

모노머 조성 변화에 따른 음이온교환막 합성 및 구조 분석

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Preparation and morphology control of anion-exchange membrane by monomer composition

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1. Introduction

The performance of ion-exchange membrane (IEM) depends largely on its nature and the conditions of the surrounding liquid medium. The former includes the type of a membrane (cationic or anionic), the amount of fixed charges and its distribution. The latter includes the operating condition and the flow field near the liquid-membrane interface. Increment of fixed charges in membrane can improve the performance of an IEM. With the same total fixed charges, the distribution of these charges is also important for the performance. In these views, a number of synthesis of ion-exchange membranes have been reported and developed [1,2]. More recently, a new preparation method combined by monomer sorption and UV-polymerization was proposed, designing a simplified process [3]. The objectives of this study are to synthesize morphologically controllable anion-exchange membranes, and to investigate the relationship between its charge distribution and its electrochemical properties. While anion-exchange membranes are prepared by monomer sorption and UV-radiation polymerization reported previously, morphology of a membrane can be controlled by monomer composition based on swollen effect between substrate and monomers. When using hydrophilic monomer (F-monomer) only, hydrophobic substrate dose not swell because hydrophobic substrate prevents hydrophilic monomer (F-monomer) from absorbing into the free volume of substrate. The phenomena may allow F-monomer to be

polymerized only on the membrane surface to cross-sectional direction. After introduction of anion-exchange function, the membrane carrying anion exchange functions on the surface of membrane only will be prepared. When using hydrophilic / hydrophobic monomers mixture, hydrophobic substrate does swell because hydrophobic substrate allows hydrophilic monomer (F-monomer) to absorb in the free volume of substrate while the hydrophobic monomer is penetrated into the substrate. The phenomena may allow F-monomer to be polymerized on the membrane to cross-sectional direction. After introduction of anion-exchange function to the base membrane, the membrane the membrane bearing anion exchange functions uniformly to the cross-sectional direction is prepared.

2. Experimental

Non-porous low-density polyethylene film was swollen in vinylbenzyl chloride (VBC)/styrene/divinyl benzene (DVB)/benzophenone (BP) mixture, for 1 day. The film was polymerized by UV-radiation under 400 W (110-400 nm) mercury lamp for 30~50 min. After removing unreacted monomer, the base membrane was quaternarized in 0.5 M trimethyl ammine (TMA) solution for 1~2 hr. The prepared anion-exchange membranes were stored in 0.5 M NaCl solution. The content of styrene (hydrophobic monomer) in the monomer solution was varied by 0~28 wt %. The morphological change of prepared membranes was investigated by the differential scanning calorimeter (DSC 2010, TA Instrument, US) and FTIR ATR/TR method. The membrane electrical resistance (MER), transport number, ion-exchange capacity (IEC), I-V curve and chronopotentiogram were obtained referring to the literature [4]. A commercial anion-exchange membrane, AMX (Neosepta, Tokuyama Co., Japan) was used as a reference membrane.

3. Results and Discussion

With the increasing styrene content, the ratio ATR to TR approached to unity (Fig. 1), indicating that the increase of styrene allowed to distribute the monomer homogeneously in the cross-section. Due to the hydrophilic nature of VBC (F-monomer), they were absorbed only on the surface of LDPE (hydrophobic nature) when LDPE was immersed in VBC (hydrophilic) monomer solution. On the other hand, VBC monomers were absorbed into the free volume of LDPE by adding styrene monomer to monomer solution because the

