

Preparation of Poly(vinylidene fluoride)-*g*-poly(methacrylic acid) Composite Nanofiltration Membrane

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Abstract: Amphiphilic graft copolymer from poly(vinylidene fluoride) (PVDF) was synthesized using atom transfer radical polymerization (ATRP) for composite nanofiltration membranes. Direct initiation of the secondary fluorinated site of PVDF facilitates grafting of *tert*-butyl methacrylate (tBMA). Amphiphilic PVDF-*g*-PMAA graft copolymer with a 51:49 wt ratio was obtained by hydrolyzing poly(*tert*-butyl methacrylate) (PtBMA) to poly(methacrylic acid) (PMAA). Wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) confirmed the decrease of crystallinity of PVDF upon graft copolymerization. Composite nanofiltration membranes were prepared from PVDF-*g*-PMAA as a top layer coated onto PVDF ultrafiltration (UF) support membrane. The morphology and hydrophilicity of membranes were characterized using scanning electron microscopy (SEM) and contact angle measurement. The rejections of composite membranes were 80.2% for Na₂SO₄ and 28.4% for NaCl, and the solution flux were 9.5 and 14.5 L/m² h at 1.0 MPa pressure.

Keywords: atom transfer radical polymerization (ATRP), graft copolymer, composite membrane, nanofiltration.

1. Introduction

Composite nanofiltration (NF) membranes have received great attention in recent years [1-3]. The NF membrane process has been widely used for water treatment applications such as water softening, wastewater reclamation, and separation of organic compounds having different molecular weights. The performance characteristics of the NF membrane lie between those of reverse osmosis (RO) and ultrafiltration (UF) membranes. NF membranes are often negatively charged, and thus ionically charged polymers are of interest as a membrane material, which should be proven to be resistant to chlorine, high and low pH, high temperature and possessing good chemical stability.

NF membranes are usually prepared by coating a charged polymer on top of a porous substrate [4,5]. NF membranes have a looser skin layer structure en-

abling higher fluxes and lower operating pressures than RO membranes. Donnan effect is known to be responsible for a difference in rejection in salt separation [6]. Usually rejection is lower for monovalent ions and higher for divalent ions.

Atom transfer radical polymerization (ATRP) has been widely used to prepare graft copolymers from polymeric macroinitiators, polymer chains with regularly spaced, pendant chemical groups containing radically transferable halogen atoms [7,8]. The halogen atoms serve as initiation sites for the polymerization of side chains by ATRP. This "grafting from" method based on ATRP technique has been, thus, effectively used as an efficient polymerization for preparing well-defined graft copolymer [9-11]. Side chains are directly grafted from the backbone via ATRP initiated by the pendant initiating groups on the backbone polymers. Commercial halogenated polyolefins, such as poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), poly(chlorotrifluoroethylene) (PCTFE), and

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their copolymers are potential ATRP macroinitiators [12,13].

ATRP has also been used by a number of groups to polymerize hydrophilic monomers, including poly(oxyethylene) methacrylate (POEM) macromonomers [14, 15]. Recently Mayes group at MIT directly synthesized the graft copolymer of methacrylates from PVDF via ATRP using secondary fluorine as the initiator [16,17]. They demonstrated the direct preparation of amphiphilic graft copolymers having PVDF backbones by ATRP of hydrophilic side chains initiated at the secondary halogenated sites of PVDF. ATRP of a polyoxyethylene methacrylate (POEM) macromonomer incorporating roughly nine ethylene oxide (EO) units was used to prepare an amphiphilic graft copolymer, PVDF-*g*-POEM.

