Abstract: Physical and gas transport properties of the asymmetric hyperbranched polyimide (HBPI) -silica hybrid membranes prepared with a dianhydride, 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and an asymmetric triamine, 2,4,4’-(triaminodiphenyl)ether (TADE), were investigated and compared with those of the symmetric HBPI-silica hybrid membranes prepared with a symmetric triamine, 1,3,5-tris(4-aminophenoxy)benzene (TAPOB). The HBPI-silica hybrid membranes were prepared via sol-gel reaction using hyperbranched polyamic acid of which end groups were modified with silane coupling agents, water and tetramethoxysilane. The thermal mechanical and dynamic mechanical analysis measurements confirmed that the rigidity of asymmetric HBPI was higher than that of symmetric HBPI because of the rigid and asymmetric structure of TADE monomer. In addition, the degree of branching of asymmetric HBPI is lower than that of symmetric HBPI because of the different reactivity of the three amino groups included in TADE. The rigidity and linearity of HBPIs had an effect on the progression of sol-gel reaction, consequently the gas transport properties. The increasing of the gas permeability coefficient of the asymmetric dianhydride(DA)-HBPI-silica hybrid membranes with increasing silica content was smaller than those of symmetric DA- and amine(AM)-HBPI-silica hybrid membranes. In addition, the gas permeability coefficient of the symmetric AM-HBPI-silica hybrid membranes decreased with increasing silica content. This was due to the fact that the dispersibility of silica in the asymmetric HBPI-silica hybrids, of which polymer chain was more rigid and linear than that of symmetric HBPI-silica hybrid, was not as fine as in the symmetric HBPI-silica hybrids, and that the long and tortuous diffusion path was newly formed by hybridization with silica.

Keywords: Hyperbranched Polyimide, Silica hybrid, Gas permeability, Asymmetric, Symmetric.

1. INTRODUCTION

Aromatic polyimide (PI) is one of the super engineering plastics which have been used in many high-technology fields. Especially, in recent years, aromatic PI have been of great interest in gas separation membranes because of their excellent mechanical and thermal property, and high gas permeability and selectivity [1-4]. PIs can take various kinds of structures by combining various monomers (diamines and dianhydrides).

For the asymmetric type PIs prepared from asymmetric dianhydrides and symmetric diamines, it has been reported that the resulting PIs exhibited increased solubility, reduced viscosity, and higher glass transition temperatures ($T_g$s) than the symmetric type PIs. The increased $T_g$s were ascribable to their rigid and bent structure, and the steric hindrance [5-8]. In general, it is said that the increase in gas permeability is also induced by the rigid molecular chain.

Hyperbranched polymers are highly branched three-dimensional dendritic polymers possessing unique properties (e.g., good solubility, reduced viscosity, higher fractional free volume, and multifunctionality) arising from multiple end groups. Hyperbranched polyimides (HBPIs) can be synthesized from either the self-polycondensation of AB$_2$-type monomers or the polycondensation reaction of A$_2$ + B$_3$ monomers, where A$_2$ represents a dianhydride monomer and B$_3$ represents a triamine monomer. In the case of an A$_2$ + B$_3$ type polycondensation reaction, a variety of HBPIs can be synthesized by changing the monomer ratio and combining A$_2$ and B$_3$ monomers [9-11]. Fang et al. were the first to report the synthesis of HBPIs derived from a triamine, tris(4-aminophenyl)amine (TAPA), and commercially available dianhydrides [12,13]. We have also studied physical and gas transport properties of the HBPI membranes which have benzene ring-centered symmetric structure; i.e. we have synthesized the HBPIs by polycondensation reaction of 4,4’-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) as a dianhydride monomer and triamine monomers, 1,3,5-tris(4-aminophenoxy) benzene (TAPOB), 1,3,5-tris(4-aminophenoxy) triazine (TAPOTZ) and 1,3,5-...
tris(4-aminophenyl)benzene (TAPB) and found that the HBPI(6FDA-TAPB) membranes exhibit the highest gas permeability coefficient arising from the highest fractional free volume (FFV) [14].

