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# Hemocompatibility and ultrafiltration performance of surface-functionalized polyethersulfone membrane by blending comb-like amphiphilic block copolymer

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ABSTRACT

While polyethersulfone (PES) represents outstanding oxidative, thermal and hydrolytic stability as well as good mechanical and film-forming properties, the hemocompatibility of PES membrane must be dramatically enhanced to reduce injections of anticoagulants during hemodialysis. In this study, a comblike amphiphilic block copolymer poly (vinyl pyrrolidone)-*block*-poly (acrylate-*graft*-poly (methyl methacrylate))-*block*-poly-(vinyl pyrrolidone) (PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP) was synthesized via reversible addition-fragmentation chain transfer polymerization and used to modify PES membrane via a liquid–liquid phase separation technique. The surface structure of the modified membrane were characterized by using X-ray photoelectron spectroscopic analysis, fourier transform infrared and water contact angle measurement. The modified PES membrane showed low hemolysis ratio, improved hydrophilicity, suppressed platelet adhesion and prolonged activated partial thromboplastin time. And the modified membranes showed high PBS solution (or water) flux and good protein anti-fouling properties. The dramatic performance enhancement is attributed to its unique surface architecture, which may be formed by migration and self-assembly of PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP during phase separation. In the surface layer of the modified membrane, PVP chain formed functional brush while PMMA chain embedded in the membrane substrate. The highly branched chains of P(AE-*g*-PMMA) block endowed the modified membrane with good stability, which has potential to be used in blood purification.

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## 1. Introduction

Among the polymeric materials for biomedical devices, polyethersulfone (PES) was widely used due to its outstanding biocompatibility, mechanical properties and processing characteristics [1–3]. However, long-term clinical application of this kind of blood-contacting material may result in thrombogenic formation, response of immune system, or other tissue responses for the inadequate hemocompatibility [4–6], which has limited the application of PES membrane [7]. Therefore, the modification of PES membrane is necessary for improving the hemocompatibility [8].

Various modification methods for PES membrane have been developed in recent decades, such as bulk modification, blending method, surface-coating, surface physical treatment and surface grafting method [9–12]. Among these methods, blending is the simplest method to modify PES membrane and is widely used in industry. By directly blending hydrophilic polymers, such as poly (vinyl pyrrolidone) (PVP) [13–15], polyethylene glycol (PEG) [16], and poly (acrylic acid-*co*-vinyl pyrrolidone) [17], the surface hydrophilicity and its relative performance of the membranes could be increased. In fact, as the same series of polymer, polysulfone (PSf) modified by PVP were developed since more than 30 years ago and were commercially available. Cabasso et al. blended PVP into PSf membrane and the introduction of PVP to the spinning dope helps to eliminate the formation of dense skin on the fiber surface and contributes to the wall porosity [13]. Recently, Wang et al. used PVP as additive to modify PES membrane; the result showed that the PVP-added PES membrane has higher water flux, water adsorption, and lower water contact angle than the pristine PES membrane; adding PVP as an additive could also effectively reduce bovine serum albumin adsorption and prolong the blood coagulation time, thereby improving hemocompatibility of PES membrane [14]. Hollow fiber

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membranes were prepared from PES and PVP (PES/PVP=18/3 and 18/6 by weight) solution in N, N-dimethylacetamide by the dry wet spinning method. The performances of the PES/PVP hollow fiber hemodialysis membranes were improved by heat-treatment [15]. However, the elution of water-soluble additives from membranes was a challenge to the preparation and repeated use of the modified membranes [18].

To overcome the elution of hydrophilic additives, many studies have focused on blending amphiphilic copolymers as additives to modify the membrane surface [19–23]. When the phase separation began, the amphiphilic copolymers migrated to the surface of membrane and assembled with the hydrophilic block directed to the surface and the hydrophobic block mingled in the polymer matrix, since the amphiphilic nature of the block copolymer and the fast solvent exchange [24]. The enrichment of the hydrophilic polymers can improve the membrane performance as measured using the flux, protein adsorption and platelet adhesion [25]. Lee et al. synthesized a triblock copolymer of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) PEO-PPO-PEO, which was used as additive to prepare polyethylene oxide (PEO) surfaces. The film surface containing additives with long PEO chains was particularly effective in preventing platelet adhesion [26]. Higuchi et al. synthesized hydrophilic PSf membranes (PVP-PSf) covalently conjugated with PVP on the surface. The hydrophilic surface of the PVP-PSf membranes causes suppression of the platelet adhesion on the PVP-PSf membranes; and the long hydrophilic side chain of PVP on PVP-PSf membranes contributes to the hydrophilic and hemocompatible wipers on the surface of the hydrophobic PSf membranes [27]. In our previous study, we have synthesized a linear block copolymer of poly (styrene-*co*-acrylic acid)-*b*-poly (vinyl pyrrolidone)-*b*-poly(styrene-*co*-acrylic acid) (P(St-*co*-AA)-*b*-PVP-*b*-P(St-*co*-AA)) for PES membrane modification [28]. The modified membranes showed depressed platelet adhesion, increased coagulation time and good hemocompatibility.

