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Synthesis and Gas Permeability of PDMS/PEO Alternately Grafted Aromatic Polyamides

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The syntheses of novel graft copolyamides containing both of poly(ethylene oxide) (PEO) and polydimethylsiloxane (PDMS) in the side chains were carried out by a macromonomer method, in order to develop a new functional membrane material which were expected to possess the high permeability of PDMS and the functionality of PEO-metal complex. For this purpose, 3,5-bis(4-carboxyphenyloxy)phenyloxy-terminated PEO (BCPP-PEO) and 3,5-bis(4-aminophenoxy)benzyloxypropyl-terminated PDMS (BAPB-PDMS) were synthesized as macromonomers. The polycondensations of BCPP-PEO and BAPB-PDMS yielded the desired PDMS/PEO alternately grafted aromatic polyamide (PA-*g*-SE). Copolymer membranes were prepared by solvent casting method, and the gas permeability of these membranes was evaluated. As a result, PA-*g*-SE membrane exhibited the higher gas permeability than PEO-grafted polyamide membrane (PA-g-PEO). Furthermore, the selectivity of olefin gas through the membrane was effectively advanced by the addition of Ag ion to the copolymer membrane.

Key words: *polydimethylsiloxane / poly(ethylene oxide) / aromatic polyamide / graft copolymer / separation membrane*

1. INTRODUCTION

Facilitated transport has been receiving enormous attention as energy-saving separation technology, because it can improve both of the permeability and the selectivity [1]. The separation of olefin/paraffin mixtures by facilitated transport membranes containing silver salts is a promising method alternative to energy-intensive distillation processes, as a result, it has attracted considerable interests [2]. Recently, the facilitated transport of olefin gases has been actively researched using polymer electrolyte membranes such as poly(ethylene oxide) (PEO) containing silver ions [3]. PEO based polymeric electrolyte are the most extensively studied polymer ionic conductors due to the beneficial structure of PEO in support of a fast ion transport.

On the other hand, polydimethylsiloxane (PDMS) has the unique properties derived from its siloxane bond, which include the low glass-transition temperature, the low surface energy, the high thermal stability, the biocompatibility and the highly permeability to most gases and organic liquids [4]. In our previous study, PDMS-grafted copolyamides were prepared from a novel 3,5-bis(4-aminophenoxy)benzyloxypropyl terminated PDMS macromonomer (**BAPB-PDMS**) to obtain the highly permeable and durable membrane material [5, 6]. In fact, the copolyamide membranes exhibited the permeability of several gases and the high selectivity for organic components in pervaporation of aqueous organic liquid solutions, which also possessed the high mechanical strength, durability and processability.

In this study, a novel membrane material has been investigated to prepare grafted copolyamides containing both of PDMS and PEO side chains, which is expected to show the high gas permeability of PDMS and the functionality of PEO-silver ion complex with a durability of main-chain aromatic polyamide. For this purpose, 3,5-bis(4-carboxyphenyloxy)phenyloxy terminated PEO (**BCPP-PEO**) macromonomer was synthesized as a comonomer to **BAPB-PDMS**. In this paper, the synthetic procedure of a dicarboxylic acid terminated PEO macromonomer (**BCPP-PEO**) and the polycondensation of **BCPP-PEO** with **BAPB-PDMS** are described to obtain the desired PDMS/PEO alternately grafted aromatic polyamide, which would exhibit the high gas permeability and the selectivity to olefin gases by the addition of Ag ion. Then, the permeability coefficients of several gases through the copolyamide membrane were evaluated in detail. In addition, the separation performance of olefin/paraffin by the silver salt complex with the copolyamide membrane will be discussed.

2. EXPERIMENTAL

2.1 Materials

PEO methyl ether (Mw = 350) was purchased from Aldrich Co., Ltd., and it was dried at 150℃ *in vacuo* for 6 h before use. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium and calcium hydride, respectively, to remove the small amount of water. Other reagents were used as received. The synthetic method of **BAPB-PDMS** was described in our previous paper [5].

