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Synthesis of Polyketone-*g*-Sodium Styrene Sulfonate Cation Exchange Membrane *via* Irradiation and Its Desalination Properties

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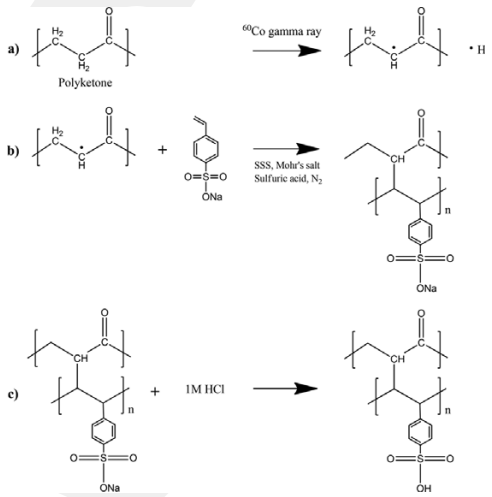
Abstract: Using the radiation grafting technique, polyketone membranes were graft copolymerized with sodium styrene sulfonate (SSS) in the presence of additives such as Mohr's salt and H_2SO_4. Fourier-transform infrared (FT-IR) spectroscopy was used to characterize the grafted membranes. Water uptake (WU), ion exchange capacity (IEC) and electrical resistance (ER) of the prepared membranes were measured in order to evaluate their physical properties The prepared membranes were applied to the membrane capacitive deionization (MCDI) process, in which their salt removal rates were evaluated and compared to those of CDI (capacitive deionization) process. The degree of grafting rose from 14.4% to 81.4% as the irradiation dose and the monomer concentration were increased. The water uptake ranged from 7.9% to 34.2%. The ion-exchange capacity was observed between 0.43 meq/g and 1.1 meq/g, and the electrical resistance had values ranging from 12.2 Ω·cm^2 to 2.1 Ω·cm^2. The electrical resistance decreased as the ion-exchange capacity was extended. When the prepared cation exchange membrane was used in the MCDI process, the salt removal rate reached 87.6%, which was much higher than 28.8% of CDI process.



Keywords: cation exchange membrane, MCDI, radiation, graft copolymer, desalination.

1. Introduction

Recently, depleting fresh water resources and increasing demands require us to look for alternative water supplies such as waste water treatment and fresh water production from sea and brackish waters. Desalination is known to be one of the most strategic solutions to the increasing global water demand and decreasing natural fresh water resources due to climate change and rising industrial use of fresh water. In particular, a desalination process for seawater and underground water which contain various ions has emerged as a technology to solve global water shortage. There are several desalination technologies such as reverse osmosis, multi-stage flash and multi-effect distillation, crystallization, ion-exchange membrane separation, solvent extraction and pressure adsorption.[1-5] Membrane technologies, such as reverse osmosis[6,7] and electrodialysis method,[8] are widely used for the production of safe drinking water and the recovery of reusable water from industrial streams. The most commonly encountered phenomenon in these processes is membrane contamination, which consequently increases energy consumption during the operation and also causes regular replacement of the membrane.

Capacitive deionization (CDI) technology has been developed as an alternative technology to overcome the drawbacks of membrane technology.[9-12] However, in the CDI process, the ions adsorbed onto the electrode surface do not move back towards the bulk solution efficiently during desorption, and the ions remaining at the electrode interface are re-adsorbed onto the electrode surface to decrease the efficiency of the system consequentially. This problem has been solved by the introduction of membrane capacitive deionization (MCDI) process. This process uses an electrode and an ion-exchange membrane to increase the salt removal rate.[13,14] Commercially most common ion-exchange membranes and key components of MCDI systems such as those manufactured by Dupont (Nafion), Asahi Chemical (Aciplex) and Tokuyama (CMX) are considerably expensive products. High cost of the membrane increases the operation cost significantly. Inexpensive and non-fluorinated membranes have recently been explored as an alternative. However, it is known that such developed membranes do not have sufficient properties to be applicable for MCDI process yet.

