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Syntheses of PEO/PDMS Graft Copolymers and the Membrane Properties

by

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Abstract

Novel graft copolymers, which consisted of polyamide or polyimide backbone attached with polydimethylsiloxane (PDMS)/poly(ethylene oxide) (PEO) block segments, were prepared by the polycondensation of diamino-terminated PEO/PDMS macromonomers with terephthaloyl chloride or 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane. Then, the effect of the composition on the physical properties of graft copolymers was investigated. The obtained copolymers were soluble in THF and some solvents, and the self-standing membranes could be prepared by a solvent-casting method. Gas permeability and ethanol permselectivity in pervaporation of ethanol/water mixture decreased with the increase of the PEO component in the side chain. In addition, the protein adhesion on the membrane surface increased with the decrease of the PEO component in the side chain. Therefore, it was revealed that the PEO component was effective for reducing the protein adhesion, although the trade-off relation was observed between the ethanol permselectivity and the protein resistance.

Keywords: Graft copolymer, Polydimethylsiloxane, Poly(ethylene oxide), Polyimide, Pervaporation

1. Introduction

Separation technique through a polymer membrane is one of the most promising achievements of energy-saving technology. In particular, pervaporation (PV) is considered to have the greatest potential for the separation technology because of its energy-saving and efficiency. It is able to separate the azeotropic mixtures or the similar molecular size compounds.[1)] Because of the global energy crisis, the organic permselective pervaporation membrane has been receiving increased attention in recent years.[2)] Pervaporation technique would enable to concentrate ethanol continuously from a culture medium of fermentation. It has been reported that silicalite membrane concentrated the aqueous ethanol solution from 5-20 wt.% to over 80 wt.% of ethanol.[3-5)] However, the permeability of these membranes was gradually decreased due to the adsorption of protein, peptone, and organic acid, which were contained in a culture medium.[6),7)] Therefore, the resistance to those bio-components was necessary for a practical separation membrane in addition to the ethanol permselectivity.

Polydimethylsiloxane (PDMS) has been known to show unique properties derived from its siloxane bond. In particular, the cross-linked PDMS membrane is well-known to exhibit selective permeation and high permeability of organic gases and liquids owing to its hydrophobicity and high diffusivity.[8)] Recently, some researches have been reported about the PV recovering of *n*-butanol from the mixture of acetone, butanol and ethanol (ABE) or the fermentation broth using PDMS membrane.[9)] On the other hand, poly(ethylene oxide) (PEO) has been known to provide a facility of repellent to protains on the polymer surface.[10),11)] Therefore, it is expected that the combination of PDMS and PEO having high organic-permeability and high biocompatibility, respectively, would be reliable to achieve a new functional material for pervaporation membranes to separate fuel ethanol from a fermentation culture. However, PDMS and PEO possessed poor processability to from membranes by themselves due to their low *T*g.

In our previous studies,[12-15)] it has been revealed that the membranes of PDMS graft aromatic polymers exhibited the high mechanical strength and the high permeability of gases and liquids, which was derived from the aromatic main chain and the flexible PDMS side chain, respectively. Furthermore, the preparations of PDMS and PEO graft copolyamides have been reported.[16-18)] Interestingly, the obtained membranes showed the organic-permselectivity in pervaporation as well as the good biocompatibility, where the membrane efficiently reduced the amount of adhered platelets or proteins on the surface. No other research had been seen for the pervaporation membrane material exhibiting both of alcohol-selectivity and biocompatibility. However, the alcohol-selectivity of these polymer membranes was not enough, which decreased by the excistance of hydrophilic PEO component.

In this study, we attempted to introduce a novel structure

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of PEO/PDMS block segment into the side chain of aromatic polyamide or polyimide, in order to develop the alcohol-permselectivity with maintaining biocompatibility. In such a block graft copolymer consisted of the three components, we have expected that the high permeability of PDMS units could be exhibited easily according to the high content of PDMS segment in each component regularly. Then, the effects of the side chain structure on the permselectivity in PV and the adsorption of protein of the copolymer membranes has been investigated.

2. Experiment

2.1 *Materials*

The synthetic procedures of 3,5-bis(4-nitro-3-methylphenoxy)benzoic acid (BNMPB) and hydrosilyl-terminated polydimethylsiloxane (PDMS-H) were described in our previous papers.[13),17)] Allyl-terminated poly(ethylene oxide) (*M*w = 400) was kindly supplied from Nichiyu Co. Ltd, and it was dehydrated by heating over 130°C in vacuo for 10 h before use. Terephthaloyl chloride and 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane (6FDA) was purchased from Tokyo Kasei Co. and Aldrich Co., respectively, and used as received. Other chemical reagents were used without further purification. Antibody of bovine fibrinogen was purchased from Wako Chemical Co.

