

## 중간기공을 갖는 미세다공성 탄소 분리막의 기체 투과 특성

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### Gas Separation Properties of Microporous Carbon Membranes Containing Mesopores

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**요약:** Poly(imide siloxane)(Si-PI)와 polyvinylpyrrolidone (PVP)를 혼합한 고분자를 사용하여 실리카가 함유된 탄소 분리막을 제조하였다. 고분자 혼합물의 열분해에 의해 제조된 다공성 탄소 구조의 특성은 두 고분자의 미세 상 분리 거동과 관련이 있다. Si-PI와 PVP의 고분자 혼합물의 유리 전이 온도( $T_g$ )는 시차 주사 열량계를 사용하여 단일  $T_g$ 로 관찰되었다. 또한 C-SiO<sub>2</sub> 막의 질소 흡착 등온선을 조사하여 다공성 탄소 구조의 특성을 규명했다. Si-PI/PVP로부터 유도된 C-SiO<sub>2</sub> 막은 IV형 등온선을 나타내었고 중간기공의 탄소 구조와 관련된 히스테리시스 루프를 가지고 있었다. 분자 여과 확인을 위해서, Si-PI/PVP의 비율과 열분해 온도 및 등온 시간과 같은 열분해 조건을 다르게 하여 C-SiO<sub>2</sub> 막을 제조하였다. 결과적으로, 120 분 간의 등온 시간 동안 550°C에서 Si-PI/PVP의 열분해에 의해 제조된 C-SiO<sub>2</sub> 막의 투과도는 820 Barrer ( $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \cdot \text{s} \cdot \text{cmHg}$ )이었으며, O<sub>2</sub>/N<sub>2</sub> 선택도는 14이었다.

**Abstract:** The silica containing carbon (C-SiO<sub>2</sub>) membranes were fabricated using poly(imide siloxane)(Si-PI) and polyvinylpyrrolidone (PVP) blended polymer. The characteristics of porous carbon structures prepared by the pyrolysis of polymer blends were related with the micro-phase separation behaviors of the two polymers. The glass transition temperatures ( $T_g$ ) of the mixed polymer blends of Si-PI and PVP were observed with a single  $T_g$  using differential scanning calorimetry. Furthermore, the nitrogen adsorption isotherms of the C-SiO<sub>2</sub> membranes were investigated to define the characteristics of porous carbon structures. The C-SiO<sub>2</sub> membranes derived from Si-PI/PVP showed the type IV isotherm and possessed the hysteresis loop, which was associated with the mesoporous carbon structures. For the molecular sieving probe, the C-SiO<sub>2</sub> membranes were prepared with the ratio of Si-PI/PVP and the pyrolysis conditions, such as the pyrolysis temperature and the isothermal times. Consequently, the C-SiO<sub>2</sub> membranes prepared by the pyrolysis of Si-PI/PVP at 550°C with the isothermal time of 120 min showed the O<sub>2</sub> permeability of 820 Barrer ( $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \cdot \text{s} \cdot \text{cmHg}$ ) and O<sub>2</sub>/N<sub>2</sub> selectivity of 14.

**Keywords:** Carbon-silica membrane, Gas separation, Carbon, Polyvinylpyrrolidone, Poly(imide siloxane)

## 1. Introduction

One of the superior gas separation materials, carbon membranes have focused in the last decade because of their high permeation performances and separation factors, which jump over the polymeric membranes' upper bound[1-3]. In addition, carbon membranes have the

excellent thermal and chemical stabilities as compared with polymeric membranes[4-5].

Up to now, many researchers studied the carbon membranes using various polymer precursors, such as polyimide[6-11], phenolic resin[12-13], and poly(furfuryl alcohol)[14]. Also, the pyrolysis conditions[10,11,15,16] and the chemical structures of polymer precursors hav-

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ing side pendent groups[15-18] significantly affected their gas separation performances. Basically, carbon membranes are divided into carbon molecular sieve (CMS) membranes and adsorption-selective carbon (ASC) membranes, which depend on the pore diameters. The former with pore diameters 3-5 Å have ideal separation factor and the latter have the pore diameters in the range of 5-7 Å[19]. Therefore, many researchers focused on the optimization of the pyrolysis conditions using various homo- or co-polymer precursors to control the porosity of carbon structures and successively prepared the carbon membranes having high permeabilities and selectivities.

