Characterizations of PDMS-graft copolyimide membrane and the permselectivity of gases and aqueous organic mixtures

Cheol Min Yun a, 1, Eiichi Akiyama b, Takeshi Yamanobe c, Hiroki Uehara c, Yu Nagase a, *

a Graduate School of Science and Technology, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan
b Sagami Chemical Research Institute, 2743-1 Hayakawa, Ayase, Kanagawa 252-1193, Japan
c Department of Chemistry and Chemical Biology, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

Article info
Article history:
Received 1 July 2016
Received in revised form 8 September 2016
Accepted 15 September 2016
Available online 15 September 2016

Keywords:
Polydimethylsiloxane
Polyimide
Graft copolymer
Gas permeability
Pervaporation
Thermal treatment

Abstract
Polydimethylsiloxane (PDMS)-graft copolyimides were synthesized by polycondensation of 3,5-bis(4-aminophenoxy)benzyloxypropyl-terminated PDMS macromonomer with 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) followed by chemical imidization to investigate the effects of PDMS segment length of copolyimides on the membrane characteristics, the gas permeability and the pervaporation performance. The copolyimide membranes, which were prepared by solvent-casting method from the chloroform solutions, became insoluble in any solvents after the thermal treatment over 150 °C in vacuo. It was confirmed from TEM observation of these membranes that the phase separation of flexible PDMS domains and hard polyimide backbones. The gas permeability coefficients of copolyimide membranes were increased as the PDMS segment length increased, but decreased after thermal treatment at 200 °C. It would be due to the chain scission and the rearrangement of PDMS segments in the side chain to become a cross-linked structure, which make the membranes insoluble. From the results of pervaporation of dilute aqueous solutions of organics, it was found that the copolyimide membranes exhibited the excellent permselectivity toward several organics, such as ethanol, acetone, benzene, chloroform and dichloromethane with a high and stable permeation. Furthermore, it was confirmed that the removal of dichloromethane from its saturated aqueous solution was efficiently achieved by the pervaporation.

1. Introduction

Pervaporation is a promising membrane-based technique with potential savings in the cost of energy for the separation of liquid mixtures. One application of organic-permselective membrane is the removal and the recovery of volatile organic components (VOCs) and solvents from waste fluid, industrial drainage or fermentation broths [1–5]. Especially, the water pollution due to VOCs has become a serious environmental problem. Polydimethylsiloxane (PDMS) has been known to show the high permselectivity for organic liquids against water in pervaporation, which is derived from the higher affinity for organic compounds than water with the high diffusivity [6–9]. To make a self-standing thin membrane, however, an improvement of the processability of PDMS is necessary, which would be achieved by the copolymerization with a high Tg or Tm component. Some researchers have investigated the improvement of processability of PDMS by controlling the chemical structure such as blends and block copolymers [10–16], although the PDMS content was limited to make a tough membrane. Meanwhile, the durability of membrane against VOCs is very important, because the organic components were concentrated in the membrane during permeation. Therefore, the PDMS rich polymer exhibiting high organic-permselectivity, processability and durability would be an ideal material to develop as a practical pervaporation membrane for the separation of VOCs.

From these points of view, we have attempted to synthesize novel PDMS-graft copolymers, the backbone structure of which consists of aromatic polyimide. Aromatic polyimides are well known to show the excellent mechanical strength, processability and the durability for several organic solvents, which have been studied for various applications in electronic devices, coating, composite materials and separation membranes [17–21]. In our...
previous study, PDMS/polyimide graft copolymer was prepared by polycondensation of 3,5-diaminobenzyl-terminated PDMS macromonomer with aromatic diamine and dianhydride monomers [22–24]. Then, the obtained membrane exhibited the high organic-permselectivity with durability derived from the backbone component. However, the PDMS content was also limited due to the poor reactivity of 3,5-diaminobenzyl terminal group of the macromonomer, which should be copolymerized with other diamine monomers. In these years, we have developed the highly reactive PDMS macromonomers, which consisted of 3,5-bis(4-amino-3-methylphenoxy)benzyloxypropyl-terminated PDMS diamine monomers. In these years, we have developed the highly reactive PDMS macromonomers, which should be copolymerized with other component. However, the PDMS content was also limited due to permselectivity with durability derived from the backbone [22].

Polycondensation of 3,5-diaminobenzyl-terminated PDMS macromonomer, which we prepared in the previous study, PDMS/polyimide graft copolymer was prepared by polycondensation with terephthaloyl chloride, trimellitic anhydride chloride, 4,4′-oxydiphthalic anhydride (6FDA) and 4,4′-hexafluoroisopropylidenedipthalic anhydride (6FDA) [25]. Although the obtained polymers possessed the long PDMS segment in every repeating unit, the tough self-standing membranes could be prepared by a solvent casting method. Furthermore, the PDMS contents of PDMS-graft aromatic copolyimides based on 3,5-bis(4-amino-3-methylphenoxy)benzyloxypropyl-terminated PDMS copolymer membranes were also investigated to reveal the effect of PDMS segment length on the permeability and the selectivity.

