Control of the Fixed Charge Distribution in an Ion-Exchange Membrane via Diffusion and the Reaction Rate of the Monomer

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The fixed charge distribution of the ion-exchange membranes was controlled by introducing ion-exchangeable groups onto the glycidyl methacrylate (GMA)-*g*-polypropylene (PP) membranes. The membranes were prepared by plasma-induced graft polymerization with uniform or nonuniform graft distributions over the cross section. The effects of reaction conditions on the graft distribution in plasma-induced graft polymerization were investigated to obtain the GMA-*g*-PP membranes with different graft distributions. The examined reaction conditions were plasma power, gas pressure of the plasma, solvent, concentration of the monomer solution, and reaction temperature. The graft distribution of the membranes was directly observed by a microscopic Fourier transform infrared mapping method and field-emission scanning electron microscopy. Also, the graft distribution was correlated with the relative magnitude of the reaction rate to the diffusion rate, which may determine the grafting yield as a function of the distance from the surface. A high rate of diffusion compared to the reaction rate resulted in a more uniform graft distribution. Among the grafting conditions, control of the reaction temperature was found to be the most effective for selectively preparing both uniform and nonuniform graft distribution. Uniform graft distribution was achieved when the reaction was conducted at 1 °C because of the relatively rapid diffusion and the slow reaction of the monomer, while nonuniform graft distribution occurred at higher reaction temperatures. Consequently, uniformly and nonuniformly charged cation-exchange membranes were prepared through sulfonation of the corresponding GMA-*g*-PP membranes at temperatures of 1 and 40 °C, respectively

Introduction

The properties of an ion-exchange membrane are determined by its chemical or physical characteristics, such as the type of fixed charge (cationic or anionic), ion-exchange capacity, the fixed charge distribution, and the hydrophobic or hydrophilic nature of the base polymer.[1,2] Despite extensive studies on the effect of the characteristics on the properties of an ion-exchange membrane, the studies on the effect of the fixed charge distribution (uniform or nonuniform) over the cross section of an ion-exchange membrane on its properties have involved only a theoretical approach because of the difficulties associated with the preparation of an ion-exchange membrane having controlled fixed charge distributions using currently available techniques.[3−11] Therefore, the control of the fixed charge distribution during the preparation of an ion-exchange membrane makes it possible to study the effect of the fixed charge distribution from an experimental point of view, which can provide useful information for applications.

Plasma-induced graft polymerization (PIGP) is a well-known method for modifying a polymer surface. PIGP consists of two steps; the first step is a plasma treatment to generate polymer radicals on the base membrane, and the second is grafting and polymerization of the monomer with the radicals. When a porous substrate is utilized as a base membrane, PIGP occurs on both the outer surface of the membrane and on the surfaces of internal pores in the membrane.[12,13] PIGP can be an effective method for preparing an ion-exchange membrane with a controlled fixed charge distribution because graft distribution (uniform or nonuniform) over the cross section of a membrane is determined by the relative ratio of the reaction rate to the diffusion rate of the monomer. Uniform graft distribution can be obtained in the case of a high diffusion rate and low reaction rate, while nonuniform graft distribution is obtained when these conditions are reversed. The diffusion and reaction of monomers through the membrane can be interpreted by the concept of mass transport. According to Fick's second law of diffusion, the mass balance for a monomer including a thickness of infinitesimal size within the membrane (x) is given by

$$R_p + \frac{dc}{dt} = D\frac{d^2c}{dx^2} \quad (1)$$

where c is the monomer concentration, t is the time, D is diffusion coefficient, R_p is the rate of monomer disappearance with thickness, dc/dt is the change in the monomer concentration with thickness with time, and $D(d^2c/dx^2)$ is the change in the rate of diffusion in and out of the thickness. In ordinary

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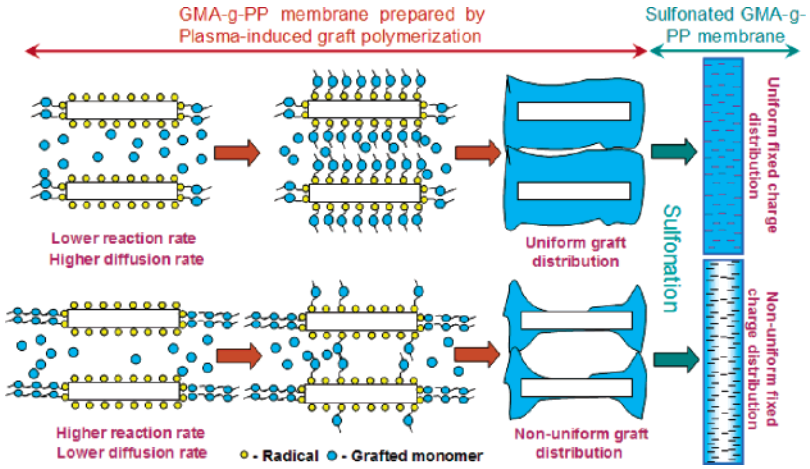
SCHEME 1: The Control of the Fixed Charge Distribution of the Ion-Exchange Membrane



free-radical polymerization, the grafting rate at any membrane thickness is given by

$$R_p = \left(\frac{k_p}{k_t^{1/2}}\right) R_i^{1/2} c \qquad (2)$$

where R_i is the rate of initiation and k_p and k_i are the rate constants for propagation and bimolecular termination. As is known from eqs 1 and 2, transport of the monomer through the membrane is determined by the diffusion rate and reaction rate.[14] Therefore, graft distribution can be controlled by appropriate regulation of the experimental parameters, such as the amount of the radical sites initiated, the solvent used, the concentration of monomer solution, and the reaction temperature, all of which can affect the diffusion rate and/or the reaction rate. An ion-exchange membrane with a controlled fixed charge distribution can be prepared by introducing ion-exchangeable groups onto the membranes with uniform and nonuniform graft distributions, which were controlled by the experimental parameters of PIGP.

