Positively charged nanofiltration membranes prepared by the co-deposition of polydopamine and poly(ethylene imine)

Pei-Bin Zhang（张培斌, 11229027）, Li-Ping Zhu*（朱利平）, Bao-Ku Zhu（朱宝库）

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

*** Contact to: Li-Ping ZHU, Email: lpzhu@zju.edu.cn, Tel/Fax: +86-571-87953011**

Introduction

In recent years, mussel adhesive proteins (MAPs) attracts much attention for its universal surface modification abilities. Dopamine (DA), a derivative of mussel adhesive proteins, has been reported to self-polymerized and cross-linked under weak alkaline conditions. The self-polymerization of DA can form a robust polydopamine (PDA) coating layer onto almost all the materials without any damage. We have previous fabricated a novel nanofiltration (NF) membrane based on multiple deposition process of DA onto polysulfone (PSf) ultrafiltration membranes. The advantages of dopamine modification can be taken more to make better performance of the NF membrane .

Here we report a novel method to prepare the nanofiltration membrane by co-deposition of DA and PEI onto PSf substrates and then cross-linking by epichlorohydrin (ECH), showed in Fig. 1. The effect of co-deposition condition and cross-linking condition were investigate in detail. The successful introduction of PEI to the surface by co-deposition method made the NF membrane perform better cations separation abilities. Moreover, the NF membranes showed better stability under alkaline condition due to the covalent and non-covalent interaction between DA and PEI during co-deposition and cross-linking process.

Method

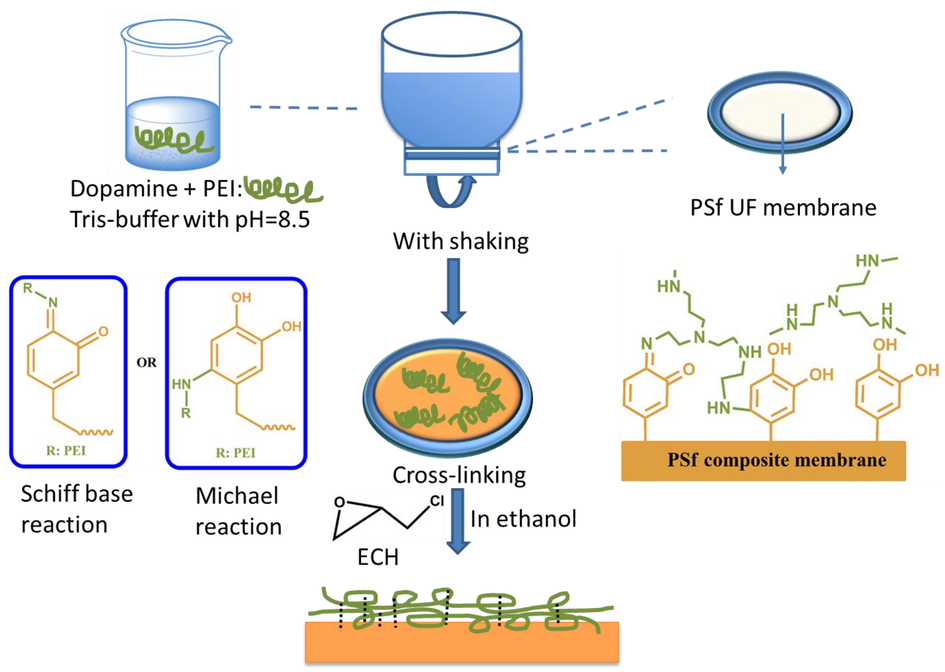

Fig. 1 Experiment process and possible reaction mechanism.

Results and Discussions

1. Analysis of chemical compositions

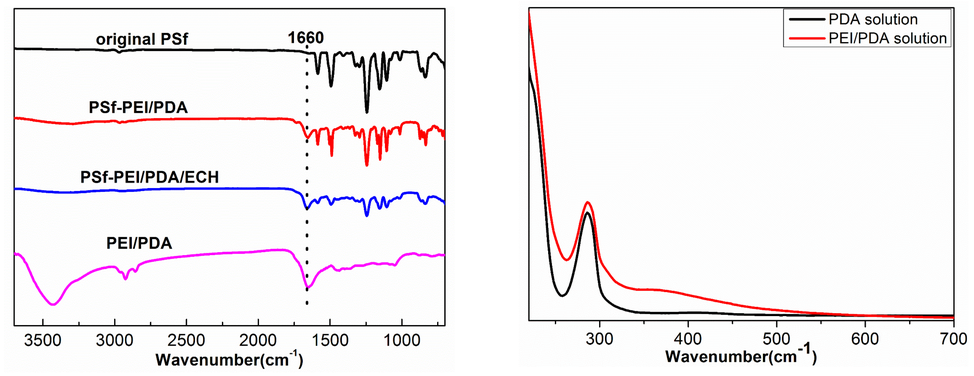

Fig. 2 ATR-FTIR spectra of the studied membranes and UV-vis spectra of reaction solutions

Table 1 XPS results of the membranes

	C	O	N	S	Cl	N/C	N/O
PSf	80.2%	15.3%	1.8%	2.7%	--		
PSf-DA	65.9%	25.9%	7.9%	0.3%	--	0.120	0.305
PSf-DA/PEI	65.8%	22.4%	11.2%	0.6%	--	0.169	0.497
PSf-DA/PEI-ECH	67.6%	19.7%	11.9%	0.2%	0.6%	0.176	0.604

2. Membrane surface morphology

After co-deposition of PEI and dopamine, the surface of the membrane was covered with aggregates. The nano-aggregates formed here presumably due to PEI participant in the aggregation of PDA. In addition, high temperature (60℃) for cross-linking gave chance to adjust the conformation of molecular chain.

