Polymer 55 (2014) 1333-1340

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Poly(vinylidene fluoride) ultrafiltration membranes containing hybrid silica nanoparticles: Preparation, characterization and performance



polyme

Suo-Hong Zhi, Jun Xu, Ran Deng, Ling-Shu Wan, Zhi-Kang Xu*

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

ARTICLE INFO

Article history: Received 28 August 2013 Received in revised form 9 December 2013 Accepted 16 December 2013 Available online 4 January 2014

Keywords: Poly(vinylidene fluoride) PHEMA-*b*-PMMA@SiO₂ Composite membrane

ABSTRACT

Poly(vinylidene fluoride) (PVDF) ultrafiltration membranes were prepared by immersion precipitation method using poly(hydroxyethyl methacrylate)-block-poly(methyl methacrylate) grafted silica (PHEMA*b*-PMMA@SiO₂) nanoparticles as additives. The hybrid nanoparticles were synthesized by the surface initiated atom transfer radical polymerization (SI-ATRP), and they were characterized in detail by FT-IR, TEM, DLS and GPC. Results confirm that core-shell structure is formed after grafting PHEMA-b-PMMA brushes on the silica nanoparticles. Their average hydrodynamic diameter also increases with the prolongation of grafting time. After blending PVDF with the hybrid silica nanoparticles, the composite PVDF membranes exhibit high porosity and improved water permeation. Especially, when the molecular weight is 1.73×10^5 g/mol for PHEMA-*b*-PMMA on the hybrid nanoparticles, the water flux of the PVDF composite membrane is 2.5 times than that of the control PVDF membrane, while the rejection to bovine serum albumin (BSA) remains at a high level (>90%). In addition, all the composite PVDF membranes show lower BSA adsorption and larger water flux recovery ratio than the control PVDF membrane. The improvement of membrane performance is attributed to the good hydrophilicity of PHEMA-b-PMMA@SiO₂ nanoparticles. Our results suggest that PHEMA-b-PMMA@SiO₂ nanoparticles with moderate molecular weight of PHEMA-b-PMMA are suitable for the property optimization of PVDF-based composite membranes.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is one of the most extensively used materials for ultrafiltration and microfiltration membranes because of its excellent antioxidation, good thermal stability, and high hydrolytic resistance as well as fine mechanical property [1– 3]. However, its hydrophobic nature, which is often liable to membrane fouling, has become a conspicuous drawback for wide application as membrane materials in water treatment [4]. Therefore, extensive efforts have been devoted to improving the surface hydrophilicity of PVDF membranes through a variety of methods such as surface grafting and additive blending. Surface grafting includes plasma treatment [5–7], UV-induced polymerization [8], electron beam irradiation [9,10], and living/controlled radical polymerization [11,12]. Blending usually involves amphiphilic copolymers [13,14] and inorganic particles [15-24] as additives. Much attention has been paid to organic-inorganic composite membranes which are fabricated through blending PVDF with

0032-3861/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2013.12.035 inorganic nanoparticles such as Al_2O_3 [17,18], SiO_2 [19,20], TiO_2 [21,22], Fe_2O_3 [23] and montmorillonite (MMT) [24].

SiO₂ is one of the most widely used inorganic materials for organic-inorganic composite membranes due to its stability, hydrophilicity, mechanical strength, and chemical property [25]. Recently, several studies have been carried out to focus on the fabrication of PVDF/SiO₂ composite membranes via blending method [19,25,26]. The porous structure could be developed and the hydrophilic property was enhanced for the composite membranes [19,26]. However, high specific surface area and reactivity are well known reasons for the aggregation of SiO₂ nanoparticles. These factors make the SiO₂ nanoparticles dispersed poorly in PVDF matrix. Therefore, it is necessary to modify the surface of SiO₂ nanoparticles. In general, the SiO₂ nanoparticles can be modified to form hybrid nanomaterials by chemically bonding or physically adsorbing polymers on their surface [27-30]. The chemically bonding method usually anchors polymer chains on the nanoparticles via "grafting to" [27,31,32] or "grafting from" [28-30,33-42] processes. The so-called "grafting from" process was commonly used to covalently anchor vinyl polymers by free radical polymerization in conjunction with surface-bound initiators [34-36].



^{*} Corresponding author. Fax: +86 571 8795 1773. *E-mail address:* xuzk@zju.edu.cn (Z.-K. Xu).