2.2 *Characterizations*

^{1}H-NMR spectra were conducted with a JEOL NM-TH5SK 400MHz FT-NMR spectrometer, and the chemical shifts were estimated in ppm units with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded with a Shimadzu FTIR-8400 spectrometer. The molecular weights of polymers were determined by a Tosoh HLC-802A instrument by using THF as eluent, equipped with four columns of TSK gels, G5000H_6, G4000H_6, G3000H_6 and G2000H_6. Standard polystyrenes were used to calibrate the molecular weights.

2.3 *Synthesis of α-allyl-ω-tosyl PEO (1)*

Under an argon atmosphere, allyl-terminated PEO (*M*w = 400, 20.0 g, 50.0 mmol) and triethylamine (16.1 ml, 120 mmol) were dissolved in 110 ml of tetrahydrofuran (THF). Tosyl chloride (11.4 ml, 60.0 mmol) was added in the solution, and the mixture was stirred at room temperature for overnight. After the mixture was poured into excess water, the organic product was extracted with chloroform to obtain 20.1 g of **1** as a transparent colorless liquid.

Yield: 91.4 %, x = 8.1.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 2.50 (3H, s), 3.67 (4xH, m), 4.02 (2H, d, J = 5.85 Hz), 5.27 (2H, m), 5.91 (1H, m), 7.34 (2H, d, J = 7.80 Hz), 7.80 (2H, d, J = 7.80 Hz).

The compounds **1** with different segment length (x = 3.0) was prepared by the same procedure as above using allyl-terminated triethylene glycol instead of allyl-terminated PEO (*M*w = 400).

2.4 *Synthesis of α-allyl-ω-3,5-bis(4-nitro-3-methylphenoxy) benzoyloxy PEO (2)*

To a solution of BNMPB (10.0 g, 23.6 mmol) and **1** (x = 8.1, 9.08 g, 15.7 mmol) dissolved in 39 ml of 2-butaone, K_2CO_3 (3.26 g, 23.6 mmol) was added, and the mixture was stirred at 80°C for overnight. Then, the organic products were extracted with chloroform, and purified by column chromatography on silica gel with ethyl acetate/hexane (1/1 by volume) to obtain 9.93 g of **2** as a yellow liquid.

Yield: 76.1 %, x = 8.2.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 2.67 (6H, s), 3.64 ((4x-4)H, m), 3.80 (2H, m), 4.02 (2H, d, J = 1.46 Hz), 4.47 (2H, m), 5.27 (2H, dd, J = 10.2, 17.6 Hz), 5.92 (1H, m), 6.92 (1H, m), 6.97 (4H, m), 7.79 (2H, m), 8.09 (2H, m).

IR, ν (KBr, cm^{-1}): 2870, 1724 (C=O), 1581, 1559, 1506, 1304 (-NO_2), 1230 (C-O-C).

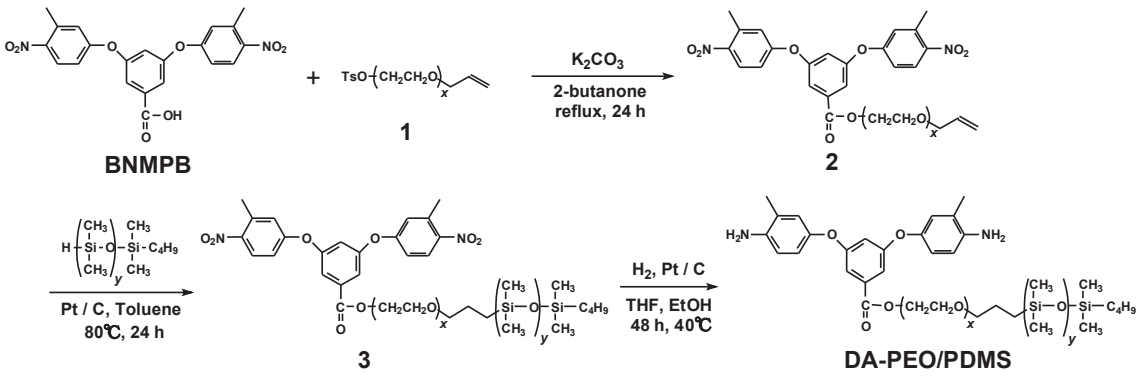
The compounds **2** with different segment length (x = 3.0) was prepared by the same procedure as above using **1** (x = 3.0) instead of **1** (x = 8.1).

2.5 *Synthesis of 3,5-bis(4-nitro-3-methylphenoxy)-benzoyloxy-terminated PEO/PDMS (3)*

PDMS-H (y = 10.0, 6.74 g, 7.88 mmol), **2** (x = 8.2, 5.45 g, 6.57 mmol) and Pt/C powder (5%, 0.256 g) were mixed in 6.6 ml of dry toluene under an argon atmosphere, and the mixture was stirred at 80°C for overnight. The product was purified by column chromatography on silica gel with chloroform to obtain 6.93 g of **3** as a pale yellow liquid.