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Alternating polyketones represent a new family of organic polymers that offers a combination of useful chemical and physical characteristics such as photo-degradability, biodegradability, chemical resistance, and ease of functionalization.[15,16]

In this study, polyketone was used for its strong chemical resistance and shock resistance abilities, which make it a favorable material for ion-exchange membranes.[17] Polyketone is an environment-friendly polymer material that is composed of carbon monoxide, ethylene and propylene. It also exhibits many desirable engineering thermoplastic properties similar to those of polybutylene terephthalate (PBT), polyoxymethylene (POM) and polycarbonate (PC), *etc*. Outstanding properties of polyketone make this polymer an interesting thermoplastic for engineering applications. It is used to manufacture interior and exterior materials, such as parts of fuel system in automotive industry, and numerous products in the electric and electronics industries. Several studies on aromatic polyketone membranes[18] and aromatic polyketone composite membranes[19] have recently been reported. However, there have been no detailed reports on the application of aliphatic polyketone to ion exchange membrane.

Radiation-induced graft copolymerization is an efficient and convenient technique which can be used to modify the chemical and physical properties of polymer materials.[20] This technique has attracted much interest because desirable properties such as higher quality of membrane, superior ion-exchange ability as well as facility of immobilization of bioactive materials were acquired upon its application to polymerization. The grafting process needs free radicals, *e.g.* those of peroxides, whose generation requires either of UV, plasma, radiation and chemicals. Radiation is one of the most effective methods on account of *in situ* generation of radical sites in the polymer matrix in a rapid and uniform fashion. Grafting by irradiation can be achieved by either of two methods: *mutual irradiation* and *pre-irradiation*. When organic polymers are subjected to ionizing radiation, trapped radicals form in huge amounts. Thereby, homopolymerization usually accompanies copolymerization as an undesirable side reaction. It is known that the addition of certain metal salts to the reaction mixture can suppress the formation of homopolymers, and mineral acids can enhance the grafting reaction. In this study, the grafting of SSS monomer onto polyketone was performed by mutual grafting process in the presence of Mohr's salt and H_2SO_4. Consequently, ion exchange groups have been attached to aliphatic polyketone chain effectively.

Effects of absorbed dose and monomer concentration on the degree of grafting were examined to find out the optimum conditions for the synthesis of the polyketone-*g*-styrene sodium sulfonate membrane. Each grafted membrane was characterized by Fourier transform infrared spectroscopy (FT-IR). Data for the ion-exchange capacity, water uptake ability, electrical conductivity and electrical resistance (ER) were collected to evaluate the eligibility of each membrane sample for MCDI process.

2. Experiments

2.1. Reagents and materials

Polyketone (PK, MW≤200,000) used in the study was purchased from HYOSUNG (Korea). Sodium styrene sulfonate (SSS) which was used as the monomer for grafting, ammonium iron(II) sulfate hexahydrate as Mohr's salt, zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$) and lithium chloride (LiCl) were obtained from Sigma Aldrich. Dimethyl sulfoxide (DMSO), which was the main solvent for grafting, was purchased from Samchun Chemical and used as received.

2.2. Methods

2.2.1. Preparation of polyketone membrane

A metallic salt solution was prepared by dissolving $ZnCl_2$, $CaCl_2$, and LiCl (22:30:10 wt%) in distilled water. Polyketone was dissolved in the metallic salt solution to prepare a 4 wt% polyketone solution. The polyketone solution was cast on a glass plate. Doctor blade was used to prepare a film with a thickness of 75 μm, and the film was immersed in distilled water subsequently. The membrane was washed with a 0.05% HCl solution at 60 °C to remove the metallic salts, and then dried in a vacuum oven at 50 °C for 24 h. An anion exchange membrane (polyvinylidene fluoride-*graft*-vinylbenzyl chloride: PVDF-*g*-VBC) which was reported in a previous study was used for CDI process.[21]

2.2.2. Synthesis of polyketone-*g*-sodium styrene sulfonate cation exchange membrane

Polyketone-*g*-sodium styrene sulfonate (PKs-*g*-SSS) ion-exchange membranes were synthesized at various conditions as shown in Table 1. For the grafting experiment, 50 mL of a sodium styrene sulfonate/DMSO solution was added first in a 100 mL glass bottle with a stopper, followed by Mohr's salt and H_2SO_4. A uniformly-cut PK membrane was put into the glass bottle which contains the monomer solution. The solution was purged with nitrogen for 30 min to remove any dissolved oxygen. Finally so-prepared glass bottles were closed by their stoppers and exposed to γ-ray irradiation at various doses (Table 1, Figure 1) at the dose rate of 10 kGy/h to initiate the grafting reactions.

