Influence of Random and Block Sequence of Tertiary Amine Based Amphiphilic Copolymer on Structure and Property of Porous Blend PVDF Membrane Formed via NIPS Process

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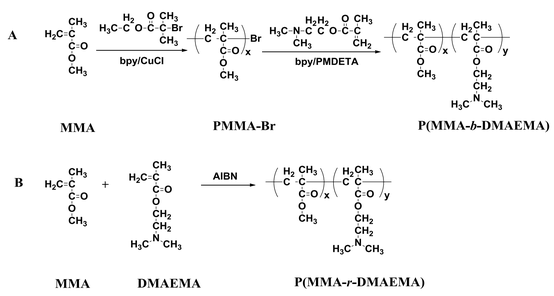
Introduction

Poly(vinylidene fluoride)(PVDF) is one of the most popular materials for microfiltration(MF)[1] and ultrafiltration(UF)[2] membranes with regard to its excellent properties such as high thermal stability, mechanical strength, chemical resistance, etc. But the hydrophobic nature limits its application in aqueous solution treatment. Recently more and more attentions have been paid to enhance the hydrophilicity and even to endow the PVDF membrane with other novel properties through various ways, for example surface coating, surface grafting and blending.

Blending is a single-step and industrialization-potential method to modify PVDF. The PVDF membrane with improved hydrophilicity and some other noble properties can be fabricated by blending with additives during the membrane preparation process [3].

Method

1.Synthesis of P(MMA-*b*-DMAEMA) (A) and P(MMA-*co*-DMAEMA) (B)



Scheme 1 A The synthesis process of P(MMA-*b*-DMAEMA) copolymer via ATRP;
B The synthesis process of P(MMA-*r*-DMAEMA) copolymer.

2. Membrane fabrication

Table 1 PVDF membranes with different compositions

Membrane ID	Polymer			Solvent
	Additives(w.t.%)		PVDF(w.t.%)	DMAc(w.t.%)
M0	-	-	16%	84%
MA	Copolymer(A)	2%	16%	82%
MB	Copolymer(B)	2%	16%	82%

Results and Discussions

1. Synthesis of the amphiphilic polymers

Table2 Molecular weight and DMAEMA content for the synthesized amphiphilic copolymers.

ID	Polymer	Mn (GPC)	Mw(GPC)	PDI(GPC)	DMAEMA content (w.t.%) (NMR)
Copolymer(A)	P(MMA_{86}-*b*-$DMAEMA_{52}$)	16830	21698	1.29	64.9%
Copolymer(B)	P(MMA_{77}-*co*-$DMAEMA_{102}$)	23811	52423	2.20	67.6%

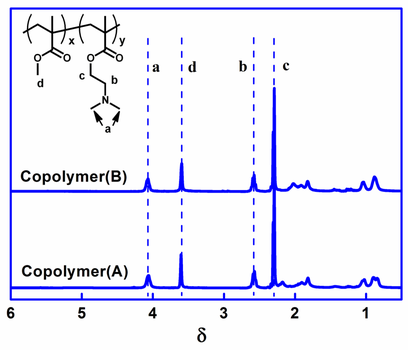


Fig. 1 ^{1}H-NMR spectra of copolymer(A) and copolymer(B).

Two copolymers with different sequence structures and nearly the same DMAEMA content were successfully synthesized.

2.Morphologies of the blend membranes

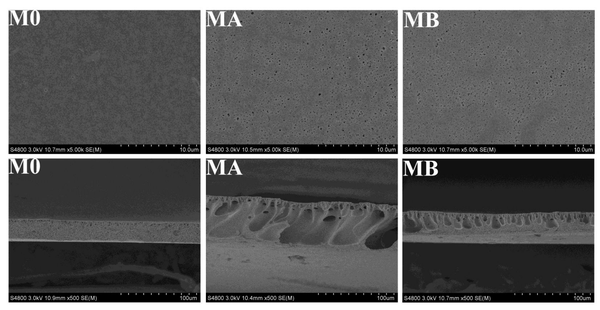


Fig. 2 SEM images of pure PVDF membrane(M0) and blend membranes with Copolymer(A)(MA) and Copolymer(B)(MB). First line: surface; second line: cross section.

3. Chemical compositions of the blend membranes

Table.3 The Chemical compositions of the whole membranes and the separation surfaces of the blend membranes

Membrane ID	Copolymer content (w.t.%)			Retention ratio of copolymer	Enrichment ratio of Copolymer
	In Casting solution	In whole membrane	In surface layer		
MA	11.1	8.2	50.0	74.0%	4.5
MB	11.1	7.5	22.2	67.8%	2.0

Comparing with the additives with random structure, the additives with block structure retain in the membrane stably and have high surface enriching ratio.

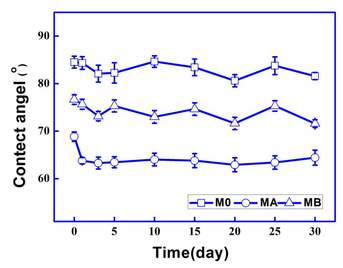


Fig.4 Water contact angle changes of the membrane after shaken in water (60℃) for different time span.

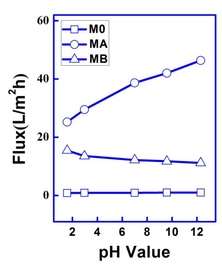


Fig.5 Water permeation operated at different pH.

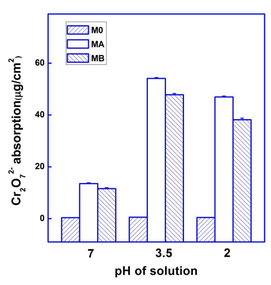


Fig.6 Cr(Ⅵ) adsorption capacity of membranes at different pH

4. Hydrophilicity stability of the blend membranes

The water contact angle for blend membranes (69°, 76°) was much lower than that of pure PVDF membrane (90±5°), and expressing hydrophilicity stability.

5. PH stimuli-responsive investigation

The flux of blend membrane was much higher than pure PVDF membrane and the flux of the membranes blending with block copolymers was much higher than the one blending with random copolymers. Blending with block copolymer endow the membranes with flux significant pH stimuli-responsive property.

6. Heavy metal ions adsorption evaluation

Blending with both block copolymer and random copolymer, endow the membranes with the ability to absorb Cr(Ⅵ) .

Conclusion

Amphiphilic block copolymers P(MMA-*b*-DMAEMA) and amphiphilic random copolymers P(MMA-*r*-DMAEMA) were successfully synthesized and blended with PVDF to fabricate porous membranes via phase inversion method.

The copolymers with block structures show enhanced performance compared with random structure one. The substantial coverage of PDMAEMA on the membrane surfaces and pore channels endow the membranes with flux pH stimuli-responsive property as well as the ability to absorb Cr(Ⅵ) .

Acknowledgements

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References

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2. L. Yu et al., *J MEMBRANE SCI*, **2009**, 337: 257.
3. J. Yu et al., *J MEMBRANE SCI*, **2011**, 366: 176.