Yield: 62.6 %, x = 7.9, y = 10.0.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 0.05 ((6y+6)H, m), 0.45 (4H, m), 0.81 (3H, t, J = 6.83 Hz), 1.25 (4H, m), 2.67 (6H, s), 3.34 (2H, m), 3.56 ((4x-4)H, m), 3.73 (2H, m), 4.40 (2H, m), 6.85 (4H, m), 7.50 (2H, m), 7.50 (2H, m), 7.99 (2H, m).



Scheme 1 Preparation of DA-PEO/PDMS.

IR, ν (KBr, cm^{-1}): 2874, 1724 (C=O), 1582, 1520, 1488, 1346 ($-NO_2$), 1261 (Si-C), 1094, 1026 (Si-O-Si), 802.

The compounds **3**'s with different segment length (x = 8.6, y = 5.8 and x = 3.0, y = 10.0) were prepared by the same procedure as above using PDMS-H (y = 5.8) and **2** (x = 3.0) instead of PDMS-H (y = 10.0) and **2** (x = 8.2), respectively.

2.6 *Synthesis of 3,5-bis(4-amino-3-methylphenoxy)benzoxy-terminated PEO/PDMS (DA-PEO/PDMS)*

Pt/C powder (5 %, 0.342 g) were dispersed in a solution of **3** (x = 7.9, y = 10.0, 6.93 g, 4.38 mmol) in 83 ml of THF and 55 ml of ethanol. The reaction vessel was purged with hydrogen and the mixture was stirred at 40°C for 48 h. Then, Pt/C was filtered off, and the solvents were evaporated *in vacuo* to obtain 4.87 g of DA-PEO/PDMS as a brown viscous liquid.

Yield: 87.5 %, x = 8.7, y = 10.1.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 0.05 ((6y+6)H, m), 0.45 (4H, m), 0.82 (3H, m), 1.24 (4H, m), 3.34 (2H, m), 2.16 (6H, s), 3.42 (2H, m), 3.64 ((4x-2)H, m), 3.77 (2H, m), 4.39 (2H, m), 6.67 (1H, m), 6.74 (4H, m), 6.78 (2H, m), 7.20 (2H, m).

IR, ν (KBr, cm^{-1}): 3450 ($-NH_2$), 2961, 2860, 1725 (C=O), 1593, 1504, 1454, 1259 (Si-C), 1094, 1022 (Si-O-Si), 798.

DA-PEO/PDMSs with different segment length (x = 8.8, y = 5.8 and x = 3.0, y = 9.6) were prepared by the same procedure as above using **3** (x = 8.6, y = 5.8 and x = 3.0, y = 10.0), respectively, instead of **3** (x = 7.9, y = 10.0).

2.7 *Synthesis of methyl 3,5-bis(4-nitro-3-methylphenoxy)-benzoate (4)*

To a solution of methyl 3,5-dihydroxybenzoate (4.28 g, 26.6 mmol) dissolved in 80 ml of *N,N*-dimethylacetoamide (DMAc), K_2CO_3 (7.35 g, 53.2 mmol) and 5-fluoro-2-nitro-toluene (9.30 g, 60.0 mmol) were added. After the mixture was stirred at 85°C for overnight, the reaction mixture was poured into excess water to precipitate the product. Then, the product was washed with methanol to obtain 10.4 g of **4** as a pale yellow powder.

Yield: 90.0 %.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 2.62 (6H, s), 3.91 (3H, s), 6.94 (4H, m), 6.99 (1H, t, J = 1.95 Hz), 7.55 (2H, d, J = 2.44 Hz), 8.08 (2H, d, J = 9.27 Hz).

2.8 *Synthesis of 3,5-bis(4-nitro-3-methylphenoxy)benzoic acid (5)*

The compound **4** (4.60 g, 10.5 mmol) was added to a solution of acetic acid (30.6 ml) and sulfuric acid (13.0 ml) dissolved in 8.0 ml of distilled water. After the mixture was stirred at 120°C for overnight, the reaction mixture was poured into excess water to precipitate the product to obtain 5.50 g of **5** as a pale yellow powder.

Yield: 98.0 %.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 2.49 (6H, s), 7.06 (2H, m), 7.17 (2H, m), 7.25 (1H, t, J = 2.43 Hz), 7.40 (2H, d, J = 1.95 Hz), 8.04 (2H, d, J = 8.29 Hz).

2.9 *Synthesis of allyl 3,5-bis(4-nitro-3-methylphenoxy) benzoate (6)*

To a solution of **5** (2.10 g, 4.95 mmol) dissolved in 15 ml of 2-butanone, allyl bromide (1.20 g, 9.90 mmol) and K_2CO_3 (1.03 g, 7.42 mmol) were added, and the mixture was stirred at 98°C for overnight. Then, the organic products were extracted with chloroform, and purified by column chromatography on silica gel with chloroform to obtain 1.96 g of **6** as a white solid.

Yield: 91.2 %.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 2.62 (6H, s), 4.82 (2H, d, J = 1.46 Hz), 5.34 (2H, dd, J = 1.46, 18.5 Hz), 5.99 (1H, m), 6.91 (4H, m), 6.93 (1H, t, J = 2.44 Hz), 7.57 (2H, d, J = 1.95 Hz), 8.09 (2H, d, J = 8.29 Hz).

