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Hydrophilic and anti-fouling polyethersulfone ultrafiltration membranes with poly(2-hydroxyethyl methacrylate) grafted silica nanoparticles as additive

Li-Jing Zhu, Li-Ping Zhu*, Jin-Hong Jiang, Zhuan Yi, Yi-Fan Zhao, Bao-Ku Zhu, You-Yi Xu

MOE Key Laboratory of Macromolecule Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

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ABSTRACT

Here we report the preparation and properties of polyethersulfone (PES) ultrafiltration (UF) membranes with poly(2-hydroxyethyl methacrylate) (PHEMA) grafted silica (SiO_2) nanoparticles (PHEMA@SiO_2 NPs) as the blending additive. The PHEMA@SiO_2 NPs were first prepared by grafting PHEMA brushes onto SiO_2 NPs via a surface-initiated reversible addition fragmentation chain transfer (RAFT) polymerization. The organic–inorganic hybrid membranes of PES with PHEMA@SiO_2 NPs were fabricated via the traditional non-solvent induced phase separation (NIPS) process. During membrane formation, the hydrophilic PHEMA@SiO_2 NPs tended to migrate toward the membrane top surfaces. The membrane surface porosities were increased and the surface hydrophilicity was enhanced after introducing PHEMA@SiO_2 NPs. More importantly, the water permeability, solute rejection and anti-fouling ability of PES membranes were improved significantly. This phenomenon indicated that the trade-off between permeability and selectivity of PES UF membranes was broken by the incorporation of PHEMA@SiO_2 NPs. Different from traditional neat inorganic NPs additive, the PHEMA@SiO_2 organic–inorganic NPs could be held in/on PES membrane for a long period of time due to the intertwisting of polymer chains. The present work provides a simple approach for stable and nearly permanent hydrophilization of PES UF membranes, which can also be extended to more membrane materials prepared by NIPS process.

1. Introduction

Polyethersulfone (PES) is a thermoplastic polymer having excellent chemical and thermal stability, and high mechanical strength [1]. It is well dissolvable in some aprotic polar solvents and can conveniently be processed into a porous membrane by a simple phase inversion method. Actually, PES membrane is one of the most popular polymer ultrafiltration (UF) membranes and widely used in water purification, beverage filtration, protein separation, pretreatment of reverse osmosis (RO) etc. [2–4]. Despite the advantages as a membrane material, PES itself is not enough hydrophilic and thus the water permeability of PES membrane is not satisfactory in practical application. Furthermore, neat PES membrane is often easy to be hit by serious membrane fouling, leading to the gradual decrease of permeation flux and frequent membrane washing [5,6]. In addition, the current PES membrane as well as other polymer membrane materials commonly suffers from the inherent trade-off effect between selectivity and permeability. Therefore, PES membrane often has to be modified to improve its hydrophilicity, anti-fouling ability and filtration properties before its practical use.

Numberless papers have been published on the modification of PES UF membranes. The reported methods in literatures mainly include blending, coating, adsorption, surface chemical or plasma treatment, surface grafting etc. [7–9]. These techniques have brought a great success in enhancing membrane surface properties such as hydrophilicity and fouling resistance. However, they also have some shortcomings and problems hindering their further popularity in membrane industry. For example, coating and grafting techniques often require substantial post-treatment process, increasing membrane fabrication costs. The long-term durability of coated and adsorbed hydrophilic layers on membrane surface is limited, especially during operation and aggressive chemical cleaning. Some hydrophilic polymeric additives e.g. poly(ethylene glycol) (PEG), poly(*N*-vinyl pyrrolidone) (PVP) introduced into membrane bulk by blending are easy to be dissolved away in membrane fabrication and use.

In recent years, inorganic materials have received more and more attention in membrane modification. By introducing inorganic materials into the organic membrane matrix, the obtained organic–inorganic hybrid membranes combines the basic properties of

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* Corresponding author. Tel./fax: +86 571 87953011.
E-mail addresses: lpzhu@zju.edu.cn, julinpin@hotmail.com (L.-P. Zhu).

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organic and inorganic materials and shows excellent separation performance, anti-fouling ability, good thermal and chemical stability and adaptability to the harsh environments [10–12]. Various inorganic materials such as nanoparticle [13–17], carbon nanotube [18,19] and graphene oxide [20] have been incorporated into PES membrane to prepare the organic–inorganic hybrid membranes. And most of the studies indicate that the addition of inorganic materials prominently improved the water permeability and fouling resistance of polymer membrane. However, when inorganic materials are directly blended into the polymer matrix without further modification, it is difficult to achieve excellent miscibility between two phases due to the aggregation of inorganic materials and the huge difference in surface energy of two phases. Therefore, inorganic materials should be modified before use to enhance their compatibility and dispersity in the membrane matrix.

Grafting polymer chains onto the inorganic material surface is a feasible and effectual strategy to enhance the miscibility between organic matrix and dispersed inorganic phase. For example, Sun et al. reported the modification of SiO_2 NPs by coating the PVP layer to improve the dispersity of SiO_2 in PES membranes [21]. Madaeni et al. grafted poly(acrylic acid) (PAA) onto TiO_2 NPs and prepared anti-fouling polyvinylidene fluoride (PVDF) membranes with PAA functionalized TiO_2 NPs [22]. Compared to water soluble polymers such as PVP, PAA etc., PHEMA has better miscibility with the hydrophobic polymer membrane matrix. Therefore, in this work, PHEMA grafted SiO_2 NPs (PHEMA@SiO_2) were used as the blending additive of PES membranes prepared by the non-solvent induced phase separation (NIPS) process. PHEMA is a favorable water-soluble polymer which can be easily obtained by the homopolymerization from its monomer by a number of ways. Moreover, PHEMA has well biocompatibility, suitable to a range of applications in biomedical field [23–25]. Actually, PHEMA has been used in the modification of polymer membranes to improve membrane hydrophilicity, anti-fouling and separation properties [26,27]. However, to our knowledge, so far rare work has been reported on the modification of PES membrane using the SiO_2 NPs grafted with PHEMA.