After the grafting reaction, the grafted membranes were washed with methanol several times to remove any unreacted starting materials and homopolymers, and then dried in a vacuum oven at 50 °C for 12 h. The grafting degree of the copolymer was calculated by Eq. (1).

$$\text{Degree of grafting (\%)} = (W_g\text{-}W_0)/W_0\times 100 \quad (1)$$

Where W_0 is the weight of the membrane prior to grafting, and W_g is the weight of the dried membrane after graft copolymerization.

2.2.3. Chemical structure

FT-IR was used to monitor the radiolytic polymerization of SSS to polyketone. A Shimadzu FT-IR spectrometer was used for FT-IR spectrum analysis. The spectra were collected by ATR with 20 scans and a resolution of 4 cm^{-1} from 4000 to 600 cm^{-1}. X-ray photoelectron spectra (XPS) measurements were carried out using Multilab 2000 XPS system with a monochromatic Al Kα source (Multilab 2000 XPS, Thermo Scientific, America).

Table 1. Synthesis conditions of PKs-*g*-SSS copolymer by ^{60}Co γ-ray mutual irradiation-induced copolymerization

Trunk polymer (g)	Irradiation conditions				Graft copolymer		
	Total dose (kGy)	Dose rate (kGy/h)	Atmosphere	Temp. (°C)	Monomer concentration (wt%) SSS/DMSO	Mohr's salt (mg)	Sulfuric acid (mL)
PK	30	10	N_2	R.T	20	2.5	5.0
					25		
					30		
					35		
PK	40				20		
					25		
					30		
					35		
PK	50				20		
					25		
					30		
					35		
PK	60				20		
					25		
					30		
					35		
PK	70				20		
					25		
					30		
					35		

2.2.4. Water uptake

To measure the water uptake capacity of the PKs-*g*-SSS cation exchange membrane, the membrane was cut into 3 cm×3 cm size. The cut membrane was immersed in distilled water for 24 h to achieve sufficient swelling. Then, the water on the membrane surface was blotted, and the membrane was weighed. The water uptake of the PKs-*g*-SSS cation exchange membrane was calculated by Eq. (2).

$$\text{Water uptake (\%)} = (W_{wet}\text{-}W_{dry})/W_{dry}\times 100 \quad (2)$$

Where W_{wet} is the weight of the swollen membrane, and W_{dry} is the weight of the dried membrane.

2.2.5. Ion-exchange capacity

The ion-exchange capacity of the PKs-*g*-SSS cation exchange membrane was measured with titration method. The PKs-*g*-SSS cation exchange membrane was immersed in 1 M HCl solution for 24 h to convert SO_3Na form to SO_3H form, followed by washing with distilled water. The membrane was impregnated and stirred in 300 mL of 0.1 M NaOH standard solution for 24 h. In the equilibrated state, 50 mL of the supernatant was collected and placed in a 250 mL Erlenmeyer flask. Then, 2-3 drops of phenolphthalein solution were added, and a 0.1 M standard solution of HCl was used for the titration. Finally, the ion-exchange capacity of the PKs-*g*-SSS membrane was calculated by Eq. (3).

$$\text{IEC (meq/g)} = [(V_{NaOH}\times C_{NaOH})\text{-}(V_{HCl}\times C_{HCl}\times 6)]/W_{dry} \quad (3)$$

Where C_{NaOH} and C_{HCl} are the concentrations (mol/L) of the standard solution used in the titration. V_{NaOH} and V_{HCl} are the volumes (mL) of the solution, and W_{dry} is the weight (g) of the dried membrane.

2.2.6. Electrical resistance of the membrane

An LCR meter of model 3522-50 (HIOKI, Japan) was used to measure the electrical resistance of the PKs-*g*-SSS cation exchange membrane. The PKs-*g*-SSS cation exchange membrane was placed in 1 M NaCl standard solution for 24 h, and then cut into 1.5 cm×1.5 cm size. The cut membrane was fixed to each cell. Each cell was filled with 1 M NaCl standard electrolyte. The electrical resistance of PKs-*g*-SSS cation exchange membrane was measured by Eq. (4).

$$\text{ER } (\Omega\cdot\text{cm}^2) = (R_1\text{-}R_2)\times A \quad (4)$$

Where R_1 is the electrical resistance of the membrane in the electrochemical cell, and R_2 is the electrical resistance of the electrolyte after removal of the membrane. A is the effective area of the membrane used in the measurement (1 cm×1 cm in this study).

