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Manipulating membrane permeability and protein rejection of UV-modified polypropylene macroporous membrane

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ABSTRACT

A three-step photo-induced graft polymerization of 2-hydroxylethyl acrylate (HEA) on the polypropylene macroporous membrane was carried out by using the chain transfer agent (CTA) benzyl dithiobenzoate (BDTB). Firstly, benzophenone was immobilized on the membrane surface; secondly, polyHEA (PHEA) was grafted on the membrane surface under UV irradiation in the presence of HEA and BDTB; thirdly, the PHEA grafted membranes with and without CTA moieties were respectively immersed in a thermostated water bath at 55 °C for the further grafting polymerization of HEA; in this step, PHEA was also grafted on the second-step modified membrane, with the grafted membrane containing CTA moieties served as macro-CTA and azodiisobutyronitrile (AIBN) as initiator.

The degree of grafting (DG) of PHEA increased with UV irradiation time in the first step. In the second step, DG increased with UV irradiation time and monomer concentration, and with the decrease of CTA concentration. In the third step, DG continuously increased with reaction time under thermostated conditions without adding the free radical initiator; for the PHEA grafted membranes with CTA moieties on the grafting chain, DG was relatively higher than that for the PHEA grafted membranes without CTA moieties; also PHEA was grafted on the membrane surface by using the second-step modified membrane as the macro-CTA and AIBN as initiator, DG continued to increase with the reaction time.

The pure water flux increased with the rise of DG up to 4.48 wt.%, then it decreased gradually, which shared the same trend with the water flux during the filtration of protein dispersion. The flux recovery ratio after water cleaning also increased with the rise of DG. But the rejection of protein dispersion followed the reversed trend of the pure water flux: it decreased down to 4.48 wt.% then increased with the rise of DG.

1. Introduction

Membranes, especially polypropylene porous membranes, were widely used in many fields such as ultrafiltration and microfiltration because of the low cost and easy processing. However, some disadvantages (hydrophobicity, poor antifouling characteristics and so on) limit its wider application. Surface modification of membranes becomes more and more important in the membrane science to endow membranes with desired properties.

There are many methods to modify the membrane surface, such as UV irradiation [1,2], plasma treatment, grafting polymerization and physical adsorption [3]. The surface grafting polymerization is a very effective approach to permanent surface hydrophilization among these methods [4,5]. However, the degree of grafting in these methods is not controllable and is often too high. As a result, the micropores on the membrane surface were jammed; membrane permeability was decreased after modification. This loss of membrane permeability has been widely observed and has been linked to the blockage of membrane pores by the grafted polymer chains, and is deteriorated by a high grafted chain density and long chain length [6]. Grafting short polymer chains may be one approach to improving the modified membrane permeability after modification. A high grafted chain density and long graft chain length may be essential to impart the necessary surface hydrophilicity to decrease membrane fouling. Accordingly, the graft chain density and chain length should be optimized to impart the necessary surface hydrophilicity and improve the permeability as high as possible. However, as a result of the traditional free radical nature of the polymerization processes it is not easy to control molecular weight of the grafted chains or to prepare block grafting chains, therefore it is difficult to design and standardize the properties of the final product [7].

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Recently, controlled free radical polymerization, such as reversible addition-fragmentation polymerization (RAFT), atom transfer radical polymerization (ATRP) [8], and nitroxide-mediated radical polymerization (NMP), has been involved to improve membrane surface modification. RAFT technique is, in principle, closest to the conventional radical polymerization, and hence perhaps is the most versatile controlled radical polymerization technique [9]. The industrial importance and robustness, relatively mild reaction conditions make RAFT route an appealing option [10]. A polymeric chain with an active site at one or two ends can be synthesized with RAFT method readily [11]. The active site can initiate the sequential addition of another vinyl monomer to the reaction system. Therefore, RAFT method is possible to introduce a block grafting chain onto the backbone of polymers [12,13], and allows relatively tight control over the amount of surface modification easily through variation of the reaction conditions. However, much work has been done to introduce the initiating sites by plasma treatment, ozone treatment and γ-irradiation, followed by the controlled graft polymerization [14–17]. In our lab, surface modification of polypropylene membranes by the reversible addition-fragmentation chain transfer (RAFT) polymerization combined with UV irradiation was conducted, and the block grafting chains with different functionalities were obtained, multi-stimulus membranes were thus acquired [18].

Many functional monomers, including 2-hydroxylethyl acrylate (HEA) were widely used to modify the surface of membranes or polymers for the improvement of hydropholicity, antifouling and biologic property. Guan et al. introduced hydrophilic groups onto PU membrane by surface grafting of HEA [19]. Mun et al. modified chitosan by graft-polymerization of HEA to improve water solubility of the polymer [20].

