Pervaporation Characteristics of Methyl Methacrylate–Methacrylic Acid Copolymer Membranes Ionically Crosslinked with Metal Ions for a Benzene/Cyclohexane Mixture

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ABSTRACT: Methyl methacrylate–methacrylic acid copolymer (MMA–MAA) membranes ionically crosslinked with Fe^{3+} and Co^{2+} ions (MMA–MAA–Fe^{3+} and –Co^{2+}) were prepared, and characteristics of permeation and separation for a benzene/cyclohexane mixture of 50 wt % benzene through these membranes in pervaporation (PV) were studied. Although the introduction of the metal ions to the MMA–MAA membrane enhanced both benzene permselectivity and permeability for a benzene/cyclohexane mixture, the PV characteristics between the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were significantly different. The difference in the PV characteristics between these membranes was strongly governed by the difference of these membrane structures based on the glass transition temperature, contact angle to methylene iodide, degree of swelling, and mixture composition absorbed in the membrane, and so on. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 233–241, 1999

Key words: pervaporation; polymer–metal complex membrane; benzene/cyclohexane mixture; benzene permselectivity; crosslinked structure

INTRODUCTION

Recently, much attention has been paid to pervaporation (PV), one of membrane separation technique, in the separation and concentration of organic liquid mixtures. Since the separation mechanism in PV is based on the difference in the solubility of permeants into polymer membranes and in the diffusivity of permeants in polymer membranes, namely, the solution–diffusion model,[1] PV is advantageous for the separation of the close boiling point and azeotropic mixtures which cannot be directly separated by distillation. When organic liquid mixtures containing one component that has a high solubility for the membrane material are permeated through the polymer membrane by PV, however, the swelling of the polymer membrane by the component lowers the permselectivity. Accordingly, in order to enhance permselectivity of the polymer membranes for organic liquid mixtures, it is very important to control the swelling of the membrane.

It is well known that polymers having amino, carboxyl, hydroxyl groups, and so on, form polymer–metal complexes with metal ions.[2–5] Particularly, when the intermolecular polymer–metal complexes between the polymer chains and the metal ions are formed, the polymers are ionically crosslinked with the metal ions. The crosslinked polymers are insoluble in solvents. Therefore, it is expected that polymer–metal complex membranes crosslinked with the metal ions are very

effective to control the swelling of polymer membranes for organic liquid mixtures in PV.

Many polymer–metal complex membranes were applied to separations of gas and liquid mixtures.[6–14] For example, in the separation of olefin/paraffin gas mixtures, the polymer–metal complex membranes with Ag^+ ion exhibited a high olefin permselectivity based on the formation of an Ag^+ ion–olefin complex.[6–9] Furthermore, since Schiff-base complexes of the Co^{2+} ion play as oxygen carriers, various polymer–metal complex membranes based on Schiff-base complexes of Co^{2+} ion were prepared and their oxygen permselectivity were studied in the separation of oxygen/nitrogen gas mixtures.[10–12] Furthermore, it was reported that poly(vinyl alcohol)/poly(allyl amine)–Co^{2+} chelate-complex membranes had a high benzene permselectivity for the benzene/cyclohexane mixtures in PV. An enhancement of the benzene permselectivity of these polymer–metal complex membranes was dependent on coordinating interactions between the π orbital in the benzene molecule and the third orbital of cobalt.[5] From these facts, it is expected that the introduction of metal ions to the polymer membranes enhances the permselectivity for the organic liquid mixtures in PV.

In this study, the methyl methacrylate (MMA)–methacrylic acid (MAA) copolymer membranes ionically crosslinked with Fe^{3+} and Co^{2+} ions (MMA–MAA–Fe^{3+} and –Co^{2+}) are prepared and the effect of the metal ions on the PV characteristics of these membranes for a benzene/cyclohexane mixture is discussed from the viewpoints of physical and chemical structure of the polymer–metal complex membrane.

EXPERIMENTAL

Copolymerization of MMA and MAA

MMA and MAA were purified by distillation under a reduced pressure. 2,2′-Azobisisobutyronitorile (AIBN) recrystallized from benzene solution was used as an initiator.