2.2.7. Application in membrane capacitive deionization (MCDI) process

The PKs-*g*-SSS cation exchange membranes were applied to the MCDI cells, in which their efficiencies to remove TDS (Total Dissolved Solids) were compared to those of CDI cells. Desalination tests were carried out in an electrochemical cell as shown in Figure 2. The electrochemical cell was composed of a nylon spacer, silicon barrier, cation exchange membrane, anion

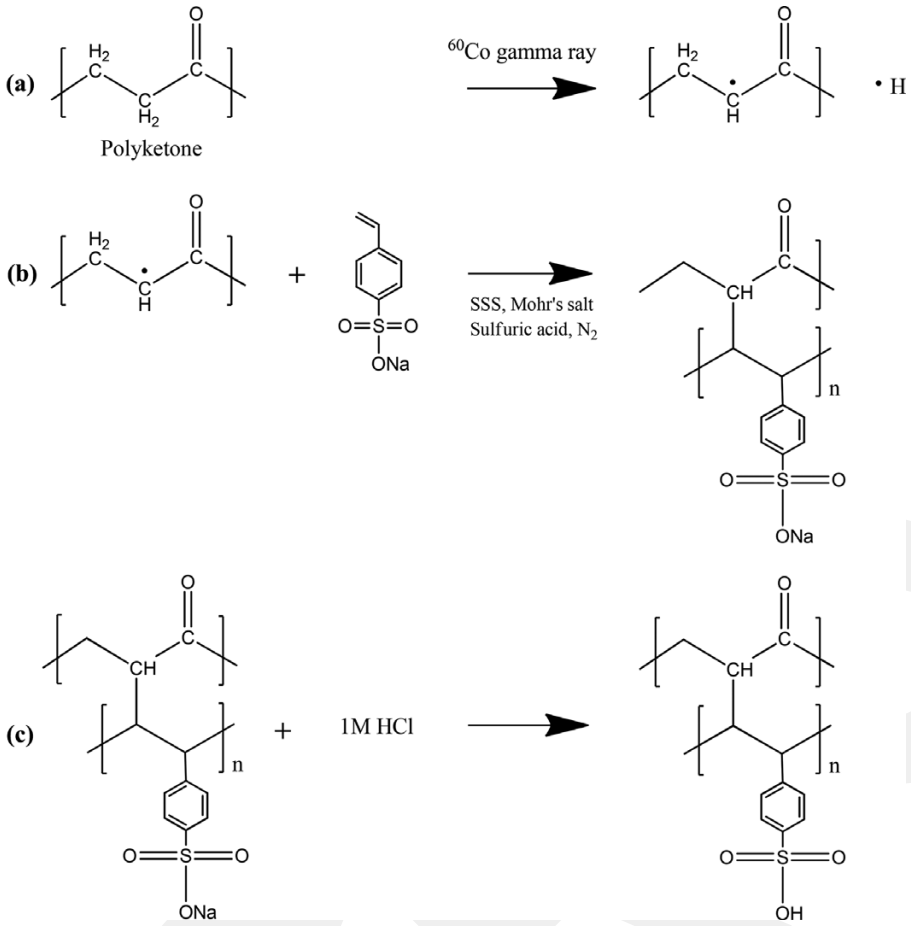

Figure 1. Reaction scheme of PKs-*g*-SSS by γ-ray irradiation.

exchange membrane cathode and anode which are both composed of carbon.[22] 250 mg/L solution of NaCl was supplied to the cell through a peristaltic pump at 20 mL/min rate. The anode was connected to the working electrode and the sensor electrode. The cathode was connected to the counter electrode and the reference electrode. A constant potential of +1.5 V for adsorption and a potential of -1.5 V for desorption were repeatedly applied to the MCDI cell for 120 s and 180 s, respectively, by using a potentiostat (WEIS 500, WonA Tech Corp.). The NaCl concentration was measured by using a TDS sensor, and the result was recorded by a midi Logger GL220 (Graph-Tech) at one second intervals. The salt removal rate (%) was calculated by Eq. (5).[23]

$$\text{Salt removal rate (\%)} = [(C_f\text{-}C_p)/C_f]\times 100 \quad (5)$$

Where C_f is the concentration of raw water, and C_p is the TDS value of the lowest concentration.