IR, ν (KBr, cm^{-1}): 2963, 1709 (C=O), 1612, 1574, 1481, 1439, 1342 ($-NO_2$), 1273, 1238, 1204, 1169, 1126, 1076, 995, 841.

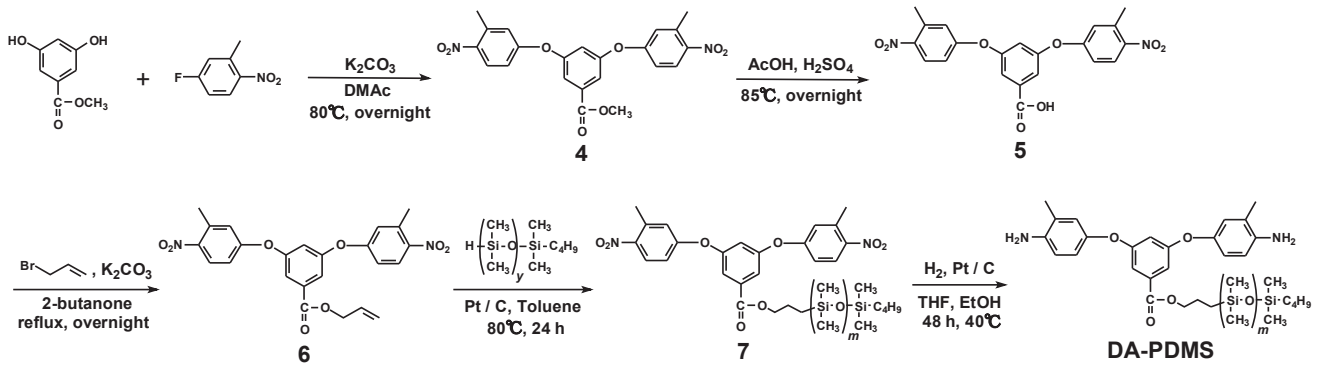
2.10 *Synthesis of 3,5-bis(4-nitro-3-methylphenoxy)-terminated PDMS (7)*

PDMS-H (y = 12.1, 12.7 g, 12.9 mmol), **6** (5.00 g, 10.8 mmol) and Pt/C powder (5 %, 0.420 g) were mixed in 11 ml of dry toluene under an argon atmosphere. Then, the mixture was stirred at 80°C for overnight. After the solvent was evaporated, the product was purified by column chromatography on silica gel to obtain 2.80 g of **7** as a yellow liquid.

Yield: 18.0 %, y = 12.1.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 0.05 (6yH, m), 0.48 (4H, m), 0.81 (3H, m), 1.24 (4H, m), 1.71 (2H, m), 2.55 (6H, s), 4.20 (2H, t, J = 6.83 Hz), 6.87 (5H, m), 7.48 (2H, m), 8.01 (2H, d, J = 8.29 Hz).

IR, ν (KBr, cm^{-1}): 2963, 2923, 1724 (C=O), 1578, 1524, 1481, 1443, 1342 ($-NO_2$), 1300, 1261 (Si-C), 1161, 1022 (Si-O-Si), 864.



Scheme 2 Preparation of DA-PDMS.

2.11 ***Synthesis of 3,5-bis(4-amino-3-methylphenoxy)-benzoxy-terminated PDMS (DA-PDMS)***

The compound **8** (2.80 g, 1.85 mmol) was dissolved in 20 ml of ethanol, and Pd/C powder (5 %, 0.0788 g) was suspended in the solution. Then, the reaction vessel was purged with hydrogen and the mixture was stirred at room temperature for 2 days. After Pd/C powder was filtered off, the product was purified by column chromatography on silica gel to obtain 2.63 g of DA-PDMS.

Yield: 77.6 %, y = 12.2.

^{1}H-NMR, δ (400 MHz, $CDCl_3$, ppm): 0.05 (6yH, m), 0.48 (4H, m), 0.81 (3H, m), 1.24 (4H, m), 1.69 (2H, m), 2.09 (6H, s), 4.13 (2H, t, J = 6.83 Hz), 6.65 (7H, m), 7.16 (2H, d, J = 8.29 Hz).

IR, ν (KBr, cm^{-1}): 3568 (-NH_2), 2963, 1717 (C=O), 1624, 1597, 1504, 1439, 1419, 1261 (Si-C), 1161, 1022 (Si-O-Si), 798.

2.12 ***Synthesis of PEO/PDMS graft copolyamides (PA-ES1, PA-ES2)***

Under an argon atmosphere, DA-PEO/PDMS (x = 8.8, y = 5.8, 0.620 g) was dissolved in 0.6 ml of anhydrous *N*-methylpyrrolidone (NMP), and it was frozen at -78°C. Then, the solution of terephthaloyl chloride (0.12 g) dissolved in 0.57 ml of NMP was added dropwise. The reaction mixture was gradually defrosted to room temperature with stirring. After the stirring for few minutes, the reaction mixture was poured into excess methanol to produce a yellow precipitate. The product was purified by the reprecipitation from its NMP solution to excess methanol, and dried *in vacuo* to afford PA-ES1 as a yellow powder.

