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Synthesis of Polyketone-*g*-Vinylbenzyl Chloride Anion Exchange Membrane *via* Irradiation and Its Properties

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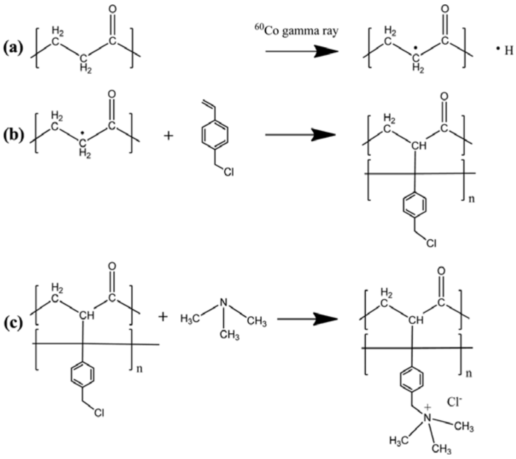
Abstract: A novel anion exchange membrane composed of aminated polyketone-*g*-vinylbenzyl chloride was synthesized *via* ^{60}Co γ-ray irradiation grafting technique. Total irradiation dose and concentration of monomers were set as variables to determine degree of grafting. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy equipped with energy dispersive X-ray spectrometer (SEM-EDS) were used to characterize the grafted membranes. Water uptake (WU) and swelling ratio (SR) were measured with a gravimetric method. A titration method was used to detect ion exchange capacity (IEC), whereas electrical resistance (ER) and ion conductivity (IC) were measured with a LCR meter. Our method has boosted the degree of grafting up to 97.6% from 3.7% as total irradiation dose and monomer concentration have been increased. WU and SR were in the ranges 1.5%-35.6% and 0.35%-20.9%, respectively. Also, IEC has taken values ranging between 0.2 and 1.19 meq/g. IC has varied within the range 0.01-0.3 S cm^{-1}, and it has shown a rising trend as IEC increased. In this study, the optimum synthesis conditions have been 70 kGy of total irradiation dose and 50wt% of monomers. The membrane synthesized here is potentially superior to Nafion membrane in terms of several properties.



Keywords: polyketone, anion exchange membrane, irradiation.

1. Introduction

Membranes have become a well-established tool for air cleaning and water treatment in addition to its widespread usage in energy, environment, biopharmaceutical, semiconductor industries. Therefore, membrane technology has received a vast amount of attention in recent years. In the present paper we would like to draw the reader's attention chiefly to the ion-exchange membranes. One characteristic feature of ion-exchange membranes is their ability to separate ions with a high selectivity. Thereby, they are used for various processes such as fuel cells as polymer electrode membrane (PEM),[1] continuous deionization for rare metal recovery,[2] separation,[3] and seawater desalination.[4,5]

Ion exchange membranes can be classified into three types: fluorinated membranes, hydrocarbon membranes and complex membranes. Fluorinated membranes, such as Nafion, appear to be more popular among aforementioned membrane types. Considering the fact that fluorinated membranes are considerably more expensive and inappropriate particularly for functionalization processes, it is required to develop a state-of-the-art membrane that is able to cure mentioned shortcomings.

In conventional ion-exchange membrane studies, Lee *et al.*[6] constructed partially fluorinated ion-exchange membranes by grafting vinylbenzyl chloride (VBC). They used irradiation method to synthesize polymer films which is followed by amination reaction. Although the performance of the membranes was poor, their production was rather straightforward. Fei *et al.*[7] also synthesized partially fluorinated membranes *via* grafting reaction and measured their performance, which in turn was exceptionally high for fuel cell applications. However, the obtained membranes were suffered from economical issue, which was hindering the implementation of fuel cells. Carbonated membranes are the low price alternatives of Nafion. While good performance of the carbonated membranes are known well, significant problems like high water uptake and high swelling ratio restrict their use substantially.

Thus, in order to improve such insufficient properties, a lot of research have been conducted on engineering plastics such as polybenzimidazole (PBI), polyamide (PA), polyethersulfone

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(PES), poly(etheretherketone) (PEEK), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The surface of these polymers has been chemically modified to gain them superior physical properties.[8,9]

Ion exchange membranes were prepared through sulfonation of PEEK (sPEEK), and tested as polymer electrode membrane (PEM) in fuel cells.[10] The resulting membranes exhibited excellent electrical and physical properties yet yielded a brittle structure. Kang's group[11] has reported that sulfonated PES membranes have outstanding thermal resistance, and are comparatively less brittle, albeit much less durable, than sPEEK membranes. Moreover, Tongwen *et al.* used PPO, which has highly stable molecular structure, as matrix and synthesized SPPO and APPO ion exchange membranes with chemical methods.[12,13]

Polyketone is recently used in automobile industry since it has excellent physical, chemical, and thermal properties.[14,15] Multi-ring structured polyketone copolymer has been reported. It has been sulfonated by Yoon *et al.* to be used as electrolyte membrane in fuel cells.[16] The recent work has produced promising results, however, these membranes require complicated synthesis steps and display steric hindrance due to their complex structures. Thus, to solve these difficulties arising from synthesis, aliphatic polyketone membranes are focused on. Aliphatic polyketones are composed of ethylene and ketone so that, to the best of our knowledge, there are no detailed reports on the aliphatic polyketone membranes since it is hard to functionalize the surface of polyketone chemically due to its stability.