In this paper, the synthesis of PDMS-graft copolyimides having different PDMS segment length was carried out by the polycondensation of BAPB-PDMS with 6FDA, and the basic characterizations of the copolyimide membranes were investigated. In particular, the influence of the thermal treatment on the membrane characteristics was investigated in detail to clarify the reason why this membrane became insoluble after the thermal treatment, as compared with polyimide derived from 1,3-bis(4-aminophenoxy) benzene and 6FDA. Furthermore, the gas permeability and the pervaporation performance through the obtained PDMS-graft copolyimide membranes were also investigated to reveal the effect of PDMS segment length on the permeability and the selectivity.

2. Experimental

2.1. Materials

3,5-Bis(4-aminophenoxy)benzyloxypropyl-terminated PDMS (BAPB-PDMS) with different PDMS segment length was prepared according to the procedure described in our previous paper [25]. 4,4′-Hexafluoroisopropylidenediphalic anhydride (6FDA) was purchased from Tokyo Kasei Co., Ltd., and used as received. Anhydrous N,N-dimethylacetamide (DMAc) was purchased from Aldrich Co., Ltd. Silicone membrane (thickness: 340 μm) was kindly supplied from Shin-Etsu Chemical Co., Ltd., and used as a reference sample.

2.2. PDMS graft copolymides (PIS6, PIS11 and PIS19)

The syntheses of PDMS-graft polyimides containing different PDMS segment lengths were performed according to the procedure described in our previous paper [27], as shown in Scheme 1. PIS6, PIS11 and PIS19 were obtained as a pale brown powder by the reprecipitation of the chloroform solution into excess methanol. 1H NMR and IR spectra of the obtained polymers were added in supporting information as Figs. S1 and S2, respectively. Typical data are shown below.

1H NMR δ (CDCl3, ppm): 6.05 (6H, m, J = 8.0 Hz), 7.15 (2H, d, J = 8.78 Hz), 7.35–7.4 (1H, m), 7.46 (4H, d, J = 8.78 Hz), 7.83 (2H, s), 7.97 (2H, d, J = 7.80 Hz), 8.07 (2H, d, J = 7.80 Hz).

IR, v (KBr, cm⁻¹): 3400 (NH2), 2972, 2885, 1570, 1506, 1478, 1342 (NO2), 1223 (C–O–C), 1032, 847.

2.3. 1,3-Bis(4-aminophenoxy) benzene (BAPB)

To a solution of resorcinol (2.50 g, 22.7 mmol), p-fluorotoluene (6.72 g, 47.6 mmol) in 50 ml of DMF and K2CO3 (6.57 g, 47.6 mmol) were added. After the mixture was stirred at 140 °C for 15 h, the reaction mixture was poured into excess iced water to precipitate the product. Then, the product was purified by washing with chloroform to afford 6.81 g of 1,3-bis(4-fluorotoluene)benzene as a white powder. Yield: 85.2%.

1H NMR δ (CDCl3, ppm): 6.84 (1H, t, J = 2.43 Hz), 6.79 (2H, d, J = 2.43 Hz), 6.88 (4H, d, J = 8.70 Hz), 7.20 (1H, t, J = 8.29 Hz), 8.17 (4H, d, J = 8.70 Hz).

IR, v (KBr, cm⁻¹): 3120, 3092, 2936, 2860, 1578, 1507, 1487, 1342 (NO2), 1223 (C–O–C), 1032, 847.

1,3-bis(4-fluorotoluene)benzene (5.0 g, 17.1 mmol) was dissolved in 150 ml of THF/ethanol (1/1 by volume), and Pd/C powder (5%, 0.59 g) was suspended in the solution. The reaction vessel was purged with hydrogen, and the mixture was stirred at room temperature for overnight. After Pd/C powder was filtered off, the product was purified by washing from ethanol for three times to give 4.59 g of 1,3-bis(4-aminophenoxy)benzene (BAPB) as a white powder. Yield: 92.0%.

1H NMR δ (CDCl3, ppm): 6.35 (3H, m), 6.45 (2H, d, J = 8.29 Hz), 6.58 (4H, d, J = 8.70 Hz), 6.73 (4H, d, J = 8.70 Hz), 7.14 (1H, t, J = 8.29 Hz).

IR, v (KBr, cm⁻¹): 3403 (NH2), 2972, 2885, 1570, 1510, 1221 (C–O–C), 1045, 850.