Controlled free radical polymerizations were further applied to modulate the molecular weight, polydispersity, and chain-end structure and length (thickness) of the anchored polymers [37–42]. Among the most used controlled free radical polymerizations, surface-initiated atom transfer radical polymerization (SI-ATRP) has been the preferred one for the synthesis of hybrid SiO₂ nanoparticles [39]. These hybrid nanoparticles are expected as suitable additives for organic–inorganic composite membranes, however, there is rare report focusing on the composite membranes fabricated from PVDF and hybrid SiO₂ nanoparticles.

We report a series of composite PVDF membranes containing poly(hydroxyethyl methacrylate)-*block*-poly(methyl methacrylate) grafted SiO₂ (PHEMA-*b*-PMMA@SiO₂) nanoparticles. The hybrid SiO₂ nanoparticles were prepared by grafting PHEMA-*b*-PMMA copolymer via SI-ATRP. PMMA was selected to firstly graft due to its excellent compatibility with PVDF [43–45]. PHEMA was subsequently grafted to form PHEMA-*b*-PMMA block copolymer for improving the hydrophilicity of the composite PVDF membranes. We aim to evaluate the effects of PHEMA-*b*-PMMA@SiO₂ nanoparticles on the surface hydrophilicity, water permeation, and protein resistance of the composite membranes.

2. Experimental

2.1. Materials

PVDF ($M_{\rm n} = 1.53 \times 10^5$, $M_{\rm w}/M_{\rm n} = 2.3$) was purchased from Solvay Solexis Inc., (Belgium). Sinopharm Chemical Reagent Co. Ltd. provided other chemicals including methyl methacrylate (MMA. 99%), copper (I) bromide (CuBr, 99.9%), copper (II) bromide (CuBr₂, 99.9%), 2,2'-bipyridine (Bpy, 99%), tetraethyl orthosilicate (TEOS, 99%), N,N-dimethyl formamide (DMF, 99%), ammonium hydroxide solution (28 wt% NH₃•H₂O), acetone, methanol, toluene, tetrahydrofuran (THF), triethylamine (Et₃N) and hydrofluoric acid solution (HF, 49%). MMA was purified by distillation under reduced pressure. CuBr was treated with 3 wt% acetic acid aqueous solution and acetone before use. 3-aminopropyltriethoxysilane (APTES) was a commercial product of Aladdin Reagent Company (China). Hydroxyethyl methacrylate (HEMA, 99%), 2-bromoisobutyl bromide (97%) and methyltrioctylammonium chloride (Aliquat 336) were purchased from Sigma-Aldrich Chemicals (USA). HEMA was purified by flash chromatography over activated neutral alumina. Ultrapure water was produced with an ELGA LabWater system (France) and used in all experiments.

2.2. Synthesis and characterization of PHEMA-b-PMMA@SiO₂ nanoparticles via SI-ATRP polymerization

Scheme 1 shows the synthesis process of PHEMA-*b*-PMMA@-SiO₂ nanoparticles. In brief, the process includes three steps. First, bare SiO₂ nanoparticles were prepared through Stöber method [46] and the silanol (Si–OH) groups on the particle surface were converted to primary amine groups by direct condensation with APTES. Second, the initiator-functionalized SiO₂ nanoparticles were obtained via a reaction with 2-bromoisobutyl bromide. Third, SI-ATRP was then adopted to synthesize PHEMA-*b*-PMMA@SiO₂ nanoparticles in monomer solution using SiO₂–Br as the initiator and CuBr/CuBr₂/Bpy as the catalyst and ligand system. More details are described in Supplementary Material.

2.3. Preparation of the PVDF/PHEMA-b-PMMA@SiO₂ organic inorganic composite membranes

PHEMA-*b*-PMMA@SiO₂ nanoparticles (2 wt% based on the weight of PVDF) were added to DMF and dissolved under



Scheme 1. Synthesis of PHEMA-*b*-PMMA@SiO₂ nanoparticles via surface-initiated ATRP.

ultrasonication for 30 min. PVDF (15 wt% based on the whole casting solution) was then added to the mixture and stirred at 60 °C for 12 h to obtain a homogeneous casting solution. The casting solution was further heated at 60 °C without stirring for 12 h to remove bubbles. This casting solution was cast onto a clean glass plate using a doctor blade, and then immersed into water bath at 35 °C for phase separation. After the membrane was detached from the glass plate, it was taken from the bath and subsequently soaked in ultrapure water for at least 24 h. To avoid the shrinkage of membrane pores, the membrane was immersed in ethanol aqueous solution with different concentrations for dehydration and then soaked in *n*-hexane overnight. Finally, the membrane was dried in air at room temperature and used for characterization. The prepared composite PVDF membranes were denoted as M12, M18, M24 and M30 according to the used PHEMA-b-PMMA@SiO₂ nanoparticles synthesized with different polymerization times. A pure PVDF membrane, M0, was used as the control sample. M1 was the composite PVDF membrane containing bare SiO₂ nanoparticles.

