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A facile approach toward multi-functional polyurethane/polyethersulfone composite membranes for versatile applications

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ABSTRACT

The complex synthesis through multistep reactions and tedious purifications based on different monomers or macromolecules limits the practical applications of functional polymers. Herein, a facile approach toward a series of functional polyurethanes (PUs) is designed for versatile biological applications within fewer step reactions under mild conditions. The tertiary amino groups in the PU are converted into zwitterions or quaternary ammonium salt via simple one-step synthesis, and then used to prepare PU/polyethersulfone composite membranes. The composite membrane with tertiary amine groups exhibits significant adsorption capability to anionic dye Congo red (CR) and toxin bilirubin. The membrane bearing zwitterionic PU displays excellent blood compatibility; while which with quaternary ammonium salts has antibacterial property. Furthermore, carboxybetaine-functional composite membrane is exploited to bear Ag nanoparticles to endow with dual functions of antibacterial and antifouling properties. This work demonstrates the potential of PUs as readily available, multi-functional, and easy-to-use materials for biological applications.

1. Introduction

With the development of polymeric materials, desired properties could be achieved flexibly by utilizing either different common monomers or some specific monomers with elaborate modifications [1–3]. Besides, the macromolecules could be further modified for extensive applications using the functional groups such as –COOH, –OH and $–NH_2$ on the macromolecular chains [4–6]. For example, the macromolecules or monomers that contained quaternary ammonium salt or Ag nanoparticles [7] could endow the materials with broad-spectrum antimicrobial property; while antifouling property was generally achieved using the monomers or macromolecules with zwitterions, hydroxyl groups and/or PEG chains, such as Sulfobetaine methacrylate (SBMA) [8], Hydroxyethyl methacrylate (HEMA) [9–11] and Poly(ethylene glycol) methacrylate (PEGMA) [12,13], which could also improve biocompatibility of materials [14]. On the other hand, for the polymers like polyesters and polyurethanes, most of the active functional groups like –OH, $–NH_2$ or –COOH in monomers are usually sacrificed in the polymerization process, thus the possibility of further modifications is less than the polymers prepared by vinyl monomers [15,16].

Despite that the types of monomers and macromolecules have been increasingly diversified through the modification, a considerable amounts of synthetic processes generally required multistep synthesis with many reactants or catalysts [17,18], restricting the practical applications due to the lack of efficiency and universality. Regarding this concern, developing different functions based on the same monomers or macromolecules through fewer step reactions under mild conditions is an indispensable strategy for both the productions and the applications.

The aim of this study is to develop a facile strategy to combine various functions in polyurethane (PU) via straightforward reactions. 4,4′-Diphenylmethane diisocyanate (MDI) was used as the hard segment to enhance the miscibility of PU with other polymeric materials; while N-methyldiethanolamine (MDEA, containing tertiary amino group) was used as the soft segment. Additionally, citric acid (CA) was used as blocking agent to endow with anticoagulation property. Different from the modification of the macromolecules that contained –OH, $–NH_2$ or –COOH, the various functionalities in this study are based on the tertiary amino groups, which could be further converted into zwitterions (sulfobetaine and carboxybetaine) [19,20] or quaternary ammonium salt [21]. The process was performed through one-step reaction without any catalysts or additional reactants. The synthesized PUs were exploited to prepare composite membranes with polyethersulfone (PES), and the adsorption capability of the composite membrane that contained tertiary amino groups was evaluated firstly by using dye Congo red (CR) and toxin bilirubin. The blood compatibility and antifouling property of the zwitterionic composite membranes were then evaluated in terms of clotting times, protein adsorption and platelet adhesion; while the activities of *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were performed to demonstrate the

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antibacterial property of the membrane bearing quaternary ammonium salts. Furthermore, it was found that the carboxybetaine could load silver, which has been seldom reported [22]; thus the carboxybetaine membrane was used to bear Ag nanoparticles to endow with dual functions of antibacterial and antifouling properties.

2. Experimental

2.1. Materials

4,4′-Diphenylmethane diisocyanate (MDI, 98%, Aladdin), N-methyldiethanolamine (MDEA, 98%, Aladdin), 1,3-propanesulfonate (98%, Aladdin), 3-bromopropionic acid (98%, Aladdin), and iodomethane (98%, Xiya) were used without further purification. N,N-dimethylformamide (DMF, 99%, Kelong), 1-methyl-2-pyrrolidinone (NMP, 99%, Kelong) and dimethyl sulfoxide (DMSO, 99%, Kelong) were distilled under vacuum. Deionized water (DI water) was used throughout the study. Congo red (CR) and methylene blue (MB) were obtained from Kelong Inc. Bilirubin (98%) was purchased from Aladdin Industrial Inc. The LIVE/DEAD BacLight Bacterial Viability Kit L-7012 was purchased from Thermo Fisher Scientific Inc.