In this work, we synthesized amphiphilic graft copolymer from PVDF via ATRP for composite nanofiltration membranes. The grafting of *tert*-butyl methacrylate (tBMA) onto PVDF by ATRP is used to prepare a polymer precursor which is subsequently hydrolyzed to obtain an amphiphilic, PVDF-based copolymer having poly(methacrylic acid) side chains, PVDF-*g*-PMAA. The structural change of PVDF graft copolymer was characterized using wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC). Composite nanofiltration membranes were prepared from PVDF-*g*-PMAA as a top layer coated onto PVDF ultrafiltration (UF) support membrane. Nanofiltration performance of membrane was tested for 1,000 mg/L Na₂SO₄ and NaCl aqueous solutions.

2. Experimental

2.1. Materials

PVDF (M_n : 107,000 g/mol), *tert*-butyl methacrylate (tBMA), copper(I) chloride (CuCl), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA), *p*-toluenesulfonic acid monohydrate (TSA) and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich. All solvent and chemicals were reagent grade, and were used as received.

2.2. Synthesis of PVDF-*g*-PtBMA

1 g PVDF was dissolved in 10 mL NMP in a round flask at 80°C. The solution was cooled to room temperature, after which tBMA (50 mL), CuCl (0.04 g), and HMTETA (0.23 mL) were added and the flask was sealed with a rubber septum. After N₂ purging for 30 min, the reaction vessel was immersed in an oil bath at 90°C. The reaction was allowed to proceed for 24 h. The resultant polymer solution was precipitated into a mixture of 1 part methanol, 1~2 parts petroleum ether, and a small amount of HCl and recovered by filtration. The polymer was purified by redissolving in NMP and reprecipitating in methanol. Finally, the PVDF-*g*-PtBMA graft copolymer with 51:49 wt ratio was dried under vacuum overnight at room temperature.

2.3. Synthesis of PVDF-*g*-PMAA

Hydrolysis of PVDF-*g*-PtBMA (5 g) was performed in anhydrous toluene (300 mL). Pieces ~2 mm in size were immersed in toluene, causing the polymer to swell visibly but not dissolve. 30 g of *p*-toluenesulfonic acid monohydrate (TSA) was added to the reaction vessel, after which the reactor was immediately sealed with a rubber septum and the TSA was dissolved by vigorous stirring. N₂ gas was bubbled through the reaction mixture for 15 min, after which the reactor was placed in an oil bath preheated to 85°C. After 7 h, the heterogeneous reaction mixture was poured into excess methanol (a good solvent for TSA). The graft polymer PVDF-*g*-PMAA was recovered by filtration, redissolved in DMF, precipitated in a mixture containing 4 parts hexane and 1 part ethanol, and again recovered by filtration. For further purification, the polymer was stirred overnight in a large volume of THF, washed again in hexane/ethanol, and dried in a vacuum oven overnight at room temperature.

2.4. Membrane Preparation

Composite membranes were prepared by coating a 2 μ m thick PVDF-*g*-PMAA layer onto porous PVDF ultrafiltration membrane (Pall Corp. DV-20) using an RK

Control Coater (Model 101, Control Coater RK Print-Coat Instruments LTD, UK). The resulting membranes were dried in a convection oven at 80°C for 24 h and further dried in a vacuum oven for 24 h at 120°C. The composite membranes were stored in water until ready to be used.

2.5. Nanofiltration Performance

The membranes were characterized in the module after pretreatment with pure water under 1 MPa pressure for 30 min. The pure water flux and the rejection of 1,000 mg/L Na₂SO₄ and NaCl solutions were measured under a pressure difference of 1 MPa at room temperature. The permeation flux, F , is calculated as Equation (1):

$$F = \frac{V}{At} \quad (1)$$

where V is the total volume of the water or solution permeated during the experiment; A represents the membrane area; and t denotes the operation time. Rejection, R , is calculated as Equation (2)

$$R = \frac{1 - C_p}{C_f} \quad (2)$$

where C_p and C_f are permeate concentration and feed concentration, respectively.

