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Highly efficient antifouling coating of star-shaped block copolymers with variable sizes of hydrophobic cores and charge-neutral hydrophilic arms

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ABSTRACT

Star-shaped block copolymers (SPs) have shown promises as an antifouling coating material on the water purification membranes. The unique architectural design of these SPs, composed of covalently linked hydrophobic core and hydrophilic arms, offers the flexibility of tailoring the core and/or arm compositions to achieve properties on demand. Here, three different sizes of SPs with increasingly hydrophobic polystyrene cores (PSCs) and longer hydrophilic polyethylene glycol (PEG) arm were synthesized to evaluate their coatability on polysulfone ultrafiltration (PSF UF) membranes based on an increasingly higher degree of hydrophobic interaction, and to study the effect of the hydrophilic PEG arm lengths on the antifouling properties of the SPs coated membranes. The oleophobicity measured from the under-water hexadecane contact angle (CA) of SPs coated membranes increased by about 3 times leading to 6-7 times improvement in permeation flux during oil emulsion filtration. No flux recovery was observed for the pristine PSF membrane, which is in sharp contrast to the 100% flux recovery ratio (FRR) achieved for SPs coated membranes. The filtration of bovine serum albumin (BSA) protein solution exhibited an improvement in the permeation flux by 2.7-8.9 times for SPs coated membranes. The FRR was only 64% for the pristine PSF membrane, as opposed to about 100% FRR for all 3 SPs coated membranes. Finally, the stability of the SPs coating was tested by rigorous washing with Tween 80 surfactant and 3 cycles oil emulsion filtrations. Surfactant washing only removed the loosely bound extra layers of SPs coating, leaving the surface-bound and pore entrapped stable SPs coating with remarkable antifouling properties. Overall, SPs with larger hydrophobic PSCs and lower arm density were found to be more effective for coating stability, and the ones with longer PEG arms were more efficient in fouling mitigation. The largest size SP3 with the longest PEG arm was found to be the optimum antifouling coating.

1. Introduction

Wastewater treatment is the forefront of research for decades, and new developments are frequently emerging due to the growing concern on environmental pollution imposed by the rapid industrialization and household activities associated with an increasing population and their luxurious lifestyle.^{1–4} Membrane technology is considered as a feasible and efficient technology

for the treatment of wastewater yielding high quality water.^{1,5–7} However, the long-term operation of membrane technology is impeded by fouling; a phenomenon that reduces the water permeation through the membrane due to the accumulation of pollutants on the surface and within the pores of the membrane.^{8–11} The fouling can be mitigated by incorporating hydrophilic materials on the membrane surface or into the polymer blend used to fabricate the membrane via phase inversion method.^{12–21} Membrane surface modification is the viable process for enhancement of antifouling property since it can be applied on existing highly optimized and subtly devised commercially available membranes.^{22,23}

In the quest of the development of membrane surface modification techniques, a host of physical and chemical modification processes have been explored, out of which physical modification, especially preadoption of a hydrophilic material on the membrane surface, is found to be more efficient, and technologically and/or economically feasible.^{23–26} Chemical grafting of hydrophilic polymers suffers from many inherent limitations, including incomplete surface coverage, limited compatibility of the membrane with many chemicals used in grafting reactions, requirements for expensive and/or destructive membrane pre-activation process, and alteration of membrane permeation properties if the chemical grafting reactions are not properly controlled.²² In contrast, physical coating processes offer superior control over membranes' antifouling properties without adversely affecting the permeation properties if the coating materials are carefully designed.^{22,23} Commonly used coating materials include linear polyelectrolytes^{20,27–30}; however, numerous limitations of polyelectrolyte-based coatings have led to the exploration of the various smart architectural design of coating materials that include hyperbranched polyelectrolytes,^{31,32} charged inorganic nanomaterials,^{33–39} carbon nanotubes,⁴⁰ and graphene oxides.^{41–44} Despite achieving promising results in terms of fouling-resistance, these developments could not overcome many of the limitations related to the stability of the coatings, necessities for membrane pre-activations, and increase in the membrane surface roughness via agglomeration of coating materials.²²

Recently, a new type of antifouling material, the star-shaped block copolymers (SPs) was introduced for membrane modification processes.^{22,45} The SPs were coated on commercial PSF membrane using layer-by-layer (LbL) self-assembly method, and the modified membrane exhibited high antifouling properties against model wastewater pollutants, including dyes, oil emulsion, BSA, and humic acid. The architectural design that featured the superiority of these SPs over many other coating materials in many aspects is the flexible nature of the core crosslinked arms of block copolymers consisting of hydrophobic PS and hydrophilic cationic blocks facilitating the alignment of hydrophobic PS segments on the hydrophobic membrane surface via presumably resembling the structure of a jellyfish. The proper alignment of SPs, via hydrophobic interaction, followed by the electrostatic interaction of the cationic arms on the SPs with the negatively charged membrane surface provides superior stability. Meanwhile, a high density of charged segments of hydrophilic arms per SP permits high antifouling properties from a thin layer of SPs coating on the membrane with minimal losses in its water permeation properties. In the previous studies on SPs coatings, the first monolayer coating was comprised of SPs bearing cationic segments (e.g., amine groups) in the hydrophilic arms, which gave additional stability of the coating along with the hydrophobic interaction of the PS cores. It should be noted that the monolayer coating of amine-containing SPs is not suitable to provide appreciable antifouling properties since the positive charges can rather attract the abundant negatively charged foulants and the oil emulsions present in wastewater. Therefore, SPs with versatile charge-neutral hydrophilic (e.g., PEG) arms could be very promising as antifouling materials irrespective of the nature of the charges on the foulants. However, the coating stability of these types of SPs yet to be

explored. The question that arises here is whether the electrostatic interaction of the SPs with membrane surface is necessary for coating stability, particularly when the architecture of the SPs offers the flexibility of tuning its structure to achieve high coating stability. We hypothesize that increasing the length and/or the number of hydrophobic PS arms used to build crosslinked PSCs should provide large-area alignment on the hydrophobic membrane surface (e.g., PSF), and the corresponding long-range hydrophobic interaction should be strong enough for the stability of the coating. It is also well-known that the larger sizes of any polymeric or nanomaterials, the poorer their dispersibility in the respective solvents. Therefore, it will be increasingly difficult to delaminate the larger sizes SPs from the surface. In addition to the enhanced stability provided by the larger hydrophobic PS core, we also hypothesize that the longer hydrophilic barrier to hydrophobic foulants preventing their approach to the membrane surface since the hydrophilic arms are extended outwards underwater.

To examine the hypotheses stated above, three different SPs (labeled as SP1, SP2, and SP3, respectively) having variable core sizes, arm numbers, and arm lengths were synthesized by a combination of anionic and atom transfer radical polymerization (ATRP) adapting the procedures from our previously published papers.^{46,47} The charge-neutral PEG was chosen as the hydrophilic arm of the SPs to evaluate the coatability of the SPs on the hydrophobic membrane surface via only hydrophobic interaction of the PSC. Charge neutral PEG is considered as a versatile antifouling material against membrane foulants irrespective of the nature of the charge the foulants are bearing.⁴⁸ It also prevents nonspecific binding of biomolecules (e.g., proteins) on solid surfaces.^{49–52} In particular, the PEG arms grafted from the SPs are of branched structure that is expected to block the access of foulants to the membrane surface more effectively than linear PEG

arms. The synthesized SPs were thoroughly characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy, gel-permeation chromatography (GPC), dynamic light scattering (DLS), bright-field scanning transmission electron microscopy (BF-STEM), and atomic force microscopy (AFM) phase mode imaging to evaluate their structural composition, molecular weight, sizes, self-assembly and extent of hydrophilicity. Afterward, the coatability of the SPs on the PSF membrane was studied, and the corresponding antifouling properties of the SPs coated membranes were evaluated from the under-water oleophobicity and filtration performance against a model organic foulant (e.g., hexadecane oil), and a model bio-foulant (e.g., BSA). Finally, the coating stability was evaluated by rigorous surfactant washing followed by scanning electron microscopy (SEM), AFM, and under-water oil contact angle analysis as well as 3-cycle filtration of hexadecane oil-in-water emulsions.

