



# Methoxypolyethylene glycol grafting on polypropylene membrane for enhanced antifouling characteristics – Effect of pendant length and grafting density



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## ABSTRACT

Grafting density and pendant length are recognized as decisive roles in membrane performance; however, they are not easy to control in widely employed free radical grafting polymerization. Herein, methoxypolyethylene glycol (MPEG) brushes with predetermined chain lengths and grafting densities were prepared from hydrophobic macroporous polypropylene membrane (MPPM) by click chemistry.

The grafting density of MPEG on the membrane rose with MPEG concentration and click reaction time, while with the decrease of pendent length. Under the same reaction conditions, the densities were 88.065, 13.116 and 7.070 chains/100 nm<sup>2</sup> for MPEG-200/600/1000, respectively. The normalized pure water flux through MPEG-200 modified membrane (grafting density of 9.250 chains/100 nm<sup>2</sup>) was 222.0, twice that through the pristine one. Pearson correlation analysis indicates that the longer the pendent length and the higher grafting density are, the lower the normalized water fluxes of BSA solution and tap water are, while the better antifouling characteristics are.

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## 1. Introduction

Hydraulic pressure-driven membrane technologies are generally considered quite effective for producing a high-quality water effluent [1]. However, membrane fouling remains a bottleneck for comprehensive applications [2,3]. Hence, developing fouling-resistant membranes is a key for using membrane technologies. Membrane surface modification has been traditionally employed as an effective means to improve membrane's antifouling properties [4].

The surface modification techniques are currently used, like decreasing membrane surface hydrophobicity and roughness,

tethering anti-adhesive monomers, polymers and inorganic particles to the membrane surface [5]. Among these methods, the surface grafting is an efficient access to enduring surface hydrophilization. It is universally accepted that the antifouling property would increase with surface hydrophilicity, which stems from the strong interaction between water and membrane surface. To this end, a variety of hydrophilic polymers have been grafted to the surfaces of various membranes. For example, polyhydroxyethyl methacrylate, polyacrylic acid etc [6] on the surfaces of polypropylene microporous membrane, PTFT membrane, polyethersulfone membrane and PVDF membrane [6].

Nevertheless, these methods (usually grafting-to technique via conventional free radical polymerization) offered little modulating of pendant length (molecular weight) and grafting density (number of chains per unit area), both of which are recognized as decisive roles in membrane performance [7,8]. Whether the membrane permeability decreases or increases and whether the antifouling characteristics improve or deteriorate depends on the modification effect. However, the relations between membrane performance and these parameters are lacking deep exploration [9]. As a result, it is of importance to modify the membranes with determined grafting density and pendent length. Polyethylene glycol (PEG)

*Abbreviations:* MPPM, macroporous polypropylene membrane; MPPM-N<sub>3</sub>, azido functionalized MPPM; MPPM-Br, brominated MPPM; PEG, polyethylene glycol; MPEG, methoxypolyethylene glycol; pro-MPEG, alkynyl-terminated MPEG; PEGMA, poly(ethylene glycol methacrylate); BSA, bovine serum albumin; GD, grafting density; ATR-FTIR, attenuated total reflectance-Fourier transform infrared spectroscopy; XPS, X-ray photoelectron spectroscopy.

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could be one of the most suitable candidates due to its well-known structure.

PEG is one of the broadly investigated polymers, capable of reducing interactions with foulants due to its high excluded volume, flexibility and hydrophilicity. Its promising antifouling properties allow PEG a favorable material for membrane surface modification. So far, the efforts to explore PEG-related surface modification have been made, including grafting-to (adding prepared side chains to the backbone) and grafting-from (growing side chains from the backbone) [10]. Grafting-to and grafting-from are the two general approaches to grafting functional polymer chains to the substrate membrane surface [11–13]. The former couples a specified polymer to an activated surface, enables the synthesis and the characterization of the backbone and side chains respectively, but often comes into low grafting densities because of steric hindrance and being difficult to embellish the polyolefin membranes due to the lack of functionalities. Whereas, the latter originates from a surface fixed initiator, and has been extensively and thoroughly studied due to its capability of preparing brushes with high grafting density. However, tailoring complex macromolecular architectures with specific properties remains a challenge.

It is found that the pendent length and grafting density play significant roles in membrane performance [14]. However, it is difficult to control the chain structure via widely employed free radical grafting polymerization. Delightedly, click chemistry may be the best solution for the problem.

Click chemistry could be a perfect grafting-to route, capable of providing superior site selectivity and almost complete reaction under benign conditions nearly without side reactions or by-products [15]. Click chemistry is a modular synthetic approach to linking small blocks together. In particular, the azide-alkyne click reaction has received a growing interest for its rather high yield (usually > 95%), high tolerance to functional groups, moderate reaction temperature requirement (25–70 °C). The click chemistry yields a well-controlled product without formatting inter-/intra-molecular crosslink, which would jeopardize the correlation between grafting chain structure and membrane performance. Besides, the resulting aromatic 1,2,3-triazoles linkages are rather stable and thus make the functional grafting chain covalently linked to the substrate membrane [16]. Therefore, the azide-alkyne click reaction promisingly offers a more cost-friendly and sustainable approach to modifying membrane surface.

