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Physical and Gas Transport Properties of Novel Hyperbranched Polyimide – Silica Hybrid Membranes

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Summary

Physical and gas transport properties of novel hyperbranched polyimide – silica hybrid membranes were investigated. Hyperbranched polyamic acid as a precursor was prepared by polycondensation of a triamine monomer, 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), and a dianhydride monomer, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and subsequently modified the end groups by 3-aminopropyltrimethoxysilane (APTrMOS). The hyperbranched polyimide – silica hybrid membranes were prepared using the polyamic acid, water, and tetramethoxysilane (TMOS) via a sol-gel technique. 5 % weight-loss temperature and glass transition temperature of the hyperbranched polyimide – silica hybrid membranes determined by TG-DTA measurement considerably increased with increasing silica content, indicating effective cross-linking at polymer – silica interface mediated by APTrMOS moiety. CO_2, O_2, and N_2 permeability coefficients of the hybrid membranes increased with increasing silica content. It was pointed out that the increased gas permeabilities are mainly attributed to increase in the gas solubilities. On the contrary, CH_4 permeability of the hybrid membranes decreased with increasing silica content because of decrease in the CH_4 diffusivity and, as a result, CO_2/CH_4 selectivity of the hybrid membranes remarkably increased. It was concluded that the 6FDA-TAPOB hyperbranched polyimide – silica hybrid membranes have high thermal stability and excellent gas selectivity, and are expected to apply to a high-performance gas separation membrane.

Introduction

Polyimide membranes have been of great interest in gas separation applications because of their high gas selectivity and excellent thermal and mechanical properties [1-7]. In recent years, novel hyperbranched polyimides have been synthesized and characterized. Fang et al. have prepared hyperbranched polyimides derived from a triamine, tris(4-aminophenyl)amine (TAPA), and commercially available dianhydrides and investigated their physical and gas transport properties [8, 9]. On the other hand, hyperbranched polyimides with another triamine, 1,3,5-tris(4-aminophenoxy)benzene (TAPOB) have been polymerized and characterized for the first time by Chen et al [10]. In our previous report, gas transport properties of hyperbranched polyimide prepared by polycondensation of a triamine monomer, TAPOB, and a dianhydride monomer, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) have been investigated [11]. It has been found that the 6FDA-TAPOB hyperbranched polyimide exhibits high gas permeability and O_2/N_2 selectivity arising from the characteristic hyperbranched structure.

Organic – inorganic hybrids are attractive materials since they generally possess desirable organic and inorganic characteristics such as heat, mechanical, and electrical advantages. In this regard, the organic – inorganic hybrids have been focused on the modification of structure and composition of polyimides in order to improve their gas selectivity and/or permeability [12-16]. In this study, physical and gas transport properties of novel 6FDA-TAPOB hyperbranched polyimide – silica hybrid membranes were investigated. The hybrid membranes were prepared using the hyperbranched polyamic acid as a precursor and tetramethoxysilane (TMOS) via a sol-gel technique.

Experimental

Monomers

TAPOB was synthesized by reduction of 1,3,5-tris(4-nitrophenoxy)benzene with palladium carbon and hydrazine in methanol [17]. 6FDA was purchased from Aldrich. These monomers were dried at 80 ºC for 24 h *in vacuo* before used.

Polymerization of 6FDA-TAPOB hyperbranched polyamic acid

3 mmol of 6FDA was dissolved in 30 ml of DMAc in a 100 ml three-neck flask under N_2 flow at room temperature. To this solution, 1.6 mmol of TAPOB in 20 ml of DMAc was added dropwise through a syringe with stirring. After that 0.4 mmol of 3-aminopropyltrimethoxysilane (APTrMOS, Aldrich) was added in the reaction mixture with further stirring for 3 h. Schematic representation of the hyperbranched polyamic acid is shown in Figure 1.

