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Poly(m-phenylene isophthalamide) (PMIA): A potential polymer for breaking through the selectivity-permeability trade-off for ultrafiltration membranes

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ABSTRACT

The selectivity-permeability trade-off represents a limitation to the performance of ultrafiltration (UF) membranes. Theoretically, this trade-off is mainly determined by the pore structure, including the porosity, pore radius distribution and skin layer thickness. Benefiting from its high rigidity and high surface free energy, poly(m-phenylene isophthalamide) (PMIA) is proposed for preparing a high-performance UF membrane. In this work, PMIA membranes with various effective pore radii (6.58 nm, 6.84 nm and 9.28 nm) were fabricated via nonsolvent-induced phase separation (NIPS). Through selectivity-permeability analysis, the PMIA membrane was found to break through the trade-off between selectivity and permeability. Compared with other UF membranes, the PMIA membrane exhibited a high porosity, narrow pore radius distribution and excellent hydrophilicity, leading to its high performance in the filtration process. This phenomenon could probably be attributed to the high rigidity, which confined the motion of the PMIA chain to suppressing pore collapse during pore formation, as well as to the high surface free energy that caused the hydrophilicity. All of these results clearly indicated that PMIA might be the most appropriate polymer for fabricating the UF membrane.

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1. Introduction

Ultrafiltration (UF) membranes are widely used in water purification [1], wastewater treatment [2], protein product concentration [3], hemodialysis [4], and more. Currently, commercial UF membranes are mostly made from polysulfone (PSF), celluloses, polycarbonate (PC), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC) and other inorganic materials. Each series contains membranes that have a range of pore size or molecular weight cut-off. Generally, the performance characteristics of UF membranes mainly contain permeability and selectivity that are inversely related. Because the steric (size exclusion) effect acts as the main separate mechanism [5], the selectivity of UF membrane is determined by pore radius (R) and pore radius distribution (σ) [6], while the permeability is governed mainly by the pore radius (R), porosity (ϵ) and skin layer thickness (δ_m). To identify the underlying relationship between the selectivity and permeability, Mehta and Zydney [7] developed a

trade-off that known UF membranes cannot permeate.

Structurally, an ideal UF membrane should have a high porosity, narrow pore radius distribution and thin skin layer. Additionally, taking the surface property into consideration, hydrophilicity endows the UF membrane with excellent wettability, which effectively improves the water permeation in the filtration process [8,9]. The block copolymer (BCP) membrane, which is supposed to possess high selectivity due to its uniform pore size, has attracted substantial attention in recent years. Nevertheless, limited by their relatively low permeability, the benefits did not outweigh the limitations [10]. Additionally, the synthesis complexity and high cost of BCP make it difficult to produce on a large scale. Therefore, it is important to seek a suitable material for preparing a high-performance UF membrane.

Poly(m-phenylene isophthalamide) (PMIA), due to its hydrogen bond network, has excellent mechanical properties and an outstanding thermal stability [11]. The glass transition temperature (T_g) of PMIA is up to 558 K (shown in Table 1), resulting in a broad range of temperature and high rigidity, which is necessary for membranes with high porosity. Meanwhile, the PMIA membrane is supposed to be hydrophilic due to the high surface free energy provided by the amide bond. Additionally, its high solubility in a common organic solvent (such as DMF and DMAc) makes it

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Table 1
Glass transition temperature and surface free energy of polymers.

Polymer	Glass transition temperature (K)	Surface free energy (mN m ⁻¹)	Δ (mN m ⁻¹)	Ref.
PMIA	558	50.5 ^a	22.3	[13]
PSf	458	42.3	30.5	[14,15]
PP	~260	29	43.8	[14]
PAN	398	38.6	34.2	[14,16]
PTFE	303–399	19.5	53.3	[14,17]
PVC	344–371	41	31.8	[14,17]
PVDF	238	25	47.8	[14,17]
Nylon	320–330	44	28.8	[14,17]
Cellulose	503	56.7	16.1	[14,18]
Cellulose acetate	243–473	45.9	26.9	[14]
H ₂ O	/	72.8	/	[18]

Δ , the difference value of the surface free energy between polymers and water.

^a 50.5, the surface free energy for PMIA, which was obtained from measurements using the two liquid method.

possible to prepare the PMIA membrane by nonsolvent-induced phase separation (NIPS), which is favorable for developing large scale UF membranes [12]. Therefore, PMIA may be a promising material for preparing UF membranes because of these prominent physiochemical properties. However, to the best of our knowledge, there are few (if any) reports about PMIA ultrafiltration membranes via NIPS.

In this work, PMIA ultrafiltration membranes with various effective pore radii (6.58 nm, 6.84 nm, and 9.28 nm) were prepared by varying the temperature of the coagulation bath during the NIPS process. As expected, the prepared PMIA membrane achieves remarkable performance, breaking through the selectivity-permeability trade-off, which can be ascribed to their excellent pore structure and surface hydrophilicity.