In this study, we synthesized aminated PK-*g*-VBC ion exchange membranes *via* γ-irradiation at room temperature based on our previous experiences. As a result, we evaluated the optimum synthesis conditions based on the results mentioned.

Morphology of the synthesized membranes was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Ion exchange capacity was measured by acid-base titration. For measuring water uptake and swelling ratio gravimetric method was employed. LCR meter was used to measure electrical resistance.

2. Experiments

2.1. Materials

Polyketone (M_w≧200,000) composed of ethyl carbonyl sequence used in the study was obtained from HYOSUNG (Korea). Vinylbenzyl chloride (VBC, assay≧96%) monomer was purchased from Acros. Chloroform (assay≧96%) solvent and trimethylamine (TMA, assay 4.5%) solution for amination reactions were purchased from Sigma Aldrich. Metal salts such as lithium chloride (LiCl), zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$) were obtained from SAMCHUN (Korea).

2.2. Preparation of polyketone membrane

A metallic salt solution was prepared by dissolving $ZnCl_2$, $CaCl_2$, LiCl (22:30:10 wt%) in distilled water. Polyketone was dissolved in 300 mL of the metallic salt solution to prepare a 4 wt% polyketone solution. The polymer solution was then cast on a glass substrate at a thickness of 50 μm using a doctor blade. The membrane was washed with a 0.05% HCl solution at 60 °C repeatedly to remove the metallic salts. Finally it was dried in a vacuum oven at 50 °C for 24 h.

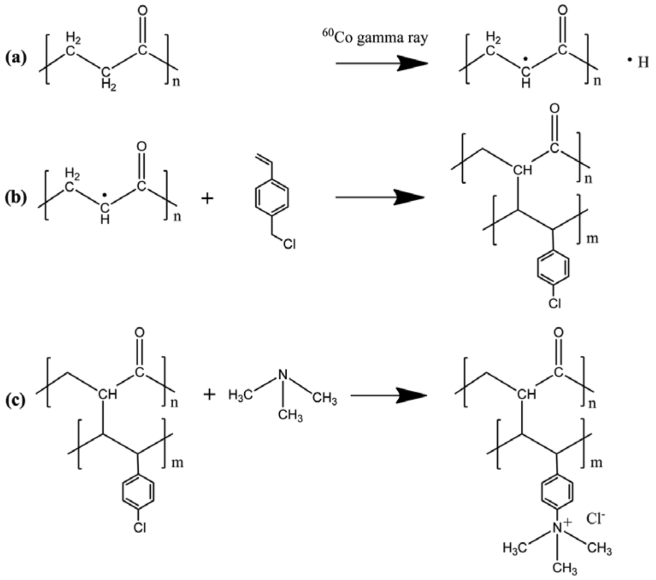


Figure 1. Reaction scheme for the synthesis of PK-*g*-VBC by ^{60}Co γ-ray mutual irradiation-induced copolymerization. (a) irradiation on PK, (b) graft polymerization for PK-*g*-VBC copolymer, and (c) amination reaction for aminated PK-*g*-VBC.

2.3. Graft copolymerization of PK-*g*-VBC

Membranes of PK-*g*-VBC were synthesized at various conditions. The mechanism of the synthesis was depicted in Figure 1. For the grafting experiment, polyketone membranes were cut into 15 cm × 10 cm size, and these pieces were immersed in 100 mL glass bottles containing 50 mL VBC/chloroform mixtures.

VBC concentration was varied from 10 wt% to 70 wt%. The solution was then purged by nitrogen for 30 min to remove the oxygen. Each glass bottle containing the solution and the membrane was exposed to ^{60}Co γ-ray irradiation at various irradiation doses from 30 kGy to 90 kGy to synthesize PK-*g*-VBC copolymers *in situ*.

The synthesized copolymers were washed with toluene and methanol in an ultrasonic bath to remove unreacted monomers, homopolymers and any other contents. After washing, the membranes were dried in a vacuum oven at 50 °C for 12 h. The grafting degree of the copolymers was calculated using below equation (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 the grafting, and W_g is the weight of the dried membrane after graft copolymerization.