On the other hand, Ozaki *et al.*[20] developed membranes by controlling the pores of carbon membranes using two kinds of polymers, one giving a high carbon yield and the other creating a very low carbon yield. According to this concept, Hatori *et al.*[21] prepared carbon membranes derived from polyimide/poly(ethylene glycol) blended polymer and characterized the mesoporous carbon structures using nitrogen-adsorption isotherm method. The properties of porous carbon structures (pore size, pore size distribution, pore volume, and bulk density) using polymer-blending method importantly are depended on the phase separation behavior between two polymers because the phase separation domain of thermally labile polymer acted as a pore-forming agent.

In our previous studies[3,22-24], we prepared the carbon membranes containing silica derived from poly(imide siloxane). The pyrolytic carbon-silica (C-SiO<sub>2</sub>) membrane was consisted of the carbon-rich phase and siloxane-rich phase because of the micro-phase separation between the polyimide (carbon-rich aromatic phase) domain and the polyimide siloxane (siloxane-rich phase) domain. Furthermore, we fabricated the CMS membranes using polyimide/polyvinylpyrrolidone blended polymer. This CMS membrane did not exhibit any characteristics of mesoporous carbon structures by thermal decomposition of polyvinylpyrrolidone evidenced from the nitrogen adsorption isotherms even though polyimide was hydrophobic and poly-

vinylpyrrolidone showed hydrophilic. Consequently, the permeation performance of the CMS membranes was enhanced with the less reduction of their separation factor[25].

To control the porosity of carbon membranes using polymer-blending method, the miscibility of two polymers is a major concerning element to control phase separation behavior. In the polymer blends, polymer-polymer interaction is an important factor for determining the phase separation of blends since phase behavior of blends is dominated by these interactions [26]. Therefore, the micro-phase separation domain of the thermal labile polymer might be related with the characteristics of porous carbon structures during the pyrolysis. In this study, we blended hydrophilic polyvinylpyrrolidone (PVP) in hydrophobic poly(imide siloxane) (Si-PI). In addition, the gas separation properties of the fabricated C-SiO<sub>2</sub> membranes derived from Si-PI/PVP blended polymers were investigated using single gases, He, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> as functions of the ratio of Si-PI/PVP and pyrolysis conditions, such as final pyrolysis temperature and isothermal time. It is also our intention to compare the sorption isothermal behaviors as well as the gas separation performance between carbonized membranes prepared from PI/PVP and Si-PI/PVP.

## 2. Experimental

### 2.1. Materials

Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were purchased from Tokyo Kasei Co., Inc., Tokyo, Japan and  $\alpha, \omega$ -aminopropyl poly(dimethyl siloxane) (PDMS, Shinetsu Co. Inc., Tokyo, Japan), which had  $M_n = 900$  and  $n = 10$  was used. Polyvinylpyrrolidone (PVP, M.W. 10,000, Aldrich Chem. Co., Milwaukee, WI, USA) was used as a thermally labile polymer. Tetrahydrofuran (THF) and *N*-methylpyrrolidinone (NMP) were obtained from Aldrich Chem. Co., Milwaukee, WI, USA and used after drying in 4 Å molecular sieves

## 2.2. Fabrication of C-SiO<sub>2</sub> membranes

Poly(imide siloxane) (Si-PI) copolymer was synthesized using PMDA, ODA, and PDMS. The chemical composition of PMDA/ODA/PDMS was 10/8/2 by mmol for the Si-PI. Firstly, PDMS was dissolved in tetrahydrofuran (THF, Aldrich Chem. Co., Milwaukee, WI, USA) and then *N*-methylpyrrolidinone (NMP, Aldrich Chem. Co., Milwaukee, WI, USA) solution of ODA was added. Finally, powder of PMDA was added to THF/NMP solution of PDMS and ODA, and then the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 6 h to obtain homogeneous siloxane-containing poly(amic acid)(Si-PAA) solution. The solid concentration of Si-PAA was kept at 15% by weight. To prepare the Si-PAA/PVP solutions, powders of PVP were added 0% (denoted SiPI-P0), 2% (denoted SiPI-P2), and 5% (denoted SiPI-P5) by weight in the each of Si-PAA solutions. The Si-PAA/PVP solutions were cast onto a glass plate and then thermally imidized. The thermal imidization protocol used in this study was illustrated in our previous study[22]. The synthesized Si-PI/PVP precursors were kept in the vacuum oven to isolate from the moisture due to the hydrophilic properties of PVP and then used to prepare the pyrolytic C-SiO<sub>2</sub> membranes.