MMA and MAA (molar ratio: 95 : 5) with AIBN (0.5 wt % relative to the monomers) were dissolved in benzene to make 50 wt % solution. The mixture was then transferred into a glass tube. The copolymerization was carried out at 60°C for 6 h under nitrogen atmosphere. The resulting MMA–MAA copolymers were purified by reprecipitation from copolymer solution that was di-

luted with tetrahydrofuran into n-hexane and dried at room temperature *in vacuo.*

Composition of MMA–MAA

The MMA–MAA copolymers were dissolved in acetone and these solutions were diluted with distilled water. The aqueous acetone solution of the MMA–MAA-added phenolphthalein as an indicator was titrated with an aqueous solution of 0.01M NaOH and the compositions of the MMA–MAA copolymers were determined by

$$x = W \times 10^5/a \tag{1}$$

where x is the molar fraction of MAA in the MMA–MAA copolymer, W is the weight of the copolymer, and a is the titer of 0.01M NaOH. The compositions of the MMA–MAA copolymer were the same as those in the feed.

Preparation of MMA–MAA Membranes Ionically Crosslinked with Metal Ions

The MMA–MAA–Fe^{3+} and –Co^{2+} membranes were prepared by casting a dimethyl formamide solution of 3 wt % MMA–MAA, adding a desired amount of $FeCl_3 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ on a rimmed glass plate, and evaporating the solvent completely at 50°C. The MMA–MAA–Fe^{3+} and –Co^{2+} membranes were immersed in distilled water at 25°C for 48 h to remove excess metal ions and dried at room temperature *in vacuo.* The thicknesses of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were 30–60 μm. The metal ion contents in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were determined by the atomic absorption analysis (Nippon Jarrell Ash, AA-855). The complex formation in the MMA–MAA–Fe^{3+} membranes was identified by UV–VIS spectra (Shimadzu, UV-2500PC).

Glass Transition Temperature of Membrane

Determinations of glass transition temperature (T_g) of the membranes were carried out with a differential scanning calorimetry (Rigaku, TAS-200) at 20°C/min.

Contact Angle on Surface of Membrane

The contact angles to methylene iodide on the surface of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were measured by means of a contact angle meter (Erma, Optics Model G-1) at 25°C.

Degree of Membrane Swelling

The dried membranes were immersed in a benzene/cyclohexane mixture of 50 wt % benzene at 40°C. After the weight of the membranes became constant, a sample membrane was taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of swelling (DS) of the membrane for a benzene/cyclohexane mixture was determined by

$$DS = W_s/W_d \qquad (2)$$

where W_s and W_d are the weights of the membrane swollen in a benzene/cyclohexane mixture and the dried membrane, respectively.

Sorption Selectivity of Membrane for a Benzene/Cyclohexane Mixture

A sample membrane prepared in a similar manner as the measurement of the degree of swelling of the membrane was put on a boat of pyrolyzer. The composition of benzene/cyclohexane sorbed in the membrane was determined by measuring the vaporized mixtures on a boat of pyrolyzer with gas chromatography.[15] The sorption selectivity ($\alpha_{sorp,B/C}$) was calculated from

$$\alpha_{sorp,B/C} = (M_B/M_C)/(F_B/F_C) \qquad (3)$$

where F_B and F_C are the weight fractions of benzene and cyclohexane in the feed solution and M_B and M_C are those in the membrane, respectively.

PV Measurements

The PV experiments were carried out using the cell and apparatus described in a previous paper.[16] The effective membrane area was about 13.8 cm². The PV experiments were carried out at 40°C. The pressure at the downstream side was maintained at 0.01 Torr. The permeate was collected in a U-tube at liquid nitrogen temperature. After the permeation reached the steady state, the weight and composition of the permeate were measured. The permeation rate in the steady state was determined from the weight of the permeate (w), permeation time (t), and effective membrane area (A). In this study, in order to compare the permeation rates of membranes with different thicknesses, a normalized permeation rate (NPR) (kgm/m² h), which is the product of the permeation rate and the membrane thickness (l), was used. The NPR was calculated by

Table I   Metal Ion Molar Ratio in the Feed and Membrane to MAA in the MMA–MAA Membranes

Membrane	Metal Ion Molar Ratio in Feed	Metal Ion Molar Ratio in Membrane
MMA–MAA–Fe³⁺	0.33	0.32
	0.67	0.60
	1.67	1.23
	2.50	1.59
	3.33	1.85
	5.00	1.90
MMA–MAA–Co²⁺	0.50	0.48
	1.00	0.81
	2.50	1.33
	5.00	2.01

$$NPR = wl/At \qquad (4)$$

The compositions of the feed solution and permeate were determined by gas chromatography. The separation factor ($\alpha_{sep,B/C}$) was calculated from

$$\alpha_{sep,B/C} = (P_B/P_C)/(F_B/F_C) \qquad (5)$$

where F_B and F_C are the weight fractions of benzene and cyclohexane in the feed solution and P_B and P_C are those in the permeate, respectively.