2.6. Characterization

The WAXS experiment was carried out on a Rigaku 18 kw rotating anode x-ray generator with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 300 mA. The 2θ range was from 5° to 40° with a scanning speed of 3°/min, and the distance from the sample to detector was 185 mm. Differential scanning calorimeter (DSC 2920, TA Instruments, Inc.) was used to characterize the materials at a heating rate of 10°C/min under N₂ environment. Water contact angle measurements were performed on membranes using an Advanced Surface Technologies, Inc. Each sample was

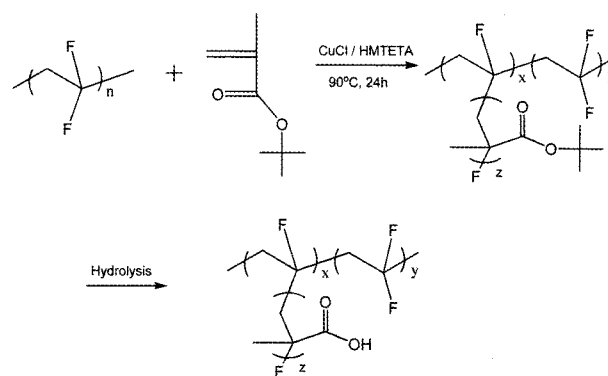


Fig. 1. Graft copolymerization of PtBMA from PVDF via ATRP and hydrolysis to form PVDF-g-PMAA.

raised toward a 1 μ L droplet of deionized water suspended from the tip of the syringe until the droplet was transferred to the sample surface. Advancing contact angles were then measured after adding deionized water to the droplet in 1 μ L increments until its edges were observed to advance over the surface. Scanning electron microscopy (SEM) was used for the characterization of membrane separation surface and cross-sectional morphologies. Fracture surfaces for cross-sectional imaging were prepared by cracking membranes under liquid nitrogen. Samples were sputter-coated with silver and examined at an accelerating voltage of 1 kV using a JEOL 6320.

3. Results and Discussion

The reaction scheme for the synthesis of PVDF graft copolymer via ATRP is illustrated in Fig. 1. The "grafting from" method using ATRP technique has been widely used as an efficient polymerization method for preparing well-defined graft copolymers. It has been generally believed that the secondary halogen atoms such as chlorine and fluorine in the halogenated polyolefins are too strongly bonded to serve as ATRP macroinitiators for the preparation of functionalized derivatives [18,19]. However, Mayes group recently reported on the direct synthesis of amphiphilic graft copolymers consisting of PVDF backbone and methacrylate side chains by the ATRP using secondary

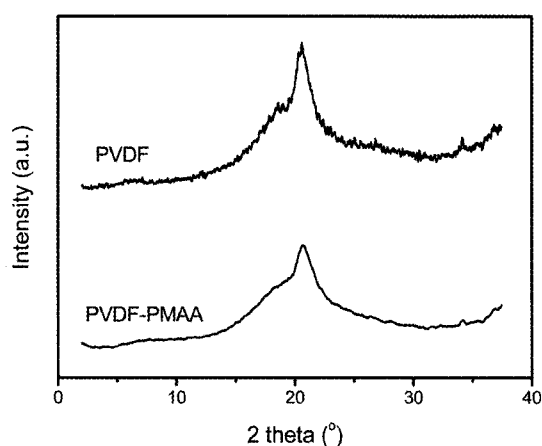


Fig. 2. WAXS patterns of pristine PVDF and PVDF-g-PMAA.

fluorine as the initiator [12,16,17].

The PVDF-g-PMAA graft copolymer with a 51:49 wt ratio was prepared using a two-step synthesis. In the first step, PtBMA side chains were graft copolymerized onto PVDF using ATRP. PVDF backbone was directly grafted with tBMA monomer at 90 °C for 24 h using ATRP. It should be noted that ATRP does not require stringent experimental conditions, as in the case of cationic and anionic polymerization [20]. In the second step, the PtBMA side chains were hydrolyzed to yield PMAA. It is well-known that PtBMA can be selectively and quantitatively hydrolyzed to PMAA in the presence of TSA [21,22]. Despite the heterogeneous nature of the hydrolysis reaction, hydrolysis of the PtBMA side chains to PMAA was quantitative. The amphiphilic PVDF graft copolymers are expected to molecularly self-assemble into continuous nanophase domains of semicrystalline PVDF interweaved with hydrophilic domains of PMAA brush layer [23].