Additionally, we have studied the syntheses and gas transport properties of symmetric HBPI-silica hybrid membranes. Organic-inorganic hybrid materials have been recognized as a new class of high performance materials because they combine the advantages of the inorganic material (e.g., rigidity and thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility, and processability) [15, 16]. The synthesis of PI–silica hybrid materials and the investigation of their physical and gas transport properties have also received much attention [17-19]. In our previous researches about the symmetric HBPI-silica hybrid membranes, we found that the gas permeability and CO₂/CH₄ selectivity of these membranes prepared via sol-gel reaction using tetramethoxysilane (TMOS) increased with increasing silica content, suggesting the characteristic distribution and interconnectivity of free volume holes created by the incorporation of silica [14, 20-26].

In this study, physical and gas transport properties of the asymmetric HBPI-silica hybrid membranes prepared with a dianhydride, 6FDA, and an asymmetric triamine, 2,4,4’-(triaminodiphenyl)ether (TADE), were investigated and compared with those of symmetric HBPI-silica hybrid membranes prepared with a symmetric triamine, TAPOB.

2. EXPERIMENTAL

2.1. Materials

TAPOB was synthesized by the reduction of 1,3,5-tris(4-nitrophenoxy)benzene with palladium carbon and hydrazine in methanol[27]. Triamine monomer, TADE, and dianhydride monomer, 6FDA, were kindly supplied from Wakayama Seika Kogyo Co. (Wakayama, Japan) and Daikin Industries (Osaka, Japan), respectively. TMOS was purchased from AZmax, Co., Ltd (Tokyo, Japan). 3-Aminopropyltrimethoxysilane (APTrMOS) and 3-(triethoxysilyl)propyl succinic anhydride (TEOSPSA) were purchased from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA) and Gelest Inc. (Morrisville, PA, USA), respectively. N, N-Dimethylacetamide (DMAc) used as a solvent was purchased from Nacalai Tesque (Kyoto, Japan). The chemical structures of the monomers, silane coupling agents and silicon alkoxide are shown in Figure 1.

2.2. Polymerization

2.2.1. Dianhydride-Terminated Hyperbranched Polyamic Acids (DA-HBPAA)

Three mmol of 6FDA was dissolved in 30-40 ml of DMAc in a 100-ml three-neck flask under N₂ flow at room temperature. 1.6 mmol of triamine (TADE or TAPOB) in 20 ml of DMAc was then added dropwise through a syringe with stirring. The monomer content was controlled to ca. 3.5 wt%. After stirring for 3 h, 0.4 mmol of APTrMOS as a coupling agent was added into the reaction mixture with further stirring for 1 h to afford

![Figure 1: Chemical structures of monomers, silane coupling agents, and silicon alkoxide.](image-url)
asymmetric and symmetric DA-HBPAA. The degree of terminal modification was 1/3.

2.2.2. Amine-Terminated Hyperbranched Polyamic Acids (AM-HBPAA)

Three mmol of triamine (TADE or TAPOB) was dissolved in 30-34 ml of DMAC in a 100-ml three-neck flask under N₂ flow at room temperature. 3.0 mmol of 6FDA in 28-40 ml of DMAC was then added dropwise through a syringe with stirring. The monomer content was controlled to ca. 3.5 wt%. After stirring for 3 h, 1.0 mmol of TEOSPSA as a coupling agent was added into the reaction mixture with further stirring for 1 h to afford asymmetric and symmetric AM-HBPAA. The degree of terminal modification was 1/3.

2.3. Membrane Formation

The asymmetric and symmetric HBPI-silica hybrid membranes were prepared by the reaction of asymmetric or symmetric HBPAAs with silicon alkoxide, TMOS, via sol–gel reaction, and then followed by thermal imidization. Appropriate amounts of TMOS and deionized water (TMOS : deionized water = 1 : 6 as a molar ratio) were added into the DMAc solution of the asymmetric or symmetric HBPAAs. The mixed solutions were stirred for 24 h and then cast on PET films and dried at 85°C for 3 h. These prepared membranes were peeled off and subsequently imidized and hybridized at 100°C for 1 h, 200°C for 1 h, and 300°C for 1 h in a heating oven under N₂ flow. The average thickness of the asymmetric or symmetric HBPI-silica hybrid membranes was about 30 μm.

