

(Short Paper)

Preparation of Cation-exchange Membranes from Polysulfone with Poly (sodium *p*-styrenesulfonate) Graft Chains

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Abstract

Cation-exchange membranes (CEMs) were prepared from polysulfone (PSF)-based graft copolymers with graft chains of poly (sodium styrene sulfonate). The graft-copolymers were synthesized by grafting ethyl *p*-styrenesulfonate (EtSS) on macro-initiators of chloromethylated PSF with different chloromethyl (CM) groups, thus changing the EtSS content in the polymers by using atom transfer radical polymerization. The transport number of the CEM (CM content = 8.4 mol %, and EtSS ratio = 46 wt. %) was 0.98, almost the same as that of a commercial CEM, Neosepta® CMX (ASTOM Corp., Japan), 0.98. The membrane resistance of the PSF-based CEM was $2.3 \Omega \cdot \text{cm}^2$, and lower than that of CMX, $3.0 \Omega \cdot \text{cm}^2$.

Key Words : Polysulfone, Cation-exchange membranes, Dynamic state transport number, Membrane resistance, Graft copolymer

1. Introduction

Donnan dialysis (DD) is a diffusion dialysis process using ion-exchange membranes (IEMs) ¹. Recently, DD process has been performed with expensive flat sheet membranes in plate-and-frame (PF) stacks. This configuration also requires expensive spacers, which makes the process rather costly². On the other hand, hollow fiber (HF) configurations do not require any spacers and have a higher packing density (ratio of membrane area to membrane module) than a PF configuration; hence, HF configurations will be more suitable for DD processes because the processes need a larger membrane area than electro dialysis processes due to their low ionic fluxes. Nowadays, almost all HF membranes for hemodialysis and water treatment applications have been prepared from a hydrophobic matrix such as polysulfone (PSF), polyether sulfone, etc. One of the methods for introducing ion-exchange groups into such aromatic polymers is to synthesize a graft copolymer by performing chloromethylation of the polymers and then use the chloromethylated polymers as a macro-initiator of the atom transfer radical polymerization (ATRP) technique³.

The goal of our study is to prepare novel HF type CEMs from PSF-based graft copolymers. To this end, in this study, PSF with graft chains of poly (sodium *p*-styrenesulfonate) (PSF-*g*-PSSS) were synthesized, and flat sheet PSF-based CEMs were prepared from the graft copolymers. We measured the ionic transport properties of the obtained CEMs to evaluate the relationship between the transport properties and the preparation conditions.

2. Experimental

The graft copolymers were prepared according to the

same method as those used in a previous study⁴. The chloromethylated PSF (CM-PSF) was synthesized by the chloromethylation of PSF ($M_w = 75,000 \text{ g/mol}$) with chloromethyl methyl ether (CMME), thus changing the CMME content. The graft-copolymer (PSF-*g*-PSSS) was synthesized by grafting ethyl *p*-styrenesulfonate (EtSS) on the CM-PSF using ATRP technique, thus changing the ratio of EtSS monomer to the CM-PSF in the reaction mixture (r_{EtSS}), and then by immersing the obtained polymer in hot water (95 °C) for 24 h to remove the ethyl groups of EtSS by hydrolysis reaction. After drying the obtained copolymer, we performed structure analysis by taking nuclear magnetic resonance (NMR) spectroscopy.

PSF-based CEMs were prepared by casting a 1-methyl-2-pyrrolidinone solution of the graft copolymers on a teflon sheet and drying them in a vacuum at 80 °C for 24 h. The water uptake (WU), dynamic state transport number (t_{d+}) and membrane resistance (R_m) of the CEMs were measured with the same methods as described elsewhere^{5,6}.

3. Results and Discussion

Based on ¹H NMR spectrum of CM-PSF macro- initiator, whose data are not shown here, the content of CM groups in the macro-initiator (C_{CM}^{P}) is defined as the number of CM groups per repeat unit and is calculated by comparing of the integration values of $-\text{CH}_2\text{Cl}$ protons at 4.6 ppm with those of aromatic protons at the $-\text{CH}_3$ in PSF at 1.7 ppm. C_{CM}^{P} increased with an increase of CMME content in the reaction mixture. The ¹H NMR spectrum of PSF-*g*-PSSS, whose data are also not shown here, confirmed the proposed structure of the graft copolymer shown in **Fig. 1**: Grafting of EtSS monomer on the CM-PSF resulted in the appearance of peaks in the region of 1.4-1.6 ppm due to the CH_2CH_3