In this study, the effect of the grafting conditions in PIGP on the graft distribution using glycidyl methacrylate (GMA) as a monomer and microporous polypropylene (PP) as a base membrane was studied. The investigated conditions were plasma power, the gas pressure used for the plasma, the solvent, the concentration of monomer solution, and the reaction temperature. The graft distribution in the prepared GMA-*g*-PP membranes was characterized by determining the change in membrane thickness, field-emission scanning electron microscopy (FESEM), and microscopic Fourier transform infrared spectroscopy (micro-FTIR). It should be noted that membranes with a uniform or nonuniform graft distribution were selectively prepared by controlling the reaction temperature. In particular, the effect of reaction temperature on graft distribution was quantitatively confirmed by a comparison of the rate of diffusion of the monomer with its reaction rate. Finally, the uniformly and nonuniformly charged membranes were prepared by sulfonation of the corresponding GMA-*g*-PP membranes, which were obtained by regulating the reaction temperature. The procedure used for the preparation of membranes with controlled fixed charge distributions was summarized in Scheme 1.

Experimental Methods

Membrane Preparation. A microporous PP membrane (Celgard 2500, Hoechst Celanese, Germany) was used as the base membrane. The base membrane had the following specifications: porosity of 55%, pore size of 0.05 μm × 0.21 μm, and thickness of 20 μm. GMA (Aldrich, U.S.A.) was used as a grafting monomer. Inhibitors of GMA were eliminated by means of an inhibitor removal column (Aldrich, U.S.A.). A monomer solution was then prepared by dissolving the purified GMA in the following solvents: diphenyl ether (DPE) (Aldrich, U.S.A.), *N*,*N*-dimethylformamide (DMF) (Junsei, Japan), and a mixture of water and methanol (MeOH) (Aldrich, U.S.A.) (100:0, 85:15, and 60:40 weight (wt) ratios). The GMA solutions were frozen and thawed repeatedly with liquid nitrogen under a vacuum of 4 Pa to remove traces of reactive gases.

Free radicals were generated on the surface of the base membrane (19 cm^2) by plasma treatment with argon (Ar) for 30 s. The radio-frequency plasma generator (model YSE-03F, Youngsin-RF, Korea) was operated at 13.65 MHz. After the plasma treatment, the base membrane was immediately immersed in the monomer solution to initiate the reaction of the GMA monomers with the free radicals of the base membrane. The graft polymerization proceeded without contact with air for a predetermined time. The grafted films were rinsed for 24 h with tetrahydrofuran (Aldrich, U.S.A.) to remove the unreacted monomers and then washed with methanol/water for 24 h. The prepared GMA-*g*-PP membranes were dried in a vacuum oven at 50 °C to eliminate residual solvents and impurities. The degree of grafting (DG), which was obtained by measuring the weight of the membrane before (W_0) and after (W_f) grafting, was defined using the following formula

$$\text{Degree of grafting (DG)} = \frac{W_f - W_0}{W_0} \times 100\ [\%] \qquad (3)$$

The thicknesses of the dried membranes were measured with a micrometer (Mitutoyo, Japan). The GMA-*g*-PP membranes were sulfonated by immersing them in a mixture of sodium sulfite (Aldrich), isopropyl alcohol (Aldrich), and water (10/15/75 wt %) at 50 °C for 24 h. The ion-exchange capacity was evaluated by measuring the number of ion-exchange groups in the membrane by titration.

Chemical Verification and Morphological Evaluation. The surface and cross section of the membranes before and after grafting were observed using a field-emission scanning electron microscope (FESEM, S-4700, Hitachi, Japan). The graft distribution of the membrane over the cross section was analyzed using a mapping method in conjunction with micro-FTIR with an automatically controlled stage (IPS-30, Jasco, Japan). The aperture size was 5 μm × 20 μm, and the area of measurement was scanned in 3 μm steps during the analysis of the cross

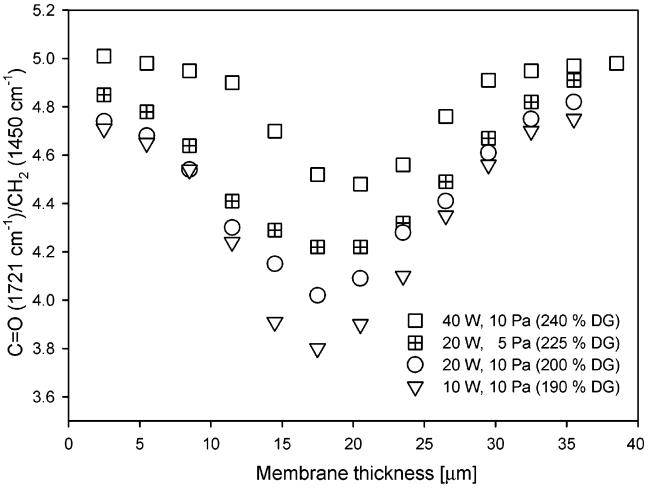


Figure 1. Graft distribution of GMA-*g*-PP membranes with a variation in plasma power and Ar pressure. Solvent, water/MeOH (60:40 wt ratio); concentration of monomer solution, 2.0 wt %; reaction temperature, 40 °C.

section of the prepared membranes. The profile of the graft layer was calculated by measuring the FTIR peak height ratio at 1721 cm^{-1}, derived from GMA, to that at 1450 cm^{-1} derived from the substrate.