Generally, the separation mechanism in PV is based on the solution–diffusion model.[1] Since the permeability coefficient corresponds to the product of the solubility and diffusion coefficients in the solution–diffusion model, the diffusion selectivity ($\alpha_{diff,B/C}$) can be determined as shown in eq. (6)[15,17] using the separation factor ($\alpha_{sep,B/C}$) and sorption selectivity ($\alpha_{sorp,B/C}$).

$$\alpha_{diff,B/C} = \alpha_{sep,B/C}/\alpha_{sorp,B/C} \qquad (6)$$

RESULTS AND DISCUSSION

Characterization of MMA–MAA Membranes Ionically Crosslinked with Metal Ions

The metal ion contents in the MMA–MAA–Fe³⁺ and –Co²⁺ membranes are summarized in Table I. The metal ion contents in the membrane increased with increasing metal ions in the feed, but were lower than those in the feed. The difference between the metal ion contents in the feed

Figure 1 UV–VIS spectra of the MMA–MAA and MMA–MAA–Fe^{3+} (the molar ratio, Fe^{3+}/COOH = 0.32) membranes.

and membrane increased with increasing metal ions in the feed.

The UV–VIS spectra of the MMA–MAA and MMA–MAA–Fe^{3+} (molar ratio: Fe^{3+}/COOH = 0.32) membranes are shown in Figure 1. The peak assigned to the complex between the carboxylate ions and the Fe^{3+} ions in the MMA–MAA–Fe^{3+} membrane was observed around 360 nm. On the other hand, the peak of free Fe^{3+} ions (310 nm), which did not form the complex, was also observed in the MMA–MAA–Fe^{3+} membrane. The results for the MMA–MAA–Fe^{3+} membranes in Table I and Figure 1 suggest that these membranes were crosslinked with Fe^{3+} ions and also contained unreacted FeCl$_3$.

Generally, it is known that the crosslinked polymers have the higher T_g than the non-crosslinked polymers.[18,19] In order to clarify the crosslinked structure of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes, the T_g's of these membranes were measured. In Figure 2, the relationship between the metal ion content and the T_g's in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes is shown. The T_g's of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were higher than that of the MMA–MAA membrane. These results support the fact that these membranes have the crosslinked structures. Consequently, it was revealed that the crosslinked structures by the complex formation between the carboxylate ions and the metal ions existed in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes.

Effect of Metal Ions on PV Characteristics of the MMA–MAA–Fe^{3+} and –Co^{2+} Membranes

Figure 3 shows the effect of the metal ion content

Figure 2 Glass transition temperature (T_g) of the MMA–MAA–Fe^{3+} (●) and MMA–MAA–Co^{2+} (○) membranes as a function of the metal ion molar ratio to MAA in the membrane.

on the normalized permeation rate for a benzene/cyclohexane mixture of 50 wt % benzene through the MMA–MAA–Fe^{3+} and –Co^{2+} membranes by PV. The normalized permeation rate for a benzene/cyclohexane mixture through the MMA–MAA–Fe^{3+} membranes with a low Fe^{3+} ion content slightly decreased with increasing Fe^{3+} ion content but those with a high Fe^{3+} ion content drastically increased. On the other hand, the normalized permeation rate through the MMA–MAA–Fe^{3+} membrane increased remarkably with increasing Co^{2+} ion content. Furthermore, the normalized permeation rates through the MMA–MAA–Co^{2+} membranes were higher than those through the MMA–MAA–Fe^{3+} membranes.

Figure 3 Effect of the metal ion content on the normalized permeation rate for a benzene/cyclohexane mixture of 50 wt % benzene through the MMA–MAA–Fe^{3+} (●) and MMA–MAA–Co^{2+} (○) membranes by PV.

