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Preparation and characterization of pH- and thermo-sensitive polyethersulfone hollow fiber membranes modified with P(NIPAAm-MAA-MMA) terpolymer

Huijuan Li, Jianyong Liao, Tao Xiang, Rui Wang, Dongsheng Wang, Shudong Sun *, Changsheng Zhao *

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

HIGHLIGHTS

- Modified polyethersulfone membranes were prepared by blending a terpolymer.
- The modified membranes showed significant pH- and thermo-sensitivities.
- The combined pH- and thermo-sensitivities could be used in separation technique.

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ABSTRACT

pH- and thermo-sensitive polyethersulfone (PES) hollow fiber membranes were prepared for the first time by blending a terpolymer of poly(N-isopropylacrylamide-co-methacrylic acid-co-methyl methacrylate) (P(NIPAAm-MAA-MMA)) via dry–wet spinning technique based on a liquid–liquid phase separation. The terpolymer was synthesized via free radical solution polymerization. Scanning electron microscopy (SEM) results indicated that the membrane morphology had been altered after the introduction of the terpolymer. The modified PES hollow fiber membranes showed pH-sensitivity, and the pH-valve effect was observed at the pH value between 7.0 and 10.0; the modified PES membranes also showed thermo-sensitivity, the hydrodynamic permeability changed slightly while the pore sizes changed significantly when the temperature increased, which indicated that the modified membranes could be used for thermo-sensitivity separation, but not suitable for thermo-sensitivity hydrodynamic permeability control. The membranes also showed excellent pH- and thermo-reversibilities.

1. Introduction

The interest in stimulus-responsive copolymers has increased during the past decades, since they have the potential to obtain sensitive materials [1]. Depending on specific behavior and application, the polymers can be designed to sense and respond to changes in environmental conditions such as temperature [2–5], pH value [6–9], magnetic or electric fields [10–12], ionic strength [13,14], added saccharides [15,16], antigen binding [17], light [18] and so on. In aqueous systems, the stimuli-sensitive systems are generally aimed at changing the hydrophilic character of functional groups into a hydrophobic one, or vice versa [19]. Either chemical or physical stimuli (or their combination) can be employed for the purpose. Chemical stimuli include acid–base reaction, complexation, bond breaking or making, redox or electrochemical reaction, or photochemical reaction. Physical stimuli comprise the changes of pH value, ionic strength, temperature, pressure, light, electrical and magnetic fields [19].

Compared with other sensitivities, pH sensitivity gives more choices both for the materials and for the application environment, and it has been widely used in the biotechnology industry for drug delivery systems and advanced separation [20]. The most widely used pH-sensitive polymers are polymeric carboxylic acids and polymeric pyridines, which become charged by protonation/deprotonation and thus undergo a pronounced change on their hydrophilicity [19]. For polymeric carboxylic acid, such as polyacrylic acid (PAA) and polymethacrylic acid (PMAA), at low pH, the carboxyl groups protonated and the hydrophobic interactions dominate, leading to a volume shrinkage of the polymer; at high pH, the carboxyl groups dissociate into carboxylate ions, resulting in high charge density in the polymer, causing it to swell [21]. For polymeric pyridine, such as 4-vinylpyridine (4VP) and 2-vinylpyridine (2VP), contrary to polymeric carboxylic acid, it is acid-swellable. All of these polymers can be used to prepare pH-sensitive membranes, such as by blending, pore-filling, surface-grafting and surface-coating methods [22].

Meanwhile, thermo-sensitivity is also extensively studied and applied in a variety of areas including sensors, drug-devices, controlled release and solute separation [23]. The thermal transition has efficient switching of the hydrophilic–hydrophobic balance. N-isopropylacrylamide (NIPAAm) is a typical monomer for thermo-sensitive polymer that exhibits a lower critical solution temperature (LCST) in water around 32 °C [1]. The PNIPAAm-contained copolymers absorb water and exist in swollen states at the temperature below the LCST [24]. It has been

* Corresponding authors. Tel.: +86 28 85400453; fax: +86 28 85405402.
E-mail addresses: stephen9988@126.com (S. Sun), zhaochsh70@163.com (C. Zhao).