styrene made LDPE swollen. Accordingly, the cross-sectional homogeneity of membrane was increased with the increasing styrene content. By varying the composition of monomer mixture, cross-sectional charge distribution can be morphologically controlled if all VBCs are quaternarized. Also, charge distribution of the membrane was evaluated by DSC. The T_m and crystallinity of prepared membranes obtained from DSC are listed in Table 1. T_m and crystallinity decreased with the increasing of styrene content, indicating that the increased styrene cause to partially destroy crystalline of LDPE and monomers were polymerized even in the crystalline of LDPE. Fig. 2 shows the relationship between weight gain of VBC (WGvbc) and IEC as a function of styrene content at a WG of 0.29 (total weight gain). While WG was fixed at 2.9, WGvbc declined as the styrene content in the monomer mixture increased. The VBC can provide the introduction of anion-exchange sites by quaternarization. Accordingly, the increase of the styrene content led to the decrease of IEC. It is generally expected that a high IEC lowers MER. However, Fig. 3 showed that the MER decreases with increasing the IEC. Using VBC only in the monomer solution, the ion-exchange sites are covered on the surface only because the hydrophilic nature of the VBC prevents monomer from absorbing into the free volume of LDPE. Such phenomenon caused to form non-conducting region in the middle of membrane to cross-sectional direction. Accordingly, such charge distribution caused to increase MER in spite of increasing IEC.

Adding the styrene into the monomer solution, the ion-exchange sites are homogeneously distributed to the whole membrane section. Such phenomenon led to lowering MER in spite of the low IEC. The surface homogeneity of membranes prepared was evaluated by chronopotentiometry [4]. Table 2 described the chronopotentiometric results of the morphologically controlled membrane at a constant current density (35 A m^{-2}). The transition time (τ) means the potential corresponding to the complete depletion of anion Cl at the membrane surface. The shorter transition time implies the decrease in surface homogeneity at a transport number. The fraction of conducting region, ϵ , was calculated according to Choi et al' study [4]. The result indicated that surface homogeneity of membranes prepared also increased with the styrene content due to the hydrophobic nature of styrene. This study suggests that the morphology of an anion-exchange membrane can be controlled by balanced

compositions of hydrophilic and hydrophobic monomers in the monomer sorption and UV-radiation method.

4. Acknowledgements

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5. Reference

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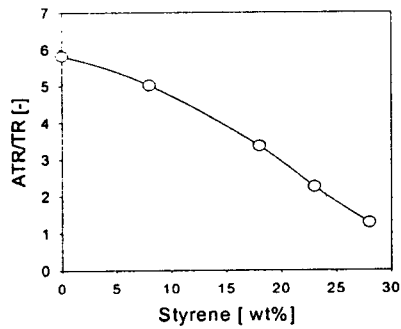


Fig. 1. Relationship between ATR/TR ratio and the styrene content.

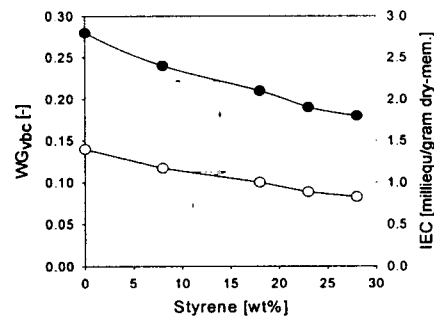


Fig. 2. Relationship between WG_{vbc} and IEC as a function of styrene content.

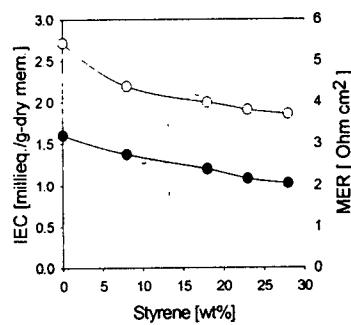


Fig. 3. Relationship between MER and IEC as a function of styrene content.

Table 1. Electrical properties using Chronopotentiometry

Membranes	LDPE/St00	LDPE/St18	LDPE/St28	AMX
τ [sec]	26.72	32.65	35.57	32.25
ϵ [-]	0.789	0.851	0.884	0.878

Table 2. T_m and Crystallinity obtained by DSC analysis

Membranes	LDPE	LDPE/St00	LDPE/St18	LDPE/St28
T _m [°C]	111.3	108.1	108.0	105.5
Crystallinity [%]	37.8	34.4	32.1	28.5