2.4. Polyimide (PI)

Under a nitrogen atmosphere, BAPB (3.30 g, 11.3 mmol) and 6FDA (5.01 g, 11.3 mmol) were dissolved in 47 ml of DMAC. After the solution was stirred for 6 h at room temperature, 4.3 ml of acetic anhydride and 6.3 ml of triethylamine were added, and the mixture was stirred for 10 h at 80 °C. Then, the mixture was poured into excess methanol to precipitate the polymer, and the obtained copolymer powder was filtered and dried. The reprecipitation of the chloroform solution into methanol gave 4.71 g of PI as a white fiber. Yield: 81.3%.

1H NMR δ (CDCl3, ppm): 6.8–6.9 (3H, m), 7.15 (4H, d, J = 8.78 Hz), 7.3–7.4 (1H, m), 7.46 (4H, d, J = 8.78 Hz), 7.83 (2H, s), 7.97 (2H, d, J = 7.80 Hz), 8.07 (2H, d, J = 7.80 Hz).

IR, v (KBr, cm⁻¹): 2913, 2846 (C–H), 1781, 1720 (C=O), 1587, 1583, 1504, 1371 (C–N), 1251, 1205, 1139, 1108, 962, 829, 721.

2.5. Characterizations of polymers

Solution 1H NMR spectroscopy was conducted with a BRUKER AVANCE-500 NMR spectrometer (500 MHz) at room temperature. Infrared (IR) spectra were recorded on a Horiba FT-720 equipped with SensIR technologies DuraSamplIR II. Gel permeation
chromatography (GPC) was carried out to determine the number-average ($M_n$) and weight-average ($M_w$) molecular weights with a Tosoh HLC-802A instrument by using tetrahydrofuran (THF) as eluent, equipped with four columns of TSK gels G5000Hg, G4000Hg, G3000Hg and G2000Hg. The elution was detected by both of refractive index (RI) and laser light scattering detectors using Tosoh LS-8000 to determine the absolute molecular weight. Standard polystyrenes were used to calibrate the molecular weights. 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.

2.6. Characterizations of polymer membranes

Copolyimide membranes with a thickness of ca. 150 μm were prepared by solvent-casting method from the chloroform solutions on the polytetrafluoroethylene sheet and dried at 40°C for 2 h. To complete the imidization, the thermal treatments of the obtained membranes were carried out at various temperatures, 80°C, 100°C, 150°C, 200°C and 250°C, for 24 h. Then, the film samples were cut into rectangular strips with a length of 40 mm and a width of 10 mm. Stress-strain curves of these films were obtained on a JF Torsi LSC-01/30, where the gauge length was 20 mm and the cross-head speed was 6.0 mm min⁻¹.

Sample membranes were cut into circular pieces with a diameter of 14 mm. The density of each membrane was determined by flotation of membrane samples in a density gradient column at 23°C. Further, the contact angles of ion-exchanged water and ethylene glycol were measured on each membrane surface. The measurements were carried out to use the sessile drop method, and their values were recorded with a Kyowa FACE AUTO DISPENSER AD-31. The reported contact angles are the average value of at least three measurements. According to Owens-Wendt equation [28], the surface free energy was calculated from the values of contact angle of water and ethylene glycol on the membranes.

The membranes were vapor-stained with an aqueous solution of 1 wt% RuO₄ at room temperature for 4 min, and the stained membranes were embedded with epoxy resin at room temperature for 24 h. Then, the stained membranes were cut into circular pieces with a diameter of 59 mm. Pervaporation of organic liquids/water mixtures through each membrane was carried out using a stainless steel cell, which was dipped in a water bath kept at 50°C. The permeate solutions were determined by gas chromatography, using Shimadzu GC-14B and GC-2014 equipped with ZS-72 and G-250 (1.2 mm × 40 m) columns, respectively. The flux ($J$, kg m⁻² h⁻¹) was calculated from the weight of permeate ($w$) in the vessel, the permeation time ($t$) and the permeation area ($A$), according to the equations shown below:

$$J = w/At$$

The separation factor, $\beta$, was defined as the equation below [29];

$$\beta = (X_{\text{organic}}/X_{\text{water}})/(Y_{\text{organic}}/Y_{\text{water}})$$

where $X_{\text{organic}}$ is the mass fraction of organic liquid in permeate, $X_{\text{water}}$ is the mass fraction of water in permeate, $Y_{\text{organic}}$ is the mass fraction of organic liquid in feed, and $Y_{\text{water}}$ is the mass fraction of water in feed.
3. Results and discussion