To confirm the structural change of the graft copolymer, the WAXS curves of pristine PVDF and PVDF-g-PMAA were measured. The results are shown in Fig. 2, where the intensity of X-ray scattering is plotted against the diffraction angle, 2θ . PVDF is a semicrystalline polymer to show sharp peaks centered at a diffraction angle of 18.4 and 20.5°. Sharp crystalline peaks can be interpreted as due to pseudo-hexagonal

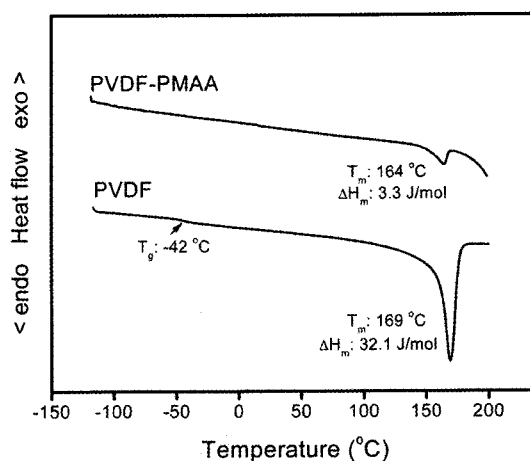


Fig. 3. DSC thermograms of pristine PVDF and PVDF-g-PMAA.

packing of the helical chains with varying degrees of lateral and chain axis disorder [24,25]. The grafting of PMAA from the PVDF alters the resulting molecular structure and physical network, leading to a decrease in its crystallinity. This can be explained by the fact that the randomness of the amorphous phase in the graft copolymers is enhanced by introducing PMAA groups, which gives rise to a perturbation of long-ranged spacing between the chains [26].

DSC thermograms for pristine PVDF and PVDF-g-PMAA are presented in Fig. 3. As seen in the figure, the crystallinity of PVDF-g-PMAA membrane was significantly decreased, which is consistent with WAXS data. For each polymer, the weight percent crystallinity, with respect to the PVDF content of the polymer, was calculated as

$$W_c = \frac{M_o^{PVDF}}{W_{PVDF}} \frac{\Delta H_m}{\Delta H_f} \quad (3)$$

where W_{PVDF} is the weight fraction of PVDF in the polymer, ΔH_m is the heat of melting observed by DSC [J/g], and ΔH_f is the heat of fusion of PVDF (6,700 J/mol). The crystallinity of PVDF-g-PMAA membrane was calculated as 16% (30% with respect to PVDF). The graft copolymer also exhibited the depression of melting point (T_m) relative to the PVDF parent

Table 1. Contact Angles of (a) Pure PVDF Membrane and (b) PVDF-g-PMAA Membrane with Time

	0 sec	10 sec	20 sec	30 sec
PVDF	93	93	92	92
PVDF-g-PMAA	65	49	43	48

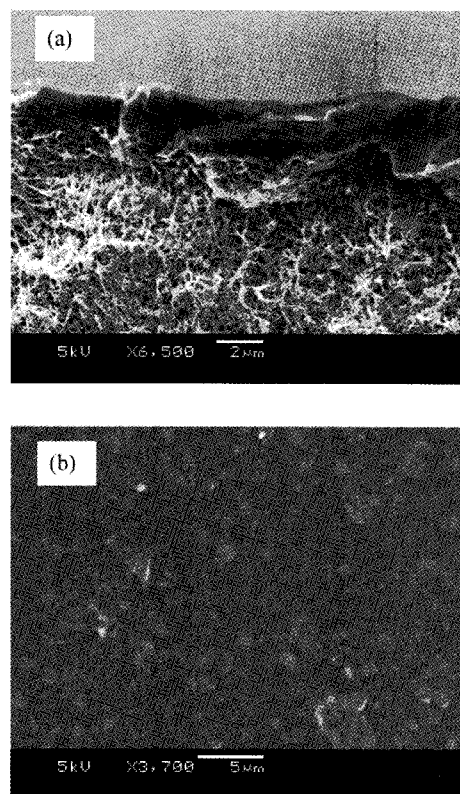
Table 2. Nanofiltration Performance of PVDF-g-PMAA Composite Membrane