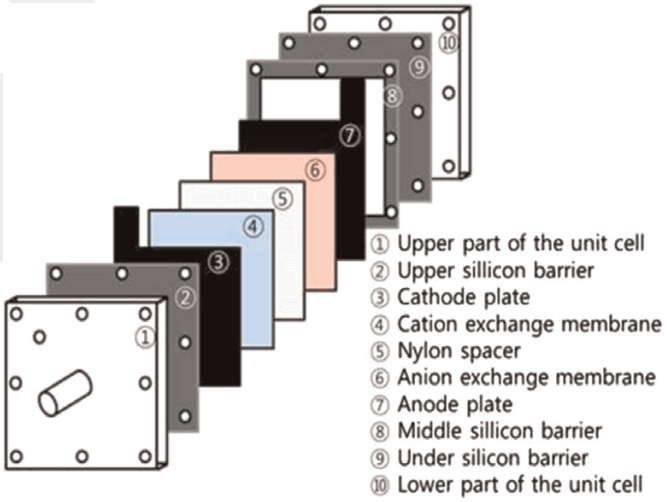

Figure 2. Schematic design of a MCDI unit cell.

3. Results and discussion

3.1. Chemical structure

Figure 3 shows FT-IR spectra of the PKs-*g*-SSS cation exchange membrane synthesized using ^{60}Co γ-ray radiation-induced grafting method and nascent PK. As shown in Figure 3, two asymmetric stretching peaks corresponding to O=S=O, which were not observed in the polyketone prior to irradiation, were observed at 1124 cm^{-1} and 1200 cm^{-1} for the PKs-*g*-SSS cation exchange membrane.[24] In addition, two stretching peaks corresponding to CH_2 were observed at 3000 cm^{-1} and 2912 cm^{-1} due to sodium styrene sulfonate, and the characteristic peak of the alkyl groups was also observed at 669 cm^{-1}. These results prove that the graft copolymerization of SSS with polyketone has been successful.[25]

XPS spectrum of PKs-*g*-SSS is shown in Figure 4. The XPS results exhibit two main peaks of S atoms at 229 (S, 2s orbital) and 167 eV (S, 2p^3 hybridization), respectively. Additionally, a

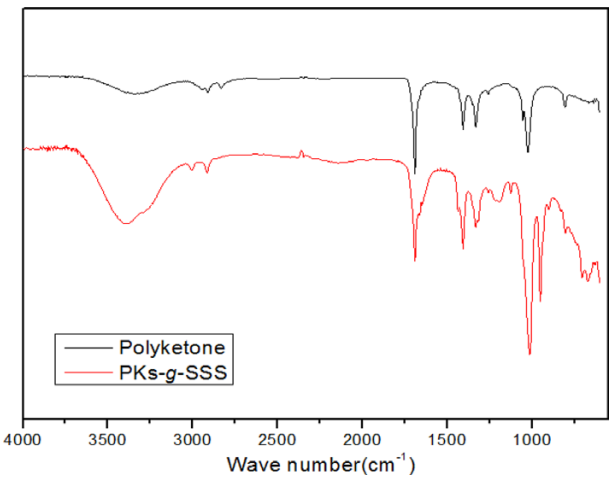

Figure 3. FT-IR spectra of polyketone membrane and PK-*g*-SSS membrane (DG=81.4%).

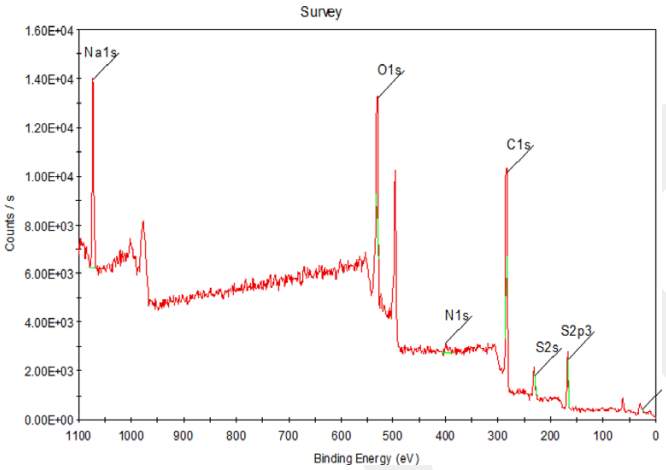

Figure 4. XPS spectrum of PKs-*g*-SSS membrane.

peak maximum centered at 1,072 eV confirms the presence of Na atoms which indicates that sodium styrene sulfate was successfully grafted on to polyketone.