2.4. Quaternization of PK-*g*-VBC copolymer

The graft copolymer membrane was cut into pieces of uniform size and subsequently immersed in a 45 mL of 45% TMA solution in three-neck flask equipped with mechanical stirrer, condenser and nitrogen purge. The solution was stirred for 18 h under nitrogen atmosphere thereafter. Figure 1 shows the mechanism of the amination reaction. The membrane was washed with DI water several times to remove unreacted TMA and then dried in a vacuum oven at 50 °C for 8 h.

2.5. FTIR spectroscopy

FTIR was used to characterize the structure of the PK-*g*-VBC anion exchange membrane. A Shimadzu FTIR spectrometer was used for FTIR spectrum analysis. The spectra were obtained by attenuated total reflectance (ATR) with a scan number of 20 and a resolution of 4 cm^{-1}. Wavelength varied from 4000 to 600 cm^{-1}.

2.6. SEM-EDS analysis

SEM-EDS (JEOKL Instrument, JSM-6700, Thermo NORAN) was used to monitor the morphology and elemental composition of the PK-*g*-VBC membrane and the aminated PK-*g*-VBC membrane. The accelerating voltage was set to 5 kV, and the sample was coated with platinum in advance by using an ion sputter.

2.7. Water uptake (WU) and swelling ratio

To measure the water uptake of the aminated PK-*g*-VBC anion exchange membrane, it was cut into 3 cm×3 cm sized piece and weighed. This piece was immersed in DI water for 24 h to achieve sufficient swelling. Water on the surface of the piece was blotted, and it was weighed as is. Water uptake (WU) of the aminated PK-*g*-VBC membrane was calculated using Eq. (2).

$$\text{WU (\%)} = (W_{wet}\text{-}W_{dry})/W_{dry}\times 100 \tag{2}$$

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

Furthermore, the cross-sectional area of the cut membrane was measured, and then, the swelling rate of the membrane was calculated using Eq. (3).

$$\text{Swelling ratio (\%)} = (A_{wet}\text{-}A_{dry})/A_{dry}\times 100 \tag{3}$$

where A_{wet} and A_{dry} are the areas of the membrane before and after swelling, respectively.

2.8. Ion exchange capacity (IEC)

The ion exchange capacity of the aminated PK-*g*-VBC membrane was measured by acid-base titration method. The membrane was cut into 3 cm × 3 cm piece and immersed in 300 mL of 1 M NaOH solution for 1 day. It was then washed by DI water. Subsequently, it was immersed in 50 mL of 1 M HCl solution for 24 h. 10 mL of the HCl solution was separated and titrated by a 0.1 M NaOH standard solution after adding a drop of phenolphthalein as indicator. Eq. (4) was used to calculate the ion exchange capacity of the membrane.

$$\text{IEC (meq/g)} = [\{(V_{HCl}\times C_{HCl})\text{-}(V_{NaOH}\times C_{NaOH})\times 6\}]/W_{dry} \tag{4}$$

where V_{HCl} and V_{NaOH} are the volumes of HCl and NaOH, respectively. C_{HCl} and C_{NaOH} are the concentrations of HCl and NaOH. W_{dry} is the weight of the dry membrane.

2.9. Electrical resistance (ER)

A LCR meter (3522 LCR HiTESTER-50, Japan) was used to measure the electrical resistance of the aminated PKs-*g*-VBC anion exchange membrane. A 1.5 cm×1.5 cm piece was cut from it, and then placed in 1 M NaCl standard solution for 24 h. The membrane piece was fixed to a cell. The cell was filled with 1 M NaCl standard electrolyte. The electrical resistance of PKs-*g*-VBC cation exchange membrane was measured using the following equation:

$$\text{ER } (\Omega\cdot cm^2) = (R_1\text{-}R_2)\times A \tag{5}$$

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 (cm^2). Ion conductivity (σ) of the membrane was calculated by Eq. (6).

$$\sigma\text{(S/cm)} = L/(\text{ER}\times A) \tag{6}$$

where ER is the electrical resistance (Ω) of the membrane and L is the thickness (cm) of the membrane.

3. Results and discussion

3.1. Degree of grafting (DG)

Figure 2 shows the effects of the VBC concentration and total irradiation dose on the degree of grafting of the PK-*g*-VBC copolymer membrane. As shown in there, the degree of grafting was related to the concentration of VBC and total irradiation dose. The degree of grafting has dramatically increased as total irradiation dose and concentration of VBC have been increased, but the effect of concentration of VBC was insignificant to the degree of grafting over the total irradiation dose of 70 kGy, which may be due to the Trommsdorff effect.[17] This effect interrupts

