biofilm formation that decreases the membrane performance [41] then could be minimized.

2. Material and methods

2.1. Materials

Tetrabutylphosphonium bromide (98%), deionized water (for TOC analysis), and methyl orange (85%) were purchased from Sigma-Aldrich Co., LLC. and used as received without further purification. Sodium *p*-styrenesulfonate hydrate (93%) was purchased from Tokyo Chemical Industry Co., LTD. and used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from Junsei Chemical Co., Ltd. and purified by recrystallization from ethanol. *n*-Hexane (95%), diethyl ether, and sodium chloride (NaCl, 99.5%) were purchased from Daejung Chemicals & Metals Co., LTD. and used as received. Ethanol was purchased from Hayman Chemical Co. and dried over a molecular sieve (4 Å). The dialysis membrane was purchased from Membrane Filtration Products, Inc. having 1000 Da of the nominal molecular weight cut off (MWCO). *Escherichia coli* (*E. coli*; ATCC 8739) were obtained from the American Type Culture Collection (ATCC). Bacto™ Agar and Difco™ Nutrient Broth were obtained from Becton, Dickinson and Company (BD). Other reagents were used as received.

2.2. Synthesis of tetrabutylphosphonium styrenesulfonate (SSP)

Tetrabutylphosphonium styrenesulfonate (SSP) was synthesized according to the reported procedures, as shown in Fig. 1 [39]. Sodium *p*-sytrenesulfonate hydrate (1.68 g, 8 mmol) and tetrabutylphosphonium bromide (4.00 g, 12 mmol) were dissolved in deionized water (10 mL) in a 100-mL round bottom flask containing a magnetic stir bar. After stirring at room temperature for 1 h, the product was extracted with dichloromethane three times, followed by drying over anhydrous magnesium sulfate. The solution was then concentrated using a rotary evaporator to obtain an oily liquid product. ^{1}H NMR of SSP [400 MHz, D_2O, δ/ppm]: 0.92 (t, 12 H, $P{-}(CH_2{-}CH_2{-}CH_2{-}\mathit{CH}_3)_4$), 1.35–1.41 (m, 16 H, $P{-}(CH_2{-}\mathit{CH}_2{-}\mathit{CH}_2{-}CH_3)_4$), 2.00–2.08 (m, 8 H, $P{-}(\mathit{CH}_2{-}CH_2{-}CH_2{-}CH_3)_4$), 5.45 (d, 1 H, $\mathit{CH}_2{=}CH{-}Ph$), 5.93 (d, 1 H, $\mathit{CH}_2{=}CH{-}Ph$), 6.83 (t, 1 H, $CH_2{=}\mathit{CH}{-}Ph$), 7.62 (d, 2 H, $CH_2{=}CH{-}\mathit{Ph}$), and 7.78 (d, 2 H, $CH_2{=}CH{-}\mathit{Ph}$).

2.3. Synthesis of oligomeric poly(tetrabutylphosphonium styrenesulfonate) (PSSP#)

A series of oligomeric poly(tetrabutylphosphonium sytrenesulfonate) (PSSP#, where # is the number of repeat units) was synthesized by varying the amount of initiator, AIBN as follows. SSP (3.0 g, 6.78 mmol) and AIBN (0.011 g, 0.07 mmol) were dissolved in ethanol (11.41 mL) in a 100-mL dried Schlenk flask containing a magnetic stir bar. The flask was sealed with a septum and deoxygenated with nitrogen for 1 h. The flask was then placed in an oil bath controlled at 60 °C and stirred with a magnetic bar for 3 h. After removing the solvent by vacuum evaporation, the polymer was dissolved in 5 mL of chloroform and precipitated in *n*-hexane three times. The resulting polymer was dialyzed against deionized water using dialysis membranes (MWCO = 1000 Da) for 3 days. After evaporating the deionized water, the product was dried under vacuum at room temperature. The molecular weight of this product was measured using a matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry found to be about 4700 Da, and it corresponds to the number of repeating units of 10.69. To distinguish this product with other PSSP having different molecular weights, it was named PSSP11, where '11' indicates the approximate number of the monomeric unit in the oligomer. Other oligomeric PSSPs were also prepared using the same procedure except for the amount of the initiator. For example, when 0.055 g (0.34 mmol) and 0.22 g (1.36 mmol) of AIBN was used, the molecular weights of the resulting product measured using MALDI-TOF mass spectrometry were found to be 2600 and 2100 Da, respectively, and they were named PSSP6 and PSSP5 because their molecular weight corresponds to 5.84 and 4.84 monomeric units, respectively. ^{1}H NMR of PSSP11 [400 MHz, D_2O, δ/ppm]: 0.82 (t, 12 H, $P{-}(CH_2{-}CH_2{-}CH_2{-}\mathit{CH}_3)_4$), 1.35–1.41 (m, 16 H, $P{-}(CH_2{-}\mathit{CH}_2{-}\mathit{CH}_2{-}CH_3)_4$), 2.00–2.08 (m, 8 H, $P{-}(\mathit{CH}_2{-}CH_2{-}CH_2{-}CH_3)_4$), 6.18–6.90 (s, 2 H, $CH_2{-}CH{-}\mathit{Ph}{-}SO_3$), 7.30–7.88 (s, 2 H, $CH_2{-}CH{-}\mathit{Ph}{-}SO_3$).

2.4. Characterization

The molecular weights were obtained using MALDI-TOF mass spectrometry (AB SCIEX TOF/TOF™ 5800 System, Applied Biosystems, USA) with a linear detector. The osmolality values of the PSSP series were obtained by measuring the freezing point depression using a semi-micro osmometer (K-7400, KNAUER, Germany). The osmolality values were