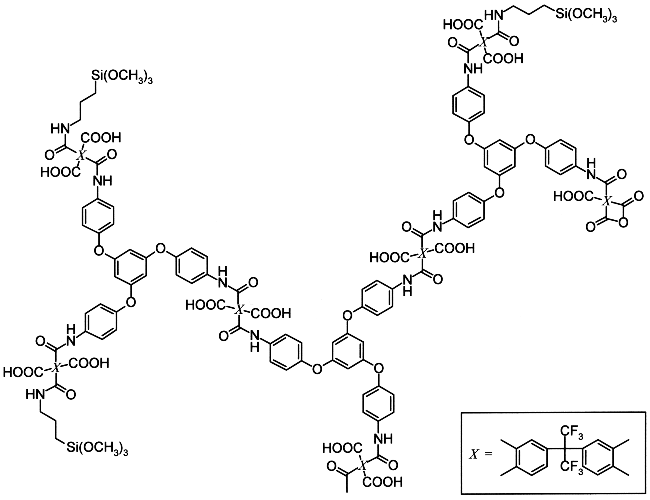

Figure 1 Schematic representation of 6FDA-TAPOB hyperbranched polyamic acid.

Membrane Formation

6FDA-TAPOB hyperbranched polyimide (HBPI) – silica hybrid membranes were prepared by sol-gel technique and thermal imidization. Desired amounts of TMOS and water (TMOS : water = 1 : 6 as a mole ratio) were added in the DMAc solution of the polyamic acid. The mixed solution was stirred for 24 h and subsequently cast on a PET sheet and dried at 80 ºC for 2 h. The prepared membrane was peeled off and subsequently imidized and hybridized at 100 ºC for 1 h, 200 ºC for 1 h, and 300 ºC for 1 h in a heating oven under N_2 flow.

Measurements

Infrared (IR) spectrum was recorded on a JASCO FT/IR-460 plus. Thermogravimetric – differential thermal analysis (TG-DTA) was performed with a Seiko TG/DTA6300 at a heating rate of 10 ºC/min under air flow. Gas permeability coefficient was determined by the vacuum-pressure method. CO_2, O_2, N_2, and CH_4 were used as permeation gases. The permeability coefficient, P ($cm^3STPcm/cm^2sec.cmHg$), can be explained on the basis of the solution-diffusion mechanism, which is represented by the following equation [18-21];

$$P = D \times S \qquad (\mathbf{1})$$

where D ($cm^2/sec.$) is the diffusion coefficient and S ($cm^3STP/cm^3_{polym.}cmHg$) is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method represented by the following equation [22];

$$D = \frac{L^2}{6\theta} \qquad (\mathbf{2})$$

where L (cm) is the thickness of the membrane and θ (sec.) is the time-lag.

Results and Discussion

Polymer Characterization

FT-IR spectra of the HBPI – silica hybrid membranes are shown in Figure 2. The bands observed around 1784 cm^{-1} (C=O asymmetrical stretching), 1725 cm^{-1} (C=O symmetrical stretching), 1378 cm^{-1} (C–N stretching), and 723 cm^{-1} (C=O bending) are the characteristic absorption bands of polyimides [8, 10]. This result indicates that the membranes are well imidized. It is also found that the bands observed around 1100 and 460 cm^{-1} assigned to Si–O–Si stretching and Si–O–Si bending, respectively [12, 23], increase with increasing silica content in the hybrid membrane, indicating sufficient formation of the three-dimensional Si–O–Si network. In addition, it can be said that the hybrid membranes have a high homogeneity because of their good transparency similarly to the pure polyimide membrane without silica

Thermal properties of the hybrid membranes were investigated by TG-DTA measurement. Figure 3 shows TG curves of the hybrid membranes. 5 % weight-loss temperature (T_d^5) and glass transition temperature (T_g), which was determined from the DTA curve, of the hybrid membranes are summarized in Table 1 in addition to the silica content determined from the residual at 800 ºC. It is confirmed that all hybrid membranes contain appropriate amount of silica. It should be noted that T_d^5 and T_g

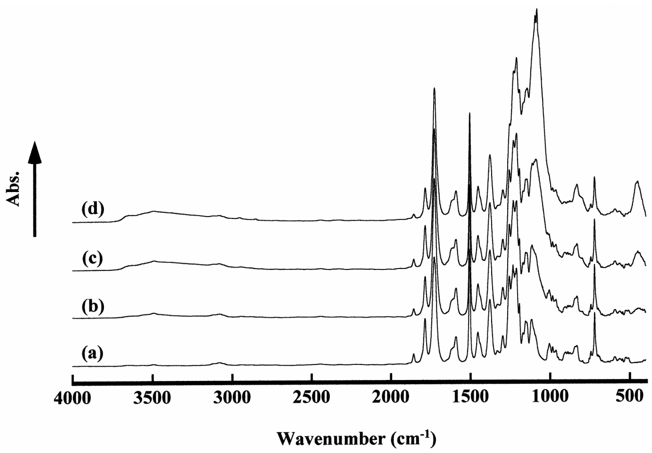

Figure 2 FT-IR spectra of HBPI – silica hybrid membranes; SiO_2 content = (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, and (d) 30 wt%.