Measurement of the Diffusion Rate. The rate of diffusion of the monomer through the GMA-*g*-PP membrane was measured, as described in the literature.[15] A two-compartment cell was used to determine the diffusion rate. The membrane was inserted between the two compartments. One compartment (V_A = 100 mL) was filled with a 9 wt % of GMA solution in a mixture of the water and MeOH (60:40 wt ratio), and the other compartment (V_B = 100 mL) was filled with a mixture of water and MeOH (60:40 wt ratio). This experiment was carried out in an oven (VISION, Korea) to maintain a constant temperature (1 and 40 °C), and the solutions in the two compartments were stirred continuously. A 500 μL aliquot was removed from the solvent compartment every 15 min for 1 h. The concentration of the diffused GMA was measured by HPLC (high-performance liquid chromatography, Waters, U.S.A.) using a C-18 column (Nova Pak, 3.9 mm × 150 mm i.d.) and an absorbance at 212 nm. The mobile phase was acetonitrile/water (60:40, v/v), and the column was eluted at a rate of 1 mL/min

Results and Discussion

Effect of Plasma Power and Ar Pressure on the Graft Distribution. The effect of plasma power and Ar pressure on the graft distribution of GMA onto a porous PP membrane was investigated, and the results are shown in Figure 1 as the relative intensity of C═O/CH_2 obtained by micro-FTIR. The membranes prepared using a high plasma power and a low Ar pressure showed a more uniform graft distribution compared to the membranes prepared using a low plasma power and a high Ar pressure, as shown in Figure 1, because sufficient electron acceleration and the high density of the plasma promoted the creation of active species on the surface of the pores of the base membrane. These results are consistent with a previous report by Choi et al.[16] In addition, another possible reason for the relatively uniform graft distribution achieved by the high plasma power (40 W) is the enlargement of the pore size. The pore of the base membrane can be enlarged by etching with a high plasma.[17] In the case of a base membrane with a large pore size or a high porosity, a relatively uniform graft distribution can be induced since the monomer can effectively diffuse into the large or numerous pores and grafting reactions occur uniformly over its cross section.[16,18] We compared the pore size of a plasma-treated base membrane, produced at 20 and 40 W, as shown Figure 2. Indeed, the pore size of the base membrane was enlarged by the high plasma power, while the pore size of the membrane that was treated with a low plasma power remained unchanged. Therefore, the enlarged pores produced by the high plasma power contributed to a uniform graft

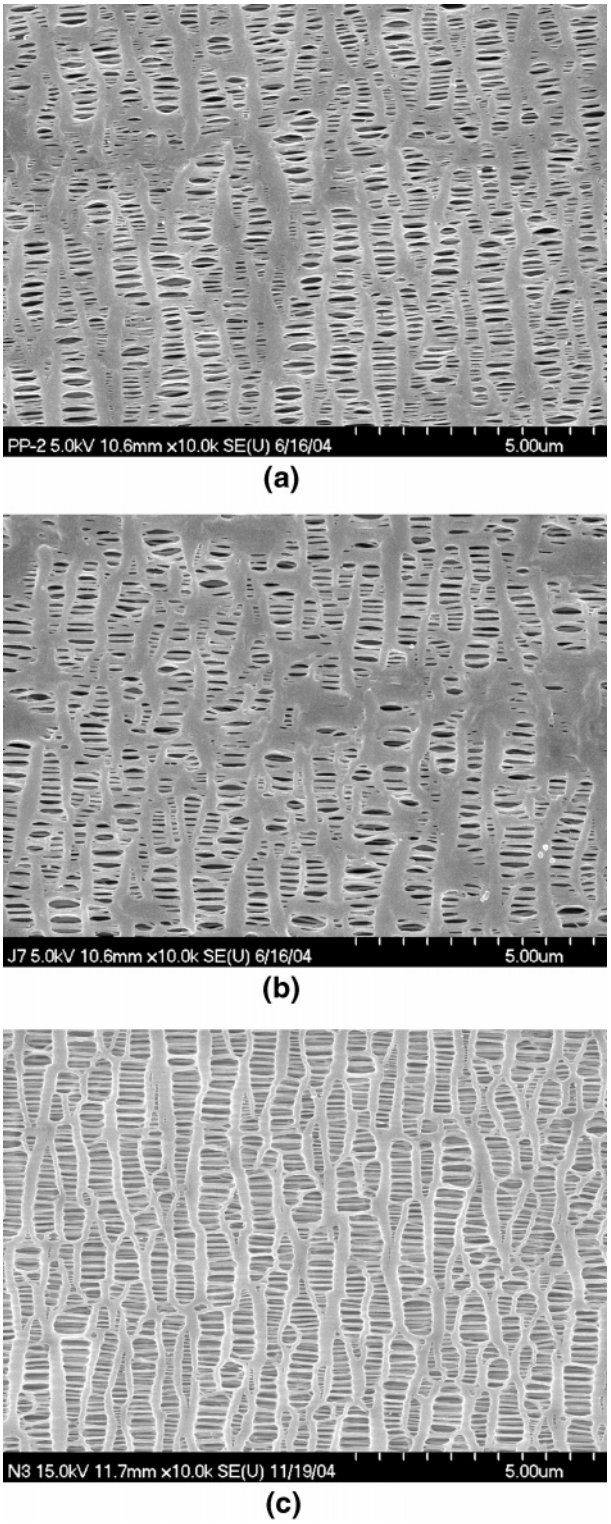


Figure 2. FESEM photographs of the membrane surface; (a) base membrane, (b) after plasma treatment at 20 W, (c) after plasma treatment at 40 W.