In this paper, we report on a three-step UV induced RAFT mediated surface modification by the grafting polymerization of HEA. Benzophenone (BP) was served as photosentisizer, benzyl dithiobenzoate (BDTB) as a chain transfer agent (CTA) and AIBN as a free radical initiator. The X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscope (FE-SEM) were utilized to characterize the surface structure and morphology of the modified membrane. Different reaction conditions, like monomer and CTA concentrations and UV irradiation time were designed to investigate the effect of reaction conditions on the degree of grafting. Control experiments were carried out and it was found that for the PHEA grafted membrane containing or not containing CTA, the reaction can last under thermostated conditions without the UV irradiation. In the third step, the further grafting polymerization of HEA can also take place by using AIBN as the initiator and the second-step modified membrane as the macro-CTA.

2. Experimental

2.1. Materials

Polypropylene macroporous membranes (PPMMs) with a porosity of 45–50% and an average pore diameter of 0.10 μm were prepared in our laboratory [21]. HEA was obtained from TCI (Kasei, Japan). Benzophenone (BP) was recrystallized twice from ethanol and used as photo-initiator. AIBN was used as received. Benzyl dithiobenzoate (BDTB) was synthesized according to the literature [22,23]. Characterization was done by ^{1}H NMR: ($CDCl_3$, 300 MHz) (ppm): 4.61 (s, 2H); 7.23–7.43 (m, 8H) and 8.02 (m, 2H). Bovine serum albumin (BSA, purity > 98%, pI = 4.8, Mw = 66 kDa) was purchased from Sino-American Biotechnology Co. and used as received. BSA dispersion was prepared in a phosphate buffered saline (PBS) solution at pH 7.4.

2.2. Photo-induced immobilization of BP on the PPMM surface

UV irradiation was conducted under argon gas environment on an UV illumination system equipped with two high-pressure mercury lamp (2 × 300 W with a wavelength range of 350–450 nm) as the light source with the strongest light emission at 365 nm. Pre-weighed PPMMs were presoaked for 10 h in 50 mL solution of 10 wt.% BP in heptane and anhydrous ethanol (5:1). UV irradiation was carried out for a given time (usually 10–60 min). The BP immobilized PPMM was designated as PPMM-BP.

2.3. Photo-induced grafting polymerization of HEA on the PPMM-BP surface

PPMM-BPs were put into flasks which were degassed by three freeze-evacuate–thaw cycles and sealed. 30 mL 0.1 mmol/L BDTB (or no BDTB) and 5–15 wt.% HEA mixed solution in anhydrous ethanol was congested by Ar gas for 30 min, then injected to the flask. After that the photo-induced grafting polymerization was carried out under UV irradiation for a prescribed time. The obtained membranes were designated as PPMM-g-PHEA-CTA (or PPMM-g-PHEA).

Finally the further polymerization was conducted by incubating the flasks in a thermostated water bath at 55 °C standing for 0–10 h.

2.4. AIBN initiated RAFT-mediated grafting polymerization of HEA on the PPMM-g-PHEA-CTA surface

To verify the ability to prepare block grafting polymer chain, the PPMM-g-PHEA-CTA was used as macro-CTA for further grafting reaction. PPMM-g-PHEA-CTA membranes were put into flasks containing 15 (v/v) % HEA and 0.1 mmol/L AIBN in isopropanol. The polymerization was performed at 80 °C for 10–60 min.

After each step of the surface modification, the membrane samples were taken out of the reaction flask and washed with ethanol and pure water in a shaking water bath at 30 °C for 24 h, dried completely in vacuum at 40 °C overnight to a constant weight, the membrane was weighed with an analytical balance to a precision of 0.1 mg. The degrees of grafting of PHEA for the second (DG2) and third step (DG3) were determined gravimetrically as follows:

$$\mathrm{DG2}\,(\%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$\mathrm{DG3}\,(\%) = \frac{W_2 - W_0}{W_0} \times 100 \quad (2)$$

where W_0 is the weight of the blank membrane, W_1 and W_2 are the weights of the membrane after the second and the third step.

2.5. Characterization of the modified membranes

X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (PerkinElmer) with Al Kα radiation ($h\nu$ = 1486.6 eV). Surface morphologies of the unmodified and modified PPMMs were observed by field emission scanning electron microscope (FE-SEM) with a Hitachi 4800 (Hitachi, Japan) operating with an accelerating voltage of 5 keV. The detailed description was similar in the literature [18].

2.6. Permeation and antifouling properties

The permeation properties of the unmodified and modified PPMMs were examined in a stirred dead-ended ultrafiltration test cell connected to a 2 L feed tank. The feed tank was pressurized by regulated N_2 gas. The active membrane area was 38 cm^2. All membrane samples were wetted and filtrated with 50 (v/v) %