3.1. Preparations of PDMS-graft copolyimides

Three kinds of PDMS-graft copolyimides (PIS6, PIS11 and PIS19) having different PDMS segment length were synthesized by poly-condensation of diamino-terminated PDMS macromonomers (BAPB-PDMS) with 6FDA followed by chemical imidization, as shown in Scheme 1. The sample codes of PDMS-graft copolyimides are represented as PISm, where m is an average degree of polymer-merization of PDMS segment in the side chain. Polyimide, PI, was prepared by the same procedure from BAPB with 6FDA as a reference sample. PDMS segment length and molecular weights of these polymers are summarized in Table 1. The average degree of polymer-merization, m, of PDMS segment in each graft copolymer was estimated by the ratio of peak intensities of 4.46 ppm (methylene protons in benzyl unit) and 0.05 ppm (methyl protons in PDMS unit) in 1H NMR spectra. As a result, the PDMS segment lengths of these polyimides were in good agreement with those of the starting macromonomers. The obtained copolyimides have the high number-average molecular weights (Mn) over 2 × 10^4. Interestingly, the weight-average molecular weights (Mw) of the graft copolymers determined by GPC were lower than the values of Mw(LS), which were the absolute molecular weight determined by light scattering method. Such branch type polymer usually becomes a compact form in the solution, therefore, the molecular weight determined by GPC mode is known to be smaller than the absolute molecular weight. The obtained PDMS-graft copolyimides were soluble in several organic solvents, such as acetone, chloroform, tetrahydrofuran (THF), toluene and N-methylpyrrolidone (NMP), but insoluble in methanol, ethanol and dimethylsulfoxide (DMSO). PI was soluble in chloroform, THF, DMSO and NMP, but insoluble in methanol, ethanol, acetone and toluene.

The thermal properties of these copolymers were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It was confirmed from DSC measurements that the thermal transitions of PDMS-graft copolymers were not observed between −100 °C and 250 °C. The thermal stability of these polymers was evaluated by TGA, as shown in Fig. 1. It was found from TGA curves that the thermal degradation of PIS6, PIS11 and PIS19 mainly occurred at around 400 °C, whereas that of PI occurred over 500 °C. Therefore, it was considered that the weight loss of these copolyimides would be derived from the degradation of the poly-mer side chain, PDMS segments. Anyway, the heat resistance of these PDMS-graft copolyimides until ca. 300 °C seems to be sufficient for the thermal imidization process by heating.

3.2. Characterizations of polymer membranes

The tough self-standing membranes could be prepared by solvent-casting method from the chloroform solutions of PDMS-

<table>
<thead>
<tr>
<th>Code</th>
<th>m</th>
<th>Mn × 10^3</th>
<th>Mw × 10^3</th>
<th>Mw/Mn</th>
<th>Mw(LS) × 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIS6</td>
<td>5.7</td>
<td>29.4</td>
<td>94.6</td>
<td>3.22</td>
<td>145</td>
</tr>
<tr>
<td>PIS11</td>
<td>11.3</td>
<td>26.0</td>
<td>90.0</td>
<td>3.46</td>
<td>123</td>
</tr>
<tr>
<td>PIS19</td>
<td>18.9</td>
<td>27.2</td>
<td>125</td>
<td>4.60</td>
<td>137</td>
</tr>
<tr>
<td>PI</td>
<td>–</td>
<td>48.5</td>
<td>112</td>
<td>2.31</td>
<td>125</td>
</tr>
</tbody>
</table>

* Average degree of polymerization of PDMS segment (m) was calculated by 1H NMR.
* Number- and weight-average molecular weights (Mn and Mw) were determined by GPC using THF as an eluent.
* Mw(LS) was determined by a light scattering detector equipped with GPC.

The morphology of PIS6, PIS11 and PIS19 membrane was investigated by TEM observation. Fig. 2 indicates the TEM images of the cross section of these membranes. In these pictures, the dark region must be PDMS domain stained by RuO4, because the dark region was increased as the increase of PDMS content. Miyata et al. have studied the morphological effects of microphase separation on the ethanol-permselectivity for the graft copolymer composed of poly(methyl methacrylate) and PDMS [11]. They have described that the PDMS domain was stained by RuO4, and the permselectivity was strongly governed by the morphology of their microphase separation. Ghosh and Banerjee also reported the micro-phase separation of PDMS/polyimide block copolymer films [31]. As can be seen in Fig. 2, TEM image clearly demonstrated that these membranes consisted of a microphase separation of backbone and side-chain components, and the continuous phase of flexible PDMS domain existed in the membrane, which was surrounded by the hard shell consisted of polyimide backbone. The surface property of the copolyimides would be due to the continuous phase of PDMS domain, and the strength of the membrane would be derived from the polyimide shell.
The gas permeabilities of these membranes were investigated to reveal the effect of PDMS segment length on the membrane permeability, which was a basic property for the use of separation membrane. Gas permeability coefficients of N$_2$, O$_2$, H$_2$, CO$_2$ and C$_2$H$_6$ through these membranes were evaluated as shown in Table 3. The gas permeability coefficients of PDMS-graft copolyimide membranes increased as the PDMS segment length became longer (PIS19 > PIS11 > PIS6), which was in good agreement with the values of density of these membranes listed in Table 2. In addition, CO$_2$ and C$_2$H$_6$ permeability of these membranes were significantly high, although the molecular diameters of these gases were larger than those of the other gases, N$_2$, O$_2$ and H$_2$. The tendency of gas permeability of these copolyimide membranes was similar to that of silicone membrane. Therefore, PDMS-graft copolyimide membranes would possess the highly permeable domains which consisted of PDMS chain with high content.