PA-ES2 was prepared as the same procedure as above using DA-PEO/PDMS (x = 7.9, y = 10.0) instead of DA-PEO/PDMS (x = 8.8, y = 5.8).

2.13 ***Synthesis of PDMS graft cpolyimide (PI-S)***

Under an argon atmosphere, DA-PDMS (y = 12.2, 1.28 g, 0.900 mmol) and 2,2-bis(3,4-anhydrodicarboxyphenyl)-hexafluoropropane (6FDA) (0.400 g, 0.900 mmol) were dissolved in 10 ml of anhydrous DMAc. After the mixture was stirred at r.t. for overnight, 0.68 ml of acetic anhydride and 1.0 ml of triethylamine were added, and the mixture was stirred at 80°C for 10 h. Then, the reaction mixture was poured into excess methanol to produce a yellow precipitate, and the product was purified by the reprecipitation from its chloroform solution to excess methanol. Finally, the product was dried *in vacuo* to afford 1.26 g of PI-S as a yellow powder.

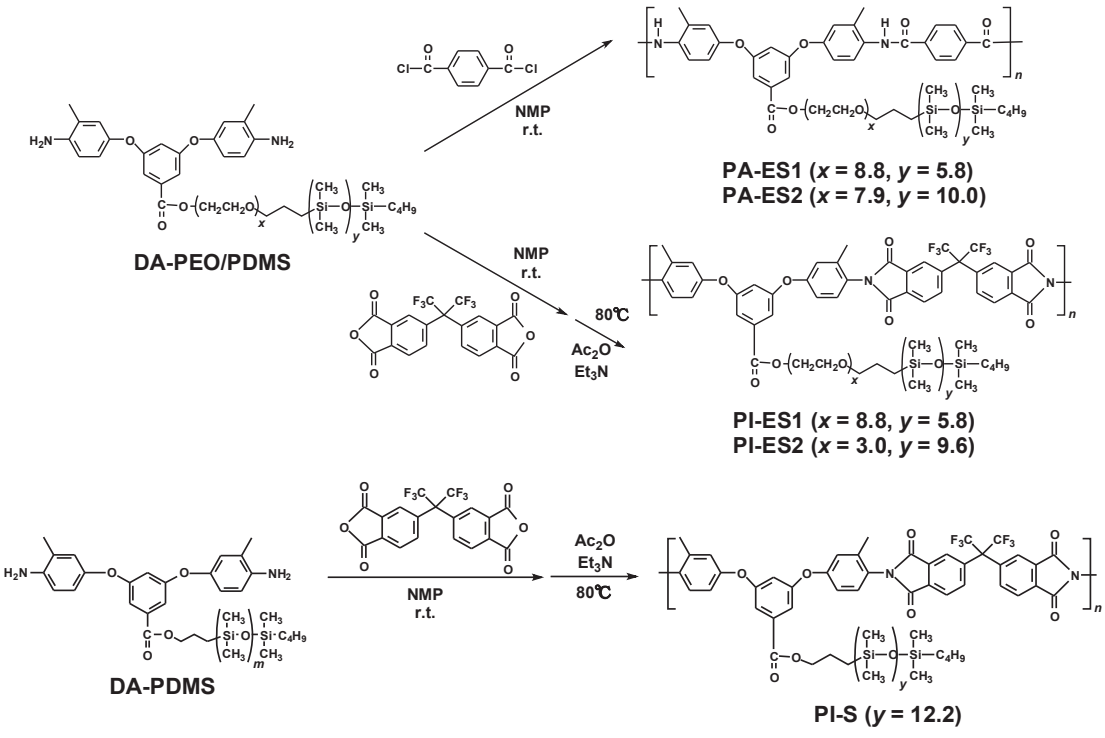
2.14 ***Synthesis of PEO/PDMS graft copolyimide (PI-ES1, PI-ES2)***

Under an argon atmosphere, DA-PEO/PDMS (x = 7.9, y = 10.0, 1.69 g, 1.26 mmol) and 6FDA (0.558 g, 1.26 mmol) were dissolved in 13 ml of NMP. After the mixture was stirred at r.t. for overnight, 1.0 ml of acetic anhydride and 1.2 ml of triethylamine were added, and the mixture was stirred at 80°C for 10 h. Then, the reaction mixture was poured into excess methanol to produce a yellow precipitate, and the product was purified by the reprecipitation from its NMP solution to excess methanol. Finally, the product was dried *in vacuo* to afford 1.54 g of PI-ES1 as a yellow powder.

PI-ES2 was prepared as the same procedure as above using DA-PEO/PDMS (x = 3.0, y = 9.6) instead of DA-PEO/PDMS (x = 7.9, y = 10.0).