*2.2 Synthesis of PEO tosylate (**Ts-PEO**)*

Under an argon atmosphere, PEO methyl ether (x = 7.83, 50.0 g, 133 mmol) and *p*-toluenesulfonyl chloride (30.4 g, 160 mmol) was dissolved in 292 ml of dry THF and 44.2 ml of dry TEA, and the solution was stirred at r.t. for overnight. Then, the reaction mixture was poured into excess water, and the organic products were extracted with chloroform and purified by column chromatography on silica gel with ethyl acetate/hexane (1/2 vol.) to afford 67.0 g of **Ts-PEO** as a yellow liquid. Yield: 95.1 %.

^{1}H-NMR, δ (400MHz, CDCl$_3$, ppm): 2.45 (3H, s), 3.38 (3H, s), 3.67 (4xH, m), 7.34 (2H, d, J=7.81Hz), 7.80 (2H, d, J=8.29Hz).

IR, ν (KBr, cm^{-1}): 3058, 2875, 1596 (C=C), 1355, 1177 (S=O), 1018, 773 (S-O-C), 1249 (C-O-C).

2.3 Synthesis of 3,5-bis(4-cyanopenyloxy)anisole (1)

To a solution of 5-methoxyresorcinol (3.00 g, 21.4 mmol) and 4-fluorobenzonitrile (5.19 g, 42.8 mmol) in 64.2 ml of *N,N*-dimethylacetoamide (DMAC), potassium carbonate (11.8 g, 85.6 mmol) was added. After the mixture was stirred at 150℃ for 5 h, the reaction mixture was poured into excess water. The organic products were extracted with chloroform and purified by recrystallization with ethanol to afford 7.47 g of **1** as a white powder. Yield: 76.7 %.

^{1}H-NMR. δ (400MHz, $CDCl_3$, ppm): 3.78 (3H, s), 6.34 (1H, s), 6.45 (2H, d, J=2.19Hz), 7.06 (4H, d, J=9.03Hz), 7.63 (4H, d, J=8.79Hz).

IR, ν (KBr, cm^{-1}): 2229 (-CN), 1633, 1504 (C=C), 1234 (C-O-C).

2.4 Synthesis of 3,5-bis(4-cyanopenyloxy)phenol (2)

Under an argon atmosphere, **1** (3.82 g, 11.2 mmol) was dissolved in 58 ml of dry dichloromethane. The solution was cooled to -78℃, and boron tribromide (4.14 ml, 44.6 mmol) was added. After the mixture was stirred at r.t. for overnight, it was poured into excess water and the organic products were extracted with ethyl acetate to afford 3.52 g of **2** as a white powder. Yield: 96.0 %.

^{1}H-NMR, δ (400MHz, DMSO-d_6, ppm): 6.24 (1H, d, J=2.20Hz), 6.34 (2H, d, J=1.95Hz), 7.16 (4H, t, J=4.40Hz), 7.79 (4H, t, J=4.40Hz).

IR, ν (KBr, cm^{-1}): 3312 (-OH), 3092, 2235, 2222 (-CN), 1591, 1501 (C=C), 1242 (C-O-C).

2.5 Synthesis of 3,5-bis(4-cyanopenyloxy)phenyloxy-terminated PEO (3)

To a solution of **2** (2.00 g, 6.09 mmol) and **Ts-PEO** (2.68 g, 5.08 mmol) in 30 ml of 2-butanone, K_2CO_3 (1.68 g, 12.2 mmol) was added. After the mixture was stirred at 80℃ for overnight, it was poured into excess water and the organic products were extracted with chloroform. The product was purified by column chromatography on silica gel with ethyl acetate/hexane (1/1 vol.) and ethyl acetate/methanol (10/1 vol.) to afford 3.00 g of **3** as a yellow liquid. Yield: 86.4 %.

^{1}H-NMR, δ (400MHz, $CDCL_3$, ppm): 3.38 (3H, s), 3.64 (4xH, m), 6.35 (1H, d, J=1.95Hz), 6.46 (2H, d, J=1.95 Hz), 7.05 (4H, d, J=8.29Hz), 7.63 (4H, d, J=8.78Hz).

IR, ν (KBr, cm^{-1}): 3508 (-OH), 2875, 2226 (-CN), 1587, 1504 (C=C), 1230 (C-O-C).

