

Surface modification of highly gas permeable membrane by nanosheets composed of ionic-functionalized polyimides

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Novel diamine monomers containing imidazolium or pyridinium groups were synthesized to prepare ionic polyimides, which were expected to have the affinity with CO₂ gases. Then, the nanosheets of these polyimides, the thickness of which were 50 - 90 nm, were fabricated by spin coating method. Furthermore, the nanosheet-coating of polydimethylsiloxane graft copolyimide membranes was carried out, and the effect of surface structure on the gas permselectivity was investigated. As a result, the nanosheet coating on the highly gas permeable membrane was effective to improve the selectivity of CO₂/N₂ and O₂/N₂ with maintaining the high gas permeability to some extent. In addition, it was found that the gas separation properties depended on the side chain structures of polyimides containing ionic groups.

1. INTRODUCTION

Recently, the climate change by the increase of carbon dioxide (CO₂) is becoming the environmental issues in the world. Then, the development of the technology for CO₂ capture and storage (CCS) has gathered much attention. The separation membrane technology has advantages in the high-energy efficiency, the low capital investments and the ease of operation [1]. Therefore, several polymers, such as poly(dimethylsiloxane) (PDMS), tetrafluoroethylene and poly(trimethylvinylsilane), have been developed as materials for CO₂ separation membranes [2]. Especially, PDMS is a well-known polymer, which shows the high gas permeability and stability. In these years, we have investigated the highly gas permeable membranes based on PDMS-graft copolymers [3-6]. Although the obtained polymer consisted of a long PDMS segment in every repeating unit, the tough self-standing membrane could be prepared by a solvent casting method. The CO₂ permeability coefficients of PDMS-graft copolyimides (PIS_m, see Fig. 1) were over 10⁷ Barrer, and the selectivity of CO₂/N₂ was almost constant at 11 [6].

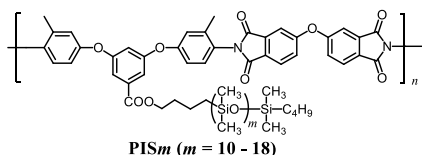


Fig. 1 Chemical structure of PIS_m.

On the other hand, as a material which had affinity with CO₂, ionic liquids were gathered much attention for CO₂ separation technology. Kammakam *et al.* have reported the synthesis of imidazolium-functionalized cardo-based poly(ether ketone)s [7] or aromatic polyimides [8, 9] and the application for CO₂ separation membrane. In order to improve the selectivity of CO₂/N₂, we have attempted the surface modification of PIS_m membrane by free-standing ultra thin films with a thickness less than 100 nm (so-called nanosheets). It has been known that nanosheets exhibit the unique properties such as high adhesive strength, flexibility and smoothness

[10]. In our previous paper [11], aromatic diamine monomers containing imidazolium group were synthesized to prepare polyimides containing ionic liquid structure. Then, the surface coating on PIS_m membrane was carried out using nanosheets composed of the obtained polyimides. As a result, it was found that the nanosheet coating with these polyimides was very effective to improve the selectivity of CO₂/N₂ and O₂/N₂ with maintaining the high gas permeability of PIS_m membrane.

In this study, we have synthesized different polyimides containing ionic groups, which were composed of alkyl imidazolium or pyridinium group. In addition, the effect of the ionic structures of polyimides on the gas permselectivity of nanosheets-coated PIS_m composite membranes was investigated.

2. EXPERIMENTAL

2.1. Materials

The synthetic procedures of PDMS graft copolyimide (PIS₁₂, $m = 12.4$), 6-tosylhexyl 3,5-bis(4-amino-3-methylphenoxy)benzoate (DA-OTs), 3-{3,5-bis(4-amino-3-methylphenoxy)benzoyloxyhexyl}-1-methylimidazolium tosylate (DA-ImCl) and PI-ImCl were described in our previous paper [11]. Tetrahydrofuran (THF) was distilled over sodium to remove a small amount of water. 4,4'-Oxydiphthalic anhydride (ODPA) was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Other chemical reagents were used without further purification.