2.4. Measurements

The inherent viscosity (ηinh) of HBPAAs was measured in a DMAc solution with a 0.5 g/dL concentration at 25°C with an Ubbelohde viscometer. Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were recorded on a JASCO FT/IR-4100 (Tokyo, Japan) at a wavenumber range of 550–4000 cm⁻¹ and a resolution of 1 cm⁻¹. Optical transmittances (ultraviolet-visible spectroscopy) were measured with a JASCO V-530 UV/vis spectrometer at wavelengths of 200–800 nm. Thermal mechanical analysis (TMA) measurements were carried out using a Seiko Instruments TMA/SS6100 (Chiba, Japan) at a heating rate of 5°C/min under N₂ flow. Dynamic mechanical analysis (DMA) measurements were performed with a Seiko Instruments DMA6100 at a heating rate of 5°C/min under N₂ flow; the load frequency was 1 Hz. Thermogravimetric-differential thermal analysis (TG-DTA) experiments were performed with a Seiko Instruments TG/DTA5200 at a heating rate of 10°C/min under air flow. The densities (ps) of the HBPIs were measured by a floating method with bromoform and 2-propanol at 25°C. According to the group contribution method, the FFV of HBPIs can be estimated by the following equation [28]:

\[
\text{FFV} = \frac{V_w - 1.3V_s}{V_w}
\]  

(1)

where \(V_s\) (cm³/mol) is the specific molar volume and \(V_w\) (cm³/mol) is the van der Waals volume of the repeating unit. CO₂, O₂, N₂, and CH₄ permeation measurements were taken with a constant volume/variable pressure apparatus under 76 cmHg at 25°C. The permeability coefficient, \(P\) [cm³(STP) cm/cm² s cmHg], was determined by the equation [29]:

\[
P = \frac{22414 L V dp}{A p RT dt}
\]  

(2)

where \(A\) is the membrane area (cm²), \(L\) is the membrane thickness (cm), \(p\) is the upstream pressure (cmHg), \(V\) is the downstream volume (cm³), \(R\) is the universal gas constant (6236.56 cm³ cmHg/mol K), \(T\) is the absolute temperature (K), and \(dp/dt\) is the permeation rate (cmHg/s). The gas permeability coefficient can be explained on the basis of the solution-diffusion mechanism, which is represented by the equation [30,31]:

\[
P = D \times S
\]  

(3)

where \(D\) (cm²/s) is the diffusion coefficient and \(S\) [cm³(STP)/cm³ polym cmHg] is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method represented by the equation [32]:

\[
D = \frac{L^2}{6\theta}
\]  

(4)

where \(\theta\) (s) is the time-lag.

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis

TADE has asymmetric structure in which two amino groups bind to one of the phenyl group of the diphenyl ether. The reactivity of the amino group in 2-position is lower than other two amino groups. Thus, it is considered that the degree of branching (DB) of the asymmetric HBPI is relatively low and the linearity is
high. Chen et al. reported that the DB of symmetric AM-6FDA-TAPOB HBPI was 0.65 [33]. In our study, the DBs of asymmetric AM-6FDA-TAPB HBPI and symmetric AM-6FDA-TAPOB HBPI measured by a same manner as Chen were 0.25 and 0.65, respectively. This result confirmed that the asymmetric HBPI is more linear than symmetric HBPI.

Table 1: Physical Properties of the Asymmetric and Symmetric HBPI-Silica Hybrid Membranes