	Na ₂ SO ₄	NaCl
Rejection (%)	80.2	28.4
Flux (L/m ² h)	9.5	14.5

polymer.

Contact angle measurements have been usually used to investigate the degree of hydrophilicity of membrane surfaces. Table 1 shows contact angles of pristine PVDF membrane and PVDF-g-PMAA membrane with time. A droplet of water placed on a pure PVDF membrane assumes a high contact angle, which changes very little over time until the drop finally evaporates. In contrast, a water droplet placed on a PVDF-g-PMAA membrane assumes a moderate initial contact angle which decreases to zero over time, and the droplet ultimately wets through the membrane. In this study, wettability was assessed based on the initial advancing contact angle of a 1 μ L water droplet placed on the membrane surface. The pristine PVDF control membrane displayed hydrophobic behavior with a constant contact angle of 92~93°, as shown in Table 1. In contrast, contact angle measurements on the PVDF-g-PMAA membrane surface exhibited instantaneous wetting as the water droplet spontaneously spread onto the surface and a contact angle was 38° after 30 second. These contact angles of composite membranes indicate an increase in surface hydrophilicity due to the introduction of -COOH groups to the membrane skin layer.

SEM micrographs of the separation surfaces and cross-sections of PVDF-g-PMAA composite membranes are presented in Fig. 4. The SEM image in Fig. 4(a) shows the cross-sectional morphology of a composite membrane comprising a 2 μ m layer of PVDF-g-PMAA

**Fig. 4.** SEM picture of (a) cross-section and (b) surface of PVDF-g-PMAA composite membrane.

coated onto a porous PVDF ultrafiltration membrane substrate. The surface of the copolymer film was smooth and nonporous to instrumental resolution as seen in Fig. 4(b), which might be highly advantageous in nanofiltration applications.

The nanofiltration performance of PVDF-g-PMAA composite membranes were tested under 1.0 MPa pressure for a 1,000 mg/L feed solution and the results were listed in Table 2. The membrane showed higher rejection for Na₂SO₄ (80.2%) than NaCl (28.4%), which is consistent with the results that rejection is lower for monovalent ions and higher for divalent ions [2,5,6]. On the other hand, the flux for Na₂SO₄ (9.5 L/m² h) is lower than for NaCl (14.5 L/m² h). This sequence represents the predictable Donnan characteristic of salt rejection for a negatively charged PVDF-g-PMAA nanofiltration membrane.

4. Conclusion

Amphiphilic PVDF-*g*-PMAA graft copolymer with a 51:49 wt ratio was successfully synthesized via ATRP technique using a two-step synthesis. The synthesis involved the graft copolymerization of PtBMA side chains onto PVDF backbone, followed by the hydrolysis of PtBMA side chains to hydrophilic PMAA. Synthesis of microphase-separated PVDF-*g*-PMAA comb copolymer was successful via "grafting from" method using ATRP, as revealed by XRD and DSC analysis. The contact angle measurements for composite membranes clearly demonstrated an increase in surface hydrophilicity due to the introduction of -COOH groups of PMAA to the membrane skin layer. The nanofiltration composite membranes exhibited rejections of 80.2 and 28.4%, and the solution fluxes of 9.5 and 14.5 L/m² h for Na₂SO₄ and NaCl, respectively, at 1.0 MPa pressure.

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