2.4. Characterization of the hybrid SiO_2 nanoparticles and the composite membranes

Chemical composition of the hybrid SiO₂ nanoparticles was analyzed by Fourier transform infrared spectra (FTIR, Nicolet Nexus 670, USA). The particle size was determined by dynamic light scattering (DLS) in DMF at 25 °C on a Malvern Zetasizer Nano ZS90 with a He-Ne laser (633 nm) and 90° collecting optics. Gel permeation chromatography (GPC) was conducted at 40 °C in THF with a flow rate of 1.0 mL/min, using a Waters 510 HPLC pump, Waters Styragel columns, and a Waters 410 differential refractometer (Millipore Corp., Bedford, MA). Poly(methyl methacrylate) was used as calibration standard. Morphologies of the hybrid SiO₂ nanoparticles were characterized by transmission electron microscopy (TEM, JEM-1230, Japan). Samples were prepared via depositing a drop of the particle suspension onto a copper grid with a carbon film and then drying prior to visualization. Thickness of the grafting layer was estimated by analyzing TEM images of the hybrid SiO₂ nanoparticles using an Image tools software.

The apparent viscosity of PVDF/PHEMA-b-PMMA@SiO₂ casting solution was measured using a rotational viscometer (NDI-79, Electrical Machinery Plant, Tongji University, China). All measurements were performed at a shear rate of 176 s⁻¹ and 60 °C. Attenuated total reflection/Fourier transform infrared (ATR/FT-IR) spectrometer (Nicolet Nexus 470, USA) was used to detect the functional groups of the membrane surface. Thirty-two scans were taken for each spectrum at a resolution of 4.0 cm^{-1} . Membrane morphologies were observed by field emission scanning electron microscope (FESEM, Hitachi S4800, Japan) under vacuum. Both the membrane surface and the cross-section were sputtered gold for 90 s before observation. Hydrophilicity of the membrane surface was evaluated by water contact angle (WCA) measurement. WCA was measured by the sessile drop method using a CTS-200 system (Mighty Technology Pvt. Ltd., China) at room temperature. The volume of droplets was 2.0 µL. Chemical composition of the membrane surface was analyzed using X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System, USA) with Mg Ka excitation radiation. Porosity (P, %) of the wet membrane was calculated according to Eq. (1) [47]:

$$P = \frac{(W_0 - W_1)/\rho_{\text{water}}}{((W_0 - W_1)/\rho_{\text{water}}) + (W_1/\rho_{\text{PVDF}})} \times 100$$
(1)

where W_0 is the weight of the wet membrane (g); W_1 is the weight of the dry membrane (g); ρ_{water} or ρ_{PVDF} is the density of water or PVDF, respectively. The dry membrane was immersed in tertiary butyl alcohol (TBA) at 30 °C for 48 h. Then the membrane was softly wiped up with filter paper and weighted quickly. Porosity of the dry membrane (P_2) was also defined according to the Eq. (1), but W_0 is the weight of the membrane refilled with TBA and ρ_{water} should be revised to ρ_{TBA} , which is the density of TBA.

2.5. Measurements of filtration and anti-fouling properties

Water permeation of the membrane was measured by a deadend filtration system. All experiments were conducted at 25 °C and a feed pressure of 0.1 MPa. A newly prepared membrane was pre-pressured at 0.12 MPa for 30 min to minimize its compaction effect before measurement, and then the pure water flux (J_w) was measured from the permeate volume until the water permeation remains constant under pressure of 0.10 MPa. For each membrane, three samples were measured at the same condition and the average J_w was reported.

Four dextrans ($M_w = 20,000, 40,000, 70,000, 100,000$, respectively) were used to characterize the molecular weight cut-off (MWCO) of the membranes. The test solution was prepared by mixing dextrans in ultrapure water at the concentration of 500 ppm. The concentration of samples from the feed and collected permeate were analyzed by means of total organic carbon (TOC) with a TOC-V_{cpn} instrument (Multin/C 3100, German). M_w which was rejected to 90% is defined as the molecular weight cut-off (MWCO) of the membrane.