2. Experimental

2.1. Materials and general methods

3-chloro-1-propanol (98%), tert-butyldimethylsilyl chloride (TBDMSCl, reagent grade, 97%), triethylamine, (TEA, \geq 99.5%), 4-(dimethylamino)pyridine (DMAP \geq 99%), lithium granules (99% tracemetals), p-divinylbenzene (p-DVB, 85%), tetrahydrofuran, (THF, anhydrous, \geq 99.9%, inhibitor-free), tetrabutylammonium fluoride (TBAF solution 1.0 M in THF), 2-bromoisobutyryl bromide (BIBB, 98%), poly(ethylene glycol) methacrylate (PEGMA, average Mn 360, contains 500-800 ppm monomethyl ether hydroquinone, MEHQ, as inhibitor), copper(I) chloride anhydrous, (beads, \geq 99.99% trace metals), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), hydroquinone (ReagentPlus®, 99%), anhydrous dichloromethane (DCM), cyclohexane (anhydrous, 99.5%), chloroform-d (99.8 atom % D), diethyl ether anhydrous, (ACS reagent, \geq 99.0%, contains butylated hydroxytoluene, BHT, as inhibitor), methanol, (for HPLC, \geq 99.9%), 2-propanol (ACS reagent, \geq 99.5%), anisole, hexanes, and acetone were purchased from Sigma Aldrich and used as received. Diphenylacetic acid (99%) was purchased from Sigma Aldrich and recrystallized from boiling benzene before use. Styrene (ReagentPlus[®], 99.9%) was purchased from Sigma Aldrich and passed though aluminum oxide (activated, neutral, Brockmann I) before use. PSF UF membranes of (20 kD molecular weight cut-off (MWCO) with polypropylene backing were kindly provided by Solecta Membranes (Oceanside, CA, USA) and were used to study the effect of SPs coating on the antifouling properties. Oil emulsion was prepared by n-hexadecane, (99%, pure, Fisher Scientific, Canada), and Tween 80 surfactant (Bio-Rad, Hercules, CA, USA). All other reagents and solvents were ACS reagent grade. DI water was used throughout the study. 1 H NMR (Varian 600MHz) in chloroform-d and gel-permeation chromatography (GPC, Malvern HT-GPC with RI, light scattering and viscometer detectors; polystyrene standard) in THF were used as the primary characterization techniques to evaluate the success of each step of the synthesis PSCs.

2.2. Synthesis of protected 1-(tert-butyldimethylsilyloxy)-3- chloropropane precursor as the organolithium initiator for anionic polymerization

1-(tert-butyldimethylsilyloxy)-3- chloropropane was prepared by silyl protection of the propanol group. Briefly, 4.4 mL (*ca.* 52.9 mmol) of 3-chloro-1-propanol was mixed with 175 mL DCM in 500 mL round bottom flask sealed with a rubber septum and equipped with a Teflon coated stir bar. 8.7 mL (*ca.* 62.5 mmol) of triethylamine was then added to this mixture after cooling it down to 0°C under nitrogen atmosphere. Next, 100 mg (0.82 mmol) of DMAP catalyst dissolved in 5 mL DCM and 7.97 g (*ca.* 52.9 mmol) of TBDMSCl dissolved in 20 mL DCM were added to the

flask. The reaction mixture was stirred at 350 rpm at room temperature for 24 hours. DCM was removed by rotatory evaporation. After that, 100 ml of distilled water was added to the residue, and the 1-(tert-butyldimethylsilyloxy)-3-chloropropane was extracted with ethylacetate using a separatory funnel, washed with brine solution, and dried with sodium sulfate. Finally, the 1-(tert-butyldimethylsilyloxy)-3-chloropropane was purified by silica gel flash chromatography using hexane as eluant, which after rotatory evaporation gave 6.16 g (29.5 mmol) product colorless liquid (purified yield 56%). ¹H NMR (600 MHz, CDCl₃, δ) = 3.75 (t, 2H, J = 5.7), 3.65 (t, 2H, J = 6.4), 1.95 (p, 2H, J = 6.2), 0.90 (s, 9H), 0.06 (s, 6H).



Scheme 1. Synthesis of protected 1-(tert-butyldimethylsilyloxy)-3- chloropropane.

2.3. Synthesis of protected 3-(tert-butyldimethylsilyloxy)-1-propyllithium initiator for anionic polymerization

Protected 3-(tert-butyldimethylsilyloxy)-1-propyllithium was prepared by lithiation at the propyl chloride group. Lithium granules (8.21 g, 2.33 mol) was placed in a rubber 250 mL two neck round bottom flask equipped with a Teflon coated stir bar under argon atmosphere, and 128 mL of anhydrous cyclohexane was added by a syringe. The round bottom flask was transferred to an oil bath preheated to 40 °C and 16.2 g (0.078 mol) of 1-(tert-butyldimethylsilyloxy)-3- chloropropane was added dropwise using addition funnel over 30 minutes under stirring at 300 rpm. After that,

the reaction mixture was heated to 60 °C and stirred at that temperature at 300 rpm for 24 hours under a balloon filled argon atmosphere. Then the reaction mixture was cooled down to room temperature and filtered through a celite pad placed in the Schlenk filter funnel under argon atmosphere, yielding a nonopalescent light yellow solution.



Scheme 2. Synthesis of protected 3-(tert-butyldimethylsilyloxy)-1-propyllithium.

The concentration of 3-(tert-butyldimethylsilyloxy)-1-propyllithium in cyclohexane was determined by titration with freshly recrystallized diphenylacetic acid before use. Briefly, about 300 mg of diphenylacetic acid was added into a rubber septum sealed round bottom flask equipped with a Teflon stir bar, and 10 mL anhydrous THF was added via a syringe under argon atmosphere. After complete dissolution of diphenylacetic acid 3-(tert-butyldimethylsilyloxy)-1-propyllithium solution in cyclohexane was added dropwise by a syringe until the appearance of a persistent yellow color.



Scheme 3. Titration of protected 3-(tert-butyldimethylsilyloxy)-1-propyllithium.

The concentration of 3-(tert-butyldimethylsilyloxy)-1-propyllithium was calculated as follows:

0.300 g diphenylacetic acid = 1.40 mmol acid = 1.40 mmol 3-(tert-butyldimethylsilyloxy)-1propyllithium. Using this titrimetric method, the concentration of 3-(tert-butyldimethylsilyloxy)-1-propyllithium was found to be 0.32 M (7.33 wt%) for a batch used to synthesize medium and largest sizes of PSCs, and 0.41 M (9.4 wt%) for another batch applied for the synthesis of smallest size PSCs.

2.4. Synthesis of protected 3-(tert-butyldimethylsilyloxy)-1-propyl-functionalizedPSCs using anionic polymerization

The first PSC (PSC1) for smallest size SP but the highest number of arms (SP1) was synthesized via crosslinking the PS arms by anionic polymerization of styrene and p-DVB following incremental addition.⁵³



Scheme 4. Synthesis of protected 3-(tert-Butyldimethylsilyloxy)-1-propyl-functionalizedPSCs.