### 3.3. Effect of thermal treatment on membrane properties

In general, the thermal imidization process is necessary to complete the conversion of amic acid components to imide bonds even after a chemical imidization in the polymerization, because the small amount of amic acid component is remained in the main chain structure. Actually, the obtained copolyimide films became more substantial after the thermal treatment over 150 °C. However, unexpectedly, it was found that the gas permeability coefficients of

### Table 2
Free surface energy and the density of polymer membranes.

<table>
<thead>
<tr>
<th>Code</th>
<th>Contact angle (degree)</th>
<th>Free surface energy (mN m$^{-1}$)</th>
<th>Density ($\times 10^{-3}$ kg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>PIS6</td>
<td>99.2</td>
<td>85.3</td>
<td>14.0</td>
</tr>
<tr>
<td>PIS11</td>
<td>99.2</td>
<td>83.9</td>
<td>14.8</td>
</tr>
<tr>
<td>PIS19</td>
<td>101</td>
<td>82.8</td>
<td>15.8</td>
</tr>
<tr>
<td>PI</td>
<td>92.8</td>
<td>77.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Silicone$^a$</td>
<td>113</td>
<td>106</td>
<td>6.60</td>
</tr>
</tbody>
</table>

$^a$ Cross-linked PDMS membrane as a reference sample.

### Table 3
Gas permeability coefficients and separation factors of polyimide membranes at 30 °C.

<table>
<thead>
<tr>
<th>Code</th>
<th>Gas permeability coefficient, $P$ (Barrer$^{-1}$)</th>
<th>Selectivity, $P$/P$_{N2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N$_2$</td>
<td>O$_2$</td>
</tr>
<tr>
<td>PIS6$^b$</td>
<td>31.8</td>
<td>80.1</td>
</tr>
<tr>
<td>PIS11$^b$</td>
<td>69.7</td>
<td>160</td>
</tr>
<tr>
<td>PIS19$^b$</td>
<td>131</td>
<td>292</td>
</tr>
<tr>
<td>PI$^c$</td>
<td>0.34</td>
<td>1.43</td>
</tr>
<tr>
<td>Silicone$^a$</td>
<td>243</td>
<td>509</td>
</tr>
</tbody>
</table>

$^a$ 1 Barrer = 7.52 $\times$ 10$^{-15}$ m$^3$ (STP) m$^{-2}$ sec$^{-1}$ Pa$^{-1}$.
$^b$ PIS membranes were heated at 150 °C for 24 h before this measurement.
$^c$ PI membranes was heated at 250 °C for 24 h before this measurement.
$^d$ Cross-linked PDMS membrane as a reference sample.
these PDMS-graft copolyimide membranes decreased by the thermal treatment at 200 °C, as shown in Fig. 3. The gas permeability coefficients of nitrogen, oxygen, hydrogen, ethane and carbon dioxide through both of PIS6 and PIS11 membranes clearly decreased after the thermal treatments at 200 °C and 250 °C in vacuo for 24 h. Therefore, in order to clarify the influence of the thermal treatment on the membrane properties, the changes of mechanical property, IR spectra and CPMAS NMR spectra were investigated for these copolyimide membranes after the thermal treatments at 80 °C - 250 °C.

Fig. 4 shows changes of Young’s modulus, the tensile strength and the elongation to break, which are determined by tensile tests of the thermally treated PI, PIS6, PIS11 and PIS19 films at each temperature. The stress-strain behaviors of these films are shown in supporting information (Fig. S3 – S6). The values of Young’s modulus and tensile strength of PISmn films slightly increased at 200 °C and 250 °C in vacuo for 24 h, whereas the elongation of PI film similarly increased. On the other hand, the values of elongation to break of PISmn films decreased at 200 °C treatment in vacuo for 24 h, whereas the elongation of PI film slightly increased. It was considered that the imidization of the small amount of amic acid component proceeded in every films at over 150 °C in vacuo for 24 h, which resulted in the increase of Young’s modulus and tensile strength. Anyhow, the great decrease of elongation values of PISmn films, as shown in Fig. 4 (C), would be caused by the other factors, for example, the change of soft segment, i.e. PDMS segment in the side chain.

