

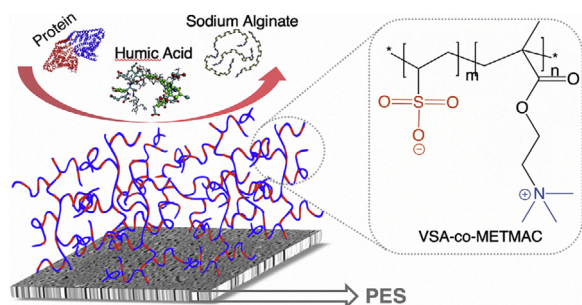
## Regular Article

## Surface and anti-fouling properties of a polyampholyte hydrogel grafted onto a polyethersulfone membrane

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Zwitterion polymers have anti-fouling properties; therefore, grafting new zwitterions to surfaces, particularly as hydrogels, is one of the leading research directions for preventing fouling. Specifically, polyampholytes, polymers of random mixed charged subunits with a net-electric charge, offer a synthetically easy alternative for studying new zwitterions with a broad spectrum of charged moieties.

Here, a novel polyampholyte hydrogel was grafted onto the surface of polyethersulfone membrane by copolymerizing a mixture of vinylsulfonic acid (VSA) and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METMAC) as the negatively and positively charged monomers, respectively, using various monomer ratios in the polymerization solution, and with N,N'-methylenebisacrylamide as the crosslinker. The physicochemical, morphological and anti-fouling properties of the modified membranes were systematically investigated.

Hydrophilic hydrogels were successfully grafted using monomers at different molar ratios. A thin-film zwitterion hydrogel (~90 nm) was achieved at a 3:1 [VSA:METMAC] molar ratio in the polymerization solution. Among all examined membranes, the zwitterion polyampholyte-modified membrane demonstrated the lowest adsorption of proteins, humic acid, and sodium alginate. It also had low fouling and high flux recovery following filtration with a protein or with an extracellular polymeric substance solution. These findings suggest that this polyampholyte hydrogel is applicable as a low fouling surface coating.

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## 1. Introduction

Zwitterionic polymers have equimolar negative (acidic) and positive (basic) charges. They exhibit excellent non-fouling

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properties in diverse environments, and have therefore been extensively studied for use in low-fouling coatings, including for membranes [1–6] as brushes [7,8], additives [6], hydrogels [9], thin-films [10], and self-assembly [11]. The non-fouling behavior of zwitterionic materials is fundamentally attributed to high hydration [12–14], but their weak intra- and inter-salt interactions (self-associations) and their weak interaction with proteins are also important [12]. In addition, the distance and nature of the charged moieties and the length of the carbon spacers between them also affect the non-fouling behavior of zwitterions [12,15]. As all these criteria are largely governed by the chemical structure of the charged moieties of the zwitterion [5,16,17], the exploration of new and improved zwitterions for use as low-fouling materials is gaining significance [18–23].

Zwitterionic polymers can be polymerized using zwitterion monomers, in which both the acidic and basic moiety are located on a single pendant substituent (e.g., betaines), or they can be copolymerized with polyampholytes—a mixture of charged monomers that have both basic and acidic functional groups. Although polyampholytes and betaines exhibit similar anti-fouling properties [24–26], betaines have received more attention in the literature. Nevertheless, research on polyampholytes as non-fouling polymers is growing [26–30] as they offer a broad spectrum of possible combinations of acid-co-base moieties, which can be easily obtained by changing one of the many available acidic or basic monomers. Unlike betaines, however, polyampholytes may acquire a charge offset (either positive or negative) [31], which can increase the fouling propensity of the coated surface [32,33]. Because the composition of the copolymer of the hydrogel may not be identical to the molar ratio of the monomers in the polymerization solution [34–36], the surface charges and their proper balancing must be determined experimentally.

To further mitigate membrane fouling, a low-fouling polymer can be grafted onto a membrane as a hydrogel. Hydrogels can absorb large amounts of water, and although they swell upon water absorption, they remain stable because of the crosslinking. The resulting three-dimensional network of crosslinked polymers exhibits a high degree of hydration, which can weaken the adhesion forces between the surface and foulants [13,30,37–40]. Furthermore, a 3D hydrogel structure grafted by photopolymerization can cover the surface uniformly [41], thus preventing internal fouling inside the membrane pores which was found to limit the efficiency of grafting of zwitterion brushes to porous membranes [7,9].