values considerably increase with increasing silica content. This fact indicates effective cross-linking at polymer – silica interface mediated by APTrMOS moiety is formed in the HBPI – silica hybrid membranes.

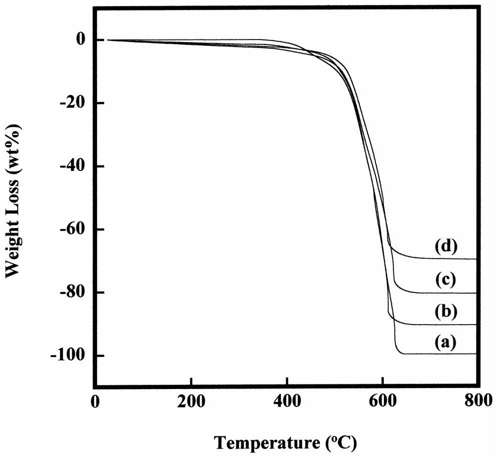

Figure 3 TG curves of HBPI – silica hybrid membranes measured under air flow; SiO_2 content = (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, and (d) 30 wt%.

Table 1 Thermal properties of HBPI – silica hybrid membranes.

Sample	T_g (°C)	T_d^5 (°C)	SiO_2 content (wt%)
HBPI	282	457	0
HBPI – SiO_2(10)	305	490	10
HBPI – SiO_2(20)	311	496	20
HBPI – SiO_2(30)	318	509	30

Gas transport properties of HBPI – silica hybrid membranes

Gas permeability, diffusion, and solubility coefficients of the HBPI – silica hybrid membranes are summarized in Tables 2 – 4 and plotted against silica content in Figure 4(a) – (c), respectively. CO_2, O_2, and N_2 permeabilities of the pure polyimide membrane without silica are slightly lower than those of the hyperbranched polyimide membrane investigated in our previous work [11]. These decreased permeabilities might be caused by the intermolecular cross-linking between APrTMOS end groups. It is found that the CO_2, O_2, and N_2 permeabilities of the hybrid membranes tend to increase with increasing silica content, which is mainly attributed to increase in the solubilities rather than the diffusivities. The increased solubilities suggest that the Langmuir sorption site favorable for CO_2, O_2, and N_2 molecules is additionally formed by the incorporation of silica particles. Similar gas transport behaviors have been observed by Park et al. for poly(imide-*co*-siloxane) – silica hybrid membranes [24], and it has been suggested that increased solubilities are caused by porous silica structure and/or free volume hole created around polymer – silica interface. On the contrary, CH_4 permeability decreases with increasing silica content, which is attributed to decrease in the diffusivity. Considering that the kinetic diameter of CH_4 (3.8 Å) is larger than those of CO_2 (3.3 Å), O_2 (3.5 Å), and N_2 (3.6 Å) [25], it is

Table 2 Permeability coefficients and ideal selectivities of HBPI – silica hybrid membranes at 76 cmHg and 25 ºC.

$P \times 10^{10}$ (cm^3STPcm/cm^2sec.cmHg)	CO_2	O_2	N_2	CH_4	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$
HBPI	7.4	1.5	0.22	0.098	6.9	75
HBPI – SiO_2(10)	10	2.0	0.31	0.092	6.6	114
HBPI – SiO_2(20)	12	2.1	0.32	0.080	6.7	150
HBPI – SiO_2(30)	19	3.0	0.46	0.080	6.6	238

Table 3 Diffusion coefficients and diffusivity selectivities of HBPI – silica hybrid membranes at 76 cmHg and 25 ºC.

