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Thermo- and pH-responsive polypropylene microporous membrane prepared by the photoinduced RAFT-mediated graft copolymerization

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ABSTRACT

Thermo- and pH-responsive polypropylene microporous membrane prepared by photoinduced reversible addition–fragmentation chain transfer (RAFT) graft copolymerization of acrylic acid and N-isopropyl acrylamide by using dibenzyltrithiocarbonate as a RAFT agent. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR/FT-IR), X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscopy (FE-SEM) were used to characterize the structural and morphological changes on the membrane surface. Results of ATR/FT-IR and XPS clearly indicated that poly(acrylic acid) (PAAc) and poly(N-isopropyl acrylamide) (PNIPAAm) were successfully grafted onto the membrane surface. The grafting chain length of PAAc on the membrane surface increased with the increase of UV irradiation time, and decreased with the increase of the concentration of chain transfer agent. The PAAc grafted membranes containing macro-chain transfer agents, or the living membrane surfaces were further functionalized via surface-initiated block copolymerization with N-isopropyl acrylamide in the presence of free radical initiator, 2,2′-azobisisobutyronitrile. It was found that PNIPAAm can be grafted onto the PAAc grafted membrane surface. The results demonstrated that polymerization of AAc and NIPAAm by the RAFT method could be accomplished under UV irradiation and the process possessing the living character. The PPMMs with PAAc and PNIPAAm grafting chains exhibited both pH- and temperature-dependent permeability to aqueous media.

1. Introduction

Graft polymerization of a functional monomer on membrane surface offers an effective approach to incorporating new properties, while retaining the desirable properties of membrane. Polypropylene microporous membrane (PPMM) possesses desirable performances, such as high void volumes, well-controlled porosity, chemical inertness, good mechanical strength and low cost [1]. However, PPMM lacks functional groups, which leads to hydrophobicity, poor biocompatibility, and also no reactivity. As a result, modification of polypropylene membrane to endow it with new functionalities is very important. Different methods have been employed to modify the membrane surface [2–6]. Those surface modification approaches, though very useful, are most commonly accomplished via the free radical process. These approaches offer somewhat limited opportunity for molecular engineering and controllable design of the grafted chain on the membrane surfaces, which is very essential to the membrane performances.

Progress in polymer science makes it possible to produce well-defined graft polymer chains with controlled lengths and specific chain architectures [7–11]. Reversible addition–fragmentation chain transfer (RAFT)-mediated polymerization is a method for achieving controlled free radical polymerization, it involves a reversible addition–fragmentation cycle, in which transfer of a thioester moiety between the active and dormant species maintains the controlled character of the polymerization. It offers many benefits over traditional free radical polymerization, including the ability to control molecular weight and polydispersity and to prepare block copolymers and other polymers with complex architecture—materials that are not readily synthesized by other methodologies. However, for the surface modification of membranes, much work has been done to pretreat the membranes by plasma treatment, ozone treatment

Abbreviations: AAc/PAAc, acrylic acid/poly(acrylic acid); ATR/FT-IR, attenuated total reflection-Fourier transform infrared spectroscopy; AIBN, 2,2′-azobisisobutyronitrile; BP, benzophenone; DBTTC, dibenzyltrithiocarbonate; FE-SEM, field emission scanning electron microscopy; LCST, lower critical solution temperature; Macro-CAT, macro-chain transfer agent; MW, molecular weight; NIPAAm/PNIPAAm, N-isopropyl acrylamide/poly(N-isopropyl acrylamide); PPMM, polypropylene microporous membrane; RAFT, reversible addition–fragmentation chain transfer radical polymerization; UV, ultraviolet; XPS, X-ray photoelectron spectroscopy.

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and γ-irradiation, functional groups were pre-introduced on the membrane surface, followed by living graft polymerization [9,12–14].

Environment-responsive membranes have stimuli-responsive moieties on the membrane surface or in their matrix. The stimuli-responsive moieties allow the membranes to change their structural, charge or affinity characteristics dynamically during filtration process by manipulation of environmental and operation conditions. Such membranes could be potentially used for the development of novel multi-component separation protocols requiring just one tunable membrane [15,16], such as liquid flow regulation, size- and charge-selective filtration, encapsulation of living cells, separation of proteins, controlled drug release, and sensors [17]. Microporous membranes consisting of PNIPAAm and PAAc can serve as a valve regulating the drug release rate in response to temperature and pH changes [18,19].

In the present work, we report on the surface modification of polypropylene microporous membranes (PPMMs) with well-defined copolymer from a photoinduced RAFT-mediated polymerization. Membranes responsive to pH and temperature were prepared. Benzophenone (BP) was first immobilized on the membrane surface by UV irradiation; then acrylic acid (AAc) was grafted on the BP immobilized membrane surface by the surface-initiated RAFT technology under UV irradiation using dibenzyltrithiocarbonate (DBTTC) as a chain transfer agent; finally, AAc grafted membrane containing living groups, which was used as macro-chain transfer agent, was further functionalized by surface-initiated block copolymerization with N-isopropyl acrylamide (NIPAAm) in the presence of free radical initiator, 2,2′-azobisisobutyronitrile (AIBN).