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pointed out that this transition resulted from not only the formation and dissociation of hydrogen bonds between the polymer networks and water molecules, but also hydrophobic interactions of PNIPAAm [23]. Thus, PNIPAAm has been widely used for preparing thermo-sensitive porous membranes [25]. Such membranes could be obtained by grafting NIPAAm on polymeric substrates such as PVDF, cellulose, PVA and PP [26], or by spin-coating PNIPAAm-contained block copolymers on the top of meso/macroporous polyacrylonitrile (PAN) support membrane [27]. The properties of the thermally induced phase transition of PNIPAAm hydrogels and micelles have also been extensively studied.

Multiple functionalities can be combined in order to respond, e.g., to both pH value and temperature due to the incorporation of two stimuli responsive polymers [1,19,24,28,29]. Zhang et al. [1] synthesized a block copolymer from ethylene glycol, 4-vinylpyridine and N-isopropylacrylamide and used as micelles. Xu et al. [24] found that crosslinked triblock copolymers of poly((2-dimethyl amino) ethyl methacrylate-*co*-2-hydroxyethyl methacrylate)-*b*-poly(N-isopropylacrylamide)-*b*-poly ((2-dimethyl amino)ethyl methacrylate-*co*-2-hydroxyethyl methacrylate) were pH- and thermo-sensitive hydrogels. Schilli et al. [29] synthesized a copolymer of poly(N-isopropylacrylamide)-*b*-poly(acrylic acid) for micellization in aqueous solutions. Most of these studies focused on the synthesis of pH- and thermo-sensitive block copolymers, as well as their hydrogel and micelle properties; however, little attention has been paid to the combination of pH- and thermo-sensitive performance for porous membranes by incorporating copolymers synthesized with both pH- and thermo-sensitive monomers.

Herein, a novel pH- and thermo-sensitive random terpolymer of poly (N-isopropylacrylamide-co-methacrylic acid-co-methyl methacrylate) (P(NIPAAm-MAA-MMA)), containing hydrophobic PMMA chains, thermo-sensitive PNIPAAm chains and pH-sensitive PMAA chains, was synthesized via free radical solution polymerization, and then blended with polyethersulfone (PES) in N-methyl-2-pyrrollidone (NMP) to prepare hollow fiber membranes. The combination of pH-sensitive PMAA and thermo-sensitive PNIPAAm creates a system that respond to combined external stimuli of pH value and temperature, while the PMMA segments provide hydrophobicity to prevent the elution of the terpolymer and miscibility of the terpolymer with the PES matrix. The membrane performance was investigated by hydrodynamic permeability testing and ultrafiltration of PEG-8000 solution.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES, Ultrason E6020P) was purchased from BASF, Germany. N-isoprorylacrylamide (NIPAAm; AR≥98.0%; CAS No. 2210-25-5) was purchased from Shanghai Wing Science and Technology Co., Ltd. (Shanghai, China). Methacylic acid (MAA; AR≥99.0%; CAS No. 79-41-4) and methyl methacrylate (MMA; AR≥99.0%; CAS No. 80-62-6) were purchased from Chengdu Kelong Inc. (Chengdu, China) and used as the monomers without any further purification. N-methyl-2-pyrrolidone (NMP; AR≥99.0%; CAS No. 872-50-4) was purchased from Chengdu Kelong Inc. (Chengdu, China), and used as the solvent. Azo-bis-isobutryonitrile (AIBN; AR; CAS No. 78-67-1) was purchased from Tianjin Kemiou Co., Ltd (Tianjin, China) and used as the initiator. Polyethylene glycol (PEG; Mw = 8000; CAS No. 25322-68-3) was purchased from Tianjin Ruijinte Co., Ltd. (Tianjin, China). All the other chemicals (analytical grade) were obtained from Chengdu Kelong Inc. (Chengdu, China), and used without further purification.