$D \times 10^8$ (cm^2/sec.)	CO_2	O_2	N_2	CH_4	$\alpha^D(O_2/N_2)$	$\alpha^D(CO_2/CH_4)$
HBPI	0.30	1.4	0.28	0.028	5.1	11
HBPI – SiO_2(10)	0.35	1.5	0.29	0.026	5.2	13
HBPI – SiO_2(20)	0.36	1.3	0.25	0.022	5.3	16
HBPI – SiO_2(30)	0.46	1.7	0.29	0.023	5.8	21

Table 4 Solubility coefficients and solubility selectivities of HBPI – silica hybrid membranes at 76 cmHg and 25 ºC.

$S \times 10^2$ (cm^3STP/$cm^3_{polym.}$cmHg)	CO_2	O_2	N_2	CH_4	$\alpha^S(O_2/N_2)$	$\alpha^S(CO_2/CH_4)$
HBPI	25	1.1	0.80	3.5	1.4	7.0
HBPI – SiO_2(10)	30	1.4	1.1	3.5	1.3	8.6
HBPI – SiO_2(20)	33	1.7	1.3	3.7	1.3	9.1
HBPI – SiO_2(30)	41	1.8	1.6	3.5	1.1	12

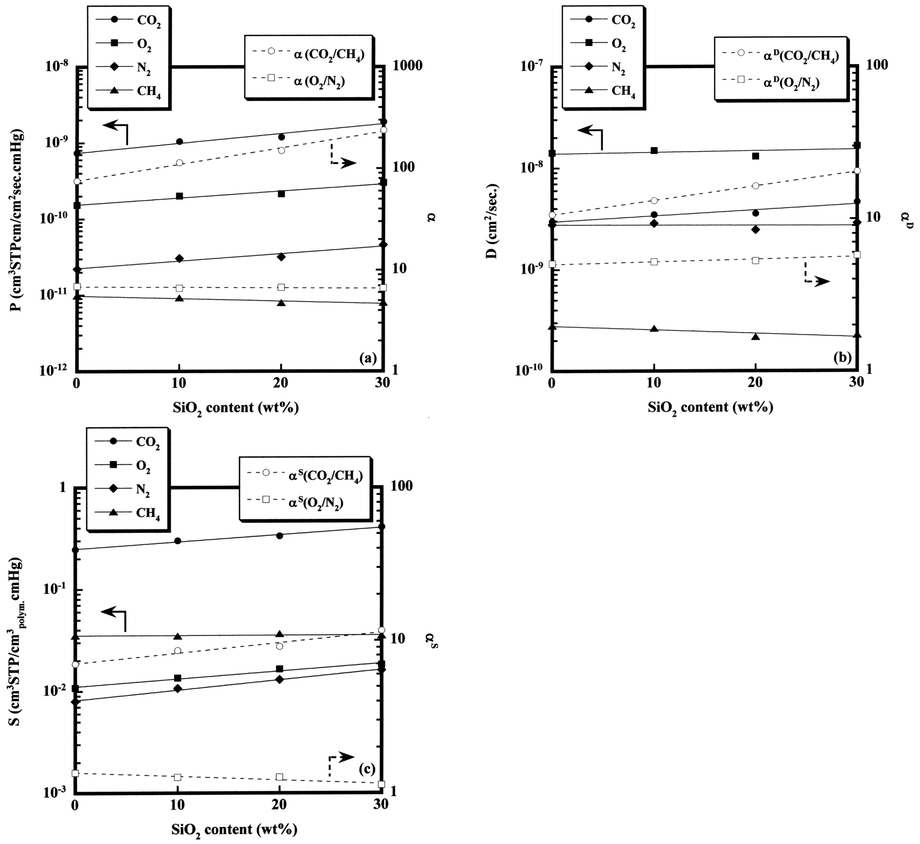

Figure 4 (a) Permeability, (b) diffusion, and (c) solubility coefficients and corresponding O_2/N_2 and CO_2/CH_4 selectivities of HBPI– silica hybrid membranes plotted against silica content in the membrane at 76 cmHg and 25 °C.

suggested that pore size of silica particles and/or free volume hole created in the vicinity of polyimide – silica interface is controlled to around 3.7 Å as a diameter.

