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# Grafting polyzwitterions onto polyamide by click chemistry and nucleophilic substitution on nitrogen: A novel approach to enhance membrane fouling resistance

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## ABSTRACT

We present a first-of-its-kind use of click chemistry to graft polyzwitterions (PZs) onto polyamide, the most widely used material to make semi-permeable membranes for desalination and water purification. We have also experimentally proven that  $S_N2$  nucleophilic substitution on nitrogen can occur on the polyamide polymer chain under mild reaction conditions, as opposed to harsh reaction conditions required by many traditional grafting approaches. To prepare the click reaction, we synthesized an alkyne-PZ via reversible addition-fragmentation chain-transfer radical polymerization, followed by functionalizing polyamide with azide functional groups through bromination and subsequently  $S_N2$  nucleophilic substitution of Br with azide. The alkyne-PZ was then grafted to azide-polyamide by an azide-alkyne cycloaddition click reaction. The PZ-grafted polyamide became much more hydrophilic than the virgin polyamide. Results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy indicated that a successful click reaction and almost full surface coverage by PZ were achieved under studied experimental conditions. Membrane flux testing in a forward osmosis mode showed that the PZ grafting did not significantly affect the water flux of a polyamide membrane, thereby demonstrating the new grafting approach as a safe route for the surface modification of polyamide membranes. Besides, the PZ-grafted polyamide membrane exhibited excellent antifouling capability, which can be attributed to the shielding of specific binding sites on membrane surface, strong hydrophilic repulsion caused by local charge-induced hydration forces, and steric repulsion introduced by the brush-like flexible PZ chains. Therefore, this study opens a new avenue to surface modification of polyamide with different functional polymers and hence paves the way to a next generation of high-performance polyamide membranes.

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## 1. Introduction

Polyamide is the most widely used material to make semi-permeable membranes for highly effective desalination and water purification and hence plays a critical role in addressing the global water and energy issues [1]. The polyamide membrane, however, has a high propensity of fouling [2–4], a long-standing problem caused by the accumulation of foreign substances on the polyamide surface. Depending on the specific type of foulants, membrane fouling can be categorized into colloidal fouling, organic fouling, scaling, and biofouling [2–4]. Membrane performance, such as water flux and effluent quality, can be severely deteriorated by fouling [5]. Because membrane surface characteristics significantly affect the process of foulant deposition and fouling layer formation [2,3], developing fouling-resistant polyamide

membranes by surface modification is key to more efficient use of membrane technology [5].

Click chemistry offers an excellent route for membrane surface modification and has previously been used for various membrane materials (e.g., polypropylene [6], polysulfone [7,8]). A salient advantage of click chemistry is its ability to provide superior site selectivity and almost quantitative transformation under mild conditions, with nearly no side reactions or by-products [7,9–14]. Instead of referring to a single specific reaction, click chemistry provides a modular synthetic approach for producing substances by joining small units together [8]. In particular, the click reaction between azide and alkyne has extremely high yield (usually above 95%), high tolerance of functional groups, and moderate temperature requirement (25–70 °C) [15]. The resulting aromatic 1,2,3-triazole ring is very stable and thus makes the grafted functional chain firmly and covalently bonded to the substrate [7,9]. Therefore, the azide-alkyne click reaction holds great promise for cost-effective, sustainable surface modification [7,10–13].

Use of click reaction for surface modification of polyamide membranes, however, has not been reported in the literature.

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Lack of such research may be attributed to the absence of suitable cationic center (e.g., carbocation) on the polyamide polymer chain where clickable functional groups (e.g., azide and alkyne) can be introduced. To circumvent this problem, we propose a novel approach to introduce clickable azide functional groups onto polyamide using  $S_N2$  nucleophilic substitution on nitrogen atom, a reaction that is particularly important in the presence of abundant amide functional groups in the polyamide polymer chain. Despite being widely employed as a means to introduce azide functional groups onto a carbocation [16,17], nucleophilic substitution reaction has focused only on the reaction of highly activated nitrogen compounds (e.g., arylsulfonamides [18–33]) but rarely been used on nitrogen. Moreover, most nucleophilic substitution reaction on nitrogen atom has been associated with harsh experimental conditions and ultra-low reaction temperature [34,35]. It is interesting to point out that the nitrogen atom in polyamide has neighboring C=O and benzene groups, which are electron-withdrawing groups and thus may facilitate the nucleophilic substitution reaction without any requirement on extreme temperature conditions. Therefore, surface modification of polyamide by nucleophilic substitution not only serves as a rare example of nucleophilic substitution on nitrogen but also provides an efficient method for modifying polyamide via click reaction.

As a new antifouling material, polyzwitterions (PZs) have received growing attention over recent years due to their high hydration capability and hence excellent anti-adhesive property against protein fouling and bacterial attachment [36]. Typically, PZ contains both positively and negatively charged functional groups within the same segment side chain while it maintains overall charge neutrality [37]. Compared with polyethylene glycol (PEG, an extensively studied hydrophilic, antifouling material) [38], PZ is able to strongly bind to water molecules with localized charges. Such electrostatically induced hydration can greatly inhibit the attachment of protein or bacteria to a polymer surface due to the physical swelling of the polymer [39,40]. This promising antifouling property makes PZs an ideal coating material for surface modification.