2.2. Synthesis of poly(N-isopropylacrylamide-co-methacrylic acid-co-methyl methacrylate)

P(NIPAAm-MAA-MMA) terpolymers were synthesized via free radical solution polymerization with three monomer feeding ratios. NIPAAm, MAA and MMA were dissolved in NMP with the mass ratios of 20:20:60, 30:30:40 and 40:40:20, respectively, and the total monomer concentration was 30 wt.%. For the synthesis, the mixture was stirred under nitrogen atmosphere and heated for 15 min until all the monomers were completely dissolved, and the system temperature reached 70 °C. Then 0.3 wt.% of the initiator (to the total monomer weight), AIBN, was introduced into the mixture, and the reaction was carried out in an airtight equipment at 70 °C for 24 h under constant stirring. After that, the products were washed for several times with double distilled water, and then immersed in double distilled water at 60 °C for several hours with stirring to remove the residual monomers, some hydrophilic homopolymers, and solvent thoroughly. The prepared terpolymers were dried at 60 °C in a vacuum oven for 72 h; then white particle products were obtained, and named as P-I, P-II, P-III, respectively.

2.3. Characterization of the terpolymers

To prepare FTIR sample, N, N-dimethylacetamide (DMAC) was chosen due to its relatively low boiling point (166 °C). The terpolymer was dissolved in DMAC, and cast on a potassium bromide (KBr) disk with the thickness of about 0.8 mm, and then the cast polymer solution was dried by an infrared light to remove the solvent DMAC thoroughly. The FTIR spectrum was measured by FT-IR Nicolet560 (Nicol, USA) with the grazing angle of 0°, the spectral resolution of 4 cm^{-1}, and the number of sample and background scans of both is 32.

The composition of the terpolymer was determined by ^{1}H NMR spectroscopy in dimethyl sulfoxide-d^{6} with a Varian Unity Plus 300/54 NMR spectrometer. The characteristic peaks were used to calculate the molar ratios of the PNIPAAm, PMAA and PMMA in the terpolymer.

Elemental analysis based on the determination of carbon (C), hydrogen (H) and nitrogen (N), was performed by means of a CARLO ERBA 1106 elemental analyzer (Italy), with a carrier gas (He, at a flow rate of 100 mL/min) at a combustion temperature of 1000 °C using the solid samples. The proportions of C, H and N for P-I, P-II and P-III were determined, respectively.

GPC measurement based on the liquid chromatography analysis was performed with HLC-8320 GPC analyzer (Japan), tetrahydrofuran (THF) was chosen as the eluent and monodispersed polystyrene standards were used to generate the calibration curve.

Differential Scanning Calorimetry (DSC) measurement was conducted on a testing machine Perkin Elmer Instruments Pyris 1 DSC. The solid sample was tightly sealed onto the DSC pan, and scanned at a temperature ranging from 0 °C to 200 °C at a heating rate of 10 °C/min under nitrogenous gas.

2.4. Preparation of PES hollow fiber membranes and filters

In the study, P-II was chosen to prepare the modified PES membranes based on preliminary experiments. PES and the terpolymer P-II were dissolved in NMP with the PES concentration of 20 wt.%, while the concentrations of P-II were 0, 0.8, and 1.6 wt.%, respectively. Then the mixtures were stirred for several hours at room temperature until pellucid solutions were obtained. After degassing, PES/P(NIPAAm-MAA-MMA) hollow fiber membranes were prepared via a widely-used dry-wet spinning technique [30,31]. In this study, three kinds of membranes were prepared, named as HFM-20-0, HFM-20-0.8, and HFM-20-1.6, respectively. HFM-x-y represents that the hollow fiber membranes were prepared from PES and the terpolymer P-II with the concentrations of x and y wt. %, respectively. All the hollow fiber membranes were immersed in water for over 24 h to remove the residual solvent. After that, the membranes were post-treated with 50% (volume fraction) glycerol aqueous solution for 2 h to prevent the collapse of porous structures when they were dried. After drying in air at room temperature, the hollow fiber membranes were prepared for further test and study.