Briefly, 8 mL of 9.4 wt% 3-(tert-butyldimethylsilyloxy)-1-propyllithium solution in cyclohexane was added to a stirred solution of 12 mL styrene in 10 mL anhydrous THF, and 200 mL cyclohexane under argon atmosphere. After 40 minutes, a 3.5 mL aliquot was withdrawn, quenched with 200 mL of degassed methanol, and the free arm sample was collected by filtration as a white solid (¹H NMR, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 84H), 6.20-6.90 (br, m, 56H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 105H), 0.90 (br, s, 9H), 0.00 (br, s, 6H)). GPC (THF): M_w = 3.5 KDa, $M_w/M_n = 1.04$, $R_h = 1.8$. A 1.3 mL portion of the p-DVB solution in cyclohexane (0.24 g/mL) was added to the remaining reaction mixture and further stirred for 1h. Two more 1.3 mL portion of the p-DVB solution in cyclohexane was added in 1h interval before the reaction mixture was quenched by slowly adding it via cannula to a rapidly stirred degassed methanol (800 mL). The crude PSC consisting of free arms was collected by filtration and dried under vacuum until a constant weight of 12.4 g was achieved. The crude product was dissolved in 80 mL DCM before the slow addition of 116 mL acetone and then 108 mL of isopropanol until the appearance of persistent turbidity. The mixture was allowed to stand undisturbed until the formation of a substantial oily layer at the bottom of the conical flask. The oily layer was collected from the bottom using a glass pipette and precipitated from 500 mL methanol. The white solid was collected by filtration and dried under vacuum until a constant weight of 9 g. GPC analysis showed the presence of about 3% of free arms. Therefore, purification was repeated by using 56 mL DCM, 85 mL acetone, and 70 mL isopropanol to yield 7.6 g pure product upon drying. ¹H NMR (600 MHz, $CDCl_3, \delta$ = 7.12 (br, s, 90H), 6.20-6.90 (br, m, 64H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 105H), 0.90 (br, s, 9H), 0.00 (br, s, 6H)). GPC (THF): $M_w = 152 \text{ KDa}$, $M_w/M_n = 1.16$, $R_h = 7.13 \text{ nm}$. The procedure for the synthesis of the other two PSCs (PSC2 and PSC3) was similar, except for the

amount of 3-(tert-butyldimethylsilyloxy)-1-propyllithium solution and a p-divinylbenzene crosslinker. Also, the required p-divinylbenzene crosslinker was added in a single step instead of incremental addition. The amount of styrene, THF, and cyclohexane was 16 mL, 16 mL, and 250 for the synthesis of both PSCs, while the amount of 7.33 wt% 3-(tert-butyldimethylsilyloxy)-1propyllithium solution in cyclohexane was 10.4 mL and 7.8 mL for the PSC2, and PSC3, respectively. ¹H NMR (free arm of PSC2, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 153H), 6.20-6.90 (br, m, 100H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 188H), 0.90 (br, s, 9H), 0.00 (br, s, 6H). GPC (free arm of PSC2, THF): $M_w = 6.0$ KDa, $M_w/M_n = 1.01$, $R_h = 2.32$ nm. ¹H NMR (free arm of PSC3, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 265H), 6.20-6.90 (br, m, 175H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 318H), 0.90 (br, s, 9H), 0.00 (br, s, 6H). GPC (free arm of PSC3, THF): $M_w = 10.2$ KDa, $M_w/M_n = 1.01$, $R_h = 3.07$ nm. The amount of 0.2 g/mL p-DVB crosslinker in cyclohexane was 5.4 mL and 4.5 mL for the PSC2, and PSC3, respectively. The crude product yield was 15.52 g and 15.27 g for the respective PSCs, which was purified in a single step solvent fractionation by dissolving the PSCs in 100 mL followed by slow addition of 150 mL acetone and 85 mL isopropanol. The purified product yields of the respective PSC2 and PSC3 were 12.51 g and 10.23 g. ¹H NMR (PSC2, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 156H), 6.20-6.90 (br, m, 110H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 182H), 0.90 (br, s, 9H), 0.00 (br, s, 6H). GPC (PSC2, THF): M_w = 137 KDa, $M_w/M_n = 1.07$, $R_h = 8.07$ nm. ¹H NMR (PSC3, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 276H), 6.20-6.90 (br, m, 190H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 303H), 0.90 (br, s, 9H), 0.00 (br, s, 6H). GPC (PSC3, THF): $M_w = 211$ KDa, $M_w/M_n = 1.05$, $R_h = 10.51$ nm.

2.5. Deprotection 3-(tert-butyldimethylsilyloxy)-1-propyl groups to prepare hydroxy functionalized PSCs

7.5 g, 12g, 10g of protected PSC1, PSC2, and PSC3, respectively, were dissolved in anhydrous THF at 0.1 g/mL concentration and 15 mL of 1 M TBAF solution in THF was added via syringe. The reaction mixture was stirred at 300 rpm at room temperature for 24 h before being heated at 50 °C for 1 h. Then the reaction mixture was cooled down to room temperature and slowly added to methanol under rapid stirring. The deprotected PSCs were collected as white solid by filtration and dried under vacuum until a constant weight of 7.08 g, 11.75 g, and 9.95 g was obtained for PSC1, PSC2, and PSC3, respectively. ¹H NMR (Deprotected PSC1, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 90H), 6.20-6.90 (br, m, 64H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 105H). ¹H NMR (Deprotected PSC3, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 2H), 1.90-1.03 (br, m, 182H). ¹H NMR (Deprotected PSC3, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 276H), 6.20-6.90 (br, m, 190H), 3.45 (br, s, 2H), 1.90-1.03 (br, m, 303H).



Scheme 5. Deprotection of 3-(tert-butyldimethylsilyloxy)-1-propyl-functional group from PSCs.

2.6. ATRP-initiator immobilization on hydroxy functionalized PSCs

A solution of 2-bromoisobutyryl bromide in anhydrous DCM was added dropwise over 20 minutes to a solution of deprotected hydroxy functionalized PSCs (7 g PSC1, 11.7 g PSC2, and 9.95 g PSC3), TEA, and DMAP in anhydrous DCM at 0 °C under argon atmosphere. The ratio of PSCs, BIBB, TEA, and DCM were 1 g : 0.28 g : 0.15 g : 6 mL. The amount of DMAP was kept fixed at 200 mg. The reaction mixture was warmed to room temperature and stirred for a total of 14 hours under static argon atmosphere before gentle reflux for 2 h. Then it was cooled down to room temperature before precipitation by slow addition to rapidly stirred methanol. The precipitate was redissolved in DCM and precipitated from methanol $(2\times)$. The white precipitate collected by filtration was dried under vacuum to a respective constant weight of 7 g, 11.2 g, and 9.8 g. ¹H NMR (ATRP-initiator immobilized PSC1, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 90H), 6.20-6.90 (br, m, 64H), 3.78 (br, s, 1.85H), 3.10 (br, s, 0.15H), 1.90-1.03 (br, m, 104H). ¹H NMR (ATRP-initiator immobilized PSC2, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 156H), 6.20-6.90 (br, m, 110H), 3.78 (br, s, 1.75H), 3.10 (br, s, 0.25H), 1.90-1.03 (br, m, 178H). ¹H NMR (ATRP-initiator immobilized PSC3, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 276H), 6.20-6.90 (br, m, 190H), 3.78 (br, s, 1.70H), 3.10 (br, s, 0.30H), 1.90-1.03 (br, m, 302H). The degree of substitution of hydroxyl functional groups with isobutyryl bromide ATRP initiator was 0.93, 0.88, and 0.85 for PSC1, PSC2, and PSC3, respectively.



Scheme 6. ATRP-initiator immobilization on hydroxy functionalized PSCs.

2.7. Grafting PEGMA from ATRP initiator immobilized PSCs

The ATRP-initiator immobilized PSCs (500 mg) were dissolved in 25 mL anisole and sonicated for 10 minutes in a Schlenk flask. Then PEGMA (15 mL each for PSC1 and PSC2, and 20 mL for PSC3) and PMDETA (18 µL, 16 µL, and 10 µL for PSC1, PSC2, and PSC3, respectively) were added and mixed by stirring. Then three freeze-pump-thaw cycles were performed, and ground powder of Cu(I)Cl beads (17.5 mg, 15.4 mg, and 11.2 mg for PSC1, PSC2, and PSC3, respectively) was added to the frozen mixture under rapid argon flow. The reaction mixture warmed up to room temperature after two more freeze-pump-thaw cycles, and the Schlenk flask was transferred to an oil bath preheated to 45 °C followed by stirring at 250 rpm for 1h, 1h 30 mins, and 1h 20 mins for PSC1, PSC2, and PSC3, respectively. It is worth noting that slow stirring is important for slow dissolution of Cu(I)Cl powders to ensure slow initiation of ATRP and minimize inter star polymer cross-coupling mediated gel formation. After the continuation of the reaction for the given time, the reaction mixture was cooled down by liquid nitrogen and opened to air. Then 200 mg of