2.15 ***Preparations of polymer membranes***

The obtained polymers were dissolved in the mixed



Scheme 3 Syntheses of PEO/PDMS and PDMS graft copolymers

solvents of NMP/THF and the solutions were poured on polytetrafluoroethylene sheets. Then, the solvents were slowly evaporated at 80°C for overnight to form the copolymer membranes, which were dried in vacuo at 80°C for overnight. The thermal treatments of the polyimide membranes were carried out at 100°C for 24 h.

2.16 ***Gas permeability***

Sample membranes were cut into circular pieces with a diameter of 36 mm and a thickness of 80 - 100 μm. Gas permeability coefficients of the pure gases, *i.e.*, hydrogen, oxygen, nitrogen, carbon dioxide, methane and ethane, were measured by the ordinary vacuum method using Tsukuba-Rikaseiki K-315N-01, where the permeation area was 7.07 cm^2. The pressures of upstream and downstream sides were about 76 and 10^{-3} cmHg, respectivity, and the cell temperature was kept at 30°C. The gas permeability coefficients (P, cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$) were calculated from the slope of the time-pressure curve, dp/dt, in the steady state.

2.17 ***Pervaporation experiments***

Sample membranes were cut into circular pieces with a diameter of 59 mm and a thickness of 80 - 100 μm. Pervaporation of aqueous ethanol solution through the membrane was carried out using a stainless steel cell, which was dipped in a water bath kept at 50°C. The pressure of the downstream side was kept at below 1.0 mmHg, and the permeation area was 20.0 cm^2. The permeated vapor was trapped in a vessel cooled with liquid N_2, and the concentration was determined by gas chromatography. The permeability coefficient (P, kg m m^{-2} h^{-1}) was calculated from the weight of permeate (w) in the vessel, the permeation time (t), the membrane thickness (L) and the permeation area (A), according to the equation shown below:

$$P = wL / At$$

The separation factor, α was defined as the equation below:

$$\alpha = (X_{ethanol} / X_{water}) / (Y_{ethanol} / Y_{water})$$

where $X_{ethanol}$ is the mass fraction of ethanol in permeate, X_{water} is the mass fraction of water in liquid in permeate, $Y_{ethanol}$ is the mass fraction of ethanol in feed, Y_{water} is the mass fraction of water in liquid in feed.

2.18 ***Measurements of contact angle***

Contact angle of water on the surface of the membranes were measured by sessile drop method using Kyowa FACE AUTO DISPENSER AD-31 at room temperature. Contact angles of the membranes after the immersion in water were measured immediately after wiped the surface with a paper.

2.19 ***Quantitative analysis of protein adhered on the membranes***

The membranes were cut into circular pieces with a diameter of 14 mm and immersed in phosphate-buffered solution (PBS, pH = 7.4) at r.t. for overnight to equilibrate the surface. The treated membranes were contacted with PBS solution (5 mg ml^{-1}) of protein, anti-human fibrinogen, for 2 h at 37°C. After 2 h, the membranes were taken out from the solution, and rinsed in excess distilled water, in order to remove non-adhered proteins. Then, 1.0 wt.% aqueous solution of sodium dodecyl sulfate (SDS) was poured to remove the adhered proteins. The concentration of fibrinogen in SDS solution was counted by a Micro BCATM Protein Assay kit (Thermo) and the number of adhered proteins on the membranes was estimated based on the absorbance of the protein-diluted system using Bio-RAD microplate reader.

3. Result and discussion

3.1 ***Syntheses of macromonomers***

The synthetic routes of diamino-terminated macromonomers, DA-PEO/PDMS and DA-PDMS, are shown in Scheme 1 and 2, respectively. A novel diamino-terminated PEO/PDMS macromonomer (DA-PEO/PDMS) was prepared by hydrosilylation of **2** with hydrosilyl-terminated PDMS oligomer (PDMS-H) followed by hydrogenation reduction of the nitro groups. The precurser, **2**, was prepared by esterification of BNMPB with allyl-terminated PEO tosylate, **1**. The three kinds of DA-PEO/PDMSs were prepared, where the average degrees of polymerization of PEO and PDMS segments, x and y, were different. The obtained DA-PEO/PDMS has a unique structure of PEO/PDMS block segment and is expected to exhibit the high reactivity in the polycondensation with diacid chloride or carboxylic anhydride, which would be due to the reactivity of *p*-aminophenyl groups in the terminal component.[13-15] In addition, it was found that the methyl group in the terminal component enabled the obtained polyamides soluble in some solvents, because it reduced the intramolecular interaction of amide bonds in the polymer solutions.[14]

On the other hand, diamino-terminated PDMS macromonomer, DA-PDMS, which consisted of the similar terminal component, was prepared to compare the membrane properties between the graft copolymers containing PEO/PDMS block segment and only PDMS segment. In the preparation of DA-PDMS, the yield of the precurser, **7**, was very low. In the hydrosilylation of **6** with PDMS-H, it was observed that a side reaction of the chain scission of ester bond occurred to produce the starting material, **5**, and PDMS compound. It would be due to the effect of silyl group connected to the ester group with propylene spacer. The improved synthetic route is now in progress to change the spacer length between ester and silyl groups.