2.2. Synthesis and characterization of polyurethanes

2.2.1. Synthesis of polyurethane with tertiary amine (PU)

All the polyurethanes were modified from original polyurethane that contained tertiary amine groups (PU) as shown in Scheme 1 and the synthetic process of PU is as follows:

MDI (6.92 g) and MDEA (3.08 g) were dissolved in DMAc with the monomer concentration of 20 wt.%, and the molar ratio of the MDI to NMDA was 16:15. The polymerization was carried out in nitrogen gas at 75 °C for 2 h, and then citric acid was introduced in the reaction system and carried out at 80 °C for another 4 h. After the reaction, the polyurethane was precipitated with deionized (DI) water and washed with ethanol for several times. The product was dried in a vacuum oven at 40 °C.

2.2.2. Synthesis of polyurethane with sulfobetaine (SPU)

1,3-Propanesulfonate (1.98 g) was added dropwise into the solution of the as-prepared PU (2.00 g) in DMSO, and the reaction was carried out at 25 °C for 24 h. Then the product was precipitated using ethanol and dried in a vacuum oven at 40 °C.

2.2.3. Synthesis of polyurethane with carboxybetaine (CPU)

3-Bromopropionic acid (2.49 g) and the PU (2.00 g) were dissolved in DMSO, and reaction was carried at 60 °C for 24 h. After the reaction, the product was precipitated using ethanol and dried in a vacuum oven at 40 °C.

2.2.4. Synthesis of polyurethane with quaternary ammonium (QPU)

CH_3I (12 mL) was added into the solution of the PU (2.00 g) in NMP and reacted at 60 °C for 12 h. After the reaction, the product was precipitated using ethanol and dried in a vacuum oven at 40 °C.

2.2.5. Characterization of the polyurethanes

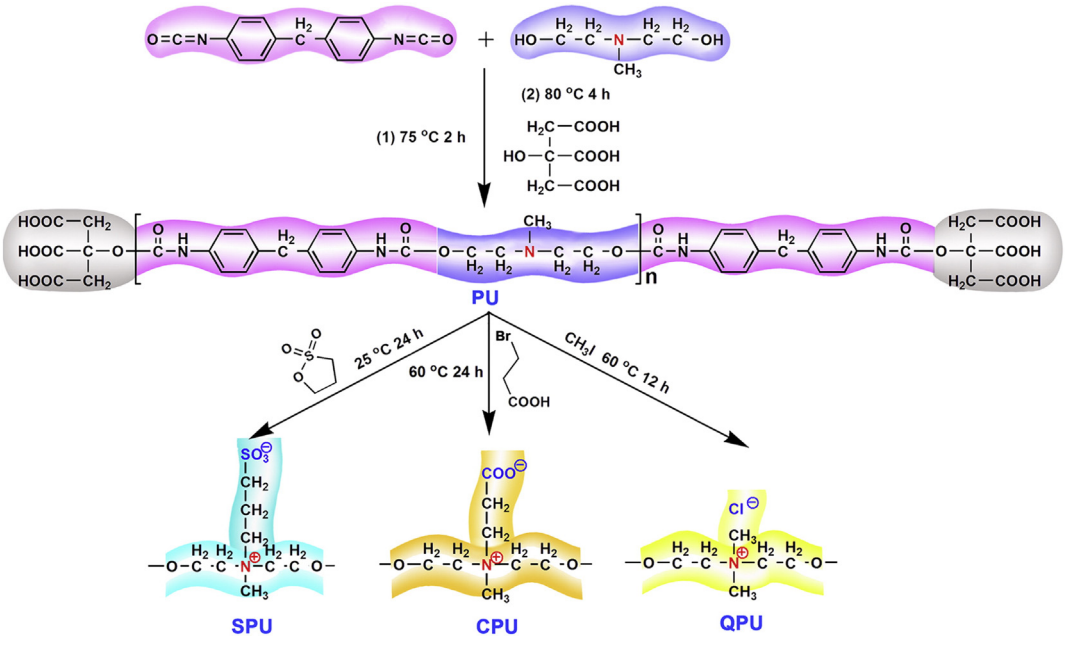
^1H NMR (400 MHz) spectra were recorded on a BrukerAVII-400 MHz spectrometer (Bruker Co., Germany), using tetramethylsilane (TMS) as the internal standard in DMSO-d_6 at room temperature.

Gel permeation chromatography (GPC) measurement was performed by using a PL220 GPC analyzer (Britain) to measure molecular weight. N,N-dimethyl formamide (DMF) was chosen as the eluent and polystyrene (PS) as the reference.

2.3. Preparation of membranes

PES was dissolved in DMSO to keep the concentration at 16 wt.%. Then the PU was added to the solution and the concentration was controlled at 4 wt.%. The solution was prepared into membranes by spin coating coupled with a phase inversion technique as described in our earlier reports [23,24]. The membranes modified with PU, SPU, CPU and QPU were termed PU/PES, SPU/PES, CPU/PES and QPU/PES, respectively.

To obtain membrane bearing Ag nanoparticles, the CPU/PES membrane was firstly immersed into 0.1 M NaOH for 10 min and rinsed 3 times in DI water. Then the membrane was immersed into 0.05 mM $AgNO_3$ solution with oscillation for 24 h in the dark, followed by rinsing with DI water for 3 times to remove the excess $AgNO_3$. Then the membrane was dipped in 0.05 mM $NaBH_4$ for 2 h to prepare Ag loaded membrane which was termed CPU-Ag/PES.



Scheme 1. Synthesis of a series of polyurethanes.