<table>
<thead>
<tr>
<th></th>
<th>( \eta_{inh} ) [dL/g]</th>
<th>Transmittance at 600nm [%]</th>
<th>TMA CTE [ppm/°C]</th>
<th>DMA Tg [°C]</th>
<th>TG-DTA ( T_d^s ) [°C]</th>
<th>Residue [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric DA-HBPI</td>
<td>0.27</td>
<td>69.4</td>
<td>47</td>
<td>350</td>
<td>471</td>
<td>0</td>
</tr>
<tr>
<td>10wt%SiO(_2)</td>
<td>-</td>
<td>88.0</td>
<td>41</td>
<td>390</td>
<td>486</td>
<td>10</td>
</tr>
<tr>
<td>20wt%SiO(_2)</td>
<td>-</td>
<td>89.3</td>
<td>33</td>
<td>394</td>
<td>492</td>
<td>20</td>
</tr>
<tr>
<td>30wt%SiO(_2)</td>
<td>-</td>
<td>92.9</td>
<td>28</td>
<td>N.D.</td>
<td>503</td>
<td>30</td>
</tr>
<tr>
<td>Asymmetric AM-HBPI</td>
<td>0.56</td>
<td>20.1</td>
<td>45</td>
<td>384</td>
<td>455</td>
<td>0</td>
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<tr>
<td>10wt%SiO(_2)</td>
<td>-</td>
<td>24.5</td>
<td>37</td>
<td>385</td>
<td>470</td>
<td>9</td>
</tr>
<tr>
<td>20wt%SiO(_2)</td>
<td>-</td>
<td>34.7</td>
<td>31</td>
<td>386</td>
<td>478</td>
<td>21</td>
</tr>
<tr>
<td>30wt%SiO(_2)</td>
<td>-</td>
<td>51.9</td>
<td>25</td>
<td>N.D.</td>
<td>495</td>
<td>30</td>
</tr>
<tr>
<td>Symmetric DA-HBPI</td>
<td>0.34</td>
<td>88.9</td>
<td>54</td>
<td>304</td>
<td>457</td>
<td>0</td>
</tr>
<tr>
<td>10wt%SiO(_2)</td>
<td>-</td>
<td>89.9</td>
<td>47</td>
<td>320</td>
<td>490</td>
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<tr>
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<td>496</td>
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<tr>
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<td>90.3</td>
<td>31</td>
<td>351</td>
<td>509</td>
<td>30</td>
</tr>
<tr>
<td>Symmetric AM-HBPI</td>
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<td>50.8</td>
<td>53</td>
<td>366</td>
<td>466</td>
<td>0</td>
</tr>
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<td>-</td>
<td>54.4</td>
<td>47</td>
<td>379</td>
<td>477</td>
<td>7</td>
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<tr>
<td>20wt%SiO(_2)</td>
<td>-</td>
<td>66.8</td>
<td>41</td>
<td>378</td>
<td>481</td>
<td>20</td>
</tr>
<tr>
<td>30wt%SiO(_2)</td>
<td>-</td>
<td>76.3</td>
<td>31</td>
<td>N.D.</td>
<td>495</td>
<td>33</td>
</tr>
</tbody>
</table>

\( \eta_{inh} \) value on corresponding HBPAAs.

The \( \eta_{inh} \) values of HBPAAs are shown in Table 1. In Table 1, it was recognized that the \( \eta_{inh} \) values of TADE system HBPAAs were lower than those of corresponding TAPOB system HBPAAs. Generally, it is said that the \( \eta_{inh} \) value of linear-type polymer is higher than that of hyperbranched polymer. Thus, it was expected that the \( \eta_{inh} \) value of TADE system HBPAAs with lower degree of branching was higher than that of TAPOB system HBPAAs. However the opposite result was obtained. This might result from the fact that it is difficult to synthesize high molecular weight asymmetric HBPAAs molecule because of low reactivity of the amino group in 2-position in TADE.

3.2. Polymer Characterization

ATR FT-IR spectra of the asymmetric and symmetric pristine HBPIs, and the asymmetric AM-HBPI-silica hybrid films are shown in Figure 2. The bands observed around 1784 cm\(^{-1}\) (C=O asymmetrical stretching), 1721 cm\(^{-1}\) (C=O symmetrical stretching), 1360-1374 cm\(^{-1}\) (C-N stretching), and 718-721 cm\(^{-1}\) (C=O bending) are characteristic absorption bands of polyimides [13, 33]. These results indicate that the asymmetric HBPIs are well imidized by thermal imidization at 300°C as well as symmetric HBPIs. The bands around 1857 cm\(^{-1}\) in Figure 2a is attributed to the stretching of C=O of the terminal anhydride groups [12, 33]. The characteristic band attributed to the stretching of N-H of the terminal amino groups in the AM-HBPIs around 3392 cm\(^{-1}\) overlapped with the peak of the O-H groups, and could not be observed. For the HBPI-silica hybrid membranes (Figure 2b), it can be observed that the broad and strong absorption bands around 1100 cm\(^{-1}\) assigned to Si-O-Si stretching are enhanced with increasing SiO\(_2\) content, indicating sufficient formation of the three-dimensional Si-O-Si network [34]. The broad absorption bands around 3480 cm\(^{-1}\) are likely attributed to silanol groups remaining in the silica domain.