The ideal selectivity for the combination of gases A and B (α(A/B)) is defined by the following equation [26];

$$\alpha(A/B) = \frac{P(A)}{P(B)} = \frac{D(A)}{D(B)} \times \frac{S(A)}{S(B)} = \alpha^{D}(A/B) \times \alpha^{S}(A/B) \qquad (3)$$

where $\alpha^D(A/B)$ is the diffusivity selectivity and $\alpha^S(A/B)$ is the solubility selectivity. These selectivities are listed in Tables 2 – 4 and plotted against silica content in Figure 4(a) – (c), respectively. For O_2/N_2 separation, it is recognized that the hybrid membranes show the O_2/N_2 selectivity ($\alpha(O_2/N_2)$) depends on the diffusivity selectivity rather than the solubility selectivity. It is worth noting that $\alpha(O_2/N_2)$ of the hybrid membranes is maintained almost constant although their O_2 permeability increases with increasing silica content. For CO_2/CH_4 separation, more noticeable enhancement of CO_2/CH_4 selectivity ($\alpha(CO_2/CH_4)$) is observed. The $\alpha(CO_2/CH_4)$ of the hybrid membranes increases with increasing silica content in connection with

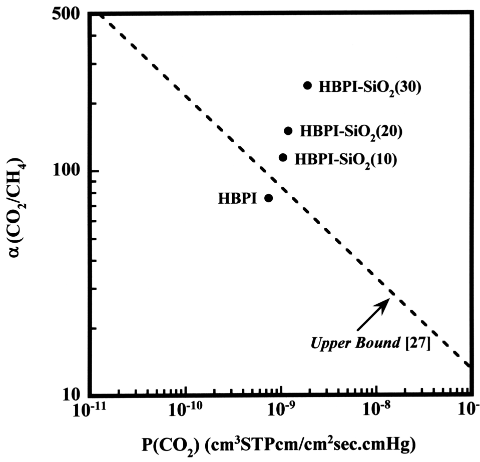

Figure 5 Ideal CO_2/CH_4 selectivity of HBPI – silica hybrid membranes plotted against CO_2 permeability of the membrane.

increased CO_2 and decreased CH_4 permeabilities. It should be mentioned that, as shown in Figure 5, the hybrid membranes containing more than 10 wt% of silica show the $\alpha(CO_2/CH_4)$ which exceeds the upper bound trade-off line for CO_2/CH_4 separation demonstrated by Robeson [27]. The anomalous behavior is considered to be due to characteristic structure of porous silica particles and/or free volume hole around polymer – silica interface which enables to develop the quite effective CO_2/CH_4 separation. Vu et al. have observed similar enhancements of O_2/N_2 and CO_2/CH_4 selectivities for polyimide – carbon molecular sieve composites by the presence of shape- and size-selective pores within the carbon molecular sieves [28, 29]. He et al. have also reported that nano-sized inorganic fillers incorporated into glassy polymers with high fractional free volumes can function as a spacer material which disrupts polymer chain packing, leading to improvement of organic vapor/permanent-gas separation properties [30]. Therefore it can be said that the HBPI – silica hybrid membranes possess the gas separation ability attributed to a size-selective molecular-sieving effect brought by the incorporation of silica particles, which is particularly effective for the CO_2/CH_4 separation.

Conclusions

Physical and gas transport properties of novel 6FDA-TAPOB hyperbranched polyimide – silica hybrid membranes were investigated. 5 % weight-loss temperature and glass transition temperature of the hyperbranched polyimide – silica hybrid membranes considerably increase with increasing silica content, indicating effective cross-linking at polymer – silica interface mediated by APTrMOS moiety. CO_2, O_2, and N_2 permeability coefficients of the hybrid membranes increase with increasing silica content. It is pointed out that the increased gas permeabilities are mainly attributed to increase in the gas solubilities. On the contrary, CH_4 permeability of the hybrid membranes decreases with increasing silica content because of decrease in the CH_4 diffusivity and, as a result, CO_2/CH_4 selectivity of the hybrid membranes remarkably increases. This fact means that a size-selective molecular-sieving effect is brought by the incorporation of silica particles in the hybrid membranes. It is concluded that the 6FDA-TAPOB hyperbranched polyimide – silica hybrid membranes have high thermal stability and excellent gas selectivity, and are expected to apply to a high-performance gas separation membrane.

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