Accordingly, FT-IR spectra and 13C and 29Si CPMAS spectra were measured for thermally treated films to reveal the change in chemical structure of PIS6 film, which exhibited the greatest change in the gas permeability and the elongation to break. Fig. 5 (A) shows the difference of FT-IR spectra of PIS6 films after treated at 100 °C and 250 °C in vacuo for 24 h. Then, the ratios of peak intensities of PDMS segment (Si–C and Si–O–Si) and the carbonyl group in the backbone component (C=O) of PIS6 were calculated from the FT-IR spectra. Fig. 5 (B) shows the relationship between the temperature of thermal treatment and the ratios of peak intensities in FT-IR spectra of PIS6 film. The intensity ratio of Si–C and Si–O–Si/C=O were estimated from the absorption peak intensities at 1253 cm⁻¹ (Si–CH₃ δ), 1012 cm⁻¹ (Si–O–Si st) and 1722 cm⁻¹ (C=O st). As a standard value, the intensity ratio of Ar/C=O was also calculated from the absorption peak intensities at 1504 cm⁻¹ (C=C st in aromatic) and 1722 cm⁻¹. As seen in Fig. 5 (B), according to the thermal treatment at 200 °C and 250 °C in vacuo for 24 h, the intensity ratios of Si–C/C=O and Si–O–Si/C=O were definitely decreased, although the ratio of Ar/C=O was not changed. Hence, it is speculated that PDMS segment was reduced by the thermal treatment at 200 °C.

13C and 29Si CPMAS NMR spectra were conducted for the thermally treated PIS6 films at various temperatures, as shown in Fig. 6. In Fig. 6 (A), the peaks between 100 ppm and 170 ppm were assigned to aromatic carbons in the backbone component of PIS6, and the peaks at 20–30 ppm were assigned to the terminal –CdH₉ groups in PDMS segments. A peak at 0 ppm is assigned to the –CH₃ groups of PDMS components. It was observed in Fig. 6 (A) that the peak intensities at 20–30 ppm and 0 ppm decreased as the temperature increased from 150 °C to 250 °C, when those were compared to the peak intensities at 100–170 ppm. This result suggested that the backbone structure was not affected by the thermal treatment, but the thermal elimination of the –CdH₉ end group in PDMS segment occurred and the reduction of PDMS segments proceeded especially at 250 °C. In addition, as shown in Fig. 6 (B), the peak intensity at 9 ppm was significantly affected by thermal treatment, where the peaks at 9 ppm and –24 ppm were assigned to –Si(CH₃)₂–CdH₉ and –Si(CH₃)₂O, respectively. The peak intensity of the terminal silyl group (9 ppm) of PIS6 film treated at 200 °C or 250 °C was obviously lower than that treated at 80 °C or 150 °C, while the peak intensities of the siloxane unit (–24 ppm) were observed without change. This NMR results indicated that the component of terminal butyldimethylsilyl group in PDMS segment was decreased by the thermal treatment at 200 °C and 250 °C in vacuo for 24 h.

From these results, it would be demonstrated that a cross-linked reaction occurred between the PDMS segments in the side chain during the thermal treatment at nearly 200 °C in vacuo for 24 h, where the elimination of terminal group of PDMS segment occurred as an initiation reaction. The speculated reaction mechanism is shown in Fig. 7. The rearrangement of PDMS chain would occur by acidic atmosphere in the presence of the very small amount of unreacted amic acid unit during the chemical imidization, even though it was not observed in 1H NMR and FT-IR spectra. Unfortunately, this phenomenon was not confirmed as a weight

---

**Fig. 3.** The effect of temperature of the thermal treatment on the gas permeability coefficients of nitrogen (●), oxygen (□), hydrogen (▲), ethane (△) and carbon dioxide (■) through (A) PIS6 and (B) PIS11 membranes.
loss in TGA measurement from 200 °C to 250 °C (Fig. 1), which would be due to the difference of heating condition. Then, the cross-linking of the side chain proceeded in the thermal treatment to make the membrane insoluble. Therefore, it was considered that the PDMS-graft polyimide membrane was expected to be an ideal material for pervaporation membrane, because of its good processability and the durability to several organic liquids.

3.4. Pervaporation performance

The effect of PDMS segment length on the pervaporation performance of PDMS-graft copolyimide membranes, which were thermally treated at 200 °C in vacuo for 24 h, was investigated as compared with silicone membrane. The dilute aqueous solutions of organic liquids, such as ethanol, acetone, benzene, chloroform and dichloromethane, were used as feed solutions in the pervaporation experiments. The saturated organic solutions in water were prepared for benzene, chloroform and dichloromethane. The pervaporation results of each membrane are summarized in Table 4.