2.2. Synthesis of 1-hexylimidazole

To a solution of 1-tosylhexane (11.2 g, 43.8 mmol) and imidazole (3.17 g, 54.8 mmol) dissolved in 50 ml of THF, 2 ml of aqueous solution containing NaOH (1.75 g, 43.8 mmol) was added, and the mixture was refluxed for 4 h. After the mixture was poured into excess water, the organic products were extracted with chloroform, and purified by column chromatography on silica gel with chloroform/methanol (9/1 v/v) to obtain 5.14 g of 1-hexylimidazole as a pale yellow liquid. (Yield: 77.1 %)

$^1\text{H-NMR}$, δ , (CDCl_3 , ppm): 0.88 (3H, t, $J = 6.75$ Hz), 1.29 (6H, s), 1.78 (2H, m), 3.94 (2H, t, $J = 7.50$ Hz), 6.92 (1H, s), 7.07 (1H, s), 7.53 (1H, s).

1-decylimidazole was also synthesized by the same procedure as above using 1-tosyldecane instead of 1-tosylhexane. (Yields. 81.2 %)

2.3. Syntheses of diamine monomers containing imidazolium group (DA-ImCx)

DA-OTs (1.28 g, 2.07 mmol) and 1-hexylimidazole (1.26 g, 8.30 mmol) were mixed in a flask, and the mixture was stirred at 50 °C for 18 h. Then, a small amount of acetone (*ca.* 5 ml) was added and excess hexane (*ca.* 50 ml) was poured into this solution. The precipitate was separated by decantation and dried *in vacuo* to obtain 1.00 g of the desired diamine monomer, DA-ImC6, as a brown viscous liquid. (Yield: 80.3 %)

$^1\text{H-NMR}$, δ ($\text{DMSO-}d_6$, ppm): 0.84 (3H, t, $J = 3.00$ Hz), 1.22-1.35 (13H, m), 1.60-1.63 (2H, m), 1.76-1.79 (4H, m), 2.02-2.09 (6H, s), 2.29 (5H, s), 4.13-4.19 (7H, m), 6.66-6.75 (8H, m), 6.97 (2H, d, $J = 2.00$ Hz), 7.11 (2H, d, $J = 8.00$ Hz), 7.47 (2H, d, $J = 8.00$ Hz), 7.79 (2H, d, $J = 1.50$ Hz), 9.17 (1H, s).

DA-ImC10 was also synthesized by the same procedure as above using 1-decylimidazole instead of 1-hexylimidazole. (Yield: 64.5 %)

2.4. Synthesis of diamine monomer containing pyridinium group (DA-Py)

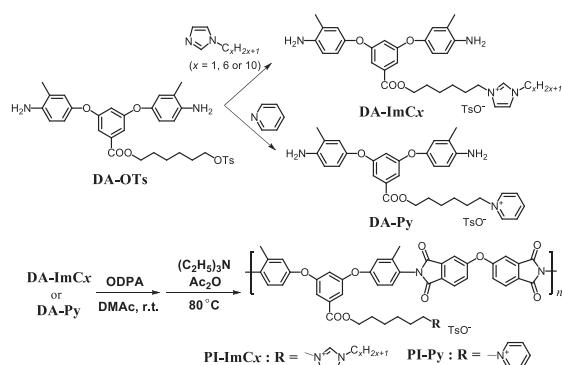
DA-OTs (0.798 g, 1.29 mmol) and pyridine (1.02 g, 12.9 mmol) were mixed in a flask, and the mixture was stirred at 65 °C for 15 h. Then, a small amount of acetone was added (*ca.* 5 ml) and excess hexane (*ca.* 50 ml) was poured into this solution. The precipitate was separated by decantation and dried *in vacuo* to obtain 0.750 g of the desired diamine monomer, DA-Py, as a brown viscous liquid. (Yield: 83.3 %)