In order to investigate the permeability of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes for a benzene/cyclohexane mixture closely, the degree of swelling of these membranes in a benzene/cyclohexane mixture of 50 wt % benzene was measured and shown in Figure 4.

The degree of swelling of the MMA–MAA–Fe^{3+} membrane for a benzene/cyclohexane mixture indicated a minimum at about the Fe^{3+} ion molar ratio of 0.32. The membrane with the Fe^{3+} ion content of >0.32 increased but was lower than that of the MMA–MAA membrane. On the other hand, the degree of swelling of the MMA–MAA–Co^{2+} membrane for a benzene/cyclohexane mixture was almost constant regardless of the Co^{2+} content in these membranes. Furthermore, the degree of swelling of the MMA–MAA–Co^{2+} membranes was higher than that of the MMA–MAA–Fe^{3+} membrane. Consequently, it is suggested that the difference of the permeability between the MMA–MAA–Fe^{3+} and –Co^{2+} membranes for a benzene/cyclohexane mixture is attributed to the difference of the swelling of these membranes.

Figure 5 shows the effect of the metal ion content on the separation factor, sorption selectivity, and diffusion selectivity for a benzene/cyclohexane mixture of 50 wt % benzene through the MMA–MAA–Fe^{3+} and –Co^{2+} membranes by PV. The separation factors of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were higher than that of the MMA–MAA membrane. The separation factor of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes indicated a maximum at around the Fe^{3+} and Co^{2+} ion molar ratio of 1.85 and 0.81, respectively. Furthermore, in a low-metal ion content in the membrane, the separation factor of the MMA–MAA–Co^{2+} membrane was higher than that of the MMA–MAA–Fe^{3+} membrane, but in a high metal ion content in the membrane, the former was lower.

Figure 4 Effect of the metal ion content on the degree of swelling of the MMA–MAA–Fe^{3+} (■) and MMA–MAA–Co^{2+} (□) membranes for a benzene/cyclohexane mixture of 50 wt % benzene.

Figure 5 Effect of the metal ion content on the separation factor (■), sorption selectivity (●), and diffusion selectivity (○) for a benzene/cyclohexane mixture of 50 wt % benzene through the MMA–MAA–Fe^{3+} and MMA–MAA–Co^{2+} membranes by PV.

The sorption selectivity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes indicated a maximum as well as its separation factor. In a low-metal ion content in the membrane, the sorption selectivity of the MMA–MAA–Co^{2+} membrane was slightly higher than that of the MMA–MAA–Fe^{3+} membrane. Park et al. reported that there was an interaction between the benzene molecule

Figure 6 Contact angle to methylene iodide on the surface of the MMA–MAA–Fe^{3+} (●) and MMA–MAA–Co^{2+} (○) membranes.

and the Co^{2+} ion.[5] In this system, the interaction between the benzene molecule and the metal ions may also exist, and that interaction between the benzene molecule and the Co^{2+} ion seemed to be stronger than the interaction between the benzene molecule and the Fe^{3+} ion. Therefore, the degree of swelling of the MMA–MAA–Co^{2+} membranes was higher than that of the MMA–MAA–Fe^{3+} membranes, and in a low-ion content in the membrane, the MMA–MAA–Co^{2+} membrane had higher sorption selectivity than the MMA–MAA–Fe^{3+} membrane. On the other hand, the diffusion selectivity of both the MMA–MAA–Fe^{3+} and –Co^{2+} membranes was almost constant regardless of the metal ion content in the membrane. The diffusion selectivity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes was lower than the sorption selectivity. Consequently, it was found that the crosslink of MMA–MAA membrane with the metal ions mainly influenced the sorption selectivity, and the benzene permselectivity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes was strongly governed by the sorption selectivity. The changes of the benzene permselectivity and sorption selectivity are mainly caused by the change of the affinity of these membranes for a benzene/cyclohexane mixture depending on the introduction of the metal ions into the MMA–MAA membrane. In order to discuss the relationship between the affinity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes for organic liquids and the metal ion content, the contact angles on the surface of these membranes were measured.