As a result, the preferential permeation of organic liquids was observed for all the membranes, and the separation factor and the flux increased as the increase of PDMS segment length. Such an organic-permselectivity would be due to the high solubility of the organic solvents on the membrane surface and the high diffusivity.
through the membrane. The high diffusivity of the membrane would be an important factor to achieve the organic-selectivity in pervaporation, because the difference between the diffusivities of the relatively large organic molecules and the small water molecule should be minimized throughout the membrane. On the other hand, it was reported that the difference of selectivity for each organic liquid through such organic-permselective membrane was strongly depended on the solubility parameters of organic liquids [25]. For example, ca. 9.5 wt% aqueous solutions of ethanol and acetone were concentrated to 50 wt% and 81 wt%, respectively, through PIS19 membrane. On the contrary, in the pervaporation of benzene, chloroform and dichloromethane solutions, PIS11 and PIS19 membranes exhibited very high separation factors, which were higher than that of silicone membrane. Especially, the saturated solution of dichloromethane in water (2.0 wt%) was concentrated to nearly 90 wt% through PIS11 and PIS19 membranes. It would be due to the high solubility of the dichloromethane on the membrane surface, the solubility parameter of which should be almost same as that of dichloromethane. Therefore, it is expected that these membranes have a great advantage for the removal of VOCs such as dichloromethane, chloroform and benzene, whose environmental standards are very strict for waste fluid or industrial drainage.

Concerning the application to a removal of VOCs from their dilute aqueous solutions, the removal efficiency of dichloromethane from its dilute aqueous solution was investigated by the similar pervaporation experiment using PIS6, PIS11, PIS19 and silicone membranes. For this purpose, the feed concentrations were determined by gas chromatography in 5 h intervals during the pervaporation of 400 g of the saturated dichloromethane solutions in water. The changes in the feed concentrations are shown in Fig. 8. These PISm membranes exhibited the better efficiency than silicone membrane, which would be due to the difference of membrane thickness as listed in Table 4. It was found that the concentration of dichloromethane was efficiently reduced by the pervaporation through these membranes with a stable permeation during 10 h, where 1.8 wt% of dichloromethane was reduced to 0.08 wt% in the case of PIS11 membrane. Kujawski et al. have also reported the detailed experiments for the effective removal of acetone, butanol and ethanol from the dilute aqueous solutions by pervaporation through PDMS membrane [31]. Thus, if the ultrathin membrane can be produced on a porous support membrane, it is
expected that a removal of organic components from waste fluid or fermentation broth would be efficiently achieved.

When these membranes were swollen with feed solutions in pervaporation, it was wondering that the microphase separation as shown in Fig. 2 might be changed to reduce the separation performance. However, the hard shell consisted of polyimide backbone would work as the linkage of PDMS domain to maintain the stable permeation during pervaporation. Actually, it was demonstrated that the gas permeability of dried PIS11 membrane, which was once used in pervaporation experiment, was not different from that of virgin membrane and the reproducibility of pervaporation results was also observed. Therefore, such a microphase separation of PDMS and polyimide phases would be stable enough for the membrane to achieve the stable permeations of gases and liquids.

**4. Conclusion**

Three kinds of PDMS-graft copolyimides having different PDMS segment lengths were successfully synthesized, and the tough self-standing membranes were prepared by solvent casting method, which became insoluble in any solvent by thermal treatment at over 150 °C. From the detailed characterizations of the thermally treated membranes, it was speculated that the rearrangement of PDMS segments occurred according to the elimination of the terminal silyl group, which resulted in the cross-linked structure between the PDMS segments to make the membrane insoluble. It was also found from TEM observations that these membranes consisted of a microphase separation of backbone and side-chain components to produce a honeycomb-like structure, where the flexible PDMS domain was surrounded by the hard shell consisted of polyimide backbone. The high gas permeability of the membrane would be caused by the continuous phase of flexible PDMS domain, and the mechanical strength would be derived from the hard shell. Furthermore, the pervaporation performance of these membranes induced the efficient removal of VOCs from the aqueous mixtures. Consequently, it is expected that PDMS-graft copolyimide membrane can be used for the removal of toxic organic components from the waste-water by pervaporation technique, due to their enough permselectivity, processability for the production of thin membrane and durability to organic liquids.

**Acknowledgment**

The authors would like to thank Dr. Takamasa Fuchikami and Dr. Takamasa Yoshida, who belong to Chemirea Co., Ltd., for their help of the determination of the dilute concentrations of dichloromethane by gas chromatography. We also express our gratitude to Professor Tomokazu Iyoda and Assistant Professor Kaori Kamata, who belong to Chemical Resources Laboratory, Tokyo Institute of Technology, for their help in TEM observations. Then, we sincerely thank Professor Takashi Asaka, who belongs to Department of Applied Chemistry, Tokai University, for his help in the measurements of stress-strain behaviors of polymer films. This work was supported by a Grant-in-Aid for Research from the Tokai University.

**Table 4**

Pervaporation of dilute aqueous organic liquids through PIS9, PIS11, PIS19 and silicone membranes at 50 °C. (Thickness: PIS6, PIS11, PIS19 – 150 mm, Silicone – 340 mm).