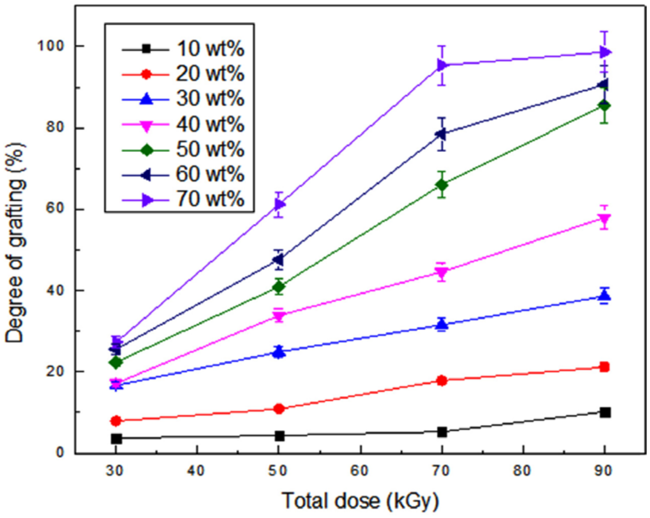


Figure 2. Effect of total irradiation dose on the degree of grafting at different monomer concentrations.

polymerization due to an increase in the viscosity of solution when radiation is applied at high monomer concentrations.[18] The increase in total dose of irradiation did not cause a significant but rather a small increment in the degree of grafting when the monomer concentration of VBC is below 50 wt%. For concentrations of VBC over 40 wt%, the degree of grafting went up dramatically as the total dose of irradiation varied from 30 kGy to 70 kGy. The maximum degree of grafting was 98% when the VBC monomer concentration was 70 wt%. From these results, it has been understood that the degree of grafting should be within 80%-110% range for preserving the properties of trunk polymer (polyketone). In this study, the optimum grafting conditions have been proved as more than 50 wt% of VBC concentration at 90 kGy of total dose of irradiation.

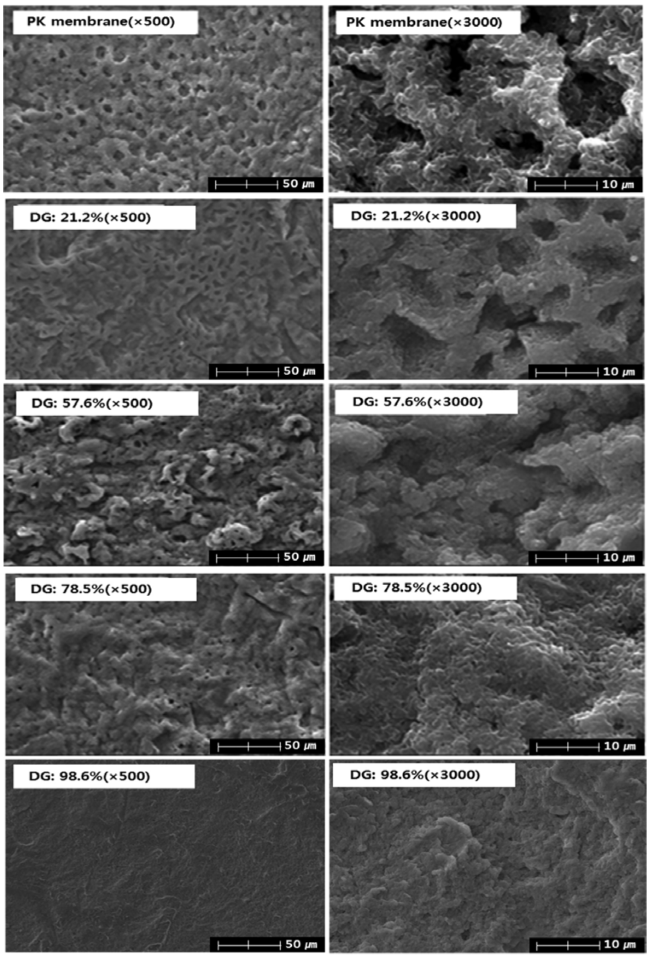


Figure 3. SEM images of polyketone and PK-*g*-VBC copolymers.