*2.6 Synthesis of 3,5-bis(4-carbonylpenyloxy)phenyloxy-terminated PEO (**BCPP-PEO**)*

To a solution of **3** (3.00 g, 4.37 mmol) in 51 ml of ethanol, the solution of KOH (5.39 g, 96.0 mmol) in 96 ml of distilled water was added, and the mixture was stirred at 120℃ for 30 min. Then, 51 ml of 30% aqueous H_2O_2 solution was added, and the mixture was stirred at 120℃ for overnight. After conc. HCl solution was added until pH of the solution was below 3.0, the reaction mixture was extracted with chloroform to afford 3.00g of **BCPP-PEO** as a yellow liquid. Yield: 94.7 %.

^{1}H-NMR, δ (400MHz, $CDCL_3$, ppm): 3.38 (3H, s), 3.64 (4xH, m), 6.32 (1H, s), 6.46 (2H, d, J=1.95Hz), 7.25 (4H, d, J=6.34Hz), 8.07 (4H, d, J=8.78Hz).

IR, ν (KBr, cm^{-1}): 3431 (-OH), 2874, 1653, 1647 (C=O), 1595, 1506 (C=C), 1229 (C-O-C).

*2.7 Preparation of PEO/PDMS-grafted polyamide membrane (**PA-g-SE**)*

Under a nitrogen atmosphere, **BCPP-PEO** (x = 8.0, 1.89 g, 2.48 mmol) was dissolved in 11 ml of thionyl chloride, and the solution was stirred at 115℃ for 3h. After the excess thionyl chloride was distilled off, the residue was dissolved in 6.2 ml of dry 1-methyl-2-pyrrolidinone (NMP). Under an argon atmosphere, the solution was cooled to -78℃, and the NMP solution of **BAPB-PDMS** (y = 11.8, 3.37 g, 2.48 mmol) was slowly added. The mixture was stirred at r.t. for 1.5 h. Then, the viscous solution was poured into excess methanol, and the precipitated polymer was dissolved in THF. Then, the THF solution was cast on a polytetrafluoroethylene sheet, and the solvent was evaporated at 70℃ for 2h to form a **PA-*g*-SE** membrane.

*2.8 Preparation of PEO-grafted polyamide membrane (**PA-g-PEO**)*

Under an argon atmosphere, **BCPP-PEO** (x = 8.0, 3.64 g, 4.81 mmol) and 3,5-bis(4-aminophenyloxy)-benzene (1.40 g, 4.81 mmol) were dissolved in 9.6 ml of dry NMP, and 0.78 ml of pyridine and 2.51 ml of triphenyl phosphite were added to this solution. The solution was stirred at 100℃ for overnight. Then, the solution was poured into excess methanol, and the precipitated polymer was dissolved in *N,N*-dimethylformamide (DMF). Then, the DMF solution was cast on a polytetrafluoroethylene sheet, and the solvent was evaporated at 80℃ for overnight to form a **PA-*g*-PEO** membrane.

2.9 Preparation of PDMS-grafted polyamide membrane (PA-g-PDMS)

Under an argon atmosphere, terephthaloyl chloride (0.62 g, 3.06 mmol) was dissolved in 6.8 ml of dry NMP. Under an argon atmosphere, the solution was cooled to -78℃, and the NMP solution of **BAPB-PDMS** (y = 11.8, 4.15 g, 3.06 mmol) was slowly added. The mixture was stirred at r.t. for 4 h. Then, the viscous solution was poured into excess methanol, and the precipitated polymer was dissolved in NMP. Then, the NMP solution was cast on a polytetrafluoroethylene sheet, and the solvent was evaporated at 90℃ for overnight to form a **PA-*g*-PDMS** membrane.