<table>
<thead>
<tr>
<th>Code</th>
<th>Organic liquid</th>
<th>Composition (wt%)</th>
<th>$\beta$</th>
<th>$J$ $\times 10^2$ (kg m$^{-2}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIS6</td>
<td>Ethanol</td>
<td>In feed 25.2</td>
<td>3.30</td>
<td>1.63</td>
</tr>
<tr>
<td>PIS11</td>
<td>Acetone</td>
<td>In feed 25.0</td>
<td>6.66</td>
<td>3.00</td>
</tr>
<tr>
<td>PIS19</td>
<td>Benzene</td>
<td>In feed 8.5</td>
<td>9.80</td>
<td>2.69</td>
</tr>
<tr>
<td>Siliconec</td>
<td></td>
<td>In feed 81.5</td>
<td>40.3</td>
<td>8.36</td>
</tr>
<tr>
<td>PIS6</td>
<td>Chloroform</td>
<td>In feed 62.3</td>
<td>205</td>
<td>4.31</td>
</tr>
<tr>
<td>PIS11</td>
<td>Acetone</td>
<td>In feed 70.1</td>
<td>291</td>
<td>8.49</td>
</tr>
<tr>
<td>PIS19</td>
<td>Benzene</td>
<td>In feed 67.2</td>
<td>254</td>
<td>9.04</td>
</tr>
<tr>
<td>Siliconec</td>
<td></td>
<td>In feed 66.9</td>
<td>250</td>
<td>5.52</td>
</tr>
<tr>
<td>PIS6</td>
<td>Chloroform</td>
<td>In feed 66.5</td>
<td>315</td>
<td>9.38</td>
</tr>
<tr>
<td>PIS11</td>
<td>Acetone</td>
<td>In feed 89.6</td>
<td>420</td>
<td>28.2</td>
</tr>
<tr>
<td>PIS19</td>
<td>Benzene</td>
<td>In feed 89.4</td>
<td>413</td>
<td>29.4</td>
</tr>
<tr>
<td>Siliconec</td>
<td></td>
<td>In feed 87.7</td>
<td>349</td>
<td>17.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>Organic liquid</th>
<th>Composition (wt%)</th>
<th>$\beta$</th>
<th>$J$ $\times 10^2$ (kg m$^{-2}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIS6</td>
<td>Ethanol</td>
<td>In feed 25.2</td>
<td>3.30</td>
<td>1.63</td>
</tr>
<tr>
<td>PIS11</td>
<td>Acetone</td>
<td>In feed 25.0</td>
<td>6.66</td>
<td>3.00</td>
</tr>
<tr>
<td>PIS19</td>
<td>Benzene</td>
<td>In feed 8.5</td>
<td>9.80</td>
<td>2.69</td>
</tr>
<tr>
<td>Siliconec</td>
<td></td>
<td>In feed 81.5</td>
<td>40.3</td>
<td>8.36</td>
</tr>
<tr>
<td>PIS6</td>
<td>Chloroform</td>
<td>In feed 62.3</td>
<td>205</td>
<td>4.31</td>
</tr>
<tr>
<td>PIS11</td>
<td>Acetone</td>
<td>In feed 70.1</td>
<td>291</td>
<td>8.49</td>
</tr>
<tr>
<td>PIS19</td>
<td>Benzene</td>
<td>In feed 67.2</td>
<td>254</td>
<td>9.04</td>
</tr>
<tr>
<td>Siliconec</td>
<td></td>
<td>In feed 66.9</td>
<td>250</td>
<td>5.52</td>
</tr>
<tr>
<td>PIS6</td>
<td>Chloroform</td>
<td>In feed 66.5</td>
<td>315</td>
<td>9.38</td>
</tr>
<tr>
<td>PIS11</td>
<td>Acetone</td>
<td>In feed 89.6</td>
<td>420</td>
<td>28.2</td>
</tr>
<tr>
<td>PIS19</td>
<td>Benzene</td>
<td>In feed 89.4</td>
<td>413</td>
<td>29.4</td>
</tr>
<tr>
<td>Siliconec</td>
<td></td>
<td>In feed 87.7</td>
<td>349</td>
<td>17.1</td>
</tr>
</tbody>
</table>

a Composition of organic liquid in feed and permeate. 
b $\beta$: Separation factor (organic liquid/water), $J$: Flux. 
c Cross-linked PDMS membrane as a reference sample.

**Fig. 8.** Changes in the feed concentrations in the pervaporation of saturated dichloromethane solution in water through PIS6 (diagonal line), PIS11 (dotted line), PIS19 (checkerboard) and silicone (dark gray) membranes. Amount of feed solution: 400 g, Permeation area: 2.0 × 10$^{-2}$ m$^2$. 

C.M. Yun et al. / Polymer 103 (2016) 214–223
Supplement Association Union.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.09.044.

References