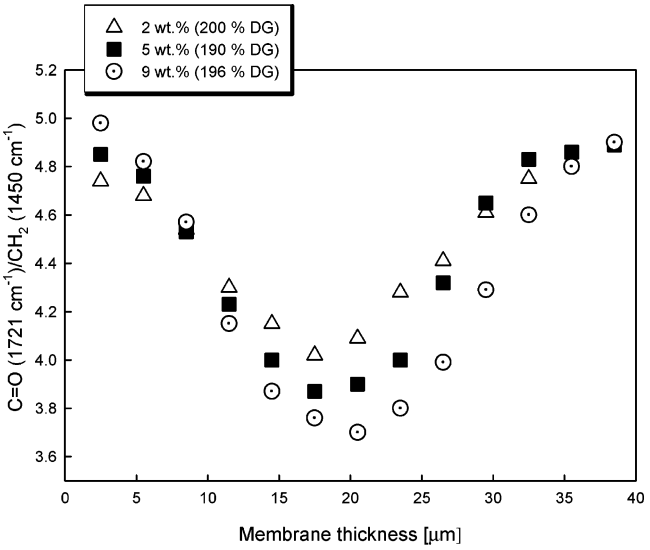


Figure 3. Graft distribution of GMA-*g*-PP membranes prepared using various concentrations of monomer solution. Plasma power, 20 W; Ar pressure, 10 Pa; solvent, water/MeOH (60:40 wt ratio); reaction temperature, 40 °C.

distribution. However, despite the increase in the pore size produced by the high plasma and the use of a thin base membrane, uniform graft distribution could not be consistently produced using similar conditions for the plasma as those of Choi et al., in which a completely uniform graft distribution with a high thickness (100 μm) was reported.[15] This result can be attributed to the lower porosity (55%) of our base membrane compared to the base membrane (70%) used by Choi et al. Despite the satisfactory amounts of the radial produced by high plasma, the low porosity prohibited the efficient diffusion of the monomer, and a nonuniform graft distribution was obtained. These results indicate that the control of graft distribution by plasma power in PIGP is not a reliable method, and its use is limited because of the porosity of the base membrane.

Effect of the Concentration of the Monomer Solution on the Graft Distribution. Figure 3 shows the effect of the concentration of the monomer solution on graft distribution. The higher the concentration of monomer solution used, the more nonuniform the distribution. The relationship between the concentration of the monomer solution and the graft distribution resulted from rapid surface grafting caused by a higher concentration of monomer on the surface of the membrane than that in the inner pores. This trend was also confirmed by the change of the membrane thickness. For membranes with a similar DG (190∼200%), the thickness of the produced membranes increased in the order of 36 (2 wt %) < 41 (5 wt %) < 44 μm (9 wt %). This indicates that surface grafting by a high concentration of the monomer solution led to an increase in the membrane thickness.

Effect of the Solvent on the Graft Distribution. In graft polymerization, the solvent plays an important role by swelling the base membrane and improving accessibility of the monomer to the grafting sites.[19] The use of a good solvent promotes the uniform graft distribution because the highly swollen base membrane provides not only an easy diffusion path for the reactive monomer but also a fast reaction. However, the use of a poor solvent leads to selective surface grafting because the base membrane swells only to a limited extent and the monomer does not diffuse into it satisfactorily. A good solvent indicates a small difference in the solubility parameter between the base membrane and the solvent. Therefore, the choice of a solvent having a similar solubility parameter to that of the base membrane can enhance the yield of grafting by the rapid diffusion of the monomer.[20−22]

TABLE 1: Solubility Parameters for Individual Species in the Grafting Conditions[a]

species			solubility parameter [MPa$^{1/2}$]
PP (base membrane)			17.5−19[b]
GMA (monomer)			20.5[c]
mixture with solvent and 2 wt % of GMA	DPE		20.9 (20.9[d])
	DMF		24.7 (24.8[d])
	water (60)	MeOH (40)	40.4 (40.5)
	water (85)	MeOH(15)	44.8 (45.1)
	water		47.5 (47.9[d])

[a] Left column of the mixture, solvent 1; right column of the mixture, solvent 2. The values in the parentheses for the solvent are the wt ratio; those for the solubility parameter are for the solvent only. [b] Obtained from the ref 22. [c] Obtained from the ref 23. [d] Obtained from the ref 24.

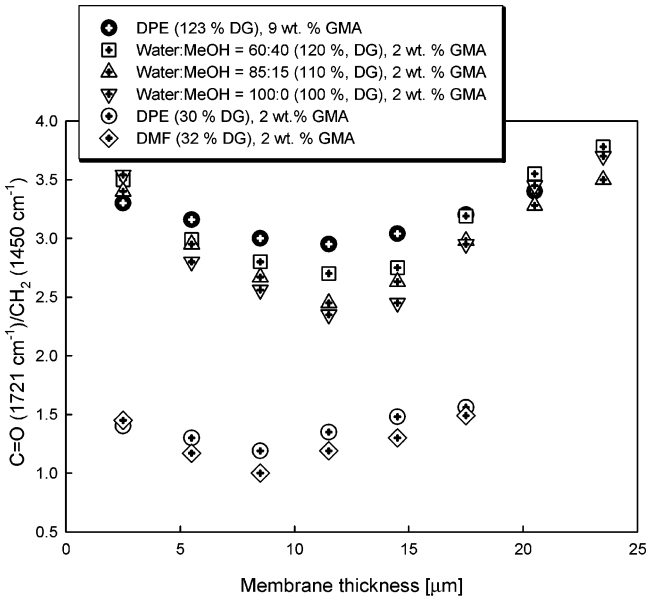


Figure 4. Graft distribution of GMA-*g*-PP membranes prepared using various solvents. Plasma power, 20 W; Ar pressure, 10 Pa; reaction temperature, 40 °C.