Altering the characteristics of the outer layer of a membrane is sufficient to reduce its fouling propensity [42], and thin hydrogel films are usually highly stable [9,43,44], allowing very thin modification layers [9,43,45]. Notably, although foulants may penetrate the hydrogel, membrane cleaning is usually more efficient for hydrogel-coated membranes because of the high water content of the hydrogel and the removal of the fouling ‘cake’ layer from the membrane surface [9,46].

Despite the potential advantages of using polyampholyte hydrogels to reduce membrane fouling, only a few such polymers using a limited number of monomers, and rarely as hydrogels, have been studied for membrane modification [33,47,48]. In the current study, a novel polyampholyte hydrogel was studied for the modification of UF polyethersulfone (PES) membranes using the UV photoinitiation method. The novel polyampholyte was copolymerized using vinylsulfonic acid (VSA) as the negatively charged monomer, [2-(methacryloyloxy) ethyl] trimethylammonium chloride solution (METMAC) as the positively charged monomer, and N,N'-methylenebisacrylamide (MBAA) as the crosslinker monomer. Then, the physicochemical properties ( $\zeta$ -potential and hydrophilicity) and morphological properties (thin-film thickness and pore size) of the grafted polyampholyte were investigated, and the

fouling propensity of the modified membranes was evaluated using bovine serum albumin (BSA), humic acid, and sodium alginate as model foulants under static conditions and BSA and external polymeric substances (EPS) from real wastewater under filtration conditions.

## 2. Experimental

### 2.1. Materials

Polypropylene/polyethylene (PP/PE, Novatexx 2471) was provided by Freudenberg, Germany, and PES (Ultrason E3010P) was provided by BASF, Germany. N-methyl-2-pyrrolidone (NMP) was purchased from J.T. Baker, PA, USA; VSA (25% in water) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan); METMAC (80 wt% in water), MBAA, ammonium persulfate (APS), tetramethylethylenediamine (TEMED), BSA, humic acid, and sodium alginate were purchased from Sigma; KCl and Na<sub>2</sub>HPO<sub>4</sub> were purchased from Merck; HCl (32%) and NaOH were purchased from Daejung Chemical and Metals Co., Ltd. (Korea); KH<sub>2</sub>PO<sub>4</sub> was purchased from Hopkin & Williams Ltd.; and NaCl was purchased from Bio-Lab (Israel). All the experiments were performed with purified water from a Milli-Q system (Millipore).

### 2.2. Copolymerization of bulk hydrogel

Free-standing bulk polyampholyte hydrogels were copolymerized by the free-radical polymerization of VSA and METMAC as the negatively and positively charged monomer, respectively, and MBAA as the crosslinker monomer (Table 1) at different molar ratios using APS and TEMED as initiators.

The polymerization solution was prepared by dissolving the monomers and crosslinker (2.5 mol% with respect to the total monomer concentration) in Milli-Q water (which was degassed with nitrogen for 10 min). Next, 44 mM of APS was added to 1 mL of the polymerization solution. The solution was then transferred to an Eppendorf tube, and 5  $\mu$ L of TEMED was added to initiate the polymerization. The reaction was allowed to proceed overnight at 25 °C, and the hydrogel was then removed from the Eppendorf tube and washed with Milli-Q water to remove unreacted monomers and salts.

Equilibrium swelling was measured using the gravimetric method. Each hydrogel was soaked for three days in aqueous NaCl (0–1000 mM, 25  $\pm$  2 °C). Upon removal, and having excess adsorbed water rapidly removed with a Kimwipe tissue, each swollen hydrogel was weighed. The hydrogel was completely dried in a vacuum at 50 °C for 48 h (until no mass change was detected) and re-weighed. The extent of swelling was calculated using the following equation:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  are the weights of the wet and dry hydrogel, respectively.

### 2.3. Surface modification of PES membranes

PES UF membranes were cast using the non-solvent phase inversion method, as previously described [49]. Briefly, PES (13% and 16% w/w) was dissolved in NMP and cast on a non-woven PP surface using an automatic casting device (Elcometer 4340 Braive Instruments, Belgium) at a 200  $\mu$ m wet thickness. The polymer film was then immersed in deionized (DI) water at 20 °C and stored in DI water until use.

Modification was performed as described in our previous study [50]. Briefly, the outer surface of the membrane was covered with

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