3.2. Degree of grafting (DG)

The radiation grafting method has been considered as a promising method for the preparation of functional polymeric materials since the desired chemical and physical properties can be conveniently achieved by selecting the proper grafting materials and optimizing the grafting conditions. This technology has been widely used in polymer industry and biomedical industry to manufacture numerous products such as adsorbents and polymer electrolyte membranes.

The changes in the degree of grafting as a function of total radiation dose and monomer concentration are shown in Figure 5. When the radiation dose was raised from 30 kGy to 70 kGy, the degree of grafting increased in proportion. As the irradiation dose and the monomer concentration increases, the monomer availability for reactive grafting sites also grows, and this leads to higher degree of grafting. This result corresponds to the previous study.[26] Since graft copolymerization with pre-irradiation method is well known to rely heavily on the amount of trapped

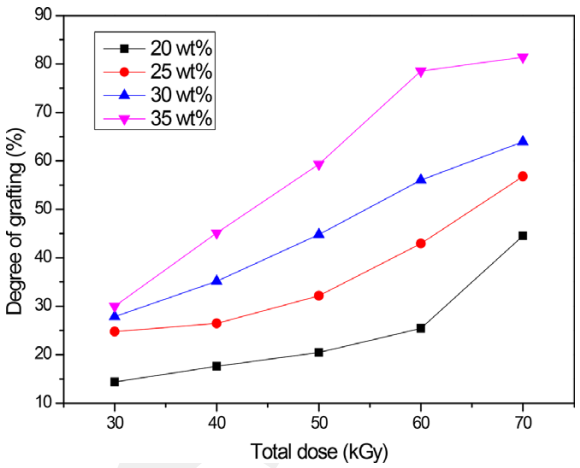

Figure 5. Effects of the total dose on the degree of grafting at different monomer concentrations.

radicals generated in the base polymer, the rising trend in DG can be attributed to the increase in the amount of efficient trapped radicals with the increase of radiation dose. This is usually accompanied by an increase in the initiation of radicals, which is followed by predominance of propagation and suppression of termination. The increase in DG with an SSS concentration at a particular dose is due to the increase in the available amount of monomers in the grafting sites synergized by acid addition.

3.3. Electrical resistance

The driving force for mass transfer in an ion-exchange membrane is the potential difference, and therefore, the low electrical resistance of an ion-exchange membrane is advantageous for MCDI systems. The electrical resistance may depend on the type of functional group in the ion-exchange membrane and the ion-exchange capacity as well. In addition, the electrical resistance may be affected by the steric conformation of the polymer. The high grafting degree is favorable in order for lower electrical resistance of a membrane, but on the other hand it may worsen its physical properties. Therefore, this counter-effect should be taken into account for developing an ion-exchange membrane with sufficient durability required for operation conditions of MCDI.

The electrical resistance of the ion-exchange membrane was measured as a function of the total irradiation dose (Figure 6). As the total irradiation dose increased, the electrical resistance tended to decrease. These results may be due to the presence of more ion exchange groups of well-stacked styrenes chain in the polyketone membrane as the degree of grafting increased. When the grafting rate was 60% or higher, its electrical resistance was lower than that of Nafion 117 (3.5 $\Omega \cdot cm^2$).

3.4. Ion-exchange capacity

The ion-exchange capacity, which is an important factor that affects the ion selectivity of an ion-exchange membrane, was measured with titration method. As shown in Figure 7, the ion-exchange capacity of the membrane tended to increase when the total irradiation dose increased. The maximum ion-exchange capacity of the PKs-*g*-SSS cation exchange mem-

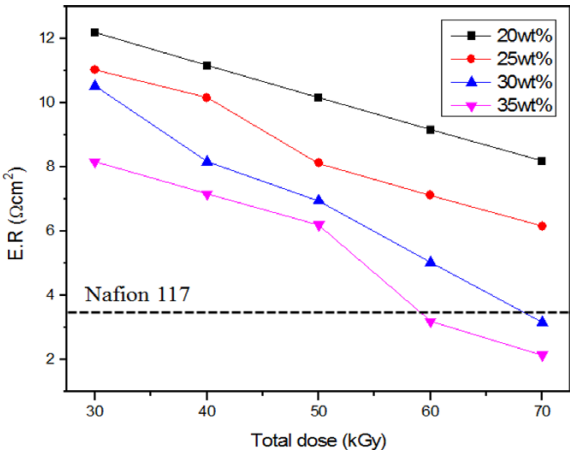

Figure 6. Electrical resistance of PKs-*g*-SSS cation exchange membranes at different monomer concentrations and total dose.