In this study, we used five solvents having different solubility parameters for the preparation of the GMA-*g*-PP membranes. The solubility parameters of the solvents used, GMA, and the base membranes are listed in Table 1. Since the solubility parameter of the monomer/solvent mixtures is unknown, they were estimated by the following equation[25]

$$\delta_{Mix} = (\varphi_M \delta_M{}^2 + \varphi_{D1} \delta_{D1}{}^2 + \varphi_{D2} \delta_{D2}{}^2)^{1/2} \qquad (4)$$

where φ_M, φ_{D1}, and φ_{D2} are the volume fractions of the monomer, solvent 1, and solvent 2 of the mixtures, respectively, and δ_M, δ_{D1}, and δ_{D2} represent the solubility parameters of the monomer, solvent 1, and solvent 2, respectively.

Figure 4 shows the graft distribution of membranes prepared using various solvents. As shown in Figure 4, a more uniform graft distribution was obtained for the membrane using DPE as a solvent compared to that using DMF. This result can be explained by the similar solubility parameter of DPE with the base membrane since a rapid diffusion by a similar solubility parameter led to a fast reaction. The faster reaction of the monomer with the membrane using DPE was also confirmed

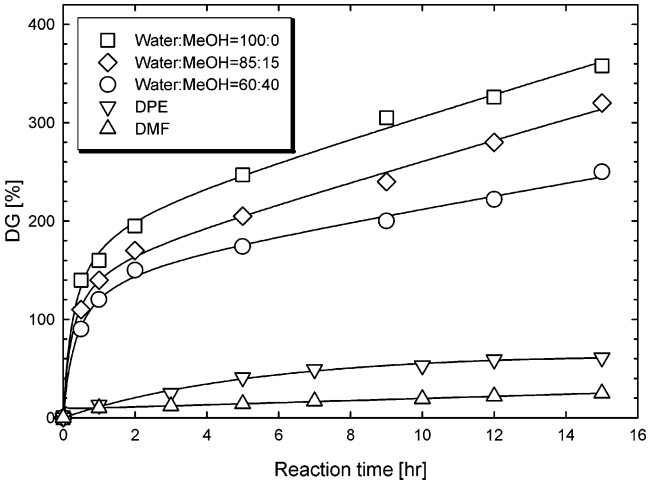


Figure 5. Effect of solvent on grafting yield. Plasma power, 20 W; Ar pressure, 10 Pa; concentration of monomer solution, 2.0 wt %; reaction temperature, 40 °C.

via the relationship between the reaction time and DG, as shown in Figure 5. Both the final DG and the reaction rate of the membrane using DPE were higher than those when DMF was used. However, membranes prepared using solvents containing water showed a much higher DG and reaction rate than the membrane using DPE of DMF, despite the large difference in the solubility parameters between the monomer solution and the base membrane, as shown in Figure 5. This result is caused by the characteristics of the water solvent, which causes the rate of polymerization to be accelerated.[16,26,27] Therefore, the membrane with the solvent containing a high ratio of water showed a high reaction rate and a final DG, which resulted in a more nonuniform graft distribution, as shown in Figure 4. In order to compare the graft distribution of the membranes prepared using DPE with that of membranes prepared using solvents containing water, the GMA-*g*-PP membranes with a high DG were prepared using a higher concentration (9 wt %) of GMA in DPE. As shown in Figure 4, the graft distribution of the membrane prepared using DPE had a more uniform distribution than the membrane prepared using the water-containing solvent. However, as shown in Figure 4, the use of a high concentration (9 wt %) of GMA in DPE resulted in a relatively nonuniform distribution due to the effect of concentration, as explained in the previous section.

Effect of Grafting Reaction Temperature on the Graft Distribution. Temperature is considered to be one of the most significant parameters in controlling the uniformity of grafting distribution since the reaction rate for grafting is strongly dependent on temperature.[19] Figure 6 shows the relationship between reaction time and DG as a function of reaction temperature. Both the DG and the reaction rate increase with an increase in reaction temperature. This result can be easily understood since an increase in reaction temperature leads to active grafting reactions.

Figure 7 presents data on the thickness of the prepared membranes as a function of DG for various reaction temperatures. Membrane thickness increased linearly with DG, and the membrane prepared at a high temperature showed a relatively larger thickness at a similar DG to those prepared at a low temperature. This indicates that the grafting reaction with GMA molecules occurred uniformly over the cross section of the membrane at a low preparation temperature, whereas the grafting reaction was favored on the membrane surface at a high reaction temperature. The effect of reaction temperature on graft distribution was also confirmed through the FESEM images

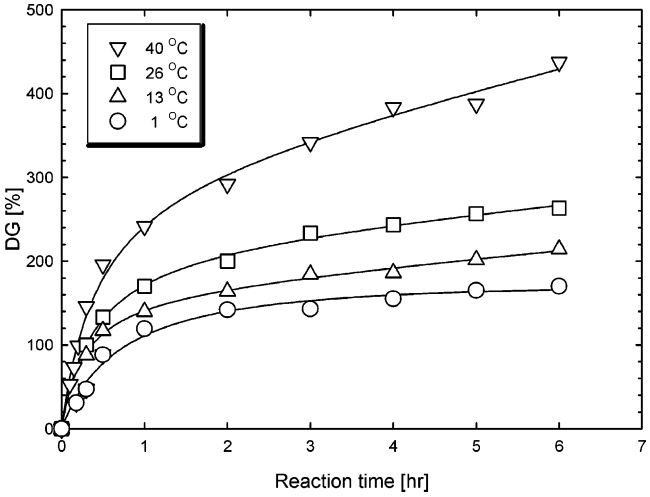


Figure 6. Effect of the reaction temperature on grafting yield. Plasma power, 20 W; Ar pressure, 10 Pa; solvent, water/MeOH (60:40 wt ratio); concentration of the monomer solution, 9 wt %.