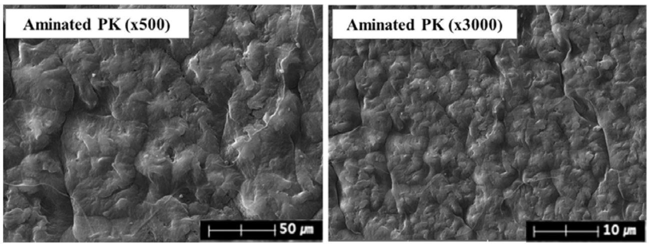


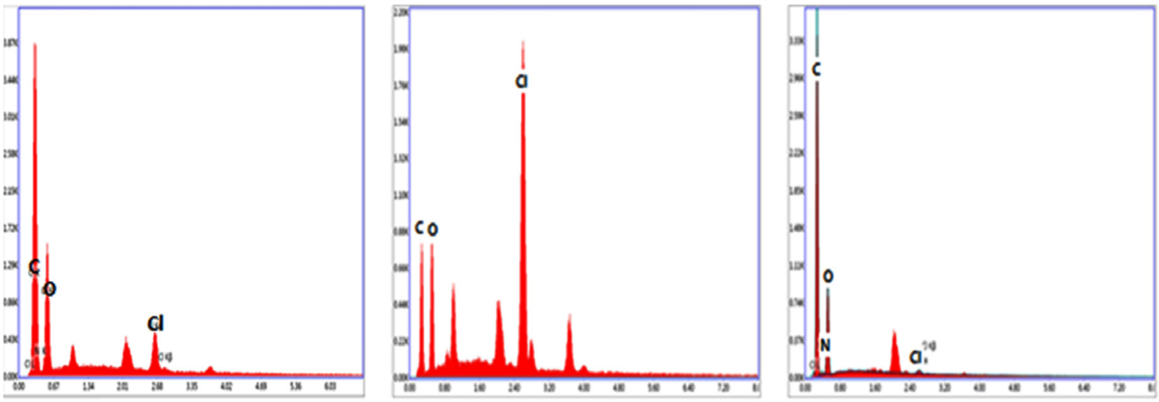
Figure 4. SEM images of aminated PK-*g*-VBC membrane.

3.2. SEM-EDS analysis

Grafting of polymers is a demonstrated surface-modification approach.[19,20] Figures 3 and 4 show the morphology of PK-*g*-VBC copolymer membranes prepared *via* ^{60}Co γ-ray irradiation and aminated PK-*g*-VBC membrane. An aminated membrane, which showed 98.6% degree of grafting, was selected. Surfaces of polyketone membrane and PK-*g*-VBC membranes which have 21.2%, 57.6%, 78.5%, 98.6% degrees of grafting, have been viewed with SEM instrument. As shown in Figure 3, nascent polyketone membrane possessed relatively uniform structure and pore apertures. However pore apertures have been observed to have smaller size as the degree of grafting increased. While the size of pore apertures appeared around 10 μm in nascent membrane, those seem to have shrunk or filled as irradiation and amination progressed (average pore sizes were measured with image J (N>30)).

Table 1. Composition of polyketone, PK-*g*-VBC copolymer (DG: 70%), and aminated PK-*g*-VBC ion-exchange membranes (DG: 70%)

	Elements (at%)			
	C	N	O	Cl
Polyketone	76.8	0.6	21.6	1.02
PK-*g*-VBC copolymer	64.8	0.0	19.5	15.7
PK-*g*-VBC membrane	71.2	4.1	24.3	0.4



(a) PK membrane (b) PK−g−VBC membrane (c) Aminated PK−g−VBC membrane

Figure 5. EDS Spectra of (a) polyketone membrane, (b) PK-*g*-VBC copolymer membrane (DG: 70%), and (c) aminated PK-*g*-VBC ion-exchange membrane (DG: 70%).

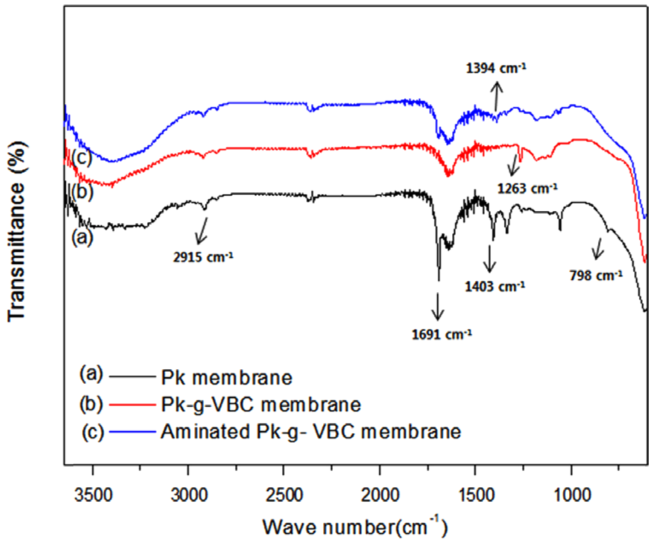


Figure 6. FTIR spectra of (a) PK membrane, (b) PK-*g*-VBC membrane (DG: 70%), and (c) aminated PK-*g*-VBC membrane (DG: 70%).