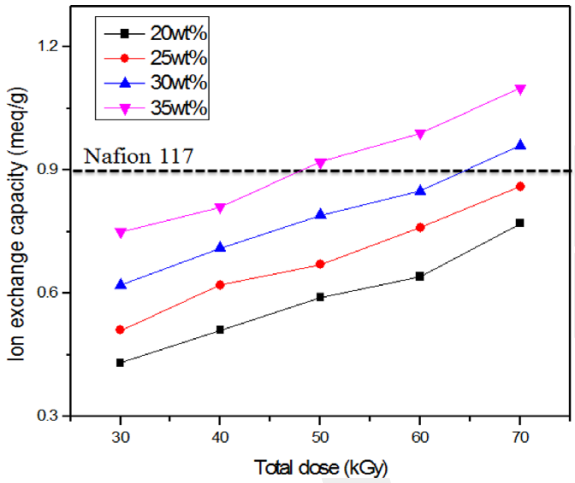

Figure 7. Effect of total does on ion exchange capacity of PKs-*g*-SSS cation exchange membrane.

brane was 1.10 meq/g. The high ion exchange capacity may be attributable to the increased number of sulfonic acid groups introduced on PK as the degree of grafting increased.

Good control of the total irradiation dose and the monomer concentration in the grafting reaction can lead to favorable changes in ion-exchange capacity and electrical resistance of membranes.

3.5. Water uptake

The ion-exchange membrane is swollen because a charged functional group is introduced in the polymer chain composing the membrane. Excessive water uptake of the membrane may decrease its dimensional stability, and also result in the formation of pinholes in the membrane. Therefore, it is important to control the irradiation dose and the monomer concentration to prepare membranes suitable for MCDI process. The water uptake of the prepared PKs-*g*-SSS exchange membrane was measured and the results are shown in Figure 8.

As shown in Figure 8, when the total irradiation dose was 70 kGy at 35 wt% SSS concentration, the water uptake of the cation exchange membrane was 34.2%, which is lower than

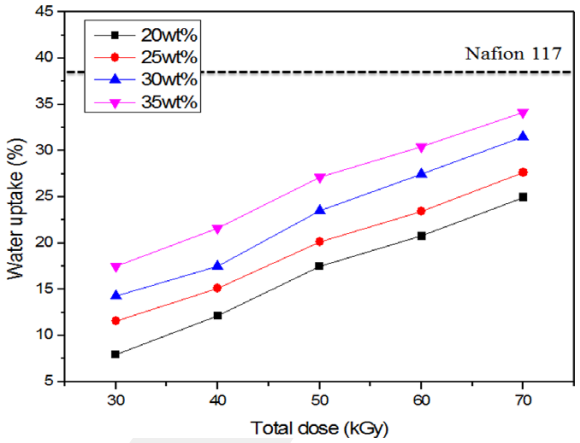

Figure 8. Effects of the total dose on the water uptake at different monomer concentrations.

38% of Nafion 117. This may imply that hydrophobicity or PKs-*g*-SSS copolymer is comparable to that of Nafion 117.

3.6. Application in the MCDI process

A PKs-*g*-SSS cation exchange membrane (DG=81.4%) with suitable ion-exchange capacity and electrical resistance was applied in the MCDI process. The process was compared to the CDI process which does not employ a membrane. The results are shown in Figures 9 and 10. The TDS adsorption concentration was evaluated when a 250 mg/L NaCl solution was supplied in the MCDI unit cell at a flow rate of 20 mL/min under implementation of +1.5 V. The TDS desorption concentration was determined under the same conditions when -1.5 V was applied to the system. During the implementation of +1.5 V in the adsorption-desorption cycles, the maximum TDS value just slightly varied from 1,081 mg/L to 1,083 mg/L. The minimum TDS value was 31.1 mg/L, which is much lower than 218.9 mg/L of raw water. The TDS removal rate of the PKs-*g*-SSS cation exchange membrane exhibited a constant pattern in several adsorption-desorption cycles. The salt removal rate which was calculated by Eq. (5) has been 87.6%.