$^1\text{H-NMR}$, δ ($\text{DMSO-}d_6$, ppm): 1.27 (3H, m), 1.35 (2H, m), 1.62 (2H, q, $J = 7.00$ Hz), 1.90 (2H, q, $J = 7.17$ Hz), 2.06 (6H, s), 2.29 (3H, s), 4.18 (2H, t, $J = 6.50$ Hz), 4.58 (2H, t, $J = 7.50$ Hz), 6.67 (2H, t, $J = 2.25$ Hz), 6.71 (3H, t, $J = 2.25$ Hz), 6.76 (2H, s), 6.97 (2H, d, $J = 2.50$ Hz), 7.11 (2H, d, $J = 8.00$ Hz), 7.47 (2H, d, $J = 8.00$ Hz), 8.15 (2H, t, $J = 7.25$ Hz), 8.60 (1H, t, $J = 7.75$ Hz), 9.07 (2H, d, $J = 5.50$ Hz).

2.5. Syntheses of polyimides

Under an argon atmosphere, a solution of ODPA (0.326 g, 1.05 mmol) dissolved in 4.0 ml of anhydrous DMAc was added dropwise to a solution of DA-ImC6 (1.97 g, 2.81 mmol) dissolved in 2.0 ml of DMAc. After the mixture was stirred at room temperature for 19 h, 0.790 ml of acetic anhydride and 1.17 ml of triethylamine were added, and the mixture was stirred at 80 °C for 5 h. Then, the reaction mixture was poured into excess ethyl acetate to produce a brown precipitate, and the product was purified by the reprecipitation from its DMAc solution to excess ethyl acetate. Finally, the product was dried *in vacuo* to afford 0.826 g of the desired polyimide, PI-ImC6, as a brown powder. (Yield: 75.3 %)

$^1\text{H-NMR}$, δ ($\text{DMSO-}d_6$, ppm): 0.81 (3H, t, $J = 6.00$ Hz), 1.20 (21H, m), 1.38 (2H, m), 1.66 (2H, m), 1.78 (4H, m), 2.14 (4H, s), 2.29 (3H, s), 4.15 (6H, m), 4.25 (3H, s), 7.11 (3H, d, $J = 8.00$ Hz), 7.19 (2H, s), 7.34 (3H, s), 7.44 (2H,



Scheme 1 Syntheses of diamine monomers and polyimides.

d, $J = 10.0$ Hz), 7.66 (2H, s), 7.78 (2H, s), 8.08 (1H, d, $J = 5.50$ Hz), 9.18 (1H, s).

IR, ν (KBr, cm^{-1}): 2929, 2858, 1716 (C=O), 1608 (C=C), 1578, 1375, 1242 (C-O-C), 1195 (S=O), 1101.

PI-ImC10 and PI-Py were prepared by the same procedures above using DA-ImC10 and DA-Py, respectively, instead of DA-ImC6.

PI-ImC10 (Yield: 80.3 %):

$^1\text{H-NMR}$, δ ($\text{DMSO-}d_6$, ppm): 0.81-0.82 (3H, t, $J = 6.00$ Hz), 1.20 (21H, m), 1.38 (2H, m), 1.66 (2H, m), 1.78 (4H, m), 2.14 (4H, s), 2.29 (3H, s), 4.15 (6H, m), 4.25 (3H, s), 7.11 (3H, d, $J = 8.00$ Hz), 7.19 (2H, s), 7.34 (3H, s), 7.44 (2H, d, $J = 10.0$ Hz), 7.66 (2H, s), 7.78 (2H, s), 8.08 (1H, d, $J = 5.50$ Hz), 9.18 (1H, s)

IR, ν (KBr, cm^{-1}): 2900, 2852, 1716 (C=O), 1600 (C=C), 1578, 1375, 1242 (C-O-C), 1167 (S=O), 1099.