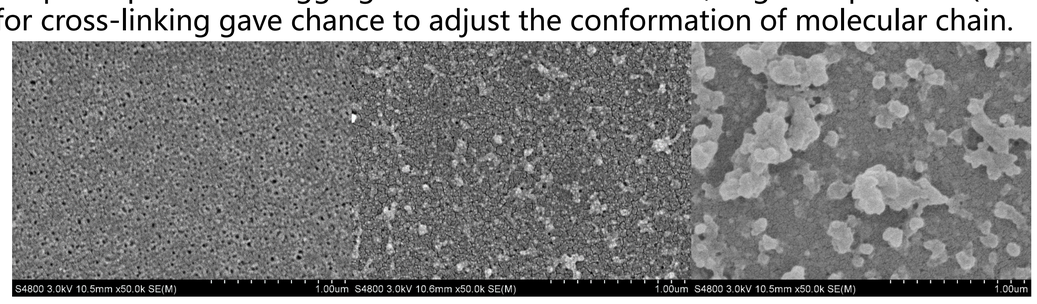

Fig. 3 SEM images of PSf membrane, PSf-PEI/PDA composite membrane and PSf-PEI/PDA/ECH composite membrane, respectively.

3. NF tests of PSf-PEI/PDA/ECH membrane

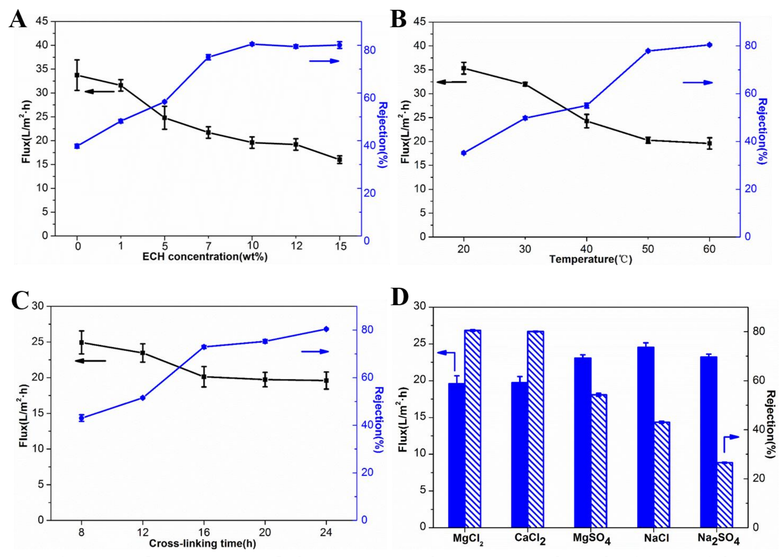

Fig.4 Separation performance of the NF membranes. (Salt solutions with 1 mmol/L concentration under 0.4 MPa)

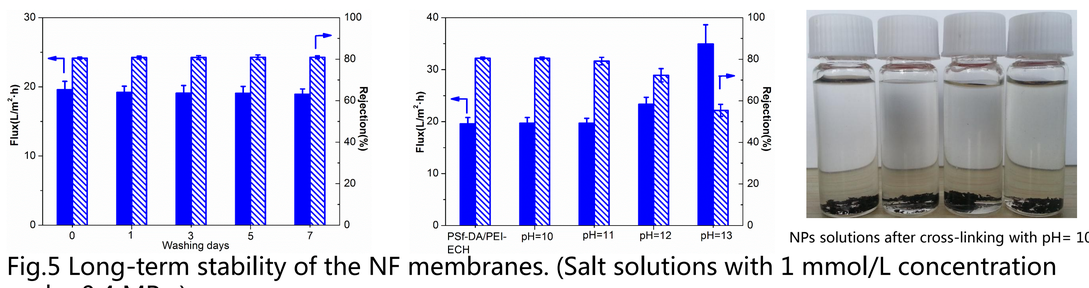

Fig.5 Long-term stability of the NF membranes. (Salt solutions with 1 mmol/L concentration under 0.4 MPa)

Conclusion

A novel positively charged composite nanofiltration (NF) membrane was prepared by the co-deposition of dopamine (DA) and poly(ethylene imine) (PEI) on a polysulfone (PSf) substrate following with epichlorohydrin (ECH) cross-linking. The rejection of the composite membrane to different salts followed the order $MgCl_2 \approx CaCl_2 > MgSO_4 > NaCl > Na_2SO_4$, which exhibited as a typical positively charged NF membrane. Furthermore, the composite membrane was found to be stable under alkaline conditions, which effectively reduced the limit to the operation environments for the dopamine-modified membranes.

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (Grants 51273176), the National High Technology Research and Development Program of China (863 Program of China, 2012AA03A602), and the Fundamental Research Funds for the Central Universities (2014QNA4038).

References

1. Y. Zhang, et al. Langmuir, 2012, 28(51): 17585-17592.
2. S. M. Kang, N. S. Hwang, J. Yeom, S. Y. Park, P. B. Messersmith, I. S. Choi, R. Langer, D. G. Anderson, and H. Lee, Advanced functional materials, 2012, 22, 2949-2955.
3. C. Feng, J. Xu, M. Li, Y. Tang, C. Gao, Journal of Membrane Science, 2014, 454, 103-110