In the present paper, we would like to report the preparation and properties of PES UF membranes using PHEMA@SiO_2 NPs as the blending additive. The PHEMA@SiO_2 NPs were first prepared by grafting PHEMA brushes onto SiO_2 NPs via RAFT polymerization to improve their dispersity and the miscibility in the PES matrix. The organic–inorganic hybrid membranes of PES with PHEMA@SiO_2 NPs were fabricated via the traditional NIPS process. The hydrophilicity, anti-fouling and separation properties of the organic–inorganic hybrid membranes were investigated in detail.

2. Experimental

2.1. Materials and reagents

Polyethersulfone (PES, A100, M_w=53,500) was supplied by Solvay Company. Tetraethyl orthosilicate (TEOS, 99.9%), (3-aminopropyl)triethoxysilane (APTES, 97%), *N*,*N*′-dicyclohexyl carbodiimide (DCC, 99%) and 4,6-dimethyl-2-pyridinamine (DMAP, 98%), 1-dodecanethiol (98%), carbon disulfide (CS_2, $\geq$ 99.9%), 4,4′-Azobis (4-cyanovaleric acid) (ACVA, 98%) and sodium hydride (NaH) were purchased from Aladdin and used directly. Azobisisobutyronitrile (AIBN) was supplied by Shanghai Chemical Regent Company and recrystallized two times from ethanol. *2*-Hydroxyethyl methacrylate (HEMA, 98%) was brought from Aladdin and passed through a column filled with basic alumina prior to use in order to remove the polymerization inhibitor. Platelet rich plasma (PRP) was obtained from the Blood Center of Zhejiang Province, China. Bovine serum albumin (BSA, M_w 67,000) was supplied by Bio Life Science and Technology Co. (Shanghai, PR China). Ultrapure water was produced by a Millipore direct-Q system. All other reagents, such as *N*,*N*′-dimethylacetamide (DMAc) and Macrogol 400 (PEG-400), were analytical grade and used without further purification.

2.2. Synthesis of PHEMA@SiO_2 NPs via surface-initiated RAFT polymerization

The synthesis route of PHEMA@SiO_2 NPs via the surface-initiated RAFT polymerization was schemed in Fig. 1. In brief, the synthesis process included four steps: (1) Bare SiO_2 NPs were prepared by the classical Stöber sol–gel method [28]. (2) Amino-functionalized SiO_2 (SiO_2–NH_2) NPs were synthesized by direct condensation of APTES with the surface hydroxyl groups of the bare SiO_2 NPs. (3) RAFT agent CDP modified SiO_2 (SiO_2-CDP) NPs were prepared by amide reaction. (4) PHEMA@SiO_2 NPs were prepared by surface-initiated RAFT polymerization of HEMA from the chain transfer agent SiO_2-CDP NPs. More details are described in Supplementary material.

2.3. Preparation of the PES/PHEMA@SiO_2 organic–inorganic hybrid membranes

The organic–inorganic hybrid membranes were prepared via the NIPS technique. PES was used as a membrane bulk material and PHEMA@SiO_2 NPs were used as additive. DMAc, PEG400 and distilled water were used as solvent, pore forming agent and coagulant, respectively. In a typical procedure for the preparation

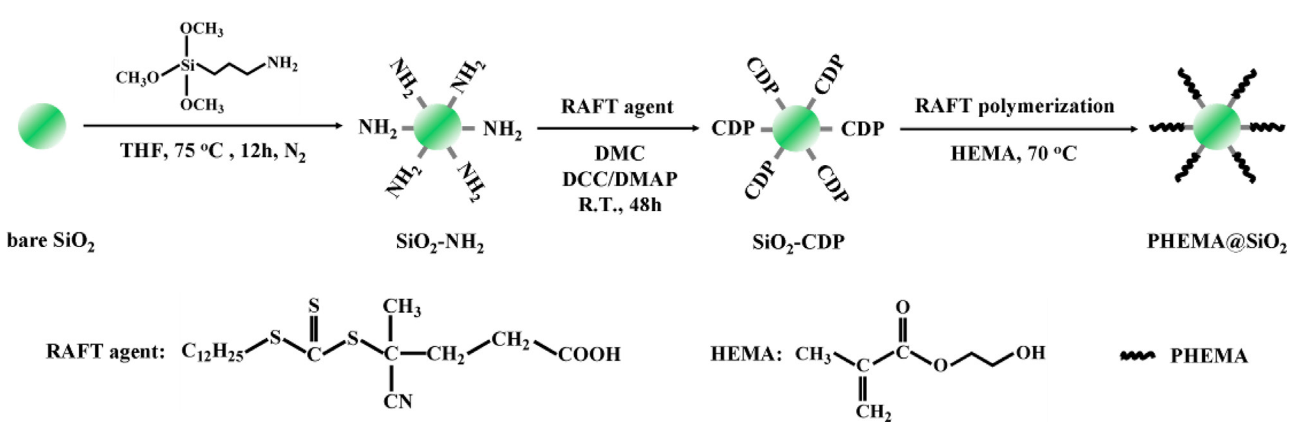

Fig. 1. The synthesis route of PHEMA@SiO_2 NPs via surface-initiated RAFT polymerization.