PI-Py (Yield: 73.6 %):

$^1\text{H-NMR}$, δ ($\text{DMSO-}d_6$, ppm): 1.31 (2H, m), 1.38 (2H, m), 1.67 (2H, m), 1.92 (2H, m), 2.09 (6H, s), 2.28 (3H, s), 4.25 (2H, t, $J = 7.25$ Hz), 4.58 (2H, t, $J = 7.25$ Hz), 7.06 (1H, s), 7.11 (2H, d, $J = 8.00$ Hz), 7.19 (4H, s), 7.32 (2H, s), 7.43 (2H, d, $J = 7.00$ Hz), 7.47 (2H, d, $J = 8.00$ Hz), 7.66 (4H, t, $J = 8.50$ Hz), 8.08 (2H, d, $J = 7.50$ Hz), 8.14 (2H, t, $J = 7.00$ Hz), 8.58 (1H, t, $J = 7.75$ Hz), 9.07 (2H, d, $J = 5.50$ Hz).

IR, ν (KBr, cm^{-1}): 2059, 2929, 2860, 1720 (C=O), 1605 (C=C), 1582, 1450, 1375, 1275, 1242 (C-O-C), 1197, 1167 (S=O), 1101.

2.6. Characterizations of monomers and polymers

$^1\text{H-NMR}$ spectroscopy was conducted with a BRUKER ADVANCE-500 NMR spectrometer (500 MHz), and the chemical shifts were estimated with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded with a Shimadzu FTIR-8400 spectrometer. Gel permeation chromatography (GPC) was carried out to determine the number-average (M_n) and weight-average (M_w) molecular weights with a Tosoh GPC system equipped with four columns of TSK gels, Multipore HXL-M, and RI detector of Tosoh RI-8010 with a pump of Tosoh CCPD using DMF solution containing 20 mM LiBr as an eluent at a flow rate of 1.0 ml min⁻¹. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were carried out on Seiko Instruments DSC-6200 and TG/DTA-6200, respectively, at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

2.7. Preparations of polymer membranes

At first, in order to produce a water-soluble sacrificial layer, an aqueous solution of sodium alginate (20 mg ml⁻¹) was dropped on a silicon oxide (SiO₂) substrate and then spin-coated at 4000 rpm for 60 s, followed by a drying step at 50 °C for 90 s. Then, ionic polyimide solutions dissolved in NMP (30-100 mg ml⁻¹) were coated on the sodium alginate-coated SiO₂ substrate at 4000 rpm for 20 s, followed by a drying step at 50°C for 4 h. The substrates were immersed in distilled water at room temperature to obtain free-standing nanosheets. Then, the obtained nanosheets (4 cm x 4 cm) were washed several times with distilled water to completely remove sodium alginate. Finally, PIS12 membrane (4 cm x 4 cm) was softly attached with each nanosheet on the surface of water to obtain the composite membranes of nanosheets/PIS12. The obtained composite membranes were dried at room temperature in desiccator followed by drying in vacuum oven at room temperature.

2.8. Characterizations of membranes

The measurements of thickness of nanosheets, which were pasted on SiO₂ substrates, were carried out using a microfigure measuring instrument ET200 (Kosaka Laboratory Ltd.). The thickness of PIS12 membrane was determined using digimatic micrometer QuantuMike IP65 (Mitutoyo Corporation). Contact angle of water on the surface of the membrane was measured by sessile drop method using Kyowa DropMaster DME-201 (Kyowa Interface Science Co.) at room temperature.

2.9. Measurements of gas permeability

Gas permeability coefficients of six kinds of pure gases, *i.e.* hydrogen, oxygen, nitrogen, carbon dioxide, methane and ethane, were measured by the ordinary vacuum method using K-315N-01 (Tsukuba-Rikaseiki Co.), where the permeation area was 7.07 x 10⁻⁴ m². The pressures of upstream and downstream sides were about 100 and 0.1 kPa, respectively, and the cell temperature was kept at 30°C. The gas permeability coefficients (P , m³ (STP) m⁻² s⁻¹ Pa⁻¹) were calculated from the slope of the time-pressure curve, dp/dt , in the steady state.