2.10 Preparations of composite membranes

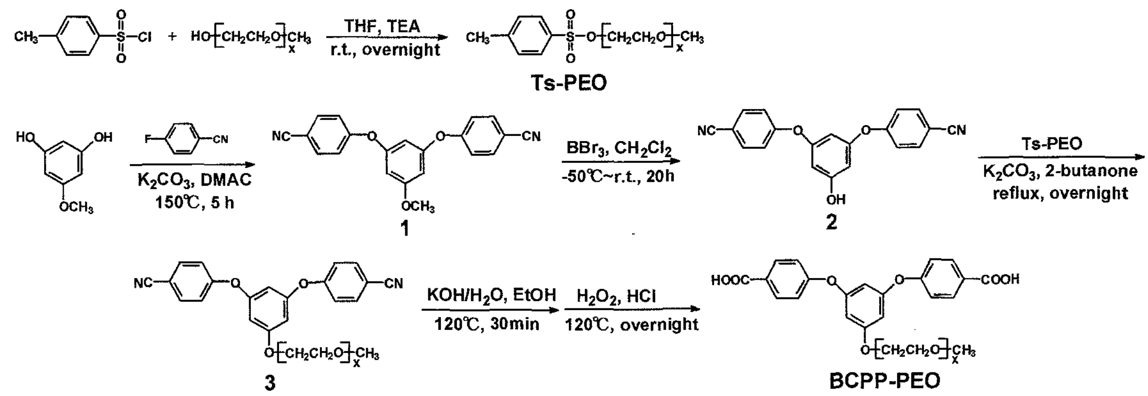
The obtained PA-*g*-PEO/PDMS and PA-*g*-PEO membranes were soaked in the solutions of $AgBF_4$ dissolved in methanol, the concentrations of which were altered based on the mole ratio of $AgBF_4$ and monomer unit of polymers, on polytetrafluoroethylene sheets at 30℃ for 6 h. Then, the membranes were dried *in vacuo* at r.t. for 4 h.

2.11 Characterizations

^{1}H-NMR spectra were conducted with a JEOL NM-TH5SK 400MHz FT-NMR. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrophotometer. The molecular weights of polymers were estimated by Tosoh gel permeation chromatography (GPC) system equipped with a pump of CCPD, five columns of TSK gels Multipore HXL-M, a column oven of CO-8010 and RI detector of RI-8010 in DMF eluent at 40℃. Average molecular weights were evaluated by polystyrene standards. Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments DSC-6200 under a nitrogen flow rate of 30 ml/min and a heating rate of 10 ℃/min. X-ray diffraction (XRD) was measured using a Philips PW1830.

2.12 Measurements of gas permeability coefficients

Sample membranes were cut into circular pieces with a diameter of 35 mm. Gas permeability was measured using the ordinary vacuum method at 30℃ with the apparatus, Tsukuba-Rikaseiki K-315N-01. Permeability coefficients were calculated from the slope of the time-pressure curve, *dp/dt*, in the steady state.



Scheme 1 Preparation of BCPP-PEO macromonomer.

3. RESULTS AND DISCUSSION

3.1 Preparation of macromonomers and graft copolymers

For the starting material of the graft copolymers, a dicarboxyl-terminated PEO macromonomer, **BCPP-PEO**, was prepared as shown in Scheme 1. Taking account of the high reactivity of the terminal group, 3,5-bis(4-carboxylphenyloxy)phenyl group was introduced into an end group of PEO via the etherification of bis(4-cyanophenoxy)phenol, **2**, with tosylated PEO, followed by the oxidation of the cyano group. These intermediates, **1**, **2** and **3**, and **BCPP-PEO** were obtained in high yields as described in the experimental section.

On the other hand, 3,5-bis(4-aminophenoxy)-benzyloxypropyl terminated PDMS macromonomer, **BAPB-PDMS**, was prepared by hydrosilylation of 3,5-bis(4-nitrophenoxy)benzyl allyl ether with hydrodimethylsilyl-terminated PDMS oligomer followed by hydrogenation reduction of the nitro groups, according to the method described in our previous report [5]. This PDMS macromonomer also showed a high reactivity with diacid chloride compounds to yield the PDMS grafted polyamides.

