

(Short Paper)

Characterization of Anion-exchange Membranes Prepared from PVA-based Block Copolymers

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Abstract

We prepared novel anion-exchange membranes (AEMs) from synthesized PVA-based block copolymers with various contents of anion exchange groups. The AEMs were cross-linked physically by annealing them and cross-linked chemically with glutaraldehyde (GA) solutions. A comparison of the block-type AEMs (bAEMs) and the random-type AEMs (rAEMs) with almost the same membrane resistance shows that bAEMs have about 20 % higher dynamic state transport number than rAEMs. The AEMs with $C^m_{\text{VB TAC}} = 13 \text{ mol. \%}$ and GA concentration = 0.01 vol. % had both the highest dynamic state transport number, 0.97 and lowest membrane resistance, 0.81 $\Omega \text{ cm}^2$ of all the bAEMs.

Key Words : Poly(vinyl alcohol), Anion-exchange membranes, Dynamic state transport number, Block copolymer

1. Introduction

Ion-exchange membranes (IEMs) has been widely applied in many fields such as the electrodialytic concentration or desalination of electrolyte solutions¹⁾ etc. Almost all of IEMs have styrene-co-divinylbenzene matrices; hence, they have difficulty to control the membrane structure, and also high production cost. One of the methods to overcome these problems in preparation of IEMs is to mix water-soluble base polymers and a polyelectrolyte, and then cross-link the base polymers. The IEMs obtained have a semi-interpenetrating network (semi-IPN) structure in which polyelectrolyte chains are immobilized in a polymer crosslinked network matrix. The ion-exchange capacity of the IEMs can be controlled easily by changing the polymer ratio of water-swollen base polymer to polyelectrolyte. Poly(vinyl alcohol) (PVA) is one of the most popular water-soluble base polymers, and PVA is a polyhydroxy polymer; hence, the polymer chains can be cross-linked using cross-linking agents such as glutaraldehyde^{2, 3)}. One of the potential disadvantages of IEMs with semi-IPN structure is low long-term stability in a solution because water-soluble polyelectrolytes will dissolve from the network into the solution⁴⁾. In contrast, in IEMs with an IPN structure, the polymer chains of membrane matrix and polyelectrolytes are cross-linked with each other; hence, these IEMs show higher long-term stability in water than IEMs with semi-IPN structure³⁾. In previous studies^{4, 5)}, PVA-based anion-exchange membranes (AEMs) were prepared from PVA and poly(vinyl alcohol-co-methacryloyl aminopropyl trimethyl ammonium chloride). However, the counter-ion permselectivity of the AEMs prepared from the random copolymer was much lower than that of commercially available AEMs^{4, 5)}.

The aim of this study is to prepare novel AEMs from synthesized PVA-based block copolymers with various contents of anion exchange groups. The AEMs were cross-linked physically by annealing them and cross-linked chemically with a cross-linker. We measured the ionic transport properties of the obtained membranes to compare the transport properties of the PVA-based AEMs with IPN

structure prepared from the block copolymer and that from the random copolymer.

2. Experimental

A PVA-based block copolymer: poly(vinyl alcohol-*b*-vinylbenzyltrimethyl-ammonium chloride) (PVA-*b*-PVBTAC) was synthesized according to the chemical reaction shown in Fig. 1 from a SH terminated PVA and vinylbenzyltrimethyl-ammonium chloride (VB TAC)⁶⁾.

2,2'-Azobis(2-methyl propionamide) dihydrochloride was used as an initiator of the reaction. PVA-*b*-PVBTAC was obtained by precipitating the reaction solution into acetone. After drying the copolymer obtained, we performed structure analysis by taking nuclear magnetic resonance (NMR) measurements.

AEMs prepared from the block copolymer (bAEMs) were obtained by casting PVA-*b*-PVBTAC aqueous solution on an acrylic plate. The bAEMs were cross-linked physically by annealing at 160 °C for 30 minutes and cross-linked chemically with 0.01 vol. % of glutaraldehyde (GA) solution.

The water content, H , dynamic state transport number, t_d , membrane resistance, R_m and mechanical strength of the bAEMs were measured with the same methods described elsewhere^{3, 4)}.

3. Results and Discussion

The characteristics of bAEMs as well as AEMs prepared from the random copolymer (rAEMs)⁵⁾ and a commercial AEM, Neosepta® AMX (ASTOM Corp., Japan) were listed in Table 1.

The content of the VB TAC group, $C^p_{\text{VB TAC}}$, increased with increasing $C^m_{\text{VB TAC}}$. This result indicates that the introduction of VB TAC groups (anion-exchange groups) on

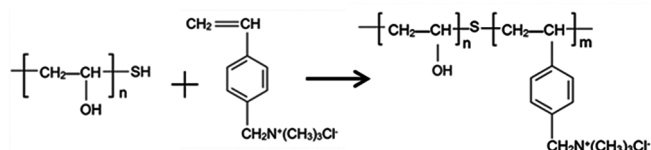


Fig. 1 Reaction scheme of PVA-*b*-PVBTAC

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Table 1 Characteristics of the AEMs: VBTAC content in a reaction mixture ($C_{\text{VBTAC}}^{\text{m}}$), VBTAC content in the copolymer ($C_{\text{VBTAC}}^{\text{p}}$), membrane thickness in wet state (d_w), water content (H), ion exchange capacity (IEC), membrane charge density (C_x), dynamic state transport number (t_d), membrane resistance (R_m), maximum tensile strength (TS), Young's modulus (YM) and elongation at break (E)

