

Preparation of hydrophilic vinyl chloride copolymer hollow fiber membranes with antifouling properties



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(2-

Methacryloyloxyethylphosphorylcholine)

(MPC)

[2-(Methacryloyloxy) ethyl] dimethyl

(3-sulfopropyl) ammonium hydroxide

(MEDSAH)

Poly(ethylene glycol) methyl ether

methacrylate (PEGMA)

ABSTRACT

Hydrophilic vinyl chloride copolymer hollow fiber membranes with antifouling properties were prepared from brominated vinyl chloride-hydroxyethyl methacrylate copolymer (poly(VC-co-HEMA-Br)). The base membrane was grafted with two different zwitterionic monomers, (2-methacryloyloxyethylphosphorylcholine) (MPC) and [2-(methacryloyloxy) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide) (MEDSAH), and poly(ethylene glycol) methyl ether methacrylate (PEGMA). The effect of the grafting on the base membrane hydrophilicity and antifouling properties was investigated. For comparison of the results, the pure water permeabilities and pore sizes at the outer surfaces of the grafted hollow fiber membranes were controlled to be similar. A poly(VC-co-HEMA-Br) hollow fiber membrane with similar pure water permeability and pore size was also prepared as a control membrane. A BSA solution was used as a model fouling solution for evaluation of the antifouling properties. Grafting with zwitterionic monomers and PEGMA improved the antifouling properties compared with the control membrane. The PEGMA grafted membrane showed the best antifouling properties among the grafted membranes

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1. Introduction

Ultrafiltration membranes have been prepared using nonsolvent induced phase separation (NIPS) from a variety of polymers, such as polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), cellulose acetate (CA), and polyvinylidene difluoride (PVDF) [1]. Polyvinyl chloride (PVC) has attracted attention as an alternative polymer for ultrafiltration membrane preparation because of its excellent mechanical strength, high resistance to corrosion and organic solvents, and low cost.

PVC flat sheet membranes prepared by NIPS have been reported in a number of studies [2–4]. Xu et al. prepared a PVC hollow fiber membrane using a ternary PVC/additive/solvent dope solution, and studied the effect of solution composition and membrane preparation conditions on the properties of the prepared membranes

[5]. Wang et al. prepared flat sheet membrane by using polyvinyl chloride-co-vinyl acetate (VC-co-VAc-OH) [6,7]. They evaluated the effect of casting solution composition and preparation conditions on the properties of the prepared membranes.

To improve the antifouling properties of PVC membranes, Babu and Gaikar prepared PVC/carboxylated polyvinyl chloride (CPVC) [8] and PVC/polyvinyl pyrrolidone (PVP) [9] flat sheet blend membranes. In these studies, the effects of process conditions on the fouling tendencies of the membranes were studied, but the effect of membrane material was not evaluated well. Liu et al. prepared membrane with lower antifouling properties by adding amphiphilic copolymer (Pluronic F 127) into PVC casting solution [10]. By increasing copolymer concentration up to 8 wt% water permeability and antifouling properties of the prepared membrane were improved. Further increment in copolymer amount was resulted in lower water permeability. They concluded that considering both the water permeability and antifouling properties, adding 8 wt% copolymer was the optimal condition to obtain membrane with high filtration properties. Although PVC blend membranes have been prepared and characterized in some studies, PVC/PAN [11] and PVC/polystyrene (PS) [12] are not completely compatible. In another study, Krishnamoorthy et al. prepared a

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PVC/CA blend membrane and studied its rejection properties [13]. They found that at a high PVC concentration, a PVC/CA blend was not compatible. These earlier studies have indicated that blending PVC with hydrophilic polymers is not easy because of a lack of compatibility. Recently Fan et al. prepared PVC/polyvinylformal (PVF) blend flat sheet ultrafiltration membranes [14]. They reported that during the phase separation process PVF was enriched to membrane surface via spontaneous surface segregation and the membrane surface hydrophilicity increased sharply which was resulted in decrease in BSA fouling.

As an alternative method for preparation of hydrophilic PVC membranes, some studies have investigated grafting with hydrophilic monomers [8,15,16]. Babu and Gaikar compared the fouling properties of a PVC membrane and an acrylic acid grafted PVC membrane [8]. They reported that grafting acrylic acid on a PVC membrane slightly decreased the PVC membrane's fouling properties. However, Liu et al. found the water permeability and antifouling properties of an acrylic acid grafted PVC membrane were higher than those of a PVC membrane [15]. Kim et al. grafted *N*-vinyl-2-pyrrolidinone (NVP) onto a PVC membrane using ultraviolet assisted graft polymerization to increase surface wettability and to decrease absorption fouling [16]. They found that reversible fouling of the grafted PVC membrane decreased sharply by combined effects of back-pulsing, cross-pulsing, and membrane surface modification.

To the best of our knowledge, few studies have investigated preparation of hydrophilic VC copolymer membranes using the grafting method. In this study, the effect of different grafting monomers on the fouling properties of hollow fiber membranes was studied. We compared the antifouling properties of membranes grafted with zwitterionic monomers with those of poly(ethylene glycol) methyl ether methacrylate (PEGMA) grafted membranes. Although both membranes showed good antifouling properties, the PEGMA grafted PVC membrane showed superior antifouling properties.