The optical transmittances at 600nm are shown in Table 1 and plotted against silica content in Figure 3. The optical transmittances of the pristine asymmetric HBPI films are lower than that of the corresponding
pristine symmetric HBPI films. This is because the molecular size of TADE, a triamine monomer of asymmetric HBPI, is smaller than TAPOB, a triamine monomer of symmetric HBPI, and therefore imide group density in a unit volume of asymmetric HBPI is higher than that of symmetric HBPI. The asymmetric and symmetric AM-HBPI films are colored to dark brown because of the partial thermal denaturation of terminal amino groups of the AM-HBPIs during thermal imidization [26]. However the optical transmittances of asymmetric and symmetric HBPI-silica hybrid films increased with increasing silica content, which might be attributed to decreased imide group density in a unit volume and favorable dispersion of silica. And this result indicated the good dispersion of silica component even in the asymmetric HBPI with high linearity. The fine and homogeneous dispersion of silica is brought not only by the characteristic hyperbranched structures of molecular chains but also by silane coupling agent which offer covalent bonds between organic and inorganic components [35].

The thermal properties of the asymmetric and symmetric HBPI-silica hybrids were investigated by TMA, DMA, and TG-DTA measurements. Coefficients of thermal expansion (CTEs) of the asymmetric and symmetric HBPI-silica hybrid films are listed in Table 1 and plotted against silica content in Figure 4. CTE values of the asymmetric HBPI-silica hybrid films were
lower than those of symmetric HBPI-silica hybrid films. This result is probably caused by the rigidity of the asymmetric HBPI molecular chains. Although only one ether unit is contained in TADE monomer, three ether units are contained in TAPOB monomer. Additionally, the steric hindrance is arisen by the asymmetric structure of TADE. Thus, the asymmetric HBPI molecules are more rigid than the symmetric HBPI molecules. With increasing silica content, CTEs of the asymmetric and symmetric HBPI-silica hybrid films decreased. This is caused by the enhancement of the thermal mechanical stability of the HBPI matrix by the formation of a robust three-dimensional Si-O-Si network and the decreased mobility of the HBPI molecular chains by hybridization with silica.

The Storage moduli (E') and tan δ of the asymmetric and symmetric HBPI-silica hybrid films are shown in Figure 5a-d. Unfortunately, DMA measurement for the asymmetric DA-HBPI-silica hybrid film containing 30 wt% of SiO₂ could not be carried out because of its mechanical brittleness. In the glassy region, no remarkable difference between the asymmetric HBPI and the symmetric HBPI was observed. In contrast, in rubbery region, we can see that the E' values of the asymmetric HBPI-silica hybrid films were higher than those of corresponding symmetric HBPI-silica hybrid films. As in the case of CTE, this is attributed to the rigidity of asymmetric (TADE system) HBPI molecules. E’s of the asymmetric and symmetric HBPI-silica hybrid films increased with increasing the silica content in both regions. This increase is caused by the increasing of inorganic behavior and the decreasing of mobility of HBPI molecular chains by hybridization with silica. Glass transition temperatures (Tgs) of the asymmetric and symmetric HBPI-silica hybrid films determined from the peak top of tan δ are summarized in Table 1 and plotted against the silica content in Figure 6. The Tg value of asymmetric pristine HBPI is higher than that of corresponding symmetric pristine HBPI. With increasing the silica content, Tgs shifted to a higher temperature along with a decrease of peak intensity and a broadening of the half-width of tan δ. This result indicates that Tgs increased with the increase of inorganic behavior and the decrease of mobility of the

![Figure 5: E’ and tan δ of a) asymmetric DA-HBPI-silica hybrid films, b) asymmetric AM-HBPI-silica hybrid films, c) symmetric DA-HBPI-silica hybrid films and d) symmetric AM-HBPI-silica hybrid films.](image-url)
HBPI molecular chains caused by crosslinking through silica domains. Particularly, the $T_g$ values of asymmetric and symmetric DA-HBPI-silica hybrids increased with increasing silica content conspicuously. This is probably because that robust three-dimensional Si-O-Si network is easily formed via sol-gel reaction in the DA-HBPI-silica hybrids [26].