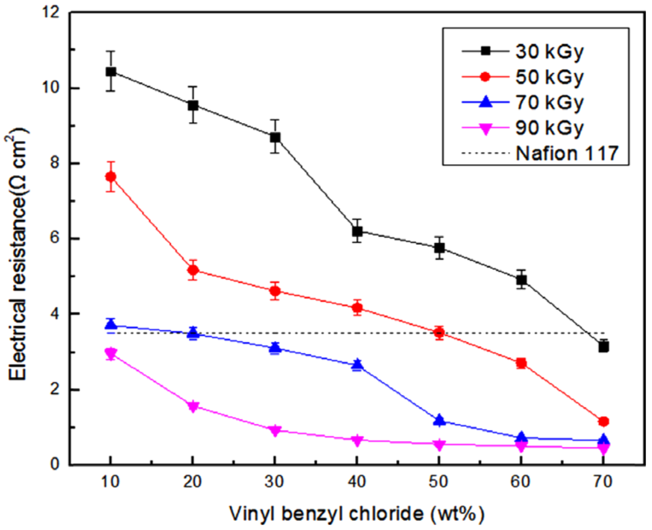


Figure 7. Effect of VBC monomer concentration on electrical resistance at various total doses.

These results corresponds well to Kwak's report which states that molecular structures with more compact micropores form due to growing steric hindrance as the degree of grafting increases.[21]

Figure 5 and Table 1 show the results of EDS analyses for nascent polyketone membrane, PK-*g*-VBC copolymer membrane (DG: 70%) and aminated PK-*g*-VBC membrane (DG: 70%). While PK-*g*-VBC copolymer membrane has shown 15.7% of Cl content, which has not been observed in nascent polyketone membrane, the aminated PK-*g*-VBC membrane has shown less Cl content and more N content. From these results, we have confirmed that synthesis of PK-*g*-VBC anion exchange membrane by ^{60}Co-γ radiation induced grafting method has been successful in terms of structure and elemental composition.

3.3. FTIR spectroscopy

FTIR spectra of the nascent polyketone membrane, PK-*g*-VBC copolymer membrane (DG: 70%) and aminated PK-*g*-VBC membrane (DG: 70%) are shown in Figure 6. A CH_2 stretching vibration peak at 2915 cm^{-1} and a strong peak corresponding to C=O at 1691 cm^{-1} have been observed in the polyketone membrane prior to irradiation. Also, peaks at 1403 cm^{-1} and 798 cm^{-1} due to deformation of CH_2 have been observed as shown in Figure 6(a). On the other hand, Figure 6(b) is a spectrum of PK-*g*-VBC copolymer membrane. A new peak that did not appear in the nascent polyketone membrane has showed up at 1263 cm^{-1} which corresponds to C-Cl wagging band. This peak is a crucial evidence for confirming the expected structure of PK-*g*-VBC copolymer. The aminated PK-*g*-VBC membrane has showed an additional peak at 1394 cm^{-1} which can be attributed to the deformation of N-CH_3. These results indicate that the aminated PK-*g*-VBC membrane was successfully synthesized.[22]

3.4. Electrical resistance

The driving force for mass transfer in the ion exchange membrane is the potential difference hence lower electrical resistance is favored for higher efficiency in ion exchange membranes. Therefore, the electrical resistance should be controlled to be lower as long as it does not affect the selectivity of an ion exchange membrane. Figure 7 shows that electrical resistance of the synthesized membranes tends to be lower as concentration of VBC and total dose increase. Also, in the case of the membrane synthesized with 30 kGy dose, the electrical resistance showed a similar value to that of Nafion when the monomer concentration was 70%. The membrane prepared with 50 kGy dose had lower electrical resistance than that of Nafion when concentration of VBC is over 50 wt%. The membranes prepared with doses of 70 kGy and 90 kGy both showed lower values than that of Nafion within the concentration range of VBC varying from 10 wt% to 70 wt%. As confirmed with FTIR and SEM-EDS analyses, these results correspond to the Shin's report[23] which argued that the electrical resistance decreases with corresponding increase in ion selectivity as amination rate increases.

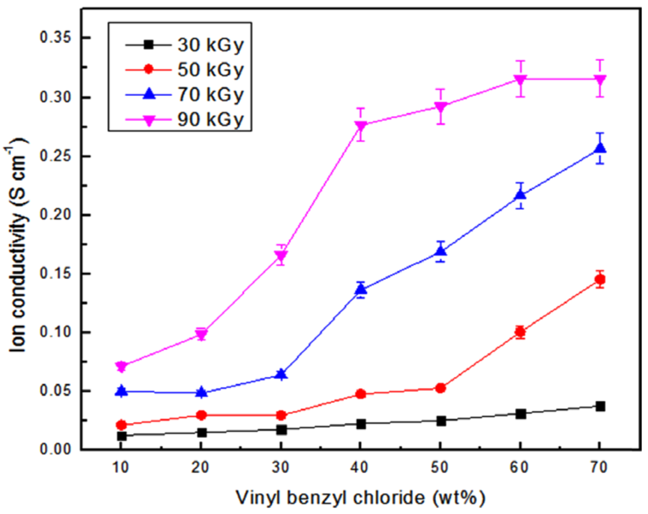


Figure 8. Effect of VBC monomer concentration on ion conductivity at various total doses.