Figure 6 shows the contact angles to methylene

iodide on the surface of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes as a function of the metal ion molar ratio to MAA in the membrane. In this figure, the higher contact angle means that the surface of the membrane is more hydrophilic because the contact angles in this study were determined by methylene iodide. The contact angles to methylene iodide on the surface of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes were higher than that of the MMA–MAA membrane and increased with increasing metal ion content in the membrane. These results suggest that the MMA–MAA–Fe^{3+} and –Co^{2+} membranes are more hydrophilic than the MMA–MAA membrane and the hydrophilicity of these membranes was enhanced by an increase of the metal ions in the membrane. As listed in Table II, benzene has a higher hydrogen bond component δ_h, the solubility parameter, than cyclohexane.[20] Therefore, it is expected that benzene is slightly more hydrophilic than cyclohexane. The increase in the hydrophilicity of polymer membranes may enhance the affinity for benzene in the benzene/cyclohexane mixture. These discussions support the fact that the MMA–MAA–Fe^{3+} and –Co^{2+} membranes exhibited higher sorption selectivity than the MMA–MAA membrane. In comparing the contact angles of the MMA–MAA–Fe^{3+} membranes with that of the MMA–MAA–Co^{2+} membranes, the former was slightly lower than the latter in a low-metal ion content but the former was remarkably higher than the latter in a high-metal ion content. These changes in the contact angle were similar to those in the sorption selectivity of both the MMA–MAA–Fe^{3+} and –Co^{2+} membranes. Therefore, it is concluded that the increase in the sorption selectivity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes are mainly caused by the increase in the hydrophilicity of

Table II   Molecular Volume and Hansen Solubility Parameter of Benzene and Cyclohexane

Solvent	Molar Volume [cm³/mol]	Solubility Parameter [(MPa)$^{1/2}$]			
		δ_d	δ_p	δ_h	δ
Benzene	89.4	18.4	0	2.0	18.6
Cyclohexane	108.7	16.8	0	0.2	16.8

δ, Hansen solubility parameter; δ_d, dispersive forces contribution component; δ_p, polar component; δ_h, hydrogen bonding component; $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$.

Figure 7 Complexes of carboxyl groups with Fe^{3+} and Co^{2+} ions in the MMA–MAA–Fe^{3+} and MMA–MAA–Co^{2+} membranes.

these membranes depending on the metal ion content.

Relationship Between Structure of MMA–MAA Membrane Ionically Crosslinked with Metal Ions and PV Characteristics

The permeability of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes increased with an increase of the metal ion content in the membrane. However, the sorption selectivity and separation factor of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes indicated maxima in a different metal ion content and lowered by the increase of the metal ion content in a high metal ion content. These phenomena are mainly attributed to the difference of the membrane structures based on both the kind of metal ions and the metal ion contents. Because the Fe^{3+} and Co^{2+} ions are the trivalent and divalent ions, respectively, the Fe^{3+} and Co^{2+} ions can form the complexes with the carboxylate ion in the MMA–MAA membrane as shown in Figure 7. In a low metal ion content, the Fe^{3+} and Co^{2+} ions with the carboxylate ion in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes mainly form the complexes such as (A) and (D), respectively. In these membranes with a high metal ion content, however, the complexes such as (C) and (E) in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes increase, respectively.[21] Namely, the increase of the metal ion content in the membrane leads to the decrease of the ionic crosslinking point. Moreover, the $FeCl_3$ and $CoCl_2$ in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes also increase and those may play as a plasticizer for the membrane. These assumptions are supported by the presence of the

UV–VIS spectrum of $FeCl_3$ in the MMA–MAA–Fe^{3+} membrane and the lower of the T_g in a high metal ion content in the MMA–MAA–Co^{2+} membrane shown in Figures 1 and 2, respectively. Therefore, it is concluded that an introduction of many metal ions into the membrane leads to the formation of more opened-membrane structures.

Consequently, the MMA–MAA–Fe^{3+} and –Co^{2+} membrane structures are illustrated as different tentative models depending on the metal ion content in the membrane, as shown in Figure 8. In the MMA–MAA–Fe^{3+} and –Co^{2+} membranes with a low-metal ion content in the membrane, the metal ions mainly act as an ionic crosslinker. On the other hand, in a high-metal ion content in the membrane, the ionic crosslinking points of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes are less than those of these membranes with a low-metal ion content and excess $FeCl_3$, and $CoCl_2$ salts play as a plasticizer for the membrane. These discussions can easily permit understanding of the PV characteristics of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes for the benzene/cyclohexane mixture. Namely, higher permeability of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes with a higher metal ion content is mainly dependent on the plasticization of the membrane. On the other hand, the benzene permselectivity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes is enhanced by the increase in the hydrophilicity of these membranes, depending on the metal ions. However, in the MMA–MAA–Fe^{3+} and –Co^{2+} membranes with a high-metal ion content, a lower T_g was observed, as shown in Figure 2. This low T_g is due to high plasticization of the membrane based on the increase of $FeCl_3$ and $CoCl_2$ salts existing in the membrane. Therefore, the benzene permselectivity of the MMA–MAA–Fe^{3+} and –Co^{2+} membranes is lowered in a high-metal ion content.