BSA solution filtration was performed at 0.1 MPa and room temperature using a flat-sheet cross-flow test cell with an effective membrane area of 4.9 cm². BSA solution with concentration of 1 g/L was flowed across the membrane. The rejection ratio was measured by collecting permeates at a given interval. The solute concentration of permeate and feed was determined using a UV–visible spectrophotometer (UV-2450, Shimadzu, Japan). For each membrane, three samples were measured and the average *R* was reported. After filtration of BSA solution, the membrane was washed with PBS and ultrapure water for 30 min, respectively. Then the pure water flux (J_R) was measured. The flux recovery ratio (FRR) was calculated as follow:

$$FRR(\%) = \frac{J_R}{J_W} \times 100$$
 (2)

Fouling resistance of the membrane was evaluated by measuring the amount of BSA absorbed on the sample. Wet membrane with 4.9 cm² was washed with the phosphate buffer saline (PBS) (pH 7.4) for 2 h, and then put into a vial filled with 10 mL BSA solution with a concentration of 1 g/L. The vial was then incubated in oscillating water bath at 25 °C for 24 h to reach adsorption equilibrium. The concentrations of BSA solution before and after adsorption were measured by UV–visible spectrophotometer (UV-2450, Shimadzu, Japan). The adsorption amount of BSA was calculated from the concentration variation. Each value reported was an average of three parallel experiments.

3. Results and discussion

3.1. Synthesis and structures of PHEMA-b-PMMA@SiO₂ nanoparticles

SI-ATRP was adopted to synthesize PMMA@SiO₂ and PHEMA*b*-PMMA@SiO₂ nanoparticles. In our cases, the number of initiators on the surface of SiO₂ nanoparticles is insufficient to generate enough Cu(II) species, especially at the early stage of polymerization. However, this problem can be addressed by the addition of a low concentration of Cu(II) species at the beginning of polymerization [42,48,49]. Therefore, CuBr₂ was used as retarder to ensure sufficient exchange between the dormant species and the active sites. FT-IR spectra (Fig. 1), TEM images (Fig. 2) and DLS analysis (Fig. 3) all demonstrate that the SiO₂ nanoparticles were step-by-step modified with PMMA and PHEMA-*b*-PMMA.

For example, FT-IR spectra of PMMA@SiO₂ and PHEMA-*b*-PMMA@SiO₂ nanoparticles appear additional peaks at 1728 cm⁻¹ (stretching vibration of C=O), 1439 cm⁻¹ (stretching vibration of – CH), 1148 cm⁻¹ (stretching vibration of C–O–C), and 3425 cm⁻¹ (bending vibration of –OH) (Fig. 1c and d). At the same time, core–shell structure has been formed by grafting polymers on the surface of SiO₂ nanoparticles. The dark SiO₂ cores have been firstly



Fig. 1. FT-IR spectra of silica (a), SiO_2 -Br (b), PMMA@SiO₂ (c) and PHEMA-b-PMMA@SiO₂ (the polymerization time is 12 h) (d) nanoparticles.



Fig. 2. TEM images of SiO₂ (a), SiO₂–Br (b), PMMA@SiO₂ (c) and PHEMA-*b*-PMMA@SiO₂ (the polymerization time is 12 h) nanoparticles (d). (Red arrows indicate the polymer grafted on the surface of SiO₂ nanoparticles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

surrounded by a thin gray PMMA layer (ca. 14 nm) (Fig. 2c). The thickness of polymer layer increases significantly (ca. 36.5 nm) (Fig. 2d) after subsequently grafting PHEMA on the surface of PMMA@SiO₂ nanoparticles with 12 h polymerization. Furthermore, the hydrodynamic diameter of PHEMA-*b*-PMMA@SiO₂ nanoparticles increases with an increase in polymerization time (Fig. 3). However, it is larger for the hydrodynamic diameter of PHEMA-*b*-PMMA@SiO₂ nanoparticles measured by DLS (446 nm, Fig. 3b) than that obtained from TEM images. This is mainly associated with swelling of the polymer chains in DMF [50].

The molecular weights of PMMA and PHEMA-b-PMMA grafted on SiO₂ nanoparticles were determined after cleaving the polymers from the surface via HF aqueous solution. Typical results indicate that the molecular weight of PMMA is 1.08×10^5 g/mol. After further grafting with PHEMA, the molecular weight of PHEMA gradually increases from 1.6 \times 10^5 g/mol to 2.01 \times 10^5 g/mol with an increase in polymerization time (Fig. 4). Furthermore, the polydispersity index (PDI) also increases slightly with the prolongation of polymerization time. It is attributed to the multifunctional nature of SiO₂-Br as initiator, which may result in the intermolecular coupling of the growing radicals and the formation of crosslinked structure when the chain radical concentration is high enough at a local area [51,52]. In fact, the viscosity of the reaction mixture increases with increasing polymerization time. Furthermore, when SiO₂-Br is used as multifunctional initiators in ATRP, intermolecular coupling of grafting chains easily takes place from different silica cores and termination occurs by neighboring surface-immobilized chains in an intramolecular fashion [49].