hydroquinone radical inhibitor was added, and the mixture was air blown for 1h under stirring, leading to a blood-red coloration. Then, the reaction mixture was stirred for 1 more hour and passed through a basic alumina column. The polymer was eluted from the column using about 200 mL DCM until all red color cleared out of the column. Then, the polymer was precipitated by slowly adding to vigorously stirred hexane. The gooey green precipitated thus formed was dissolved in about 20 mL THF and precipitated by slowly adding to vigorously stirred ether (100-150 mL). This dissolution and precipitation from ether were repeated twice to yield a white gooey solid. The white gooey solid was dissolved in about 20 mL 1,4-dioxane and freeze-dried to obtain a soft white solid of 1.7 g SP1, 1.9 g SP2, and 1.75 g SP3. ¹H NMR (SP1, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 101H), 6.20-6.90 (br, m, 64H), 4.5-4.05 (br, s, 95H), 4.05-3.45 (br, m, 677H), 3.45-3.05 (br, s, 61H), 1.90-1.03 (br, m, 307H). ¹H NMR (SP2, 600 MHz, CDCl₃, δ) = 7.12 (br, s, 129H), 6.20-6.90 (br, m, 110H), 4.5-4.05 (br, s, 142H), 4.05-3.05 (br, m, 1128H), 1.90-1.03 (br, m, 482H). ¹H NMR (SP3, 500 MHz, CDCl₃, δ) = 7.12 (br, s, 315H), 6.50-6.70 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.05 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.05 (br, m, 190H), 4.5-4.05 (br, s, 260H), 4.05-3.45 (br, m, 1795H), 3.45-3.05 (br, s, 158H), 1.90-1.03 (br, m, 858H).



Scheme 7. Grafting PPEGMA from ATRP initiator immobilized PSCs as hydrophilic segments for the synthesis of the final amphiphilic SPs.

2.8. SPs solution preparation

About 40 mg of each SP was first dissolved in 2 mL of THF placed in a 15 mL screw-capped vials by vigorous stirring, shaking, and high-intensity sonication in a sonication bath to obtain a clear solution. The ease of dissolution of SPs in THF was in the order of SP1 > SP2 > SP3. Afterward, DI water was added to the solution in 100 μ L portions every 30 seconds where the solution changed from a transparent solution to a turbid solution to a further transparent solution. After this transition period, DI water added in 500 μ L portions every 30 seconds until the vial was filled. Then, the content in the vial was transferred to a 100 mL screw-capped jar and diluted with water to 80 mL. The solution was stirred vigorously under air overnight to remove the THF. The solution volume was reduced to 20 mL to prepare 0.2 wt% solution used for dip coating on the PSF UF membrane. The solution was diluted with DI water to 0.02% for STEM imaging, and pressurized coating on PSF membrane as well as to 0.03 wt% for DLS measurements.

2.9. Characterization of SPs

The hydrodynamic diameter of the SPs (0.03 wt % aqueous solution) was measured using a Malvern Zetasizer Nano-ZS (Malvern Instruments Ltd., Worcestershire, UK) at 25 °C. The average hydrodynamic diameter was calculated against polystyrene (PS) latex standard by performing three series of 11 measurements.

The water dispersity, size distribution, self-assembly, apparent coating density, and the presence of hydrophilic PEG arms of SPs were evaluated via bright field-scanning transmission electron microscopy (BF-STEM) operated at 30 kV accelerating voltage and 30 μ A emission current on an ultra-high-resolution Hitachi S–5500 cold field emission SEM. The BF-STEM samples were prepared by depositing a droplet of SP solution (0.02%) on a carbon-coated 400-mesh copper grid (Electron Microscopy Sciences, PA, USA) and blotting using filter paper after 10 s. The samples were then stained by applying one droplet of uranyl acetate (2% aqueous solution) for 120 s, followed by blotting and air-drying.

To evaluate local hydrophilicity of the SPs, a dilute solution of SPs was drop cast on the silica wafer surface, and high resolution, soft tapping mode AFM Probes (MikroMasch USA, Inc.) with low spring constants of 5.0 N/m and 1 nm radius were used. For obtaining a clear phase mode image from the surface, a low scan rate (0.3–0.5 Hz) and amplitude setpoint were chosen during measurement.

2.10. SP coating on porous PSF UF membranes by self-assembly method

The PSF UF membrane was pretreated to remove the protective coating layer by soaking into IPA for 30 min, followed by rinsing with DI water. The membrane was finally kept in DI water overnight prior to the coating to ensure the complete removal of IPA. In order to coat the pretreated PSF membrane with SP through the self-assembly process, the substrate was first placed between two frames with sealing rubbers. Frames were held tightly with paper clips, and an SP solution (0.2 wt% aqueous solution) was poured onto the active surface of the membrane. After 1h, the solution was removed, and the membrane was immersed in DI water for 20 min to remove the loosely bound SPs. Then, the membrane was removed from the frame and was stored in DI water overnight until further characterization.

The oleophobicity of the SPs coated PSF UF membranes were evaluated by measuring their underwater n-hexadecane captive bubble contact angle measurements. Contact angle measurements were performed using a contact angle analyzer (Data Physics Instruments GmbH) with a 6 μ L captive n- hexadecane bubble in water. A 2 cm wide membrane strip was first placed face down in a custom-made holder. The membrane holder assembly was then accommodated in a small, clear cuvette so that the membrane was fully immersed in water. A high-speed computercontrolled camera was focused on the membrane surface, and at least three n-hexadecane bubbles were placed on the membrane surface using a syringe with an inverted needle. Contact angle samples were kept under deionized water and rinsed before analysis.

Filtration performance of SP self-assembled membranes was studied using hexadecane oil-inwater emulsion as a feed solution. Synthetic oily wastewater solutions were prepared using hexadecane (n-hexadecane, 99%, pure, Fisher Scientific, Canada) with Tween 80 surfactant (Bio-Red). To prepare 1000 ppm hexadecane oil-in-water emulsion, 0.75 mg of Tween 80 surfactant was dissolved in 300 mL DI water. Then 0.5 g of hexadecane was blended in this surfactant solution, and the mixture was homogenized with a homogenizer (Homogenizer 150, Fisherbrand, Canada) at the highest speed for 4 min. Then 200 mL of DI water was added to this emulsion and homogenized for a further 4 min. To evaluate the antifouling property of a representative SP1 coated PSF UF membrane, a 400 mL dead-end filtration cell (Amicon, UFSC40001) was used. Nitrogen gas was used to pressurize water through the membrane at 5 psi to obtain a stable initial pure flux of *ca*. 185 LMH. The mass of permeate water was monitored and recorded over time using a digital weighing balance (ME4002, Mettler Toledo, USA) and pure water flux (PWF) of the membrane was calculated using the following equation (1):

$$J_w = \frac{m}{\rho A_m \Delta t} \tag{1}$$

where J_w is pure water flux (LMH), m is the mass of the permeate water (kg), ρ is water density (kg/m³), A_m is the effective area of membrane (45.4cm²), and Δt is the time of permeation (hr).

After 30 min of constant pure water flux, 400 mL of hexadecane oil emulsion was added to the cell, and the filtration was performed for 1 h at 350 rpm while the cell was refilled with the permeate on demand. At the end of oil filtration, the oil emulsion was discarded, and the membrane was rinsed with 400 mL DI water for 20 min at 350 rpm. Then, pure water flux was recorded for 30 min. The oil concentrations in the feed and permeate solutions were measured using a total organic carbon (TOC) analyzer (Shimadzu TOC-L with ASI-L and TNM-L). The retention ratio (or rejection) of the oil was calculated by equation (2):

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100 \tag{2}$$

where C_f and C_p represent the oil concentration in the feed and permeate solution, respectively.

The flux decline ratio (FDR) at the end of oil filtration period and the flux recovery ratio (FRR) after a simple wash was calculated by equation (3) and (4):

$$FDR = \left(1 - \frac{J_f}{J_{w1}}\right) \times 100 \tag{3}$$

FRR (%) =
$$\left(\frac{J_2}{J_1}\right) \times 100$$
 (4)

2.11. SPs coating on porous PSF UF membranes by pressure-assisted method

To coat the membranes by the pressure-assisted method, a pretreated PSF UF membrane was first placed in the 400 mL dead-end filtration cell, and 800 mL of pure DI water was passed through the membrane at 5 psi to remove the excess IPA. Then, 200 mL of 0.02 wt% SP solution in DI water was filtered through the membrane at 10 psi. The membrane was kept under nitrogen pressure for 25 minutes for drying after all the water passed through the membrane. Then the membrane and the cell were rinsed gently with 3 portions of 100 mL DI water, left under 400 mL DI water for 1 h for realignment of the SP coatings, and stirred at 350 rpm for 16 h. The membranes were gently rinsed with DI water before further characterizations.