3.2 ***Syntheses and properties of copolymers***

As shown in Scheme 3, PEO/PDMS graft copolyamides (PA-ES1 and 2) and copolyimides (PI-ES1 and 2) were prepared by polycondensation of DA-PEO/PDMS with terephthaloyl chloride and 6FDA, respectively, followed by a chemical imidization to prepare polyimides. PDMS graft copolyimide (PI-S) was also prepared from DA-PDMS and 6FDA. The segment lengths and the molecular weights of the obtained copolymers are summarized in Table 1 with the polymerization yields. The yields of polyamides were relatively low as compared with those of polyimides. In the case of polyamides, the very fine powder was produced in the reprecipitation and difficult to be recovered by the filteration.

As we expected, all of the obtained copolymers exhibited

Table 1 Characterizations of PEO/PDMS graft copolymers.

Code	x [a)]	y [a)]	Mn x 10^{-3} [b)]	Mw x 10^{-3} [b)]	Mw/Mn [b)]	Yield (%)
PA-ES1	8.8	5.8	23.5	45.3	1.93	48.3
PA-ES2	7.9	10.0	19.2	33.4	1.74	43.5
PI-ES1	7.9	10.0	14.6	19.2	1.35	68.9
PI-ES2	3.0	9.6	15.2	27.5	1.81	68.4
PI-S	-	12.2	22.2	40.3	1.82	76.4

a) The degree of polymerization of each segment was determined by ^{1}H-NMR of the each macromonomer.
b) The number- and weight- average molecular weights (Mn, Mw) were determined by GPC using THF as eluent.

a good solubility, which were soluble in THF. But, the solubility to the other solvents was altered according to the side chain components. PEO containing polymers (PA-ES1, 2 and PI-ES1, 2) were soluble in polar solvents such as dimethylsulfoxide (DMSO) and NMP but insoluble in chroloform and alcohols. On the contrary, PDMS graft copolymer, PI-S, was insoluble in DMSO and NMP but soluble in THF and chloroform. From these results, it was considered that the solubility of the copolymers depended on the composition of PEO and PDMS segments which have different solubility parameters. Then, the self-standing membranes of PEO/PDMS graft copolymers could be prepared by the solvent casting method from the NMP/THF mixed solutions, and the membranes became stronger after the thermal treatment at 100°C. PI-S membrane was similarly obtained from the chloroform solution and heated at 200°C.

3.3 *Gas permeability of copolymer membranes*

The gas permeabilities of the copolymer membranes were investigated to reveal the effect of each segment length on the membrane permeability. The permeability or the diffusivity of the membrane is thought to be an important role in the organic permselectivity in pervaporation. Gas permeability coefficients of pure gases, *i.e.*, hydrogen, nitrogen, oxygen, carbon dioxide, methane and ethane through these membranes were evaluated as listed in Table 2.

The gas permeability coefficients of the copolymer membranes remarkably decreased as the increase of PEO content. The highest gas permeability coefficients were observed in PI-S membrane without PEO component. This result indicated that the PEO unit would be a disadvantage in the construction of PDMS permeable domains. This tendency was in good agreement with our previous report, which described the membrane properties of copoly(amide-imide) membranes prepared from the blend of PEO and PDMS macromonomers.[18] As compared with PA-ES2 and PI-ES1 membranes which consisted of the same length of PEO and PDMS segments, the gas permeability of PI-ES1 was a little higher than that of PA-ES2. Therefore, polyimide main chain would be more effective to improve the permeability than polyamide main chain. There would be an aggregation of highly polar amide units in the polyamide membrane to decrease the diffusion of gas permeation.

3.4 *Pervaporation property*

The pervaporation properties of the copolymer membranes were evaluated by using *ca.* 10 wt.% of aqueous ethanol solution as a feed solution. Unfortunately, PA-ES2 membrane was broken in the pervaporation experiment. Probably, the polyamide containing the long side chain, PA-ES2, would be highly swollen in the aquesous ethanol solution. Then, the pervaporation experiments were

Table 2 Gas permeability of each copolymer membrane at 30°C.

Code	Permeability coefficient, P (Barrer [a)])						Selectivity, P/P_{N_2}				
	H_2	O_2	N_2	CO_2	CH_4	C_2H_6	H_2/N_2	O_2/N_2	CO_2/N_2	CH_4/N_2	C_2H_6/N_2
PA-ES1	52.9	40.4	18.1	274	60.1	178	2.92	2.23	15.1	3.32	9.83
PA-ES2	86.8	72.8	33.4	450	110	330	2.60	2.18	13.5	3.29	9.88
PI-ES1	125	101	45.1	583	145	411	2.77	2.24	12.9	3.22	9.11
PI-ES2	158	123	53.7	678	171	472	2.94	2.29	12.6	3.18	8.79
PI-S	238	188	82.9	1022	259	667	2.87	2.27	12.3	3.12	8.05

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

Table 3 Results of pervaporation of aqueous ethanol solutions through each copolymer membrane at 50°C.