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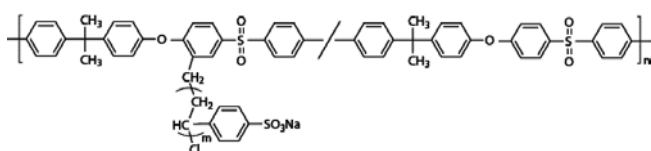


Fig. 1 Chemical structure of PSF-g-PSSS

Table 1 Characteristics of the PSF-based CEMs and CMX: CM group content in the polymer (C_{CM}^P), EtSS ratio in the reaction mixture (r_{EtSS}), thickness at a dry state (d_D), water uptake (WU), ion exchange capacity (IEC), membrane resistance (R_m), dynamic transport number for cations (t_{d+})

CEM	C_{CM}^P [mol%]	r_{EtSS} [wt.%]	d_D [μm]	WU [%]	IEC [meq/g]	R_m [$\Omega \cdot \text{cm}^2$]	t_{d+} [-]
CEM1	1.8	93	55	140	0.83	1.4	0.92
CEM2	6.7	46	40	38	0.71	6.2	0.99
CEM3	6.7	93	110	310	1.6	0.5	0.80
CEM4	8.4	46	30	78	0.61	2.3	0.98
CMX	-	-	170	30	1.8	3.0	0.98

moieties of the EtSS. The characteristics of the PSF-based CEMs prepared from the graft copolymers are listed in Table 1. The IEC of the CEMs increased as r_{EtSS} increased. The water uptake (WU) of a CEM is an important property because both the transport number and electric resistance of the CEM depend on the water uptake. The transport number can be used as an indicator of counter-ion permselectivity of a CEM, and membrane resistance is important for obtaining high ionic flux in DD processes. WU of PSF-based CEMs increased as IEC increased, excepting CEM4, which has the highest CM content of all the CEMs. The membrane resistance of the CEMs decreased as the WU increased because the size of ionic transport domains will increase with increasing WU . The dynamic state transport number of the CEMs decreased with increasing WU . CEM3 showed the lowest transport number though it had the highest IEC of all the CEMs because it had the highest WU .

Figure 2 shows the relationship between the transport number and the membrane resistance of the CEMs as well as a commercial CEM, Neosepta® CMX (ASTOM Corp., Japan). A CEM with both high transport number and low membrane resistance, in other words, located on the upper-left side in Fig. 2, is a better CEM for DD applications. The dynamic transport number of the CEMs increased as the membrane resistance increased. The transport number of CEM4 was 0.98, the same as that of CMX. The membrane resistance of CEM4 was $2.3 \Omega \cdot \text{cm}^2$, and lower than that of CMX, $3.0 \Omega \cdot \text{cm}^2$. The lower membrane resistance of CEM4 will be mainly due to it being thinner than CMX. The flat sheet PSF-based CEMs did not have any support materials, although CMX had support materials such as PVC cloth⁷⁾. Hence, HF type CEMs will be prepared from PSF-g-PSSS. The results in this paper indicate that HF type CEMs prepared from PSF-g-PSSS will have both high counter-ion selectivity and high ionic flux. Therefore, the HF type CEMs have potential applications to DD processes in many fields,

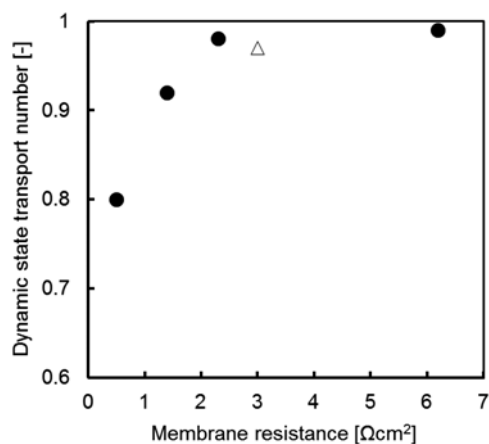


Fig. 2 The relationship between the dynamic state transport number and the membrane resistance of the CEMs. Solid circles, PSF-based CEMs; open triangle, Neosepta® CMX

such as the purification of acid or alkaline streams.

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