2. Experimental

2.1. Materials

Vinyl chloride-hydroxy ethyl methacrylate copolymer (poly(VC-co-HEMA), MW = 39,000, HEMA segment amount-of-substance fraction: 9.5%) was kindly supplied by Sekisui Chemical Co., Ltd. (Kyoto, Japan). Bovine serum albumin (BSA), pyridine, sodium dihydrogen phosphate, disodium hydrogen phosphate, copper chloride (I) (CuCl), ascorbic acid, methanol, ethanol, aqueous hydrochloric acid (1.0M), dimethylacetamide (DMAC) and polyethylene glycol (PEG, MW=600) were purchased from Wako Pure Chemical Industries (Osaka, Japan). α -Bromoisobutyryl bromide, PEGMA (MW=300), Triton X-100, 2-methacryloyloxyethyl phosphorylcholine (MPC) and [2-(methacryloyloxy) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide (MEDSAH) were purchased from Sigma-Aldrich (St. Louis, MO). Polystyrene latex particles with diameters of 20, 50 and 100 nm were purchased from Duke Scientific Corporation (Palo Alto, CA). All the chemicals were used without further purification. The structures of poly(VC-co-HEMA), MPC, MEDSAH, PEGMA and α -bromoisobutyryl bromide are shown in Fig. 1.

2.2. Synthesis and purification of materials

Brominated poly(VC-co-HEMA) (poly(VC-co-HEMA-Br)) was prepared from poly(VC-co-HEMA). The addition of Br provides a starting point for atom transfer radical polymerization (ATRP). Poly(VC-co-HEMA) (50 g) and 3.0 mL of pyridine were dissolved in

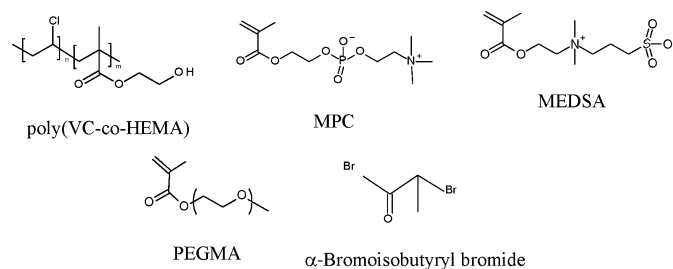


Fig. 1. Structures of polymer and monomers used for grafting.

340 g of DMAC. α -Bromoisobutyryl bromide (8 mL) and 60 mL of DMAC were mixed to obtain a homogeneous solution, and added dropwise to the poly(VC-co-HEMA) solution in DMAC with gentle stirring for 10 min. After mixing, the solution was cooled in an ice bath with gentle stirring for 2 h. The solution was then removed from the ice bath and stirred at room temperature overnight. Milli-Q water was added to the solution to precipitate poly(VC-co-HEMA-Br). The precipitated copolymer was rinsed once with ethanol and twice with Milli-Q water, and then dried at 40 °C under vacuum. The dried precipitate was dissolved in DMAC, and the precipitation procedure was repeated twice. The structures of the resulting copolymers were confirmed by ^1H NMR spectroscopy (Bruker Avance 500, Bruker Bio Spin) measurement.

2.3. Hollow fiber membrane preparation

A batch type extruder was used to prepare hollow fiber membranes via NIPS [17]. Preparation conditions for two types of membranes are summarized in Table 1. Dope solutions for preparation of hollow fiber membranes were prepared by mixing the poly(VC-co-HEMA-Br), PEG 600 and solvent at 40 °C. Before spinning the dope solution, it was left in the dope solution tank for 2 h to remove air bubbles. The hollow fiber was extruded from a spinneret with outer and inner tube diameters of 2 and 0.8 mm, respectively. After extrusion into the coagulation bath, which induced phase separation and caused membrane formation, the membrane was wound on a take up winder. Water was introduced into the inner tube to make the lumen of the hollow fiber. The solvent remaining inside the hollow fiber membrane was extracted by immersing the membrane in water. The prepared hollow fiber membrane was kept in water until it was characterized.

2.4. Atom transfer radical polymerization for monomer grafting

The prepared poly(VC-co-HEMA-Br) hollow fiber membranes were cut into 15-cm pieces. Ten pieces of hollow fiber membrane were placed in a 300-mL Schlenk flask with CuCl (0.040 g), DMDP (0.10 g), ascorbic acid (0.040 g), Milli-Q water (50 g), methanol (50 g), and monomer (0.50 g; MPC, MEDSAH, or PEGMA). The monomer was grafted onto the membrane by a grafting polymerization at 25 °C under nitrogen. The grafted hollow fiber membranes were rinsed with 10 mM HCl in methanol for 3 min and then rinsed with Milli-Q water. To assess the net effect of the grafted monomer on the fouling properties of the prepared hollow fiber membranes, we selected membranes with similar quantities of grafted monomer (0.9–1.4 g/m²) and water permeability (240–270 L/(m² h atm)) for further evaluation. The selected grafted membranes are detailed in Table 2. Each poly(VC-co-HEMA-Br) hollow fiber membrane modified with a hydrophilic monomer is abbreviated as poly(VC-co-HEMA)-g-hydrophilic monomer (i.e. poly(VC-co-HEMA)-g-PEGMA).

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