3. RESULTS AND DISCUSSION

3.1. Preparation of imidazolium-containing polymers as surface layer

As shown in Scheme 1, the new ionic diamine monomers were prepared by quaternization of DA-OTs with two kinds of 1-alkylimidazoles and pyridine. Then, three kinds of polyimides, PI-ImC6, PI-ImC10 and PI-Py were prepared to investigate the effect of differences of side chain structures on the gas permselectivity of the nanosheet-coated composite membranes. All of the polymers were soluble in aprotic polar solvents, such as

DMF, DMAc, DMSO and NMP, but insoluble in alcohols, THF and chloroform.

The molecular weights and the thermal properties of the obtained polymers are summarized in Table 1, where the weight-average molecular weights of these polyimides were in the order of 10⁴.

The glass transition temperatures (T_g) of PI-ImC6, PI-ImC10 and PI-Py were detected at 110 °C, 64 °C and 150 °C, respectively, as shown in Table 1. T_g of the polyimides containing the longer alkyl chain decreased as compared with PI-ImC1, which would be due to the higher mobility of alkyl side chains. The thermal decomposition temperatures (T_{d5}) of these polymers were estimated at around 300 °C as listed in Table 1. The decompositions of ionic imidazolium or pyridinium groups would be a trigger of the thermal degradations, because T_{d5} of polyimide without these side chains was observed over 500 °C.

3.2. Preparations of composite membranes

Polymer nanosheets were essentially fabricated using a method of Okamura *et al.* [10, 11]. Aqueous solution of sodium alginate (Na-Alg: 20 mg mL⁻¹) as a water-soluble sacrificial layer was spin-coated on the SiO₂ substrate and dried. Next, the ionic polyimide solution dissolved in NMP (30 - 80 mg ml⁻¹) was spin-coated and dried. Then, the double-layered substrate was immersed in water to obtain easily a self-standing nanosheet after Na-Alg was dissolved in water. The resulting nanosheets were flexible and transparent.

Then, PIS12 cast membranes have attached from upper side to the nanosheet on the surface of water. By using scanning electron microscope (SEM), we have observed the cross section of the obtained composite membrane as shown in Fig. 2. The ultra-thin layer of PI-ImC6 was clearly observed on the surface of PIS membrane in this SEM image.

In order to confirm the surface modification by the nanosheet-coatings, the water contact angles on the surfaces of these composite membranes were evaluated as compared with PIS12 surface. As a result, the values of contact angles on PIS12, PI-ImC1/PIS12, PI-ImC6/PIS12, PI-ImC10/PIS12 and PI-Py/PIS12 membranes were measured as 100°, 59°, 65°, 66° and 44°, respectively. It was considered that the hydrophobic PIS12 membranes covered with PDMS chains became relatively hydrophilic by the nanosheet-coatings of these ionic polymers. Furthermore, according to the difference of side chain structures in these ionic polymers, the different hydrophilicities were observed on each surface. It was found that the coatings by PI-ImC6 and PI-ImC10 resulted in the more hydrophobic surfaces than that by

Table 1 Molecular weights and thermal properties of the obtained polymers.

Code	M_w ^{a)} x 10 ⁻³	M_w/M_n ^{a)}	T_g (°C) ^{b)}	T_{d5} (°C) ^{c)}
PI-ImC1 ^{d)}	10.9	1.23	150	347
PI-ImC6	24.2	1.85	110	335
PI-ImC10	29.2	2.61	64	292
PI-Py	14.9	1.99	150	301

a) Number- and weight-average molecular weights (M_n and M_w) were determined by GPC using DMF solution containing 2.0 M LiBr as an eluent.

b) Glass transition temperature (T_g) was determined by DSC on the 2nd heating scan at a heating rate of 10 °C min⁻¹ in N₂ flow.

c) Temperature at 5 % weight loss (T_{d5}) was determined by TGA at a heating rate of 10 °C min⁻¹ in N₂ flow.

d) The data were based on the reference [11].