3.2. Structures and properties of PVDF/PHEMA-b-PMMA@SiO₂ composite membranes

The synthesized PHEMA-b-PMMA@SiO2 nanoparticles were used as hydrophilic additives for the preparation of organic-inorganic composite membranes from PVDF. It is reasonable that the addition of hydrophilic additives will influence the morphology of the composite PVDF membranes prepared by the immersion precipitation method. As depicted in Fig. 5, porous top surfaces form on the composite PVDF membranes with 2 wt% hybrid SiO₂ nanoparticles. In addition, all the membranes exhibit a typical asymmetric structure for their cross-section. Three distinct regions can be identified clearly, that is, a thin skin layer near the top surface, a parallel columnar finger-like structure extending to the central part underneath the top surface, and a cellular structure consisting of closed pores at the lower half of the membrane cross-section. MWCOs of the pristine and composite PVDF membranes were characterized by using dextran as model molecules to further determine the effective membrane surface pores. All the membranes show low rejections (<60%) when permeating dextran (20 kDa and 40 kDa) aqueous solution. However, MWCO of M24 and M30 (100 kDa) is larger than that of M12 and M18 (70 kDa) (Fig. 6). It indicates that the membrane surface becomes porous and the pore size increases with an increase in the molecular weight of PHEMA-b-PMMA. Fig. 7 indicates that the porosity becomes large after blending with SiO₂ nanoparticles. Moreover, the porosity first increases and then slightly decreases with increasing the molecular weight of PHEMA-b-PMMA.



Fig. 3. DLS results of SiO₂ (a), PHEMA-b-PMMA@SiO₂ with different polymerization time (12 h (b), 18 h (c), 24 h (d) and 30 h (e)).



Fig. 4. GPC curves of PMMA and PHEMA-*b*-PMMA etched from PMMA@SiO₂ and PHEMA-*b*-PMMA@SiO₂ nanoparticles with different polymerization time (12 h, 18 h, 24 h and 30 h).

These changes of membrane structure and porosity can be explained as follows. The addition of hydrophilic SiO₂ and PHEMAb-PMMA@SiO₂ nanoparticles enhances the affinity interaction of the casting solution and the water precipitant, which promotes solvent-nonsolvent exchange in the process of phase separation and then results in the formation of large pores. In addition, some nanoparticles can leach out from the casting solution and act as pore-forming agent during membrane formation. Furthermore, the viscosity of the casting solution was also measured for studying the effect of the molecular weight of PHEMA-b-PMMA on the diffusional aspect of the solution. The addition of hybrid SiO₂ nanoparticles increases the viscosity of the casting solution with an increase in the molecular weight of PHEMA-b-PMMA, which reveals that the overall diffusion can be kinetically inhibited with the hybrid SiO₂ nanoparticles in solutions (Fig. S1 in Supplementary Material). As we all known, the thermodynamic enhancement coexists with the rheological hindrance during the process of immersion precipitation, showing a trade-off relationship against one another. According to the results of MWCOs and membrane porosity, the thermodynamic factor prevails over the rheological hindrance due to high hydrophilic character of PHEMA-b-PMMA@SiO₂ nanoparticles. Therefore, these factors cause the formation of a porous top layer with relatively large pores.

FT-IR/ATR spectra were measured to characterize functional groups of the composite membranes surfaces in Fig. 8. Typical



Fig. 5. FESEM images of composite PVDF membranes: (a) pristine PVDF membrane, (b) PVDF/SiO₂ membrane for M1, (c) PVDF/PHEMA-*b*-PMMA@SiO₂ membrane with 1.6 × 10⁵ g/mol PHEMA-*b*-PMMA for M12, (d) PVDF/PHEMA-*b*-PMMA@SiO₂ membrane with 1.73 × 10⁵ g/mol PHEMA-*b*-PMMA for M18, (e) PVDF/PHEMA-*b*-PMMA@SiO₂ membrane with 1.84 × 10⁵ g/mol PHEMA-*b*-PMMA for M24, (f) PVDF/PHEMA-*b*-PMMA@SiO₂ membrane with 2.01 × 10⁵ g/mol PHEMA-*b*-PMMA for M30. Left column: membrane top surface; right column: cross-section.

absorption peaks of the PVDF membrane are at 1402 cm⁻¹, 1382 cm⁻¹ (bending vibration of $-CH_2$), 1210 cm⁻¹ (wagging vibration of $-CH_2$), 1172 cm⁻¹ (twisting vibration of $-CH_2$), 1070 cm⁻¹ (in plane wagging vibration of C–F), and 877 cm⁻¹ (stretching vibration of $-CF_2$) (Fig. 8a). The composite membranes show additional peaks at 800 cm⁻¹ (bending vibration of Si–O–Si) and 1728 cm⁻¹ (stretching vibration of C=O) (Fig. 8b and c), which indicate the existence of SiO₂ and PHEMA-*b*-PMMA@SiO₂ nanoparticles on the membrane surfaces.