Figure 6: Glass transition temperatures ($T_g$) of asymmetric and symmetric HBPI-silica hybrid films derived from the peak top of tan $\delta$.

5% weight-loss temperatures ($T_d^5$) were investigated by TG-DTA and summarized in Table 1 along with the silica content determined from the residues at 800°C. The residues showed that all hybrid membranes contained an appropriate amount of silica, as expected. In Figure 7, $T_d^5$ values of the asymmetric and symmetric HBPI-silica hybrids are plotted against silica content. For the symmetric pristine HBPI, the $T_d^5$ value of the AM-HBPI was higher than that of corresponding DA-HBPI. On the other hand, in the case of asymmetric pristine HBPI, the $T_d^5$ value of the DA-HBPI was higher than that of corresponding AM-HBPI. $T_d^5$ values are affected by the amount of thermally unstable units in the molecule. For the symmetric HBPI, the $T_d^5$ value was probably controlled largely by the degradation of C-F bond in 6FDA component [26]. Thus, the $T_d^5$ value of the DA-HBPI with higher content of 6FDA was lower than that of AM-HBPI. On the other hand, in the asymmetric HBPI, the rigidity of AM-HBPI molecule may have a major effect on the $T_d^5$ value. The AM-HBPI is more rigid than DA-HBPI because there are many branching units in the AM-HBPI molecular chains, and so the crosslinking reaction between silane coupling agents is hard to progress and many thermally unstable silanol groups remain in asymmetric AM-HBPI molecular terminals. The $T_d^5$ values of the asymmetric and symmetric HBPI-silica hybrid membranes increased with increasing silica content. This increased thermal stability of the HBPI–silica hybrid membranes resulted from the formation of crosslinking between the HBPI and the silica domain, the introduction of inorganic characteristics, and the radical trapping effect of silica. Even though the silica content increased, the $T_d^5$ of the asymmetric HBPI-silica hybrids did not increase so conspicuously as corresponding symmetric HBPI-silica hybrids. This was probably because there were more silanol groups left in the asymmetric HBPI-silica hybrids than the symmetric HBPI-silica hybrids due to the rigidity of the asymmetric HBPI-silica hybrids as the above-mentioned discussion about the TMA and DMA behaviour.

Figure 7: 5% weight loss temperatures ($T_d^5$) of asymmetric and symmetric HBPI-silica hybrids.

3.3. Gas Transport Properties

The gas permeability, diffusion, and solubility coefficients of the asymmetric and symmetric HBPI-silica hybrid membranes are summarized in Table 2 along with the FFVs calculated from the group contribution method. And the CO$_2$ and CH$_4$ permeability, diffusion, and solubility coefficients are plotted against silica content in Figures 8a-c and 9a-c, respectively. In general, it is well known that gas diffusivities of polymers strongly depend on the FFVs [36, 37]. In this work, the gas permeabilities and FFVs of asymmetric HBPIs also tended to be higher than those of corresponding symmetric HBPIs. This was due to the higher rigidity of the asymmetric HBPI molecules. As shown in Table 2 and Figure 8, the CO$_2$ gas
permeability coefficient of the asymmetric AM-HBPI-silica hybrid membranes decreased with increasing silica content. In addition, the increasing of the CO$_2$ gas permeability coefficient of the asymmetric DA-HBPI-silica hybrid membranes with increasing silica content was smaller than those of corresponding symmetric DA-HBPI-silica hybrid membranes. For the CH$_4$ gas transport property, from Table 2 and Figure 9, it was recognized that the CH$_4$ gas permeability of the asymmetric HBPI-silica hybrid membranes decreased with increasing silica content conspicuously. And these results on permeability greatly reflect the change in the diffusivity coefficient. In our previous research, we found that the gas permeability coefficient and the CO$_2$/CH$_4$ selectivity of the symmetric DA-HBPI-silica hybrid membranes prepared via sol-gel reaction using TMOS increased with increasing silica content, suggesting the additional formation of free volume holes and a Langmuir sorption site effective for gas transport and separation properties through hybridization with silica [23,24,38]. However, in the asymmetric HBPI-silica hybrids with the high linearity of polymer chains, the dispersibility of a silica component is not as good as in the symmetric HBPI-silica hybrids. Therefore, silica component is aggregated to the size that affects the gas permeation but doesn’t affect the optical transmittance. The more the size of a silica component is large, the more the diffusion path formed in the PI-silica interfacial region becomes long and tortuous. The effect of newly formed diffusion path was countered by the increase of total path of the gas. Similar gas transport properties have been reported in several other studies. Merkel et al. studied the effect of particle size on gas permeability of superglassy polymer-silica nanocomposites. They reported the importance of using small particles to achieve the desired effect on gas transport in the polymer; the gas permeability increases linearly with decreasing silica particle size [39-41]. Dougnac et al. also reported similar results about the transport properties of the PA6-silica nanosphere composites [42]. In addition, we have reported that in the AM-HBPI-silica hybrid membranes, it was thought that an effect of hybridization on gas permeability was hard to be taken because of the rigidity of the AM-HBPI polymer chains which inhibit the progress of the sol-gel reaction [26]. It was considered that the rigidity of asymmetric AM-HBPI was the highest of all examined HBPIs, and that the gas permeability decreased with increasing the silica content.