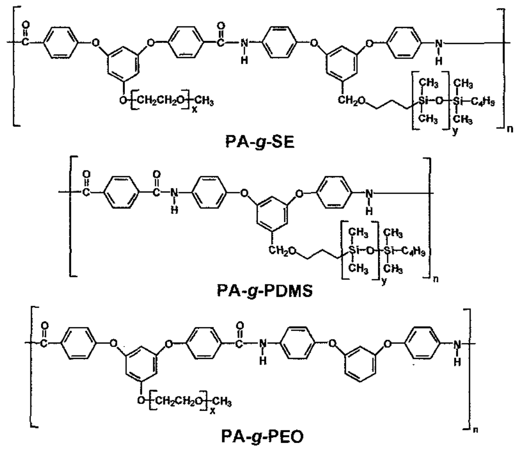


Fig. 1 Structures of graft copolymers.

Then, the polycondensation of **BAPB-PDMS** with the diacid chloride compound derived from **BCPP-PEO** proceeded smoothly to obtain a high molecular weight copolyamide, **PA-*g*-SE**, in which PEO and PDMS side chains were alternately grafted. In order to clarify the effect of side chain structure on the physical properties and gas permeabilities, PDMS grafted polyamide (**PA-*g*-PDMS**) and PEO grafted polyamide (**PA-*g*-PEO**) were prepared as comparative samples, according to the polycondensation of terephthaloyl chloride with **PA-*g*-PDMS** and that of 3,5-bis(4-aminophenyloxy)-benzene with **PA-*g*-PEO**, respectively. The chemical structures of **PA-*g*-SE**, **PA-*g*-PDMS** and **PA-*g*-PEO** are shown in Fig. 1, and the results of polymerizations are summarized in Table 1.

The obtained **PA-*g*-PEO** was soluble in polar solvents such as DMF and NMP, but insoluble in THF, alcohols, acetone and chloroform. However, in the case of **PA-*g*-SE** and **PA-*g*-PDMS**, when the reprecipitated polymers were filtered and dried *in vacuo*, they became insoluble in any solvents, whereas the polymers were soluble in THF, DMF and NMP just after the filtrations to obtain the homogeneous solutions of these polymers. Therefore, the copolymer membranes were prepared from their solutions in which the polymers were dissolved immediately after the reprecipitaions. It is considered that the amide bonds are highly aggregated after drying to make the polymer insoluble, and the aggregation would be enlarged by the phase separation of hydrophobic PDMS segments.

The physical properties of these copolymer membranes were analyzed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The broad glassy peaks were observed for every copolymer in their XRD patterns, and *Tm* and *Tg* were not observed in the range from r.t. to 300℃ on the DSC curves. Therefore, it was found that all of the copolymers gave the glassy membranes.

Table 1 Results of preparations of graft copolymers using PDMS and PEO macromonomers.

Sample code	Yield (%)	*y* of PDMS [a]	*x* of PEO [a]	$Mn\times10^{-4}$ [b]	$Mw\times10^{-4}$ [b]	*Mw/Mn* [b]
PA-*g*-SE	78.2	11.8	8.6	1.55	4.91	4.23
PA-*g*-PDMS	76.5	11.8	-	3.17	28.7	9.67
PA-*g*-PEO	78.3	-	8.5	3.65	15.4	4.23

a) Average degree of polymerization of PDMS or PEO segment.

b) Number-average molecular weight (*Mn*) and weight-average molecular weight (*Mw*) were determined by gel-permeation chromatography.

Table 2 Gas permeability of PA graft copolymer membranes at 30℃.

Sample code	Permeability coefficient (Barrer[a])							Separation factor		
	H_2	CO_2	O_2	N_2	CH_4	C_2H_4	C_2H_6	CO_2/N_2	CO_2/CH_4	C_2H_4/C_2H_6
PA-*g*-SE	141	536	93.4	44.1	132	329	376	12.2	4.08	0.88
PA-*g*-PDMS	172	759	147	66.8	214	535	602	11.4	3.54	0.88
PA-*g*-PEO	2.52	6.86	0.541	0.0647	0.331	0.891	0.698	98.0	20.8	1.28

a) 1 Barrer = 10^{-10} cm^3(STP) · cm／cm^2 · s · cmHg

Table 3 Effect of addition of $AgBF_4$ into PA-g-PEO and PA-g-SE membranes on the permeability coefficients of ethylene and ethane through the composite membranes.

