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Grafting of Poly (Cysteine Methacrylate) Brush from Polysulfone Membrane via Surface-Initiated ATRP and Their Anti-Protein Fouling Property *

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Abstract

In this paper, we first grafted the poly cysteine methacrylate (pCysMA) brush on polysulfone membrane by surface-initiated atomic-transfer radical polymerization and studied for their antifouling properties. The surface topological structure, chemical composition, and wettability of the as-prepared surface are characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), fourier transform infrared spectra (ATR-FTIR), and water contact angle (WCA) measurements. The hydrophilicity and anti-biofouling activities of the polymer brush surface were evaluated by protein adsorption test. The results displayed that the pCysMA shows better hydrophilicity and effectively resisted the adsorption of bovine serum albumin (BSA) protein.

Keywords: Polysulfone; Cysteine; ATRP; protein adsorption

1 Introduction

Due to its excellent mechanical strength, and thermal stability, polysulfone (PSU) has been used in the field of hemodialysis [1, 2], ultrafiltration [3], and fuel cells [4]. However, the hydrophobic nature of PSU membranes limited its biomedical applications. Hydrophilic surface modification of the membrane would be an effective approach to solve this problem [5-9].

The surface coatings containing zwitterionic structural units are highly resistant to nonspecific protein adsorption, bacterial adhesion, and biofilm formation. Recently, amino acids, a natural zwitterion, have shown good anti-biofouling performance [10-12]. Rosen et al. prepared a functionalized silica nanoparticles with cysteine in order to create a low-fouling surface for nano medicine applications [13]. Shen et al. used self-polymerized dopamine to form a thin and surface-adherent polydopamine layer onto poly(ethylene terephthalate) (PET) sheet, followed by covalent

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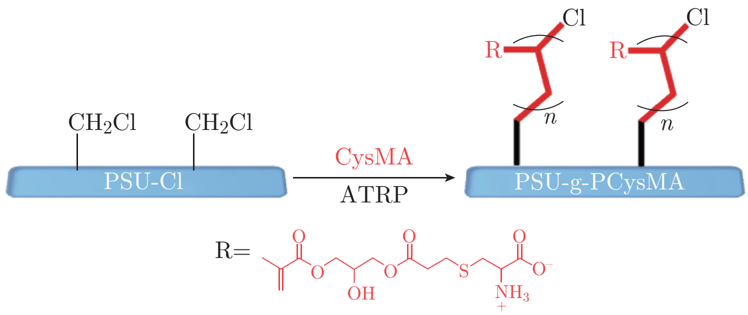
grafting cysteine (Cys) to improve hemocompatibility and anti-biofouling property [14]. Liu et al. prepared zwitterionic poly(serine methacrylate) (PSerMA) brushes on a planar gold substrate using surface-initiated photo iniferter-mediated polymerization (SI-PIMP) for evaluation as a potential antibiofouling material [15]. Very recently, Armes et al grafted the Poly(cysteine methacrylate) (PCysMA) brushes into the surface of silicon wafers by atom-transfer radical polymerization [16]. The obtained the film strongly resist cell adhesion when immersed in culture media in the presence of HDF cells.

Our interest in developing synthetic methods for the preparation and modification of polymer materials [17-21], as part of our continuous research, in the present study, we modified the PSU membrane with a cysteine-based zwitterionic poly(cysteine methacrylate) via ATRP method as shown in Scheme 1. The anti-fouling performances of modified membranes were tested by bovine serum albumin (BSA) protein absorption.



Scheme 1 Grafted zwitterionic poly(amino acid) brushes with anti-fouling properties

2 Experimental Procedure

2.1 Materials

Polysulfone (PSU Udel P1700LCD) was purchased from Solvay Advanced Polymers. 2, 2'-dipyridyl, and CuBr were purchased from Sinopharm (Shanghai, China). Cysteine and 3-(acryloyloxy)-2-hydroxypropyl methacrylate were purchased from Aladdin Reagent (Shanghai) Co., Ltd. and used without purification. Chloromethylation of PSU was performed according to the reported methods [22]. Cysteine Methacrylate monomer (CysMA) was synthesized according to the published work [16].

2.2 Grafting of pCysMA Brushes from PSU Film

Cysteine methacrylate (CysMA) monomer (1.5 g) was dissolved with 12 mL deionized water and stirred for 15 minutes, then 2,2'-dipyridyl (70 mg) was added into the mixture. After being stirred for 15 min under a nitrogen atmosphere, the mixture was degassed by three freeze–pump–thaw cycles. In the frozen state, PSU-Cl membrane ($2 * 2$ cm) and CuBr (32 mg) were placed into the glass tube. The tube was then subjected to three additional freeze–pump–thaw cycles before being kept at 60 °C. After a predetermined period of time, the modified membrane was removed from the reaction system. After being thoroughly washed with methanol and water, the membrane was dried to constant weight under vacuum.