The topography of the pristine and SPs coated membranes by the pressure-assisted method was evaluated using SEM. The SEM was operated at 30 kV accelerating voltage and 30 μ A emission current on an ultra-high-resolution Hitachi S–5500 cold field emission SEM. The membrane surface roughness was evaluated using the height mode imaging of the same AFM technique described in section 2.9. The oleophobicity of the pristine and SPs coated membranes were also evaluated by under-water n-hexadecane captive bubble contact angle measurements, as described in section 2.10.

PWF was measured at 10 psi until a constant value was achieved. The PWF measurement was repeated 3 times on each type of membranes prepared separately on 3 different days. The antifouling property against n-hexadecane oil-in-water emulsion was carried out in the same way as described in section 2.10. The pressure required to adjust the initial constant pure water flux of *ca*. 150 LMH was 2.3 psi for pristine PSF UF membrane while a higher pressure (6.1-8.2 psi) was required for SPs coated membranes. The anti-BSA fouling property of the pristine PSF and SPs coated PSF membranes were examined by a single batch filtration of 400 mL of the BSA solution in $1 \times$ phosphate buffer saline (PBS) of pH 7.4 (provided by Biochemistry lab of National Research Council Canada) for 30 min using the 400 mL dead-end filtration setup.

2.12. Evaluation of the stability of the SPs coatings on porous PSF UF membranes

After finishing the pressure-assisted coating of SPs, the membranes were stirred in the cell at 350 rpm under 400 mL of 150 ppm Tween 80 surfactant solution for two hours to examine the removal of the SPs from the surface. After decanting the surfactant solution and 3 times gentle rinsing with DI water, a fresh 400 mL portion of 150 ppm Tween 80 surfactant solution was added to the cell and passed through the membrane to remove SPs from the membrane pores. After further rinsing, the membranes were stirred under 400 mL DI water at 350 rpm for 16 hours and rinsed further before characterizations. The SEM topography, AFM roughness, and oleophobicity were evaluated in the same way as described in the earlier sections. Reusability of surfactant-washed membranes was evaluated by 3 cycles hexadecane oil-in-water emulsion filtration following the same process as described in section 2.11, except oil-in-water emulsion filtration period was 2h, and the flux recovery was recorded for *ca*. 120 min, 90 min, and, 50 min for SP1, SP2, and SP3 coated membranes, respectively. These different time periods were required to achieve 100% flux recovery.

3. Results and discussion

3.1. Synthesis and characterization of star-shaped block copolymers

To study the effect of structural and compositional variation of SPs on their coatability onto the membrane surface and their influence on the fouling resistance, three different SPs having variable core sizes, arm numbers, and arm lengths (Figure 1 and Table 1) were synthesized by a combined anionic polymerization and ATRP. Initially, living PS arms of variable lengths were prepared by using different known concentrations of 3-(tert-butyldimethylsilyloxy)-1-propyl lithium anionic polymerization initiator. The ¹H NMR analysis of quenched aliquots of PS arms demonstrated 28, 50, and 87 repeating units of styrene for SP1, SP2, and SP3, respectively, which is consistent with their corresponding increasingly higher GPC molecular weight (M_w) of 3.5, 6, and 10.2 kDa (Table 1). These PS arms were then crosslinked by adding p-DVB to prepare the star-shaped hydrophobic PSCs. The number of arms per PSC was tuned by the multistep incremental addition of the crosslinker for SP1,⁵³ and a single step addition of the variable amount of crosslinker for SP2 and SP3.⁵⁴ Residual linear PS arms were removed from the mixture by the solvent fractionation process yielding pure PSCs on a gram scale (7-12.5 g). GPC analysis provided weight average molecular weight (M_w) of 152, 137, and 211 KDa for PSC1, PSC2, and PSC3, respectively. The approximate arm numbers per PSC, calculated by dividing the M_w of PSCs by the M_w of the respective arms, were found to be 43, 23, and 21 for PSC1, PSC2, and PSC3, respectively.

After evaluating the variable sizes (in terms of M_w) and arm numbers of the hydrophobic PSCs, the emanating hydrophobic PS arms were modified to immobilize ATRP initiator, and chargeneutral hydrophilic branched PEG arms were built on these PS arms by applying ATRP of PEGMA. The approximate number of PEGMA units per PS arms was calculated by integrating the intensity of the ¹H NMR peaks for methylene proton next to the ester group of PEGMA with respect to the intensity of the peaks for proton on the 2nd and 6th position of the aromatic rings of styrene units of PS arms. This ¹H NMR integration provided *ca.* 47, 71, and 130 PEGMA units per PS arm for SP1, SP2, and SP3, respectively.



Figure 1. Schematic of the plausible structure of the star-shaped block copolymers (SPs).

Table 1. Characteristics of star-shaped block copolymers (SPs).

Sample Code	Hydrophobic	Molecular	Molecular	No. of PS arms	No. of	Hydrodynamic
	arms: No. of PS	weight (kDa) of	weight (kDa) of	per PS cores	hydrophilic	diameter (nm)
	units (m)	hydrophobic PS	hydrophobic PS		PEGMA units	
		arm	cores		(n) per arm	
SP1	28	3.5	152	43	47	26 ± 11
SP2	50	6	137	23	71	45 ± 29
SP3	87	10.2	211	21	130	47 ± 17

The water dispersibility of the SPs is pivotal for their coating on the membrane.²² The antifouling property of the SPs coating on the membrane is also governed by the hydration and extension of the hydrophilic arms in the water.²² The water dispersibility of the SPs is provided by their hydrophilic PEG arms. Meanwhile, the hydrophobicity of the PS cores and the overall sizes of the amphiphilic SPs dictates the self-assembly and coating density on the hydrophobic surfaces. All

the three SPs were dispersible in the water when assisted by pre-dispersion in a miscible organic solvent (e.g., THF) that was removed later by evaporation. A dilute (0.02 wt%) dispersion of the SPs in water was prepared and drop cast on the carbon-coated copper grid to evaluate their water dispersity, size distribution, self-assembly, apparent coating density, and the presence of hydrophilic PEG arms. As evident from the BF-STEM images (Figure 2, left panels) of the uranium stained SPs, the SPs are largely monodispersed except the presence of a few small size aggregates. The sizes of SPs are found to be 20.0 ± 5.4 nm for SP1, 22.0 ± 2.8 nm for SP2, and 28.1 ± 4.4 nm for SP3. However, these sizes are not real sizes under the operating condition of water filtration since the SPs are in the dry state on the TEM grid, where the arms are folded inward to minimize their surface energy. In contrast, the arms are extended underwater forming a solvent corona and increasing the overall sizes. DLS measurement indicated the hydrodynamic diameters of 26 ± 11 nm, 45 ± 29 nm, and 47 ± 17 nm for SP1, SP2, and SP3, respectively. The self-assembly and apparent coating density of the SPs followed the trend of their sizes. The coating density is ca. 760 SPs/ μ m² for the smallest size SP1, *ca*.610 SPs/ μ m² for a slightly larger size SP2, and *ca*.335 SPs/µm² for the largest size SP3. The existence of hydrophilic PEG arms around the hydrophobic PS cores is evident from the darker contrast on the periphery of the SPs. The darker contrast is associated with uranyl metal ion coordination to the ether oxygen of PEG arms.⁵⁵



Figure 2. BF-STEM images of uranium stained SPs demonstrating the dispersity, size distribution, self-assembly, apparent coating density, and the presence of hydrophilic PEG arms (left panels); AFM phase mode images of SPs demonstrating the difference in their extent of hydrophilicity (right panel, scale bar 20 nm).