Finally, the carbon-silica (C-SiO<sub>2</sub>) membranes were prepared by pyrolysis of the Si-PI/PVP precursors with the ratio of Si-PI/PVP and the final pyrolysis temperature (550, 600, 700, and 800°C) under argon purge flow rate of 300 [cc(STP)/min] in a tube furnace supported on an alumina holding plate. The pyrolysis protocol used in this study was also identical with that of our previous work[27]. Additionally, we employed an isothermal time of 60, 120, and 240 min at the final pyrolysis temperature of 550°C.

## 2.3. Characterization methods

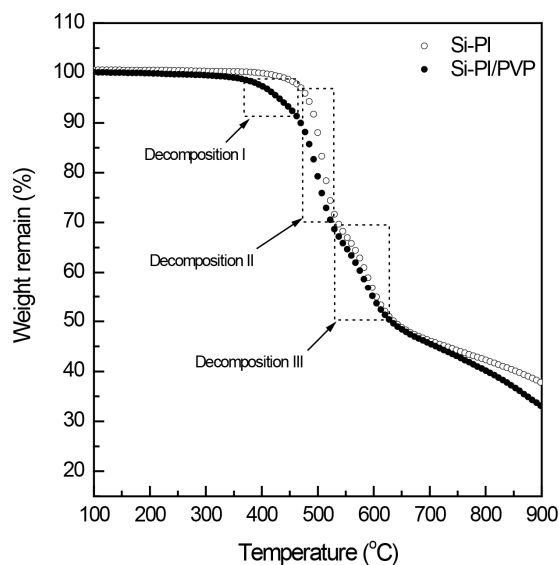
Differential scanning calorimetry (DSC, TA Instruments, New Castle, DE, USA) measurements were used from -50 to 350°C under a nitrogen gas flow with a heating rate of 10 °C/min to measure the glass transition temperatures ( $T_g$ ) of Si-PI/PVP polymer

blends, which is a useful parameter in evaluating the phase separation behavior of the two polymers. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA2050 thermogravimetric analyzer (TA Instrument, New Castle, DE, USA) to study the thermal properties of PVP and Si-PI. To investigate the structural changes of C-SiO<sub>2</sub> membranes derived from Si-PI/PVP precursor by the final pyrolysis temperature and isothermal condition with evaluated average *d*-spacing values, wide-angle X-ray diffraction (WAXD) measurement was carried out using a Rigaku Denki model RAD-C (Rigaku, Tokyo, Japan) with Cu K $\alpha$  radiation of wavelength 1.54 Å. To confirm the gas adsorption characteristics of the C-SiO<sub>2</sub> membranes derived from Si-PI/PVP precursors with the ratio of Si-PI/PVP, nitrogen adsorption isotherms [BET (Brunauer-Emmett-Teller) method] were observed at -196°C.

## 2.4. Gas permeation measurement

The permeation properties of the C-SiO<sub>2</sub> membranes derived from Si-PI/PVP precursors were measured using the high vacuum time-lag method at feed temperature of 25°C with the pressure difference of  $8.11 \times 10^6$  Pa (760 Torr) between the feed side and the permeate side. To probe the molecular sieving capability of the C-SiO<sub>2</sub> membranes prepared with the thermal labile polymer and the pyrolysis conditions (pyrolysis temperature and isothermal time), the small gas molecules [He (2.6 Å), CO<sub>2</sub> (3.3 Å), O<sub>2</sub> (3.46 Å), and N<sub>2</sub> (3.64 Å)] were used with the high purity of 99.99%. To measure the permeabilities of the flat-type C-SiO<sub>2</sub> membranes with the area of  $2 \times 2$  cm<sup>2</sup> and the thickness of 30 μm, we masked the membrane using impermeable alumina tape, and then epoxy sealant was applied at the interface between the tape and the C-SiO<sub>2</sub> membranes to prevent any gas leak.