Sample	$C_{\text{VBTAC}}^{\text{m}}$ [mol.%]	$C_{\text{VBTAC}}^{\text{p}}$ [mol.%]	d_w [μm]	H [-]	IEC [meq/g]	C_x [mol/dm ³]	t_d [-]	R_m [Ω cm ²]	TS [MPa]	YM [MPa]	E [%]
bAEM-1	4	3.85	75	0.48	0.57	0.99	0.93	5.38	7.80	58.2	14.7
bAEM-2	7	5.66	95	0.51	0.85	1.21	0.94	2.68	4.59	35.0	14.5
bAEM-3	10	8.25	96	0.58	1.10	1.14	0.94	1.06	5.25	33.9	18.8
bAEM-4	13	10.7	103	0.61	1.65	1.14	0.97	0.81	3.61	25.4	14.3
rAEM-1 ⁽⁵⁾	-	-	200	0.74	0.35	0.09	0.71	1.41	-	-	-
rAEM-2 ⁽⁵⁾	-	-	200	0.66	0.25	0.09	0.72	2.43	-	-	-
rAEM-3 ⁽⁵⁾	-	-	200	0.59	0.21	0.13	0.74	3.19	-	-	-
rAEM-4 ⁽⁵⁾	-	-	140	0.61	0.29	0.15	0.75	2.09	-	-	-
rAEM-5 ⁽⁵⁾	-	-	130	0.51	0.19	0.16	0.75	4.57	-	-	-
rAEM-6 ⁽⁵⁾	-	-	150	0.55	0.23	0.14	0.74	3.87	-	-	-
AMX	-	-	140	0.24	1.40	1.53	0.98	2.30	27.5	-	-

Annealing conditions: 160 °C, 30 min

Cross-linking conditions: 25 °C, 24 h, 3M NaCl, HCl, cross-linker (glutaraldehyde) concentration: 0.01 vol.%

The random copolymer content (wt.%) : rAEM-1, 100; rAEM-2, 90; rAEM-3, 80; rAEM-4, 70; rAEM-5, 60; rAEM-6, 50

a PVA main chain can be controlled quantitatively. $C_{\text{VBTAC}}^{\text{p}}$ was lower than $C_{\text{VBTAC}}^{\text{m}}$ in all the copolymers. This will be due to the fact that a homo-polymer (polyVBTAC) was also synthesized in the reaction.

The water content, H increases with $C_{\text{VBTAC}}^{\text{p}}$ because the osmotic pressure in the AEMs increases with increasing number of charged groups in the AEMs with the same described elsewhere^{3,4,7}.

Figure 2 shows the dynamic state transport number, t_d , of the AEMs as a function of the membrane resistance, R_m . t_d is an indicator of counter-ion permselectivity of AEMs. t_d increases with increasing $C_{\text{VBTAC}}^{\text{p}}$ while the R_m decreased with increasing $C_{\text{VBTAC}}^{\text{p}}$. Those indicate that the effect of $C_{\text{VBTAC}}^{\text{p}}$ was more than H . A comparison of the block-type AEMs (bAEMs) and the random-type AEMs (rAEMs) with almost the same R_m shows that bAEMs have about 20 % higher t_d than rAEMs, meaning that the bAEMs have higher counter-ion permselectivity than rAEMs. Higa et al.³⁾ suggested that cation-exchange membranes prepared from a PVA-based block copolymer had higher transport properties than ones prepared from a PVA-based random copolymer because the formers had higher degree of crystallinity than the latters. Therefore, the high permselectivity of bAEMs will be due to the fact that the degree of crystallinity of bAEMs is higher than that of rAEMs.

The AEMs with $C_{\text{VBTAC}}^{\text{m}} = 13$ mol.%, bAEM-4, had the highest t_d , 0.97 and lowest R_m , 0.81 Ω cm² of all the bAEMs, while t_d and R_m of AMX was 0.98 and 2.3 Ω cm² respectively. Hence, the bAEM-4 has almost the same t_d and also about three times lower R_m than those of the commercial AEM.

After all, these results indicate that the AEMs prepared from the block copolymer have higher ionic selectivity than those from the random polymer, and lower R_m than the commercial AEM. Hence, the membranes in this study will have potential application to desalination processes using ED.

Acknowledgements

SH terminated PVA used in this study were supplied by KURARAY Co., Ltd. This work was partly supported by JSPS KAKENHI Grant Number 16H01796, and by the Salt Science Research Foundation No.1617.

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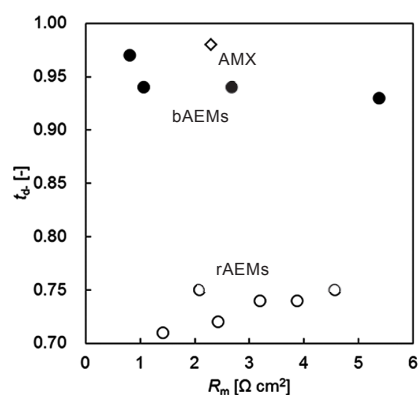


Fig. 2 Dynamic state transport number, t_d , of the AEMs as a function of membrane resistance, R_m , of the AEMs. Samples: solid circles, bAEMs; open circles, rAEMs; open diamond, AMX

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(平成 28 年 12 月 22 日受付, 平成 29 年 2 月 1 日採用決定)
(Received December 22, 2016, Accepted February 1, 2017)