As the hydrophilicity of the individual SP is an essential property governing the antifouling efficiency of the resulting SPs coating, the AFM phase-contrast images were acquired to evaluate hydrophilicity of SPs.²² The root-mean-square (RMS) value obtained from a phase image, which is the degree of the phase difference between the hydrophilic arms and the hydrophobic core, indicates the extent of hydrophilicity. It is evident from the AFM images (Figure 2, right panels) that the center of the SP is darker while the periphery is brighter. The dark phase is arising from the hydrophobic PSC, while the bright phase is from the hydrophilic PEG arms. Note that the hydrophilic PEG arms are folded inwards in the dry state to minimize the surface energy exposing part of the hydrophobic PSC. Therefore, RMS value from these contrast images is not the absolute measure of the hydrophilicity of the SPs. However, this RMS value is still very useful to estimate and compare the difference in hydrophilicity among the SPs. The RMS values of SPs are found to be in the order of SP1 (4.55) >SP2 (4.93) >SP3 (6.01). Although SP1 has a higher density of hydrophilic PEG arms compared to SP2 (ca. 43 PEG arms for SP1 vs. 23 PEG arms for SP2), its hydrophilicity is lower than that of SP2 since it has a lower number of hydrophilic PEG repeating units in each arm (ca. 47 PEG units for SP1 vs. 71 PEG units for SP2). Meanwhile, SP3, with the largest number of PEG repeating units, has the highest hydrophilicity. It is worth noting that the length of the hydrophilic PEG arms is manifested by the length of the hydrophobic PS block as well as their density per PSC. SP1 has the shortest hydrophobic PS block and the highest density per SP (Table 1). Therefore, the shortest hydrophilic PEG arms were enough to make SP1 easily dispersible in water. SP2 has almost twice as long hydrophobic PS block as SP1 while having onehalf the density per SP. Therefore, longer hydrophilic PEG arms were required to solubilize SP2. SP3 has the longest hydrophobic PS block at a similar density to SP2, and its solubility in water required the longest hydrophilic PEG arms. The observation of this variation in hydrophilicity SPs

with respect to their hydrophobic PSCs sizes suggests that larger hydrophobic PSCs and subsequently longer hydrophilic PEG arms are preferable for SPs to obtain superior hydrophilicity.

3.2. Evaluation of self-assembly driven coatings of SPs on porous PSF UF membrane

The antifouling coating material for the membrane should be hydrophilic, which brings challenges with their coating on the hydrophobic membrane. Therefore, it is necessary to have multiple segments in the coating materials that enable electrostatic, hydrophobic, and hydrogen bonding interaction with the membrane surface. In our previous study, we have shown that the flexible nature of the hydrophobic PS segment and the hydrophilic cationic segment of the arms on the SPs allows a very effective interaction (hydrophobic plus electrostatic) with the PSF membrane surface through their favorable alignment resembling an intermediary structure of a jellyfish.²² This effective dual interaction of SPs provided a stable coating on the PSF membrane. One objective of this study is to evaluate the coatability SP on the PSF membrane via only the hydrophobic interaction of the PSC with the hydrophobic PSF membrane surface. Therefore, SPs of variable hydrophobic PSC sizes and charge-neutral PEG arm sizes were coated from a 0.2 wt% solution on the PSF membrane via the self-assembly process. The SPs coated membrane should exhibit underwater oleophobicity since the hydrophilic arms are extended outwards underwater, providing a barrier for oil adsorption. Therefore, the oleophobicity of the SPs coated membranes was evaluated from the underwater captive n-hexadecane bubble contact angle measurements (Figure 3, left panels). The water contact angle (WCA), which is a complementary angle to n-hexadecane contact angle, is almost similar for all three types of SPs coated membrane. The contact angles are $90.8^{\circ} \pm 3.5^{\circ}$, $41.5^{\circ} \pm 1.8^{\circ}$, $41.1^{\circ} \pm 1.9^{\circ}$, and $43.1^{\circ} \pm 2.4^{\circ}$ for pristine PSF, SP1, SP2, and SP3 coated PSF membranes, respectively. The similar contact angles (i.e., similar wettability) of the SPs coated membranes may be arising from the mutual effect of coating density and extent of the

hydrophilicity of the SPs. As described in the earlier sections, the relative coating density of the SPs is in the order SP1>SP2>SP3 (**Figure 2, left panels**), whereas their extent of hydrophilicity follows the opposite order (**Figure 2, right panels**). Therefore, a balance between the coating density and the hydrophilicity of the SPs imparts the similar extent of hydrophilicity on the coated membranes.

Knowing that the SPs coated membrane can induce oleophobic properties, the antifouling behavior of a representative SP, that is SP3 coated membrane, was evaluated by carrying out the filtration of hexadecane oil in water emulsion. As shown in the **right panel of Figure 3**, constant pure water flux of *ca.* 183 LMH was initially recorded for 30 minutes, which was followed by oil emulsion filtration for 1 hour. The water flux declined to 146 LMH after 1-hour oil emulsion filtration. The only 20% decline in water flux verses 76% flux decline for pristine PSF against this very strong oil emulsion based foulant indicates that the SPs with charge-neutral PEG hydrophilic arms can provide high antifouling property to SPs coated the membrane. However, the flux recovery after 20 minutes of stirring at 350 rpm underwater was not appreciable. The flux recovery ratio defined as the ratio of water flux after the washing cycle over the initial pure water flux was only 84%. Meanwhile, no flux recovery was observed for pristine PSF. This low flux recovery for SP1 coated PSF membrane can be attributed to the irreversible fouling of the uncoated parts of the membrane surface and the membrane pores. Therefore, it was essential to apply an alternative coating process that can provide high coverage SPs on the membrane surface and cover the pores of the membrane.



Figure 3. Representative under water n-hexadecane captive bubble contact angles of a) pristine PSF, b), c), and d) SP1, SP2, and SP3 coated PSF membranes, respectively (left panels); evaluation of antifouling property of pristine and SP1 coated PSF UF membrane during the filtration of hexadecane oil in water emulsion (right panel). The coating of SPs was conducted via the self-assembly process.

3.3. Evaluation of pressure-assisted coatings of SPs on porous PSF UF membrane

The pressure-assisted method, using a dead-end filtration setup, enables forcing the attachment of the SPs on the membrane surface. Under the external pressure, the hydrophilic segments of the arms of the SPs are expected to fold upwards due to their unfavorable interaction with the hydrophobic membrane surface. This upward folding of the hydrophilic arms can facilitate the exposure of the hydrophobic PS core of the SPs and enhance the hydrophobic interaction with the hydrophobic membrane surface. Moreover, this external pressure can force the SPs to penetrate the membrane pores covering internal pore surface, which can provide an antifouling barrier to pore blockage with hydrophobic foulants. In this context, 200 mL of 0.02 wt% SP solutions was filtered through the PSF membrane under 10 psi transmembrane pressure. The extra loosely bound SPs were removed by stirring at 350 rpm underwater, in the same filtration setup, for 16 hours.

The coating of the SPs was first evaluated by comparing SEM topography of the SPs coated PSF membranes with that of the pristine PSF membrane (**Figure 4**, **left panels**). It is evident from the SEM images that the pristine PSF consists of highly porous structures, and these porous structures are completely covered by the SPs for all coated membranes.



Figure 4. Evaluation of pressure-assisted coating of SPs from SEM topography (left panels), AFM roughness (middle panels), and representative underwater n-hexadecane captive bubble contact angles (right panels).

The roughness of the pristine and SPs coated membranes were examined by AFM height mode imaging (**Figure 4, middle panels**). The pristine PSF exhibited a very rough surface consisting of stiff spherical features arising from the aggregation of PSF polymers during the phase inversion process used for the membrane fabrication. On the other hand, all the SPs coated membranes are showing a smoother surface and consist of softer features. The PEG arms of the SPs likely provide softness to the SPs coated membranes. The average roughness denoted as Rq is found to be 5.41 nm for pristine PSF, which decreased to 4.02, 3.80, and 3.64 nm for SP1, SP2, and SP3 coated membranes, respectively. The decrease in the roughness values of the PSF membranes after SPs coating further supports the effective coverage of the membrane surface with SPs, which is beneficial for the antifouling properties. The Rq values of the SPs coated membranes also followed variation in the sizes of the SPs. The largest SP, (i.e., SP3) effectively occupied the inter-spherical feature gaps and/or the porous structures on the membrane provided the smallest roughness value in contrast to the smallest SP (i.e., SP1).