### 3.4. O$_2$/N$_2$ and CO$_2$/CH$_4$ Selectivities

The ideal selectivity for the combination of gases A and B [$\alpha$(A/B)] is defined by the equation [43]:

$$\alpha(A/B) = \frac{P_{A/B}}{P_{B/B}}$$

where $P_{A/B}$ is the permeability of gas A through the membrane, and $P_{B/B}$ is the permeability of gas B through the membrane. This equation indicates the ratio of the permeabilities of two gases, which is a direct measure of the selectivity of the membrane.
where $\alpha^D(A/B)$ is the diffusivity selectivity and $\alpha^S(A/B)$ is the solubility selectivity. The $O_2/N_2$ and $CO_2/CH_4$ selectivities of the HBPI-silica hybrid membranes are listed in Table 3, and $\alpha(CO_2/CH_4)$ is plotted against the $CO_2$ permeability coefficients in Figure 10. In Figure 10, the open symbols represent the data of the pristine HBPI, and the darkness of filled symbols increased with increasing silica content.

In general, there is a trade-off relationship between permeability and permselectivity; the gas selectivity decreases with increasing the permeability, or vice versa [43]. In our previous study, we reported that 1) the $\alpha(O_2/N_2)$ values of the symmetric DA-HBPI-silica hybrid membranes slightly decreased and the $O_2$ permeability increased with increasing silica content along with the upper bound trade-off line for $O_2/N_2$ separation demonstrated by Robeson [44, 45], and 2) the both $\alpha(CO_2/CH_4)$ values and the $CO_2$ permeability of the symmetric DA-HBPI-silica hybrid membranes increased with increasing silica content. In this study, for the asymmetric AM-HBPI silica hybrid membranes, the plots of the $O_2$ permeability and $O_2/N_2$ permselectivity relationship shifted to the low permeability region with increasing silica content along with the upper bound trade-off line. On the other hand, the plots of the $CO_2$ permeability and $CO_2/CH_4$ permselectivity relationship shifted to the low permeability region with significant increase of selectivity with the increase of silica content (Figure 10). For this reason, it is considered that the free volume holes formed by hybridization with silica in the asymmetric AM-HBPI silica hybrid membranes have an excellent molecular sieving effect on $CO_2/CH_4$ selectivity because the $CH_4$ gas diffusivity coefficient decreased with increasing silica content conspicuously.
Table 3: \( \text{O}_2/\text{N}_2 \) and \( \text{CO}_2/\text{CH}_4 \) Selectivities of Asymmetric and Symmetric HBPI-Silica Hybrid Membranes at 76 cmHg and 25°C