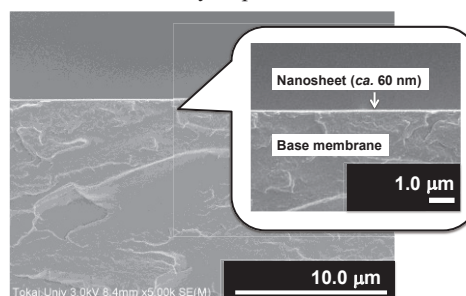


Fig. 2 SEM image of the cross section of PI-ImC6/PIS12 composite membrane.

Table 2 Gas permeability coefficients and selectivity of PIS12 and composite membranes at 30°C.

Code	Thickness (nm/ μm)	Gas permeability coefficient, P (Barrer ^a)						Selectivity, P/P_{N_2}				
		H ₂	N ₂	O ₂	CO ₂	CH ₄	C ₂ H ₆	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /N ₂	CH ₄ /N ₂	C ₂ H ₆ /N ₂
PIS12 ^b	0/134	245	92.0	204	1090	296	826	2.66	2.22	11.8	3.22	8.98
PI-ImC1/PIS12 ^b	53/106	201	6.97	44.1	218	6.80	9.43	28.8	6.33	31.1	0.976	1.35
PI-ImC6/PIS12	65/123	256	43.2	126	616	115	274	5.93	2.92	14.3	2.66	6.34
PI-ImC10/PIS12	70/103	284	60.7	167	823	160	376	4.86	2.75	13.6	2.97	6.19
PI-Py/PIS12	89/123	213	11.4	55.2	259	19.2	34.7	18.7	4.84	22.7	1.68	3.04

a) 1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² sec⁻¹ cmHg⁻¹ = 7.52×10^{-15} m³ (STP) m m⁻² sec⁻¹ Pa⁻¹. b) The data were based on the reference [11].

PI-ImC1, which would be due to the hydrophobic hexyl and decyl groups. On the contrary, the coating by PI-Py seemed to make the PIS surface more hydrophilic than those by imidazolium-containing polyimides.

3.3. Gas permselectivity of the composite membranes

Gas permeability coefficients of PIS12 and the composite membranes were evaluated for pure gases, *i.e.* H₂, O₂, N₂, CO₂, CH₄ and C₂H₆, by the ordinary vacuum method. The results are summarized in Table 2. For the composite membranes, the thicknesses of the nanosheet layers were in the range of 53 - 89 nm on PIS12 base membranes, the thickness of which were 103 - 123 μm .

As can be seen in Table 2, the gas permeability coefficients of the composite membranes for all gases except H₂ considerably decreased as compared with those of PIS12 base membrane. This phenomenon would be attributed to the dense layers composed of nanosheets, which act as barrier layers. Among these composite membranes, PI-ImC6 and PI-ImC10/PIS12 composite membranes showed the higher gas permeability coefficients than PI-ImC1 and PI-Py/PIS12 composite membranes. In addition, for the permeations of CH₄ and C₂H₆, the PI-ImC6 and PI-ImC10 layers brought about the higher permeability and selectivity than other composite membranes. Probably, the PI-ImC6 and PI-ImC10 layers would have the relatively higher gas permeability and the affinity to CH₄ and C₂H₆, because of the flexibility and the hydrophobicity of alkyl chains.