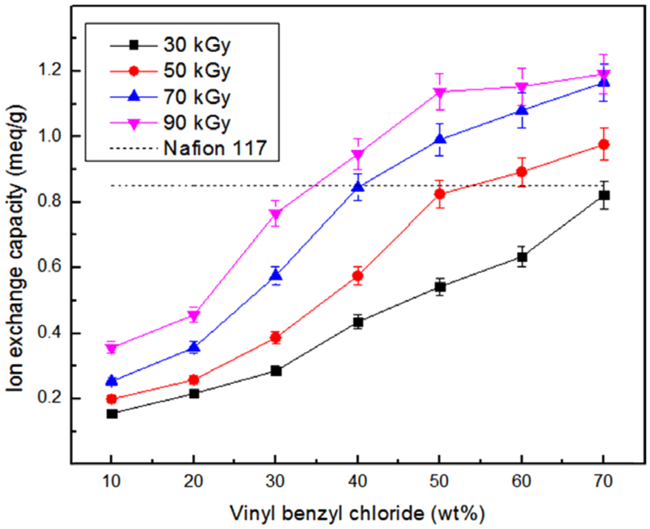


Figure 9. Effect of VBC monomer concentration on ion exchange capacity at various total doses.

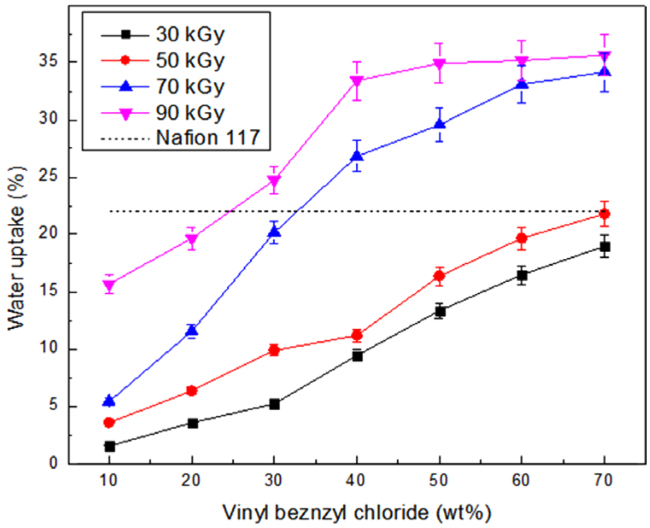


Figure 10. Effect of VBC monomer concentration on water uptake at various total doses.

3.5. Ion conductivity (IC)

Ion conductivity of PK-*g*-VBC according to VBC monomer concentration and total irradiation dose is shown in Figure 8. Differently from electrical resistance, ion conductivity of aminated PK-*g*-VBC membrane increased as VBC concentration and total irradiation dose increased. The maximum value of ion conductivity was 0.31 S/cm when the degree of grafting was 98%. These results may suggest that the ion selectivity of aminated PK-*g*-VBC membrane might be superior to that of Nafion 117 membrane (0.078 S/cm).

3.6. Ion exchange capacity (IEC)

Ion exchange capacity of the aminated PK-*g*-VBC membrane was measured with a titration method. Figure 9 plots the relationship of IEC with VBC concentration and total irradiation dose. Ion exchange capacity of the membrane tended to grow when VBC concentration and total irradiation dose have been increased. The membranes prepared with more than 40 wt% VBC concentration have been able to perform similar to Nafion. Even if they were induced by 30 kGy and 50 kGy of irradiations, better performance has been possible when VBC concentration was over 40 wt% and total irradiation dose was 70 kGy or more. In the case of membranes prepared with 70 wt% VBC concentration and 90 kGy irradiation, ion exchange capacity has reached a maximum of 1.2 meq/g. From these results, VBC concentration should be more than 50 wt% when the total irradiation dose is less than or equal to 50 kGy. In addition, more than 40 wt% VBC concentration is required to achieve outstanding IEC values when total irradiation dose is greater than or equal to 70 kGy. The successive correlation between lower total irradiation dose, less degree of grafting, less amination and lower ion exchange capacity complies well with previous reports.[21,22]

3.7. Water uptake and swelling ratio

Water uptake and swelling ratio are important factors because excessive water uptake of a membrane can worsen its dimensional stability, and also cause a decrease in ion selectivity of the membrane.[24] Figsures 10, 11 plot the change in water uptake and swelling ratio of the synthesized membrane against varying VBC concentration. When the total dose of irradiation has been 30 kGy and 50 kGy, regardless of the VBC concentration, WU has been lower than that of Nafion. At 70 kGy total irradiation dose, WU has been higher than that of Nafion, but it has been same or lower at and below 30 wt% of VBC concentration. WU has been higher at 90 kGy dose when the VBC concentration was more than 20 wt%. The maximum WU value has been 35%. Under 50 kGy dose conditions, degree of grafting has occurred insufficient for WU. Consequently, the hydrophilic amine groups have not been fully introduced into the membrane. In the same vein, higher total irradiation doses cause higher WU which is directly related to the abundance of hydrophilic amine groups in the structure. Although the maximum WU is higher than that of Nafion membrane, as long as the maximum WU is 35%, there would be no significant drawback in the practical use of this membrane.