In the present work, the grafting-to method was explored to tether MPEG chains to the membrane surface via click chemistry. To introduce MPEG to the MPPM membrane surface, click reaction was conducted between pro-MPEG and azido-MPPM (MPPM-N<sub>3</sub>), as shown in Fig. 1. Clickable MPPM (MPPM-N<sub>3</sub>) was obtained via a photochemical pathway; the introduced Br atoms then exchanged with azido groups through S<sub>N</sub>2 nucleophilic substitution. Clickable MPPM with azido groups on the membrane (MPPM-N<sub>3</sub>) is thus fabricated. Clickable MPEG, or pro-MPEG, was synthesized via Williamson reaction. Finally, click coupling pro-MPEG to MPPM-N<sub>3</sub> was performed to modify the hydrophobic MPPM surface through the azide-alkyne reaction to afford 1,2,3-triazoles, which makes the MPEG chains covalently linked to the substrate membrane [17].

The grafting chain length and grafting density can be well modulated. The brushes can be fully characterized and well controlled, therefore, the experimental data could clearly throw light on how the pendent length and grafting density affect the membrane performance [18]. The experimental results show that long pendent length and high grafting density result in reduction of membrane permeability while in the improvement of membrane antifouling characteristics.

## 2. Experimental section

### 2.1. Materials

MPEG (The MPEGs having nominal  $M_w$  of 200, 600 and 1000 were used as the macromonomers for pro-MPEG. The polydispersity indexes of MPEG200, MPEG600 and MPEG1000 by GPC are 1.10, 1.07 and 1.06, respectively), sodium ascorbate and copper sulfate (Sinopharm Chemical Reagent Co., Ltd) were purchased. Bovine serum albumin (BSA,  $M_w$  = 66 kDa, molecular size  $14 \times 4 \times 4$  nm [19]) was bought (Sino-American Biotechnology Co.) and dispersed in PBS buffer at pH 7.4. All the chemicals were used as received.

Clickable polypropylene membrane, e.g., azido functionalized MPPM (MPPM-N<sub>3</sub>), was prepared in the light of the literature [20] (MPPM, mean pore size 0.20 μm, thickness 160 μm, porosity 75%, Membrana GmbH, Germany).

Alkynyl-terminated MPEGs (pro-MPEG-200, pro-MPEG-600 and pro-MPEG-1000) were synthesized via Williamson reaction [21] and [22], respectively. The <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, in ppm): 2.35 (s, 1H, —C≡CH), 4.12 (s, 2H, —CH<sub>2</sub>C≡C), 3.64 (s, O—CH<sub>2</sub>—CH<sub>2</sub>—O), 3.37 (s, 3H, CH<sub>3</sub>O). Please see Fig. S1.

### 2.2. General procedure

#### 2.2.1. Click coupling pro-MPEG to MPPM-N<sub>3</sub>

The click reaction was conducted according to [20]. Briefly, MPPM-N<sub>3</sub> was suspended in a Schlenk flask and deoxygenized by applying three vacuum/N<sub>2</sub> charging cycles. 0.50 g pro-MPEG in 40 mL DMSO was added under Argon protection. Then the reaction was performed with an oil bath at 60 °C for 24 h using CuSO<sub>4</sub> and sodium ascorbate as the catalysts.

Grafting density (GD) of MPEG is calculated by formula (1):

$$GD \text{ (chains/100 nm}^2\text{)} = \frac{m_1 - m_0}{A_{BET} \times M_w} \times \frac{6.023 \times 10^{23}}{10^{18}} \times 100 \quad (1)$$

where  $m_1$  (g) is the weight of MPEG grafted MPPM,  $m_0$  (g) the weight of the unmodified one [23],  $A_{BET}$  (m<sup>2</sup>) BET specific surface area of the membrane (measured by Beckmann-Coulter GmbH technique, 28.5 m<sup>2</sup>/g),  $M_w$  the molecular weight of MPEG (g/mol). All results were the averages of at least 3 parallel samples.

Each of the membrane samples was sonicated for 10 min and then ethanol/water (1:1) and 0.2 M NaCl washed for respective 4 h, followed with tap water by vibration for about 24 h, finally vacuum desiccated overnight at 40 °C.

#### 2.2.2. Membrane permeation properties

The permeability was investigated with a dead-ended stirred ultrafiltration system (Amicon 8050 connected to a 1 gallon Millipore feed tank, pressure regulated with Ar [20]) at the stirring speed of 200 rpm, temperature of 20 °C and a constant transmembrane pressure of 40 kPa. 1 g/L BSA dispersion in phosphate buffer solution at pH 7.4 was used for the feed solution. Normalized flux, flux recovery ratio after tap water cleaning, the relative flux reduction were described as follows:

$$\text{Normalized flux} = J_{o,m}/J_{o,u} \quad (2)$$

$$\text{Flux recovery ratio} = J_1/J_{o,m} \quad (3)$$

$$\text{Flux reduction (\%)} = (J_{o,m} - J_p)/J_{o,m} \times 100 \quad (4)$$

The relative flux reduction includes the reversible fouling (resulted from reversible BSA adsorption and could be eliminated by hydraulic cleaning) and irreversible fouling (due to irreversible BSA adsorption or deposition and could not be removed by hydraulic washing), they can be defined as:

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