On the other hand, the selectivity of O₂/N₂ and CO₂/N₂ increased much in the cases of PI-ImC1 and PI-Py/PIS12 composite membranes, whereas the PI-ImC6 and PI-ImC10 layers were not effective. The selectivity values of O₂/N₂ and CO₂/N₂ are plotted against the values of P_{O_2} and P_{CO_2} , respectively, as shown in Fig. 3 as compared with Robeson upper bound [12]. Although the tradeoff relation between the gas permeability and the selectivity was observed, PI-ImC1/PIS12 composite membrane showed the best performance in the gas permselectivity, which were near to the upper bound of O₂/N₂. Furthermore, the PI-Py layer was also effective to improve the selectivity of O₂/N₂ and CO₂/N₂. Therefore, the introductions of compact ionic substituents such as 1-methylimidazolium and pyridinium groups would make the polymer surface layer dense, and the affinity to O₂ and CO₂ of these groups would improve the selectivity of these composite membranes.

4. CONCLUSION

Aromatic polyimides containing imidazolium and pyridinium moieties were prepared as surface layers for the surface modifications of highly gas permeable membrane composed of PIS12. It was found that such

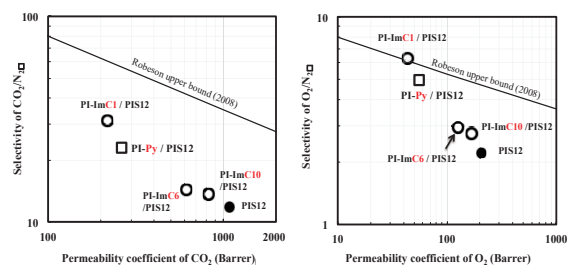


Fig. 3 Relationship between the permeability coefficients of CO₂, O₂ and selectivity of CO₂/N₂, O₂/N₂ of PIS12 and the composite membrane as compared with Robeson upper bound (2008) [12].

nanosheet-coatings by these ionic polyimides containing 1-methylimidazolium and pyridinium groups were very effective to improve the selectivity of CO₂/N₂ and O₂/N₂. In addition, the introduction of long alkyl chains into imidazolium group would bring about the increase of free volume to increase the gas permeability, although the density or free volume of nanosheets could not be confirmed. Consequently, it was speculated that the relatively dense surface layer with an affinity to a specific gas would be effective to enhance the gas separation property of the highly gas permeable membrane, as described in our previous report [11].

REFERENCES

- [1] S. Kim, Y. M. Lee, *Progress in Polym. Sci.* **43**, 1-32 (2015).
- [2] C. H. Jung, H. B. Park, Y. M. Lee, *Contribution Membrane* **31**, 161-164 (2006).
- [3] Y. Nagase, T. Ando, C. M. Yun, *React. Func. Polym.* **67**, 1252-1263 (2007).
- [4] Y. Saito, C. M. Yun, H. Ishikura, Y. Nagase, *Trans. Mater. Res. Soc. Jpn.* **34**: 145-148 (2009).
- [5] C. M. Yun, A. Abeta, S. Wirittichai, K. Yamamoto, H. Ishikura, Y. Nagase, *Trans. Mater. Res. Soc. Jpn.* **35**: 237-240 (2010).
- [6] C. M. Yun, E. Akiyama, T. Yamanobe, H. Uehara, Y. Nagase, *Polymer* **103**, 214-223 (2016).
- [7] I. Kammakakam, H. W. Kim, S. Y. Nam, H. B. Park, T. H. Kim, *Polymer* **54**, 3534-3541 (2013).
- [8] I. Kammakakam, S. Y. Nam, T. H. Kim, *RSC Adv.* **6**, 31083-31091 (2016).
- [9] B. Gye, I. Kammakakam, H. You, S. Y. Nam, T. H. Kim, *Separ. Purif. Tech.* **179**, 283-290 (2017).
- [10] Y. Okamura, K. Kabata, M. Kinoshita, D. Saitoh, S. Takeoka, *Adv Mater.* **21**, 4388-4392 (2009).
- [11] Y. Nagase, B. Suleimenova, C. Umeda, K. Taira, T. Oda, S. Suzuki, Y. Okamura, S. Koguchi, *Polymer* **135**, 142-153 (2018).
- [12] L. M. Robeson, *J. Membr. Sci.* **320**, 390-400 (2008).

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