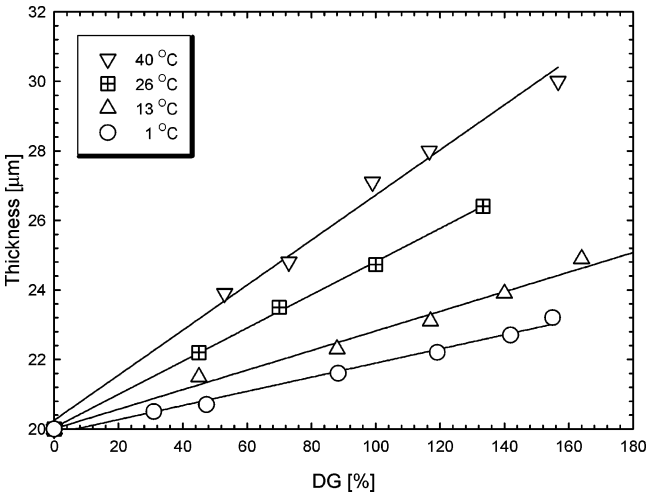


Figure 7. Variation in membrane thickness with DG for different reaction temperatures.

shown in Figure 8. The membrane prepared at 1 °C showed a uniform graft distribution, and the grafted GMA molecules filled the inner pores of the membrane, whereas the membrane prepared at 40 °C exhibited a rather nonuniform graft distribution with partially filled inner pores and a densely grafted layer on the membrane surface.

The results for the effect of reaction temperature implies that the reaction rate was effected to a greater extent than the diffusion rate by the reaction temperature, and the uniform graft distribution with the low reaction temperature was due to the significantly reduced reaction rate compared to a reduction in the diffusion rate. In order to confirm this hypothesis, the diffusion rate of the monomer through the membrane was measured and compared with the reaction rate obtained from reaction kinetics data. The diffusion rates of the monomer through the membrane were determined by a previously described[15]

$$J'_{\mathrm{Diff}} = \frac{C_{\mathrm{B}}V_{\mathrm{B}}}{A_1 t_1} = \frac{PC_{\mathrm{A}}}{L} \tag{5}$$

where J'_{Diff} is the diffusion rate of the monomer through a membrane with thickness L, C_{B} the concentration of the diffused GMA in the solvent compartment, V_{B} the volume of the solvent

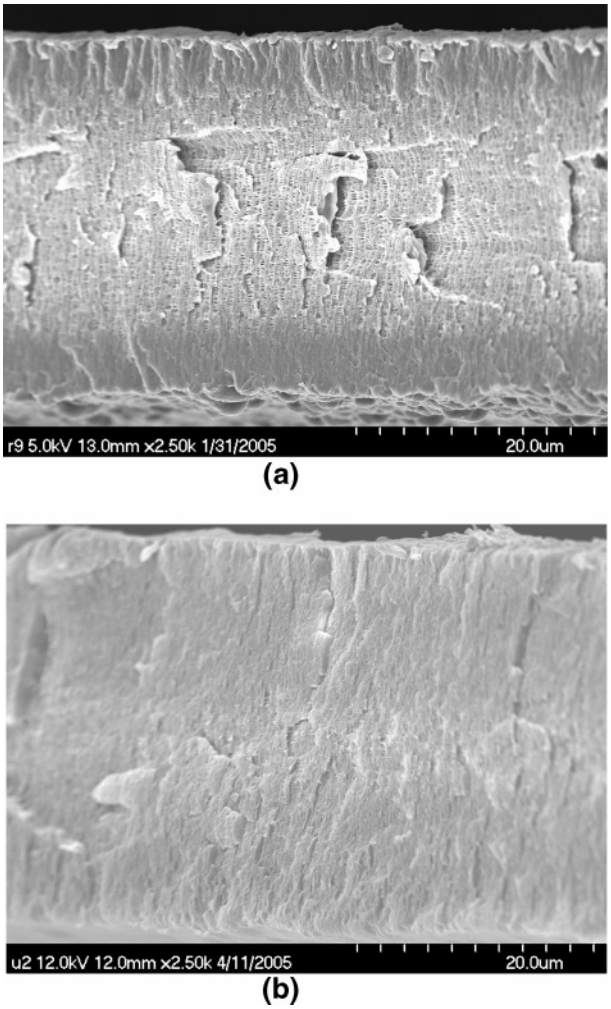


Figure 8. Cross-sectional FESEM images of GMA-*g*-PP membranes; (a) 156% DG (reaction temperature, 40 °C); (b) 156% DG (reaction temperature, 1 °C).