Code	Composition [a)] (wt%)		α [b)]	P [b)] × 10^6 (kg m m^{-2} h^{-1})	Contact angle of water (degree)
	in feed	in permeate			
PA-ES1	9.34	14.7	1.67	10.7	100
PI-ES1	11.4	28.0	3.03	8.08	101
PI-ES2	11.3	35.2	4.25	5.43	108
PI-S	11.4	38.3	4.83	4.96	106

a) Composition of organic liquid in the feed and the permeate, determined by gas chromatography.
b) α : Separation factor (EtOH/Water), P: Permeability coefficient.

conducted for PA-ES1, PI-ES1, PI-ES2 and PI-S membranes, the PEO contents of which were different (PA-ES1 > PI-ES1 > PI-ES2).

The results are summarized in Table 3 with the contact angle of water of each membrane. The contact angle of every membrane was over 100°, therefore, the surface of these membranes was hydrophobic and would be covered with PDMS segments. The permeability coefficient (P) increased with the increase of PEO content in the copolymer. However, the separation factor (α) of ethanol/water decreased with the increase of PEO content. Thus, it was speculated that the permeation of water would increase as the increase of PEO cotent.

In particular, the PDMS-rich copolymer membrane, PI-ES2, exhibited the good ethanol permselectivity in the pervaporation, the separation factor of which was almost same as that of PDMS graft copolymer membrane, PI-S. In the case of PA-ES1 membrane, the permselectivity of PDMS component in pervaporation would be inhibited by the large content of PEO component, although the PEO segment did not make the surface more hydrophilic. Therefore, the alcohol-permselectivity in the pervaporation would be based on not only the hydrophobic membrane surface but also the high diffusivity of inert of the membrane to make the difusions of ethanol and water almost same. In the case of such PEO/PDMS graft copolymer membranes, PEO segment would reduce the diffusivity of the membrane to decrease the alcohol-permselectivity.

3.5 *Protein adhesion*

Finally, the adhesion property of proteins on the membrane surface was evaluated using bovine fibrinogen as a model protein. Although fibrinogen would not be involved much in a culture medium during the production of bio-ethanol, we supposed to preliminarily evaluate the protein resistance of these copolymer membranes by using a commercially available protein. The amount of adhered proteins on the copolymer membranes was determined after contact with a solution of fibrinogen in PBS.

As shown in Figure 2, the amount of adhered fibrinogen on the film surfaces was estimated for PI-ES1, PI-ES2, PI-S and poly(ethylene terephthalate) (PET) films. The PEO-rich polymers, PI-ES1, effectively reduced the protein adhesion, where the amount of adhered protein on PI-ES1 was less than one fourth to that of PI-ES2 and PI-S. Thus, it was assumed that such a reduction of the adhered protein was derived from the property of PEO segment. On the other hand, the separation factor of ethanol/water in pervaporation decreased with the increase of PEO content. Therefore, the tendencies of the ethanol permselectivity and the protein resistance of the copolymer membranes were in trade-off relation.

4. Conclusion

Novel graft copolymers containing PEO/PDMS block segments in the side chain were successfully prepared by a macromonomer method, and the tough and flexible membranes could be prepared by a solvent-casting method. The gas permeability decreased with the increase of the PEO content, which inhibited the high permeability of PDMS component. Furthermore, it was found that the moderate introduction of PEO component into the same side chain was effective to improve the PV permeability. However, the decrease of PEO content caused the increase the amount of protein adhesion. Therefore, the ethanol permselectivity in pervaporation and the protein resistance strongly depended on the content of PEO. The trade-off relation was observed between the ethanol permselectivity and the protein resistance. Consequently, PEO/PDMS graft copolymer membrane is one of the candidates as a pervaporation membrane for the continuous separation of bio-ethanol from a culture medium of fermentation, although the further investigation is necessary to develop the selectivity in pervaporation.

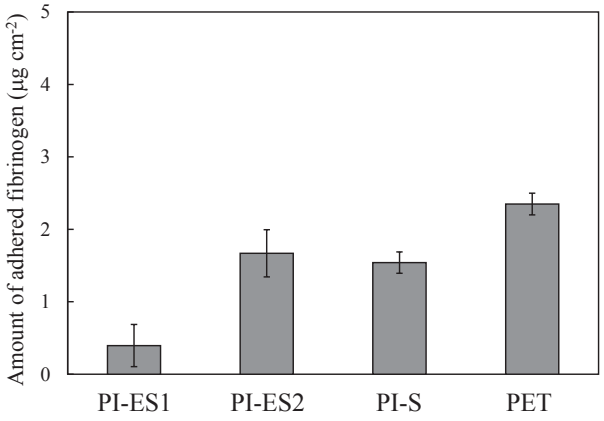


Fig. 1 Amount of adhered fibrinogen on the polymer films.

5. References

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