<table>
<thead>
<tr>
<th></th>
<th>( \alpha(\text{O}_2/\text{N}_2) )</th>
<th>( \alpha^3(\text{O}_2/\text{N}_2) )</th>
<th>( \alpha(\text{CO}_2/\text{CH}_4) )</th>
<th>( \alpha^3(\text{CO}_2/\text{CH}_4) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric DA-HBPI</td>
<td>6.7</td>
<td>5.0</td>
<td>1.4</td>
<td>70</td>
</tr>
<tr>
<td>10wt%SiO(_2)</td>
<td>6.6</td>
<td>4.9</td>
<td>1.3</td>
<td>84</td>
</tr>
<tr>
<td>20wt%SiO(_2)</td>
<td>6.5</td>
<td>5.2</td>
<td>1.4</td>
<td>100</td>
</tr>
<tr>
<td>30wt%SiO(_2)</td>
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<td>5.7</td>
<td>1.2</td>
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</tr>
<tr>
<td>Asymmetric AM-HBPI</td>
<td>5.3</td>
<td>3.3</td>
<td>1.7</td>
<td>82</td>
</tr>
<tr>
<td>10wt%SiO(_2)</td>
<td>5.4</td>
<td>4.3</td>
<td>1.3</td>
<td>88</td>
</tr>
<tr>
<td>20wt%SiO(_2)</td>
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<td>6.2</td>
<td>1.1</td>
<td>100</td>
</tr>
<tr>
<td>30wt%SiO(_2)</td>
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<td>Symmetric DA-HBPI</td>
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<td>5.8</td>
<td>1.2</td>
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</tr>
<tr>
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</tr>
<tr>
<td>20wt%SiO(_2)</td>
<td>6.7</td>
<td>5.3</td>
<td>1.3</td>
<td>82</td>
</tr>
<tr>
<td>30wt%SiO(_2)</td>
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<td>5.8</td>
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<tr>
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</tbody>
</table>

Figure 10: Ideal \( \alpha(\text{CO}_2/\text{CH}_4) \) permeselectivity of asymmetric and symmetric HBPI-silica hybrid membranes plotted against \( \text{CO}_2 \) permeability coefficient.

4. CONCLUSIONS

The asymmetric and symmetric HBPI-silica hybrid membranes were prepared via sol-gel reaction and their physical and gas transport properties were investigated. It is considered that the asymmetric HBPI molecular chain is more linear than symmetric HBPI. ATR FT-IR spectra revealed satisfactory imidization and sufficient formation of a three-dimensional Si-O-Si network in all prepared membranes. The result of optical transmittances indicated the fine and homogeneous dispersion of silica component even in the asymmetric HBPI with high linearity. From the DMA and TMA measurements, it was suggested that thermal and dimensional stability of the asymmetric HBPI-silica hybrids were higher than those of symmetric HBPI-silica hybrids because the rigidity of the asymmetric HBPI molecular chains. Besides, there were more silanol groups left in the asymmetric HBPI-silica hybrids than the symmetric HBPI-silica hybrids due to the rigidity of the asymmetric HBPI molecular chains. Thus, the \( T_\alpha \) values of the asymmetric HBPI-silica hybrids did not increase so conspicuously as corresponding symmetric HBPI-silica hybrids with increasing silica content. The \( \text{CO}_2 \), \( \text{O}_2 \), \( \text{N}_2 \), and \( \text{CH}_4 \) gas permeability coefficient of asymmetric AM-HBPI-silica hybrid membranes decreased with increasing silica content. This was because the dispersibility of a silica component in the asymmetric HBPI-silica hybrids with the high linearity of polymer chain is not as fine as in symmetric HBPI-silica hybrids, and therefore the long
and tortuous diffusion path was newly formed by hybridization with silica. Nevertheless, the asymmetric HBPI-silica hybrids demonstrate superior CO₂/CH₄ selectivity due to the excellent molecular sieving effect of the newly formed free volume holes by incorporation with silica.

ACKNOWLEDGEMENTS

The authors would like to thank Ministry of Education, Science and Culture for support of the project, Regional Innovation Strategy Support Program, “Kyoto Environmental Nanotechnology Cluster”.

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Received on 07-08-2013 Accepted on 13-11-2013 Published on 30-11-2013

DOI: http://dx.doi.org/10.6000/1929-6037.2013.02.04.3