Following the evidence of the successful coating of SPs on the PSF membrane, the oleophobicity of the SPs coated membrane was evaluated from the under-water n-hexadecane captive bubble contact angle measurements (**Figure 4, right panels**). The contact angles for pressurized SPs coated membranes reduced compared to those for self-assembly based SPs coated membranes. The contact angles are $34.7^{\circ} \pm 0.3^{\circ}$, $33.4^{\circ} \pm 0.2^{\circ}$, and $36.3^{\circ} \pm 1.1^{\circ}$ for SP1, SP2, and SP3 coated PSF membranes, respectively. This reduction in contact angles demonstrates better surface coverage of the PSF membrane with SPs under pressurized coating method. Notably, the contact angles for all three SPs coated membranes are again similar despite the application of different types of the coating process. This observation again supports the size-dependent coating density of the SPs with different degrees of hydrophilicity on the membranes.

It is known that the addition of extra layers of coating on porous MF and UF membranes always reduces the water flux due to the added resistance to water transport. High antifouling properties and separation efficiency are achieved at the expense of this flux decline. However, the goal of membrane surface modification strategies is to maintain an appreciably high-water flux during wastewater filtration. Therefore, proper coating material should not dramatically reduce the water flux. SPs, as coating materials, offer the privilege of maintaining high water flux even at high coating density. The water flux reduced from 319 ± 28 LMH for pristine PSF membrane to $211 \pm$ 12, 204 \pm 8, and 193 \pm 16 LMH for SP1, SP2, and SP3 coated PSF membranes, respectively. Although the flux decline is more than 30% for all the SPs coated membranes, the magnitudes of the fluxes are still well in the range of ultrafiltration membranes. One important observation here is that all SPs coated membranes provide similar pure water flux despite the difference in their sizes. Theoretically, larger sizes of SPs should provide higher water flux than the smaller size ones due to higher interparticle gaps for the former. However, the porous structure and inter-spherical feature gaps of the pristine PSF need to be taken into consideration to evaluate the effect of SPs on the pure water flux decline. As described in the AFM analysis of the SPs coated membrane (Figure 4, middle panels), the larger SPs occupied the inter-spherical feature gaps and/or the porous structures on the membrane more effectively than the smaller SPs, balancing the effect of larger interparticle gaps of the larger SPs.

The anti-oil fouling properties of the membranes were evaluated by filtering a highly concentrated (*ca.* 1000 ppm) hexadecane oil-in-water emulsion. The oil emulsion filtration was carried out under constant initial pure water flux mode (**Figure 5a**), and the permeate flux was recorded for 1 hour. At the end of 1-hour oil emulsion filtration period, the flux decline for pristine PSF is 142 LMH (93%) while the flux decreased by only *ca.* 20 LMH (13%), 22 LMH (14%), and 24 LMH

(16%) for SP1, SP2, and SP3 coated PSF membranes, respectively. It is worth noting that the PSF membrane is one of the most susceptible membranes to organic fouling, and oil is known as the most severe organic foulants. Therefore, 5.9 to 7.1 times lower flux decline ratio (FDR) compared to pristine PSF is outstanding for the ultrafiltration of a highly concentrated oil emulsion. Such a high antifouling property of the SPs coated membranes is endowed by an antifouling barrier created by the highly hydrated and extended PEG arms. We have also shown in our previous study that the inclusion of PEG moieties with quaternary amine or carboxylic acid moieties in the hydrophilic arms of SPs can significantly improve the hydrophilicity and antifouling properties of the SPs coated membranes.²² Remarkably, the FDR for all three SPs coated membranes is very similar, which is consistent with the previously observed similarity in their oleophobicity by contact angle measurements. A slight increase in the FDR from SP1 to SP2 to SP3 coated PSF by 1% to 2% may be due to the lower coating density of the larger SPs allowing a bit more spaces for adsorption oil emulsion and/or the free surfactant present in the oil emulsion. Another important factor in determining the antifouling properties of the membrane is the flux recovery ratio (FRR). No flux recovery was observed for the pristine PSF membrane, whereas the FRRs were 105%, 110%, and 109% for SP1, SP2, and SP3 coated PSF membranes, respectively (Figure 5b). The high FRR values for all SPs coated membranes means that the fouling is completely reversible. However, there are two likely reasons for FRR values higher than 100%. It might be due to the increased hydrophilicity of the coated membrane provided by the alignment of Tween 80 surfactant molecules among SPs. Another reason might be the surfactant induced washing and subsequent detachment of some SPs coating from the membrane surface. The former reasoning complies more with the higher FRR since the similar increasing trend in permeate flux was observed during the filtration, which would not be possible if SPs are washed off, as the space left by SPs washing should be fouled, reducing the permeate flux. Tween 80 was shown to increase the surface hydrophilicity of PEG-coated glass coverslips significantly by occupying the gaps among the PEG chains, which were observed by a reduction in the water contact angle by *ca*. 10° .⁵² Meanwhile, the oil rejections for pristine and SPs coated PSF membranes were all above 98%.

As mentioned in the earlier sections, PEG-based coating is well known to reduce nonspecific adsorption of biomolecules (e.g., proteins). Hence, the anti-biofouling properties of the membranes were evaluated by filtering 100 ppm solutions of BSA protein. Pristine PSF exhibited a flux decline of ca. 62 LMH (42%) whereas the flux declined by only ca. 23 LMH (15%), 17 LMH (11%), and 7 LMH (5%) for SP1, SP2, and SP3 coated PSF membranes (Figure 5c). This low fouling of BSA, notably only ca. 7 LMH decline in permeate flux for SP3 coated PSF membrane, is unprecedented with any other modification applied on PSF UF membranes. An increasing trend in the improvement of permeate flux for SP1 to SP2 to SP3 coated PSF membranes was also observed. This enhancement in antifouling property against BSA is consistent with the increase in the length of PEG arms from SP1 to SP2 to SP3. There is literature evidence for the higher repelling capability of longer PEG chains against proteins.^{50,56–58} Meanwhile, the FRR was only *ca*. 64% for pristine PSF, contrary to ca. 100%, 99%, and 102% for SP1, SP2, and SP3 coated membranes, respectively (Figure 5d). The FRR of about 100% for all SPs coated membranes demonstrated that their fouling by BSA was completely reversible. The rejection of BSA for pristine and SPs coated PSF membranes were in the range of 67.7-89.5%.



Figure 5. Evaluation of antifouling properties of pristine and SPs coated PSF UF membranes against a), b) hexadecane oil-in-water emulsion, and c), d) BSA.

3.4. Evaluation of the stability of the SPs coatings on porous PSF UF membrane

It was evident from the previous section that the SPs coating is stable under continuous stirring underwater at 350 rpm for 16 hours. The coatings were also stable under the BSA filtration condition, where BSA was dissolved in PBS buffer containing high concentrations of salts. However, the permeate flux during oil emulsion filtration and respective FRR was increasing. One of the possible reasons for this increase in permeate flux was attributed to the washing of some SPs by the free Tween 80 surfactant present in the oil emulsion. Tween 80 is an amphiphilic polymeric surfactant consisting of PEG and octadecenoate as hydrophilic and hydrophobic moieties, respectively. Tween 80 has a good structural resemblance to the amphiphilic SPs consisting of PEG and PS as hydrophilic and hydrophobic moieties, respectively. Therefore, it is reasonable to assume that Tween 80 surfactant will have a very strong interaction with SPs and could potentially wash out the SPs from the membrane surface. In this context, the stability of the SPs coating was evaluated by stirring the membrane in the dead-end filtration setup under Tween 80 surfactant solution at 350 rpm for 2 hours followed by passing 400 mL surfactant solution through the membranes at 350 rpm and further stirring underwater at 350 rpm for 16 hours. The SPs coatings are found to be stable even after these rigorous washing cycles. As can be seen from the SEM images that the pores of the SPs coated PSF membranes are not still visible (**Figure 6, left panels**).