Fig. 6. Molecular weight cutoff of the pristine and composite PVDF membranes.

Surface hydrophilicity is one important parameter of separation membrane for water treatment, which is often evaluated by WCA measurement. In can been seen from Fig. 9 that WCA of the composite PVDF membranes is lower than that of the PVDF membrane (92°). With increasing the molecular weight of PHEMA-*b*-PMMA, WCA of the composite PVDF membranes first decreases to minimum (71°) and then increases to 82°. It indicates that the addition of PHEMA-*b*-PMMA@SiO₂ nanoparticles enhances the surface hydrophilicity of PVDF membrane, which can be attributed to the hydroxyl groups of PHEMA segment.

Chemical composition of the pristine and composite PVDF membrane surfaces was characterized by XPS analysis to study the relationship between surface composition and hydrophilicity. The characteristic XPS signals for carbon (C) and fluorine (F) are observed for the pristine PVDF and composite PVDF membranes. Furthermore, new peaks of O 1s and Si 2p3 are observed from PVDF/SiO₂ and PVDF/PHEMA-*b*-PMMA@SiO₂ membranes (Fig. 10). Table 1 lists the atomic percentages of C, F, O and Si elements of all prepared PVDF membranes. There is no O and Si element on the neat PVDF membrane surface. PHEMA-*b*-PMMA and SiO₂ nanoparticles are the source of O and Si. XPS measurement shows that



Fig. 7. Porosity of the pristine and composite PVDF membranes.



Fig. 8. FT-IR/ATR spectra of the studied membranes (a) PVDF membrane, (b) PVDF/SiO₂ membrane for M1, and (c) PVDF/PHEMA-*b*-PMMA@SiO₂ membrane with 1.6×10^5 g/mol PHEMA-*b*-PMMA for M12.

the atomic percentages of O and Si element on the membrane surfaces increase with the blending of SiO₂ and PHEMA-b-PMMA@SiO2 nanoparticles. It indicates the existence of nanoparticles in the near surface of the composite membranes. These results clearly evidence that the hydrophilic PHEMA-b-PMMA@-SiO₂ nanoparticles are segregated to the membrane surface during membrane preparation. Generally speaking, the chemical potential of hydrophilic component in water is substantially less than that of hydrophobic component. Hydrophilic hybrid SiO₂ nanoparticles migrate faster to interface between the casting solution and water than hydrophobic PVDF chains prior to precipitation, resulting in surface enrichment of hydrophilic PHEMA chains [53]. However, the Si and O content of M30 is less than M18. It is deduced that the migration will be inhibited with an increase in the polymer chain length, which makes the surface hydrophilicity of membrane decrease slightly [54].

Ultrafiltration experiments were carried out to study the influence of PHEMA-*b*-PMMA@SiO₂ nanoparticles on the permeation performances of the composite PVDF membranes. As can be seen from Fig. 11, the pure water flux first increases to 65.96 L/m^2 h



Fig. 9. Water contact angles of the pristine and composite PVDF membranes.



Fig. 10. XPS spectra of the pristine and composite membranes.

(M18), which is two times more than that of the PVDF membrane, and then decreases to 42.78 L/m^2 h (M30). This trend is well matched with the porosity and the surface hydrophilicity of the composite PVDF membranes. An increase in these two parameters reasonably enhances water permeation of the membranes.

Protein-resistance is another important parameter that associates with the antifouling property of polymer membranes. Further investigation was focused on the effects of PHEMA-b-PMMA@SiO2 nanoparticles on the rejection and static adsorption of BSA. The BSA rejection first increases and then decreases with an increase in the molecular weight of PHEMA-b-PMMA. One major reason for the low rejection of M1 is the addition of SiO₂ nanoparticles increases the pore size. After blending with PHEMA-b-PMMA@SiO₂ nanoparticles, the PHEMA segment of PHEMA-b-PMMA@SiO₂ nanoparticles may migrate to the membrane surfaces. The hydroxyl groups of PHEMA can bind water molecules to form a hydration layer, which hinders the adsorption of BSA from 124.8 μ g/cm² to 83.83 µg/cm² (Figure S2 in Supplementary Materials). However, when the molecular weight of PHEMA-b-PMMA is high, the surface pores of M24 and M30 become large based on the results of MWCO measurement. Moreover, the surface hydrophilicity of M24 and M30 is lower than M12 and M18 (Fig. 9). All these factors result in low rejections for M24 and M30.