CONCLUSIONS

The MMA–MAA membranes ionically crosslinked with the metal ions that do not dissolve in benzene/cyclohexane mixtures were prepared by polymer–metal complex formation between the MMA–MAA copolymer and the metal ions.

Both the permeability and permselectivity of the MMA–MAA membrane ionically crosslinked with the metal ions increased with increasing metal ion content in the membrane. Furthermore, the PV characteristics of the MMA–MAA–Fe^{3+}

Low Fe^{3+} content

High Fe^{3+} content

Low Co^{2+} content

High Co^{2+} content

Figure 8 Structures of the MMA–MAA–Fe^{3+} and MMA–MAA–Co^{2+} membranes with high and low metal ion contents.

membranes for a benzene/cyclohexane mixture with an increase of the metal ion content were remarkably different from those of the MMA–MAA–Co^{2+} membranes. These differences depended on the difference of membrane structures (different complex formation) based on the valence of Fe^{3+} and Co^{2+} ions.

It was found that the use of the metal ions as a crosslinker to the MMA–MAA copolymer effectively enhanced the PV characteristics for a benzene/cyclohexane mixture.

REFERENCES

1. Huang, R. Y. M. Pervaporation Membrane Separation Process; Elsevier: Amsterdam, 1991; Chapter 1.
2. Toshima, N.; Kaneko, M.; Sekine, M. Kobunshi Sakutai; Kyoritsushuppan: Tokyo, 1990.
3. Abe, K. Kobunshi Complex; Kyoritsushuppan: Tokyo, 1994; Chapter 1.
4. Uragami, T.; Niwa, N.; Sugihara, M. Kobunshi Ronbunshu 1982, 39, 669.

5. Park, C. K.; Oh, B.-K.; Choi, M. J.; Lee, Y. M. Poly Bull 1994, 33, 591.

6. Hsiue, G.-H.; Yang, J.-S. J Memb Sci 1993, 82, 117.

7. Ho, W. S.; Dalrymple, D. C. J Memb Sci 1994, 91, 13.

8. Yang, J.-S.; Hsiue, G.-H. J Memb Sci 1997, 126, 139.

9. Adachi, K.; Wei, H.; Tanioka, A. Polymer Preprints Japan 1997, 46, 469.

10. Tsuchida, E.; Nishide, H.; Ohyanagi, M.; Kawakami, H. Macromolecules 1987, 20, 1907.

11. Delany, M. S.; Reddy, D.; Wessling, R. A. J Memb Sci 1990, 49, 15.

12. Hsiue, G.-H.; Yang, J.-M. J Poly Sci, Polym Chem 1993, 31, 1457.

13. Nishide, H.; Kawakami, H.; Sasame, Y.; Ishiwata, K.; Tsuchida, E. J Poly Sci, Polym Chem 1992, 30, 77.

14. Wei, Y.; Huang, R. Y. M. J Appl Poly Sci 1994, 53, 179.

15. Okuno, H.; Nishida, T.; Uragami, T. J Poly Sci, Polym Phys 1995, 33, 299.

16. Inui, K.; Miyata, T.; Uragami, T. Angew Makromol Chem 1996, 240, 241.

17. Miyata, T.; Iwamoto, T.; Uragami, T. J Appl Polym Sci 1994, 51, 2007.

18. Van Krevelen, D. W. Properties of Polymers; Elsevier: Amsterdam, 1990.

19. Mahesh, G. N.; Banu, P.; Radhakrishnan, G. J Appl Poly Sci 1997, 65, 2105.

20. Brandrup, J.; Immergut, E. H. Polymer Handbook 3rd Ed.; Wiley: New York, 1989.

21. Marinsky, J. A.; Marcus, Y. Ion Exchange, Vol. I; Dekker: New York, 1966.