The stability of the SPs coatings is also demonstrated by the preservation of the lower roughness values compared to pristine PSF (**Figure 6, middle panels**). The Rq values increased from 4.02, 3.80, and 3.64 nm to 4.70, 3.96, and 4.74 nm for SP1, SP2, and SP3 coated membranes, respectively, which are still considerably lower than 5.41 nm for pristine PSF. The roughness values increased more for SP1 and SP3 coated membranes compared to the SP2 coated membrane. The more increase in roughness of these membranes might be due to the higher removal of SP1 and SP3 due to enhanced interaction of the PEG moieties of Tween 80 with a double number of PEG arms on SP1 and longer chains of PEG arms on SP3. The removal of larger size SP3 from the coated membranes will leave larger gaps left behind on the membrane, leading to a larger increase in roughness value for SP3 coated membranes.

Meanwhile, the oleophobicity of the SPs coated membranes also slightly decreased after surfactant washing as evident by the increase in contact angles from $34.7^{\circ} \pm 0.3^{\circ}$, $33.4^{\circ} \pm 0.2^{\circ}$, and $36.3^{\circ} \pm 1.1^{\circ}$ to $43.7^{\circ} \pm 1.0^{\circ}$, $39.3^{\circ} \pm 0.5^{\circ}$, and $40.3^{\circ} \pm 0.7^{\circ}$ for SP1, SP2, and SP3 coated membranes, respectively (**Figure 6, right panels**). The largest decline in oleophobicity was observed for SP1

coated PSF membranes, as evidenced by the largest increase in contact angles (*ca.* 9°), which was followed by SP2 (*ca.* 6°) and SP3 (*ca.* 4°) coated membranes. The lower decline in the oleophobicity of the SP3 coated membrane suggests higher stability of coating with larger SPs than that with smaller ones.



Figure 6. Evaluation of the stability of SPs coating on PSF UF membranes upon surfactant washing from the SEM topography (left panels), AFM roughness (middle panels), and representative underwater n-hexadecane captive bubble contact angles (right panels).

All the above characterization shows that the surfactant washing removes some of the SPs coatings from the PSF membranes. This removal might only be limited to the loosely bound excess SPs layers, in which case the antifouling properties should not be altered dramatically. In this context, the antifouling property of surfactant-washed SPs coated membranes was evaluated and compared with pristine PSF by filtration of oil-in-water emulsion (Figure 7a). The stability of the SPs coating was also evaluated by three consecutive cycles of oil-emulsion filtration and washing steps. First, constant initial pure water flux was adjusted and maintained for 30 minutes, which was followed by oil emulsion filtration for 2 hours, simple water-based washing for 20 minutes, and recording flux recovery until it reached a constant value. The last 3 steps were repeated for 2 more times to complete 3 cycles. Figure 7b summarizes the FDR and FRR values of pristine and SPs coated membranes for all 3 cycles. The flux decline for pristine PSF was ca. 142 LMH (93%) at the end of 2 hours filtration, and FRR was only ca. 9%. In contrast, the flux decline for SPs coated PSF at the end of 1st cycle oil filtration was ca. 55 LMH (36%), 29 LMH (18%), and 30 LMH (19%) for SP1, SP2, and SP3 coated membranes, respectively. The flux decline rates for SP1 coated membranes on the 2nd and the 3rd cycles of oil filtration were 60 LMH (38%), and 62 LMH (41%), respectively. Meanwhile, SP2 coated membranes encountered a flux decline of ca. 34 LMH (22%) on the 2nd cycle and *ca*. 34 LMH (23%) on the 3rd cycle of oil filtration. Lastly, the 2nd and 3rd cycle of oil filtration for SP3 coated membranes exhibited a flux decline of *ca*. 42 LMH (26%), and 42 LMH (26%), respectively. The FRR for all three SPs coated membranes was nearly 100%, although reaching to this nearly complete flux recovery took about 120, 90, and 50 minutes for SP1, SP2, and SP3 coated membranes, respectively. Based on the gradual flux recovery pattern and time difference for complete flux recovery, it can be assumed that the flux decline was mainly associated with the accumulation of smaller oil droplets and/or free Tween 80

surfactant molecules within SPs coating layers which were slowly removed upon washing during FRR measurement. The coating density of SP1 was the highest, which resulted in the strongest trapping and took the longest time for the cleaning, while larger SPs of lower coating density behaved oppositely. The largest increase in flux decline among the SPs coated membranes upon initial surfactant washing followed by 3 cycle oil emulsion filtration was observed for SP1 coated membrane by *ca*. 42 LMH (28%) while SP2 and SP3 coated membranes exhibited a slight increase in the flux decline by *ca*. 14 LMH (10%) and 20 LMH (12%). These observations suggest that SP3 with the smallest hydrophobic core and an almost double number of hydrophilic PEG arms are more washable than SP2 and SP3. However, the flux decline for all SPs coated membrane was nearly constant on the 2nd and the 3rd cycles. This indicates that the strong surface-bound, as well as the pore-entrapped SPs are more stable, and the surfactant can remove only some of the loosely surface-bound SPs and extra multilayers of SP coatings.



Figure 7. Evaluation of the stability of the SPs coatings on PSF UF membranes upon surfactant washing from the recyclable antifouling properties against hexadecane oil-in-water emulsion.

4. Conclusion

In this study, three different sizes of SPs with variable hydrophobic PSCs and hydrophilic PEG arm compositions were synthesized to develop and optimize an unusually stable and versatile antifouling coating on hydrophobic PSF UF membranes. Smaller SPs provided higher apparent coating density over the larger ones. In comparison, longer PEG arms on the larger SPs provide superior hydrophilicity of the individual SP, leading to similar hydrophilicity of the SPs coated membranes. The pressurized coating method provided superior coverage of SPs on a PSF membrane resulting in improved antifouling efficiency with strong suppression of internal fouling as compared to self-assembly driven technique. The SPs coating provided substantial enhancement in the surface hydrophilicity and antifouling properties against a model organic foulant (i.e., hexadecane oil) and a model bio-foulant (i.e., BSA protein). The SPs coated membranes exhibited similar surface wettability and flux decline properties against oil emulsion owing to the balance between size-dependent coating density and the extent of individual SP's hydrophilicity. The SP3 coating with the longest PEG arms provided the highest antifouling property against BSA, indicating that the length of the PEG arms is the determinant factor to prevent the adhesion of biofoulant on the coated membrane. The SPs coating stability was tested by rigorous washing with Tween 80 surfactant and 3 cycles oil emulsion filtrations. It was found that the surfactant washing only removed the loosely surface-bound extra layers of SPs. Larger SPs, with larger hydrophobic PSC and longer hydrophilic PEG block, were found to be more effective in terms of coating stability and antifouling properties. This study provides a valuable insight into the fabrication of next-generation fouling resistant membranes using a straightforward, easily implemented, and environmentally friendly method.

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Declaration of interest

The authors declare no competing interests.

Abbreviation

SPs, star-shaped block copolymers; PSCs, polystyrene cores; PEG, polyethylene glycol; PSF UF, polysulfone ultrafiltration; CA, contact angle; WCA, water contact angle; PWF, pure water flux; FRR, flux recovery ratio; FRD, flux decline ratio; LMH, liter per square miter per hour; BSA, bovine serum albumin; DLS, dynamic light scattering; BF-STEM, bright-field scanning transmission electron microscopy; AFM, atomic force microscopy; SEM, scanning electron

microscopy; TEM, transmission electron microscopy; ¹H NMR, proton nuclear magnetic resonance; GPC, gel-permeation chromatography; TOC, total organic carbon; RMS, root-mean-square; ppm, parts per million; LbL, layer-by-layer; MWCO, molecular weight cut-off; PEGMA, poly(ethylene glycol) methacrylate; ATRP, atom transfer radical polymerization; TBDMSCl, tert-butyldimethylsilyl chloride; TEA, triethylamine; p-DVB, para-divinylbenzene; DMAP, 4-(dimethylamino)pyridine; TBAF, tetrabutylammonium fluoride; BIBB, 2-bromoisobutyryl bromide; THF, tetrahydrofuran; DCM, dichloromethane; CDCl₃, deuterated chloroform; RT, room temperature; IPA, isopropanol; PBS, phosphate buffer saline.

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