In addition, FRR was also measured to evaluate the antifouling property of the composite PVDF membranes. As depicted in Fig. 12, FRRs of the composite PVDF membranes are more than that of the PVDF membrane. The later has a low FRR (26%), implicating a poor antifouling property. In contrast, the FRR of M18 reaches 90%. Low FRR of the PVDF membrane is ascribed to the high adsorption of BSA on the membrane surfaces and the entrapment of BSA in the

Table 1

Surface chemical composition of the pristine and composite membranes detected by XPS.

| Membrane samples | Atomic relative content (mol%) | | | |
|------------------|--------------------------------|------|-------|------|
| | С | 0 | F | Si |
| M0 | 53.66 | 0 | 45.02 | 0.01 |
| M1 | 53.59 | 3.67 | 41.44 | 0.31 |
| M18 | 53.56 | 7.04 | 35.73 | 1.92 |
| M30 | 56.4 | 5.38 | 36.26 | 1.01 |



Fig. 11. Pure water flux and BSA rejection of the pristine and composite PVDF membranes



Fig. 12. Water flux recovery ratio of the pristine and composite PVDF membranes.

membrane pores (Figure S2 in Supplementary Materials). The addition of PHEMA-b-PMMA@SiO2 nanoparticles increases the hydrophilicity of the membrane surfaces and membrane pores, which result in high FRR.

4. Conclusions

PHEMA-*b*-PMMA@SiO₂ nanoparticles were synthesized through SI-ATRP and then used as a novel hydrophilic additive to prepare PVDF/PHEMA-b-PMMA@SiO2 composite membranes via immersion precipitation method. These hybrid nanoparticles influence the structure and performance of the composite PVDF membranes obviously. Nanoparticles with appropriate molecular weight of PHEMA-b-PMMA increase the pure water flux, improve the BSA rejection to a high level (>90%), and reduce the membrane fouling at the same time. The improved performances are attributed to the good hydrophilicity of PHEMA-b-PMMA@SiO2 nanoparticles. Our study provides a reasonable modification approach to prepare organic-inorganic composite membranes from PVDF and SiO₂ nanoparticles.

Acknowledgments

The authors acknowledge financial support by the National Natural Science Foundation of China (Grant no. 21174124) and the Ph.D. Programs Foundation of the Ministry of Education of China (Grant no. 20120101110123).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.polymer.2013.12.035.