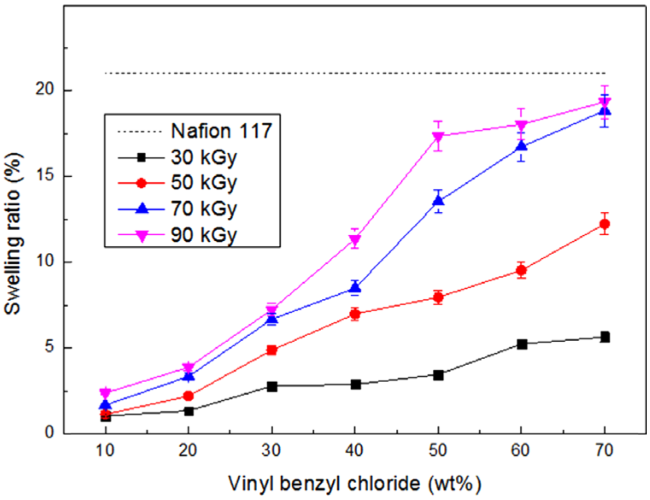


Figure 11. Effect of VBC monomer concentration on swelling ratio at various total doses.

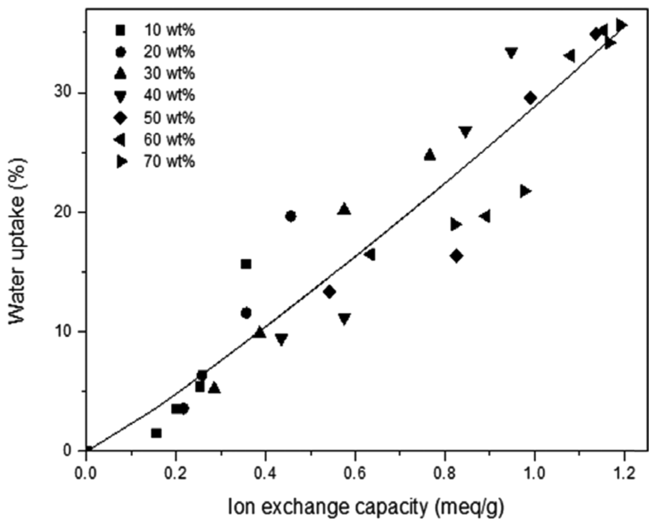


Figure 12. Relationship between ion exchange capacity and water uptake.

On the other hand, swelling ratio is a key parameter for dimensional stability. As shown in Figure 11, swelling ratio of aminated PK-*g*-VBC membrane has been related to the VBC concentration at all total irradiation dose ranges. Except at 30 kGy, the swelling ratio of the membrane increased gradually with the increase in the VBC concentration. As discussed for WU phenomenon, swelling ratio is also related to the degree of grafting followed which determines the amount of hydrophilic amine groups, consequently. The maximum swelling ratio of the membrane has been less than that of Nafion 117 membrane, indicating that the membrane synthesized in this study is suitable for practical processes.

Relationship between ion exchange capacity (IEC) and water uptake (WU) is plotted in Figure 12 WU tended to increase as IEC increased. Higher degree of grafting is a reason for the formation of more sites which amine groups can attach to.[25,26] As a result, any increase in hydrophilicity can be attributed to the increasing number of amine groups introduced onto PKs in greater numbers as the degree of grafting is increased. As discussed in previous sections, these findings indicate that both ion exchange capacity and swelling ratio are related on the hydrophilicity of ion exchange membrane.

4. Conclusions

Anion exchange membranes of aminated PK-*g*-VBC were successfully synthesized with ^{60}Co γ-ray irradiation, followed by solution casting. FTIR and SEM-EDS were used to identify amine groups along the modified PK. Our findings showed that applied total irradiation dose is more effective than monomer (VBC) concentration for achieving higher degree of grafting. Electrical resistance has tended to decrease as both or either of degree of grafting and monomer concentration have increased. Ion conductivity and ion exchange capacity of the aminated PK-*g*-VBC membrane were comparable to those of Nafion 117 membrane. Water uptake and swelling ratio of the membrane were adoptable for practical processes.

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