compartment, A_1 the membrane area for the diffusion (0.785 cm^2), t_1 the time of diffusion, P the permeability, and C_A the concentration of the monomer in the GMA + solvent compartment. The subscripts A and B refer to the GMA + solvent compartment and the solvent compartment, respectively. In the diffusion test, the monomer was allowed to diffuse from the GMA + solvent compartment to the solvent compartment, and the monomer entered and diffused from only one surface of the membrane (Figure 9a). However, the monomer diffused through both surfaces of the membrane during the actual grafting reaction. In order to correct for this difference, we calculated the diffusion rate at $x = 0$, assuming that the diffusion took place from only one side of the membrane with thickness of $L/2$ (Figure 9b). It was assumed that the concentration of the unreacted monomer at $x = 0$ was zero in the actual grafting reaction, and a comparison between the reaction rate and the diffusion rate obtained from the diffusion test was reasonable. Since the monomer diffused through both surfaces of the membrane during the actual grafting reaction, the diffusion rate, $J_{\text{Diff at } x=0}$, at $x = 0$ through the membrane with thickness, L (Figure 9a) was equal to the doubled diffusion rate, $2J'_{\text{Diff at } x=0}$, through the membrane with thickness $L/2$ (Figure 9b) and is given by

$$J_{\text{Diff at } x=0} = 2J'_{\text{Diff at } x=0} = \frac{2C_B V_B}{A_1 t_1} = \frac{PC_A}{L/2} \tag{6}$$

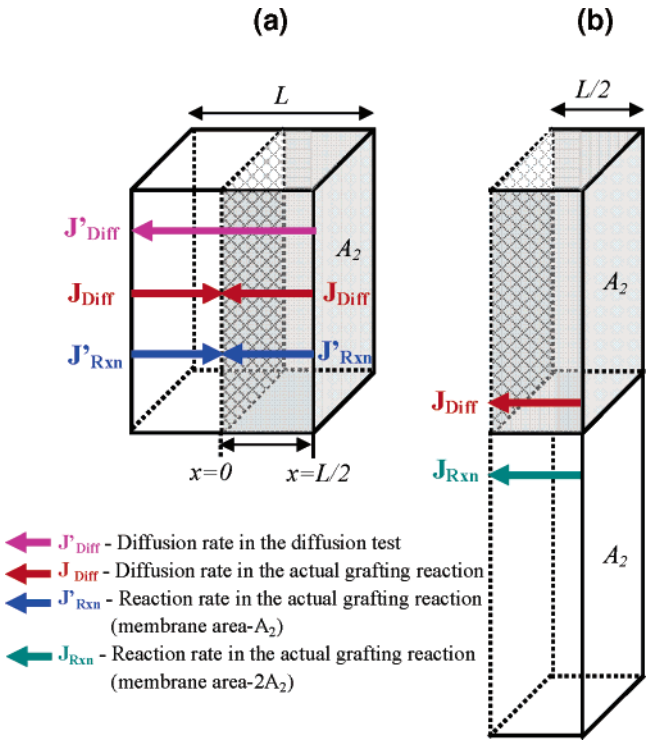


Figure 9. Membrane parameters to be considered in the estimation of the diffusion rate and reaction rate. (a) Diffusion rate and reaction rate in the experimental conditions; (b) the diffusion rate and reaction rate for the estimation.

Meanwhile, the reaction rate was obtained from the relationship between the reaction time and the weight gain ($W_f - W_0$) of the membrane after polymerization. The equation used to calculate the reaction rate is shown below

$$J'_{\text{Rxn}} = \frac{W_f - W_0}{A_2 t_2 M_w} \tag{7}$$

where A_2 is the area of the membrane (=19 cm^2), t_2 the reaction time, and M_w the molecular weight of GMA (142.15 g/mol). Since the monomer diffused through both surfaces of the membrane (Figure 9a) and polymerization occurred during the actual reaction, the reaction rate, $J_{\text{Rxn at } x=0}$, at $x = 0$ is equal to the reaction rate at $x = 0$ through the membrane with the thickness $L/2$ and the doubled area $2A_2$ (Figure 9b). The reaction rate at $x = 0$ changes

$$J_{\text{Rxn at } x=0} = \frac{W_f - W_0}{2A_2 t_2 M_w} \tag{8}$$

The calculation of the reaction rate was carried out using a selected area of data showing a linearly proportional relationship between reaction time and DG in Figure 6.

Figure 10 shows the obtained diffusion rate and the reaction rate as a function of the DG of membranes prepared at 1 and 40 °C. The diffusion rate decreased with an increase in the DG because of the reduction in the porosity of the membrane. However, the reaction rate was nearly constant with DG because of the linear relationship between the reaction time and the weight gain during the initial stages of the reaction. The diffusion rate was lower than the reaction rate at 40 °C for all DGs. However, the diffusion rate at 1 °C was higher or similar to the reaction rate at 40 °C. Therefore, the diffusion of the monomer into the inner pores was preferably promoted compared to the reaction rate at the low reaction temperature of

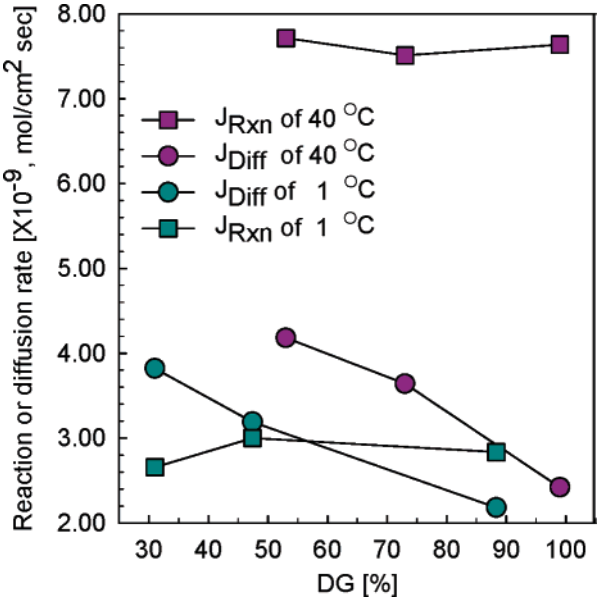


Figure 10. Diffusion rate and reaction rate of membranes prepared at 1 and 40 °C. (a) DG versus diffusion rate and reaction rate of the membranes. (b) Temperature versus diffusion rate and reaction rate of the membranes with the similar DGs (48% for 1 °C and 52% for 40 °C).