Sample code	Polymer	Thickness (μm)	Mole ratio of $AgBF_4$ /monomer unit[a)]	Permeability (Barrer[b)])		Separation factor
				C_2H_4	C_2H_6	C_2H_4/C_2H_6
PEO1	PA-*g*-PEO	201	2.0	0.35	0.11	3.29
SE1	PA-*g*-SE	180	0.5	85.8	84.8	1.01
SE2	PA-*g*-SE	202	1.0	14.7	8.10	1.81
SE3	PA-*g*-SE	147	1.5	10.0	3.57	2.80
SE4	PA-*g*-SE	144	2.0	19.7	4.97	3.97

a) The mole ratio of $AgBF_4$ in the membrane against the monomer unit of each graft copolymer shown in Fig. 1.
b) 1 Barrer = 10^{-10} cm^3(STP) · cm／cm^2 · s · cmHg

3.2 Gas permeability of copolymer membranes

Gas permeability coefficients of the copolymer membranes were evaluated as listed in Table 2. Among these membranes, **PA-*g*-PDMS** membrane showed the highest gas permeability for all gases, whose oxygen permeability was the same order as PDMS membrane [7]. Thus, the continuous phase of side-chain PDMS segment would exist in the surface and the inner part of **PA-*g*-PDMS** membrane. The gas permeability of **PA-*g*-PDMS** membrane was increased as the increase of PDMS segment length [6], then, in this study, the average degree of polymerization of PDMS segment was fixed at about 12 which was a suitable length to exhibit the high gas permeability and maintain the sufficient mechanical strength of membrane. On the other hand, the gas permeabilities of **PA-*g*-PEO** membrane was much lower than those of **PA-*g*-PDMS**, which would be due to the high density of PEO-grafted polyamide derived from the strong interactions between side chain PEO segments and amide groups in the main chain.

Interestingly, the gas permeability coefficients of **PA-*g*-SE** membrane were similar to those of **PA-*g*-PDMS** and much higher than those of **PA-*g*-PEO**. These results indicated that the gas permeability of **PA-*g*-SE** membrane was controlled by PDMS domain and the interactions of PEO segments or amide bonds were prevented by bulky and hydrophobic PDMS segments. In particular, in the case of PA-g-SE membrane, the permeability coefficient of carbon dioxide was a little higher as compared with other gases. As shown in Table 2, the separation factors of CO_2/N_2 and CO_2/CH_4 of **PA-*g*-SE** membrane were higher than those of **PA-*g*-PDMS**, which would be due to the high affinity of PEO segment against CO_2. Actually, the selectivity of CO_2 against N_2 or CH_4 reached very high value in the case of **PA-g-PEO** membrane.

The effect of the addition of silver ion to **PA-*g*-PEO** and **PA-*g*-SE** membranes on the ethylene/ethane permselectivity was investigated. The permeability coefficients of ethylene and ethane of the composite membranes were summarized in Table 3. As comparing the separation factors of ethylene/ethane of the copolymer membranes without Ag ion in Table 2, the addition of $AgBF_4$ was effective to improve the selectivity of ethylene against ethane for the composite membrane of **PA-*g*-PEO**/$AgBF_4$ (PEO1). In addition, the composite membrane of **PA-*g*-SE**/$AgBF_4$ (SE4) with the same content of $AgBF_4$ as PEO1 exhibited the higher permselectivity of ethylene than PEO1, however, the permeability coefficient of ethylene was decreased as compared with **PA-*g*-SE**. Therefore, the content of $AgBF_4$ in the composite membrane was decreased as shown as SE3, SE2 and SE1 in Table 3. As a result, the selectivity of ethylene against ethane decreased as the decrease of $AgBF_4$ content. Moreover, it was noticed that SE4 membrane exhibited the higher permselectivity of ethylene than SE2 and SE3 membranes.

Consequently, it was found that PDMS/PEO alternately grafted copolymer exhibited the high gas permeability as the same level as PDMS-grafted copolymer, however, the addition of Ag ion into the membrane decreased the gas permeability although the selectivity of ethylene against ethane was generated by a complex of Ag ion with PEO segment. The improvement of the selectivity will be investigated as a future subject.

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