2. Experimental

2.1. Materials

PPMMs with a porosity of 45–50% and an average pore diameter of 0.10 μm were prepared in our laboratory [20]. AAc was purified under reduced pressure to remove the inhibitor before use. NIPAAm, anhydrous ethanol and 2,2′-azobisisobutyronitrile (AIBN) were used as received. BP was recrystallized twice from ethanol and used as photo-initiator. DBTTC was synthesized according to the literature [21].

2.2. Photoinduced 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. Preweighed PPMMs (at least two samples per batch) were presoaked for 60 min in 50 mL solution of 10 wt.% BP in heptane. UV irradiation was carried out for a given time. The BP immobilized PPMM was designated as PPMM-BP.

2.3. Photoinduced RAFT-mediated graft polymerization of AAc on the PPMM-BP surface

PPMM-BPs (at least two samples per batch) were put into 50 mL 0–5.0 mmol/L DBTTC and 10 wt.% AAc solution in anhydrous ethanol, then the photoinduced RAFT-mediated graft polymerization was carried out in a sealed flask. The general procedure is as follows: the mixture was degassed by three freeze–evacuate–thaw cycles. After that the reaction was carried out under UV irradiation at room temperature for a prescribed time. The obtained membranes were designated as PPMM-g-PAAc.

2.4. Preparation of the PPMM-g-PAAc-b-PNIPAAm membranes

The living PAAc side chains on the surface (including the pore surfaces) of the PPMM-g-PAAc membranes were used as the macro-chain transfer agents (macro-CTAs) to further functionalize the membrane in another round of surface-initiated graft copolymerization. PPMM-g-PAAc membrane, NIPAAm monomer (10 wt.%), and AIBN (0.10 mol/L) were introduced into 40 mL of 2-propanol. The solution was saturated with purified argon for 60 min under stirring. The reactor flask was then sealed and heated to 60 °C to initiate the RAFT-mediated graft copolymerization. After the desired reaction time (10–60 min), the reactor flasks were cooled in an ice bath to stop the reaction. The obtained membranes were designated as PPMM-g-PAAc-b-PNIPAAm.

The processes of the RAFT-mediated method for the preparation of the PPMM-g-PAAc and PPMM-g-PAAc-b-PNIPAAm membranes are illustrated schematically in Fig. 1.

After each step of surface modification, the membrane samples were taken out of the chamber 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 constant weight. The grafting density (σ), grafting chain length of PAAc (γ_1) and PNIPAAm (γ_2) were calculated as follows according to [22]:

$$\sigma = \frac{(W_1 - W_0)/\mathrm{MW_{BP}}}{S} \quad (1)$$

$$\gamma_1 = \frac{(W_2 - W_0)/\mathrm{MW_{AAc}}}{(W_1 - W_0)/\mathrm{MW_{BP}}} \quad (2)$$

$$\gamma_2 = \frac{(W_3 - W_2)/\mathrm{MW_{NIPAAm}}}{(W_1 - W_0)/\mathrm{MW_{BP}}} \quad (3)$$

where σ, grafting density, mol/cm^2, in the present work σ was set at 0.224 μmol/cm^2 [23]; γ_1 and γ_2, the grafting chain length of PAAc and PNIPAAm on the membrane surface, repeating units per chain; W_0 is the weight of the blank membrane, W_1, W_2 and W_3 are the weights of the membrane after the first, the second and the third step; S is the surface area of the membrane; $\mathrm{MW_{BP}}$ (182.22 g/mol), $\mathrm{MW_{AAc}}$ (72.06 g/mol) and $\mathrm{MW_{NIPAAm}}$ (113.16 g/mol) refer to the molecular weights of BP, AAc and NIPAAm, respectively.

2.5. Characterization of the modified membranes

ATR/FT-IR spectra were recorded on an infrared spectrometer (FT-IR 8900, Shimadzu, Japan). The ATR accessory contained a ZnSe crystal at a nominal incident angle of 45°, yielding about 12 internal reflections at the sample surface. All spectra (40 scans at 4.0 cm^{-1} resolution and ratio to the appropriate background spectra) were recorded at 25 °C.

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). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 23.5, 46.95 or 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5 × 10^{-8} Pa. The whole spectra (0–1100 eV) were recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the contaminated carbon (C1s = 284.7 eV).

Surface morphologies of the unmodified and modified PPMMs were observed by field emission scanning electron microscope (FE-SEM) with a Hitachi 4800 (Hitach, Japan) operating with an accelerating voltage of 5 keV. Prior to FE-SEM analysis, the membrane was affixed to a standard sample stub by double-sided carbon conductive tape (Ted-Pella). To prevent surface charging, a thin film