So far, PZ-based surface modification efforts, including surface-initiated atom transfer radical polymerization and plasma-induced interfacial polymerization, have mostly targeted ultrafiltration membranes [41–47]. Only a very few attempts have been made to modify polyamide membranes by creating a PZ thin film on membrane surface via chemical vapor deposition [47] or concentration-polarization-enhanced radical graft polymerization [48]. These existing approaches, however, require specialized setup that is very difficult to scale up and/or involves harsh chemical conditions that are hard to control and lead to troublesome side reactions and by-products [47,48]. Therefore, an efficient, controllable, and easy to scale-up approach for grafting PZs onto the polyamide membrane is highly desirable.

In the present study, alkyne-terminated PZ as a representative zwitterionic polymer was grafted onto a thin-film composite polyamide membrane using nucleophilic substitution on nitrogen followed by click chemistry. First, alkyne-terminated PZ was synthesized via reversible addition-fragmentation chain-transfer (RAFT) radical polymerization. Azide functional groups were then introduced onto the polyamide membrane using a two-step procedure: (i) bromination of polyamide with sodium hypobromite solution under high-pH conditions; and (ii) replacement of the bromine groups by azide functional groups using  $\text{NaN}_3$  via nucleophilic substitution. Finally, PZ was grafted onto the polyamide membrane by performing azide-alkyne click reaction between the alkyne-terminated PZ and azide-functionalized polyamide. Various characterization techniques were employed to confirm the success of the PZ grafting on the polyamide membrane surface. The permeate flux and fouling performance of the

polyamide membrane before and after PZ grafting were tested in a forward osmosis (FO) membrane system.

## 2. Materials and methods

### 2.1. Materials

Unless noted otherwise all chemicals used in this study were obtained from Sigma-Aldrich (St. Louis, MO) and used as received. The polyamide membrane was synthesized in our lab by interfacial polymerization on a polysulfone membrane support, following a procedure similar to the one used in Ref. [5]. Briefly speaking, the polysulfone support was synthesized by a phase inversion process on a polyester fabric. The polysulfone (molecular weight of 22,000) was obtained from Solvay Advanced Polymers (Alpharetta, GA) and the polyester fabric sheets (40  $\mu\text{m}$ , grade 3249) from Ahlstrom (Helsinki, Finland). To synthesize the polyamide membrane, the polysulfone support was fixed in a plastic frame and subsequently placed in an aqueous 1,3-phenylenediamine (MPD) solution (3.4 wt%), surface-dried, and soaked in a 1,3,5-benzenetricarbonyl trichloride (TMC) solution (0.15 wt% in Isopar-G). The membrane was then treated in DI at 95 °C, a sodium hypochlorite (200 ppm) aqueous solution, a sodium bisulfite (1000 ppm) aqueous solution, and again in DI at 95 °C. Finally, the synthesized polyamide membrane was rinsed thoroughly with DI and ready for use.

### 2.2. Nucleophilic substitution on nitrogen

A sodium hypobromite ( $\text{NaBrO}$ ) solution was prepared by adding bromine dropwise to 0.5 M  $\text{NaOH}$  solution at 0 °C in dark environment (by using aluminum foil to shield the reaction from light) until a pH of 9.2 was reached [49]. A polyamide membrane coupon (15 cm in diameter) was fixed in a plastic frame, with the active side of the membrane in contact with  $\text{NaBrO}$  solution for 1–10 min [50]. The polyamide-Br membrane thus obtained was then submerged in 10 g/L  $\text{NaN}_3$  solution. The azide substitution reaction was allowed to continue for 24 h at 20 °C, with the solution continuously stirred in a nitrogen gas atmosphere.

### 2.3. Synthesis of PZ by RAFT polymerization

[2-(methacryloyloxy)ethyl]dimethyl-(3-sulfo)propyl ammonium hydroxide (MEDSAH) was used to synthesize the model PZ via RAFT radical polymerization. In the polymerization, azodiisobutyronitrile (AIBN) was used as an initiator, and alkyne-terminated S-1-Dodecyl-S'-(R,R'-dimethyl-R"-acetic acid)trithiocarbonate (alkyne-SDDAT) as a chain transfer agent. To perform the reaction, 5 g MEDSAH, 0.2 g alkyne-SDDAT, and 50 mg AIBN were mixed in 100 mL ethanol in a single-necked flask. Nitrogen was then bubbled through the solution for 30 min to remove oxygen from the flask. Next, RAFT polymerization was performed at 55 °C for 24 h to synthesize alkyne-polyMEDSAH, followed by the cooling of reactor in ice water. The synthesized polymer was then collected by filtering the solution via a vacuum filter (Cole Parmer, Vernon Hills, IL), rinsing with ethanol, and subsequently drying overnight in oven at 65 °C. The alkyne-polyMEDSAH thus collected was stored in a desiccator prior to use in the grafting experiments.

### 2.4. Surface grafting by click reaction

The polymer solution for the click reaction was prepared by dissolving 0.50 g alkyne-polyMEDSAH and 0.011 g  $\text{CuSO}_4$  in 50 mL methanol/water. Then, the azide-functionalized polyamide was submerged in the polymer solution in a single-necked flask and nitrogen was bubbled into the flask for 30 min to remove oxygen.

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