References

- Chin SS, Chiang K, Fane AG. J Membr Sci 2006;275(1-2):202-11.
- Yang JX, Shi WS, Yu SL, Lu Y. Desalination 2009;239(1-3):29-37. [2]
- Cao X, Ma J, Shi X, Ren Z. Appl Surf Sci 2006;253(4):2003-10.
- Lang WZ, Xu ZL, Yang H, Tong W. J Membr Sci 2007;288(1-2):123-31. [4]
- [5] Kaur S, Ma Z, Gopal R, Singh G, Ramakrishna S, Matsuura T. Langmuir 2007;23(26):13085-92.
- [6] Li SD, Wang CC, Chen CY. J Membr Sci 2008;318(1-2):429-34.
- Chen Y, Ying L, Yu W, Kang ET, Neoh KG. Macromolecules 2003;36(25):9451-7. [8] Rahimpour A, Madaeni SS, Zereshki S, Mansourpanah Y. Appl Surf Sci 2009;255(16):7455-61.
- Masuelli MA, Grasselli M, Marchese J, Ochoa NA. J Membr Sci 2012;389(0):91-8. [9] Clochard MC, Bègue J, Lafon A, Caldemaison D, Bittencourt C, Pireaux JJ, et al. [10]
- Polymer 2004;45(26):8683-94. Chen Y, Deng Q, Xiao J, Nie H, Wu L, Zhou W, et al. Polymer 2007;48(26):7604–13.
- Singh N, Husson SM, Zdyrko B, Luzinov I. J Membr Sci 2005;262(1-2):81-90. [12]
- İ13İ Hester JF, Banerjee P, Mayes AM. Macromolecules 1999;32(5):1643-50.
- Hester JF, Mayes AM. J Membr Sci 2002;202(1-2):119-35. [14]
- Liao C, Yu P, Zhao J, Wang L, Luo Y. Desalination 2011;272(1-3):59-65. [15]
- Dong C, He G, Li H, Zhao R, Han Y, Deng Y. J Membr Sci 2012;387–388(0):40–7. [16]
- Kumar GG, Kim P, Nahm KS, Elizabeth RN. J Membr Sci 2007;303(1–2):126–31. [17]
- [18] Liu F, Abed MRM, Li K. J Membr Sci 2011;366(1-2):97-103.
- Ì19Ì Liao C, Zhao J, Yu P, Tong H, Luo Y. Desalination 2012;285(0):117-22.
- [20] Liao C, Zhao J, Yu P, Tong H, Luo Y. Desalination 2010;260(1-3):147-52.
- [21] Bian X, Shi L, Yang X, Lu X. Ind Eng Chem Res 2011;50(21):12113-23.
- Shi F, Ma Y, Ma J, Wang P, Sun W. J Membr Sci 2012;389(0):522-31. [22]
- Xie QL, Liu J, Xu XX, Han GB, Xia HP, He XM. Sep Purif Technol 2009;66(1): 23 148 - 52
- [24] Li H, Kim H. Desalination 2008;234(1-3):9-15.
- [25] Ogoshi T, Chujo Y. J Polym Sci Part A Polym Chem 2005;43(16):3543-50.
- Zhao X, Zhang W, Chen S, Zhang J, Wang X. J Polym Res 2012;19(5):1-9. [26]
- Taniguchi T, Kashiwakura T, Inada T, Kunisada Y, Kasuya M, Kohri M, et al. [27] | Colloid Interface Sci 2010;347(1):62-8.
- [28] Gao B, Chen Y, Zhang Z. Appl Surf Sci 2010;257(1):254-60.
- [29] Li Y, Benicewicz BC. Macromolecules 2008;41(21):7986-92.
- [30] Huang Y, Liu Q, Zhou X, Perrier Sb, Zhao Y. Macromolecules 2009;42(15): 5509 - 17
- [31] You YZ, Kalebaila KK, Brock SL, Oupicky D. Chem Mater 2008;20(10):3354-9.
- 1321 Lindenblatt G, Schärtl W, Pakula T, Schmidt M. Macromolecules 2000;33(25): 9340-7.
- Wu T, Zhang Y, Wang X, Liu S. Chem Mater 2007;20(1):101-9. [33]
- Prucker O, Rühe J. Macromolecules 1998;31(3):592–601. Prucker O, Rühe J. Macromolecules 1998;31(3):602–13. [34]
- [35]
- Prucker O, Rühe J. Langmuir 1998;14(24):6893-8. [36]
- [37] Husseman M, Malmström EE, McNamara M, Mate M, Mecerreyes D, Benoit DG, et al. Macromolecules 1999:32(5):1424-31.
- [38] Baum M, Brittain WJ. Macromolecules 2002;35(3):610-5.
- Edmondson S, Osborne VL, Huck WTS. Chem Soc Rev 2004;33(1):14-22. [39]
- Matyjaszewski K, Xia J. Chem Rev 2001;101(9):2921–90. [40]
- von Werne T, Patten TE. J Am Chem Soc 1999;121(32):7409-10. [41]
- von Werne T, Patten TE. J Am Chem Soc 2001;123(31):7497-505. [42]
- [43] Niepceron F, Lafitte B, Galiano H, Bigarré J, Nicol E, Tassin JF. J Membr Sci 2009;338(1-2):100-10.
- [44] Huang C, Zhang L. J Appl Polym Sci 2004;92(1):1-5.
- Tomura H, Saito H, Inoue T. Macromolecules 1992;25(5):1611-4. [45]
- Stöber W, Fink A, Bohn E. J Colloid Interface Sci 1968;26(1):62-9. [46]
- [47] Liang HQ, Wu QY, Wan LS, Huang XJ, Xu ZK. J Membr Sci 2013;446:482–91.
- Matyjaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelman A, Luokala BB, [48] et al. Macromolecules 1999:32(26):8716-24.
- [49] Dong Z, Wei H, Mao J, Wang D, Yang M, Bo S, et al. Polymer 2012;53(10): 2074-84.
- [50] Ohno K, Akashi T, Huang Y, Tsujii Y. Macromolecules 2010;43(21):8805–12.
- [51] Pyun J, Kowalewski T, Matyjaszewski K. Macromol Rapid Commun 2003;24(18):1043-59.
- [52] Qin S, Matyjaszewski K, Xu H, Sheiko SS. Macromolecules 2003;36(3):605-12.
- [53] Mu CX, Su YL, Sun MP, Chen WJ, Jiang ZY. J Membr Sci 2010;350:293-300.
- [54] Chen X, Su Y, Shen F, Wan Y. J Membr Sci 2011;384(1–2):44–51.