2. Materials and methods

2.1. Materials

Poly(m-phenylene isophthalamide) (PMIA) fiber was provided by DuPont Co., Ltd. (USA) and dried at 100 °C for 12 h before use. Its chemical structure is shown in Fig. 1. Dimethyl acetylamine (DMAc), dimethyl formamide (DMF), glycerin and bovine serum albumin (BSA) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). A series of polyethylene glycols (PEGs, MW 10,000–100,000) were purchased from Sigma-Aldrich (USA). All solvents and chemicals were reagent grade and used as received. Ultrapure water (18 M Ω cm⁻¹, Millipore Milli-Q) was used in all aqueous solutions.

2.2. Membrane fabrication

The PMIA membranes were fabricated by the traditional phase inversion method. The casting solution was prepared by dissolving 12 g of PMIA in 88 g of mixed solution (DMAc/DMF/glycerin 1/1/0.8 wt/wt/wt) at 80 °C for 6 h. After filtration and removal of air

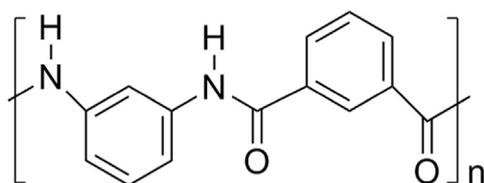


Fig. 1. Chemical structure of PMIA.

bubbles by vacuum deaeration, the solution was cast on a glass substrate with a steel knife; then, the liquid film was immersed into a water coagulation bath at 30 °C, 50 °C or 70 °C. The formed membrane was peeled off and subsequently washed in water at 60 °C for 3 d to extract the residual solvent. The as-prepared PMIA membranes were designated M30, M50 and M70, with the digits indicating the temperature of coagulation baths. Before testing, PMIA membranes were stored in 10 mM phosphate buffer solution (PBS, pH=7.4) and 5 g/L BSA/PBS solution at 4 °C. For convenience, the PMIA membrane soaked in PBS is referred to as a PMIA/PBS membrane, while that in BSA/PBS solution is referred to as a PMIA/BSA membrane. To ensure equilibrium adsorption, the PMIA/BSA membrane was soaked for 24 h before use.

2.3. Membrane characterization

2.3.1. Membrane surface properties

The surface and cross-section morphology of the membrane was characterized by field emission scanning electronic microscopy (FE-SEM, Hitachi, S-4800, Japan). Images captured at a chosen magnification (50 k) were used to measure the membrane surface pore structure characteristics. With the help of ImageJ software (National Institutes of Health, NIH), binary images were acquired with the pores in black and surface in white at a chosen threshold level [19]. In this method, the pores on the surface should be disconnected from each other and were supposed to be circular. Thus, the porosity (ϵ_{sp}) and pore area can be directly obtained from the software. Then, based on these data, the average pore radius (R_{sa}) and pore density (N_{sp}) can be calculated.

The membrane surface zeta potential was determined from the streaming potential measurement with a SurPass Electrokinetic Analyser (Anton Paar, GmbH, Austria). This measurement was performed at 20 °C in 1 mM KCl solution with the solution pH values ranging from 2 to 10, and the zeta potential was calculated using the Helmholtz-Smoluchowski equation. The water contact angle of the membrane was measured with a contact angle meter system (OCA20, Dataphysics, Germany) in the sessile-drop mode at room temperature.

2.3.2. Pore structure characterization

Polyethylene glycols (PEGs, MW 10,000–100,000) were used as solutes in the feed solution with the solute concentration kept at 200 ppm by weight. The membrane was placed at the bottom of the stirred cell and compacted for 30 min at 0.015 MPa to reach a stable flux. After the stirred cell was filled with PEG solution, the experiment was conducted under 0.01 MPa at room temperature (20 \pm 3 °C).

The rejection data for the PEG solution were plotted versus the solute radius on log-probability paper (shown in Fig. S1 in Supplementary information), showing straight lines fit with high correlation coefficients ($R^2 > 0.95$). By ignoring the concentration polarization as well as the steric and hydrodynamic interaction between pores and solutes, the average pore radius (R_a) and geometric standard deviation (GSD, σ_p) were determined. Then, the pore density (N) and porosity (ϵ) were calculated as described in Ref. [20]. Meanwhile, the effective pore radius (R_e) can be approximated using the Hagen-Poiseuille equation:

$$J_v = \frac{\epsilon R_e^2 \Delta P}{8 \eta \delta_m} \quad (1)$$

where J_v is the flux, ΔP is the pressure (Pa), η is the water viscosity (0.001 Pa s), δ_m is the skin layer thickness and ϵ is the porosity. The most probable pore radius (R_m) can be directly acquired from the probability density function curve, which was determined by the average pore radius and geometric standard deviation [6,20].

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