1 °C so that a uniform graft distribution via both grafting in the pores and on the surface of the membrane could be obtained. The degree of decrease in the reaction rate with a decrease in temperature ($\Delta J_{Rxn} = 4.71 \times 10^{-9}$ mol cm^{-2} sec^{-1}) was a much higher than that for the decrease in diffusion rate ($\Delta J_{Diff} = 0.990 \times 10^{-9}$ mol cm^{-2} sec^{-1}). This tendency for the reaction rate and diffusion rate to decrease with temperature can be explained by the well-known Arrhenius equation and the Stokes−Einstein equation, respectively.[28] According to those equations, the change in reaction rate with temperature is more sensitive than a change in diffusion rate. It is considered that these tendencies on the degree of change in the diffusion rate and reaction rate with reaction temperature sufficiently explain selective preparation of a membrane with a uniform or nonuniform grafting distribution.

Finally, uniformly and nonuniformly charged cation-exchange membranes (sulfonated GMA-*g*-PP membranes) with 2.7 mmol/g of ion-exchange capacity were prepared through sulfonation of the uniformly and nonuniformly grafted (GMA-*g*-PP) membranes with the same DG (156%) prepared at temperatures of 1 and 40 °C, respectively. Figure 11 shows cross-sectional FTIR spectra of the sulfonated GMA-*g*-PP membrane analyzed by micro-FTIR, including the fixed charge distribution. Information on the peak of the IR spectral peaks of the membranes can be found in our previous report.[29] The fixed charge ($-SO_3^-$) distribution, detected at 1030 cm^{-1}, was determined by the original graft distribution of the used GMA-*g*-PP membranes. The membrane obtained by sulfonation of the nonuniformly grafted membrane shows a nonuniform fixed charge distribution (linear decrease of the fixed charges from the surface to the center of the membrane), accordingly.

Conclusions

The sulfonated GMA-*g*-PP membranes with uniform and nonuniform fixed charge distribution were prepared by introducing cation-exchangeable groups onto the GMA-*g*-PP membranes with uniform and nonuniform graft distributions. In order to control the graft distribution of the GMA-*g*-PP membrane, the

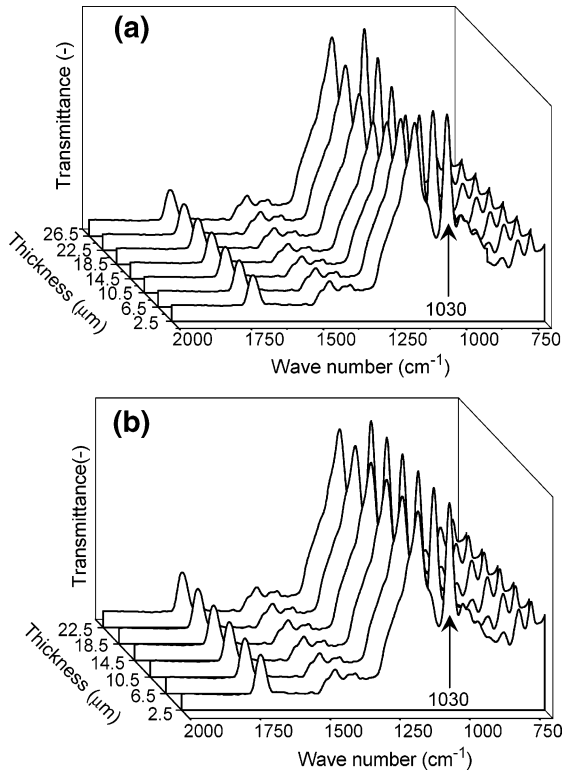


Figure 11. Cross-sectional FTIR spectra for the line mapping of sulfonated GMA-*g*-PP membranes (2.7 mmol/g of ion-exchange capacities); prepared using different reaction temperatures for the grafting reaction for GMA-*g*-PP membranes. (a) Nonuniformly charged membrane: reaction temperature, 40 °C. (b) Uniformly charged membrane: reaction temperature, 1 °C; Plasma power, 20 W; Ar pressure, 10 Pa; solvent, water/MeOH = 60/40 wt ratio; concentration of monomer solution, 9 wt %.

effects of reaction conditions on the graft distribution in PIGP were investigated in terms of plasma power, gas pressure of the plasma, solvent, concentration of the monomer solution, and reaction temperature. Reaction temperature was found to be the most effective method for selectively preparing a uniformly or nonuniformly grafted membrane. A uniform graft distribution was obtained at a low preparation temperature of 1 °C because of the drastic reduction in reaction rate and a slight reduction in diffusion rate with temperature, whereas a nonuniform graft distribution was obtained at higher temperatures because of the more rapid reaction rate on the surface of the membrane than the rate of diffusion into the inner pores. Micro-FTIR analysis revealed that uniformly and nonuniformly charged cation-exchange membranes were prepared through sulfonation of the uniformly and nonuniformly grafted (GMA-*g*-PP) membranes with the same DG prepared at temperatures of 1 and 40 °C, respectively. The preparation of an ion-exchange membrane with a controlled fixed charge can be applied to investigate the effect of the distribution of fixed charges on the performance of an ion-exchange membrane.

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