To further significantly increase the stability and hemocompatibility of the modified PES membrane, in this paper, a comb-like amphiphilic block copolymer poly (vinyl pyrrolidone)-*block*-poly (acrylate-*graft*-poly (methyl methacrylate))-*block*-poly-(vinyl pyrrolidone) (PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP) was synthesized. Compared with the similar triblock copolymer (P(St-*co*-AA)-*b*-PVP-*b*-P(St-*co*-AA)), PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP have many superiority for PES membrane modification. First of all, PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP has a comb-like macromolecular structure, but P(St-*co*-AA)-*b*-PVP-*b*-P(St-*co*-AA) is a linear block copolymer. The unique structure of PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP made it self-assemble on the PES membrane surface during the phase separation procedure, with functional branch-like –PVP chains hanged on membrane surface and with root-like -P(AE-*g*-PMMA) chains embedded in the membrane firmly, which plays an important role in the enhancement of membrane stability. Secondly, as hydrophobic chain of PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP, –PMMA can be blended with PES in good dispersion because of the principle of similar solubility parameters ($\delta_{PMMA}=22.7$; $\delta_{PES}=21.9$). The modified PES membrane with highly enhanced hemocompatibility and stability might be applied in blood purification including hemodialysis and bioartificial liver supports.

## 2. Materials and methods

### 2.1. Materials

Polyethersulfone (PES, Ultrason E6020P) was obtained from BASF, Germany. Methyl methacrylate (MMA; 99.0%) was purchased from R&LHEM, China. *N*-vinyl pyrrolidone (VP; 99.0%) was purchased from Alfa Aesar, USA, and was pretreated by activated carbons before use. Tetrahydrofuran (THF) was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China), and acryloyl chloride was purchased from Aladdin (Shanghai, China). *N*, *N*-dimethylacetamide (DMAC; AR, 99.0%) and *N*, *N*-dimethylformamide (DMF; 99.0%) were purchased from Sinopharm Chemical Reagest Co., Ltd (Biejing, China) and used as the solvents. Azo-bis-isobutryonitrile (AIBN) was purchased from Tianjin Tianhe Chemical Reagent Factory (Tianjin, China) and used as the initiator. All the other chemicals (analytical grade) were obtained from Sinopharm Chemical Reagest Co., Ltd, China, and used without further purification. The preparation of RAFT agent and macro-RAFT agent were synthesized according to the literature [22,29].

### 2.2. Polymer syntheses

#### 2.2.1. Synthesis of AE-PMMA

The general procedure was as follows: MMA, MTE, AIBN and THF were added into a 250 mL, three-necked, round-bottomed flask; After bubbling for 15 min with nitrogen, the mixture was allowed to react for 3 h under the atmosphere of nitrogen at 0 °C; Triethylamine was added into the mixture using ice-water bath to keep the constant temperature; Acryloyl chloride solution in THF was added dropwise within 20–30 min under a nitrogen atmosphere, and the polymerization was carried out for 2 h at room temperature; After filtering, the product was precipitated in petroleum ether, and washed with alkali and de-ionized water, respectively; And then the obtained AE-PMMA was dried under vacuum at 50 °C for 24 h [30].

#### 2.2.2. Synthesis of PVP-b-P(AE-g-PMMA)-b-PVP

The synthesis of PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP was carried out in a sealed tube, and shown as follows: AE-PMMA, the macro-RAFT agent (PVP), AIBN, and DMF were added to a tube, and stirred for 10 min. After bubbling with nitrogen for 30 min the reaction mixture was allowed to warm to 80 °C under a nitrogen atmosphere and polymerization was carried out for 5 h. After precipitation in ethyl ether the product was dried under vacuum at 50 °C overnight.

### 2.3. Preparation of membranes

To prepare the membranes, PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP and PES were dissolved in the solvent DMAC by vigorous stirring at 70 °C until a clear homogeneous solution was obtained, dried in a vacuum oven at 40 °C for 3 days. The concentration of PES was 16 wt%. The contents of the PVP-*b*-P(AE-*g*-PMMA)-*b*-PVP in the casting solutions were 0, 1, 3 and 5 wt%, respectively. After vacuum degassing, the casting solution was prepared into membrane by spin coating coupled with a liquid–liquid phase separation technique at room temperature. The formed membranes were washed with de-ionized water for three times to thoroughly remove the residual solvent. The resultant membranes were stored in fresh de-ionized water at 37 °C for 30 days under stirring and then dried at room temperature.

### 2.4. Characterization

FTIR spectra were measured with FTIR Nexus 670 (Nicolet American) instrument. To prepare FTIR samples, the copolymer was dissolved in DMAC and cast on apotassium bromide (KBr) disc with a thickness of about 0.8 mm. The morphologies of the membranes were observed with an XL 30ESME scanning microscope. The membranes were frozen in liquid nitrogen, and then broken and sputtered with a gold layer before scanning electron

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