For comparison, an application was carried out under the same condition for CDI process, which was not equipped with membranes. The results are shown in Figure 10. During adsorp-

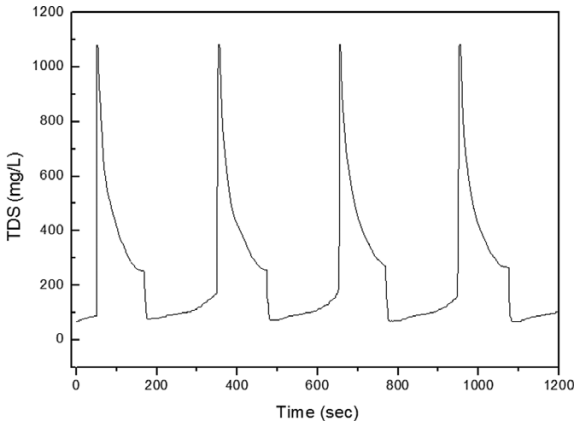

Figure 9. Amount of TDS removal in the MCDI unit process.

Table 2. Values of TDS and salt removal rates for MCDI and CDI

	1st Cycle		2nd Cycle		3rd Cycle		4th Cycle	
	MCDI	CDI	MCDI	CDI	MDCI	CDI	MCDI	CDI
Highest TDS value (mg/L)	1,081	531.1	1,082	528.1	1,082.6	514.6	1,083	503.7
Lowest TDS value (mg/L)	31.1	187.9	47.9	178	48	180.4	51.4	180.3
Salt removal rate (%)	87.6	24.8	80.8	28.8	80.8	27.8	79.4	27.9

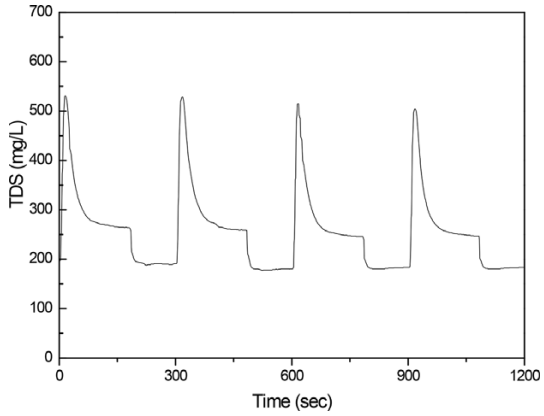

Figure 10. Amount of TDS removal in the CDI unit process.

tion-desorption cycle of CDI, the highest TDS value tended to decrease when the cycle was repeatedly carried out. These results correspond to Jeong's findings.[21]

Salt removal rate of CDI was lower than that of MCDI process in all measurements as shown in Table 2. The difference in the salt removal rate between MCDI and CDI was large. These results revealed that the introduction of the prepared PKs-*g*-SSS cation exchange membrane to CDI system increased the salt removal rate considerably.

4. Conclusions

The PKs-*g*-SSS cation exchange membrane was prepared by radiation-induced graft polymerization of SSS onto the polyketone membrane in the presence of Mohr's salt and H_2SO_4. Graft copolymerization was confirmed through FT-IR and XPS characteristic peaks associated with sodium styrene sulfonate. The properties, such as the degree of grafting, water uptake and IEC were also determined. As the total radiation dose and the monomer concentration increased, the degree of grafting increased proportionally from 14.4% to 81.4%. The ion-exchange capacity of the PKs-*g*-SSS cation exchange membrane was between 0.43 meq/g-1.1 meq/g. The ion exchange capacity increased as the degree of grafting increased. When the degree of grafting was 60% or higher, the ion exchange capacity was higher than that of Nafion 117 (0.9 meq/g), because the number of hydrophilic functional groups increased in proportion to the degree of grafting. The water uptake of the prepared PKs-*g*-SSS cation exchange membrane has values ranging from 7.9% to 34.2%, which is lower than 38% of Nafion 117. This may imply that hydrophobicity of PKs-*g*-SSS is comparable to that of Nafion 117. The electrical resistance decreased as the degree of grafting increased. Membranes which were prepared with 35 wt% monomer and irradiation dose of 60 kGy or higher outperformed Nafion 117 by as low as 2.2 $\Omega \cdot cm^2$. This may be attributed to well-stacked styrenes of SSS chain. When the prepared cation exchange membrane was applied to the MCDI process, its salt removal rate in the first cycle was 87.6%. On the other hand, the salt removal rate in the CDI process under the same conditions was 28.8%.

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