The measurement of gas permeability coefficients through the C-SiO<sub>2</sub> membranes was illustrated in our previous work[15,27]. The permeability is usually expressed in Barrers, where 1 Barrer is  $10^{-10}$  cm<sup>3</sup>(STP)cm/cm<sup>2</sup> · s · cmHg. The ideal separation fac-



**Fig. 1.** TGA curves of poly(imide siloxane) and polyvinylpyrrolidone containing poly(imide siloxane).

tor is defined as the ratio of the pure gas permeabilities of each component ( $P_A$  and  $P_B$ ) from the following equation[28]:

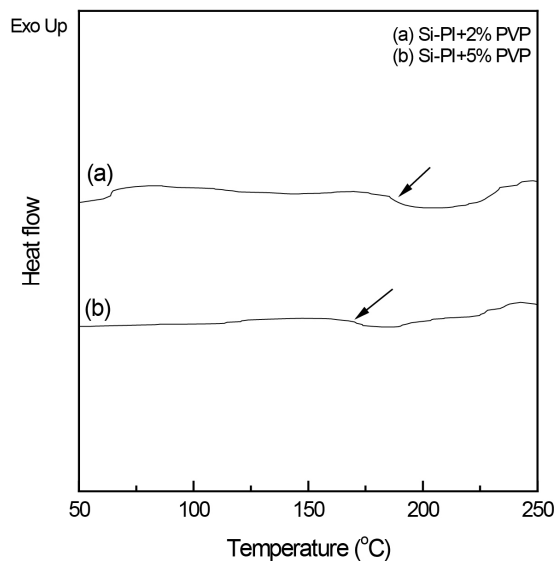
$$\alpha = \frac{P_A}{P_B} \quad (1)$$

To obtain the reasonable gas permeation results of the C-SiO<sub>2</sub> membranes, all the gas permeation experiments were measured more than three time, and the error in the permeation measurements was less than 5%.

### 3. Results and Discussion

#### 3.1. Thermal properties and phase behaviors of Si-PI/PVP

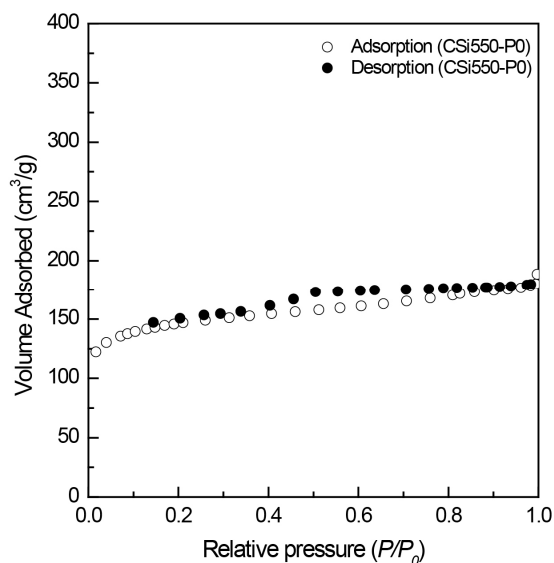
Fig. 1 shows the thermal properties of Si-PI (sample SiPI-P0) and Si-PI/PVP (sample SiPI-P5) precursors. While the sample SiPI-P0 exhibited two-step weight-loss curves, the sample SiPI-P5 showed three-step decomposition profiles. From the results, the first weight-loss appeared by the PVP decomposition was well agreed with TGA data in our previous study[26], the second and the third weight-loss curves exhibited the decomposition of PMDA-PDMS segments and



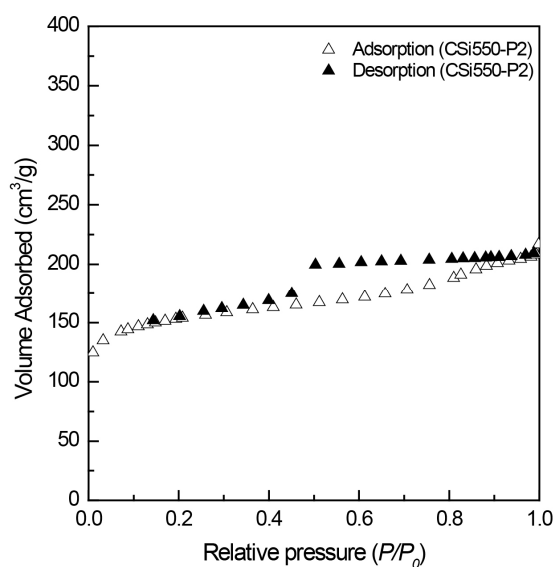
**Fig. 2.** DSC thermograms for Si-PI/PVP as a function of PVP concentration.

PMDA-ODA segments. This trend followed well with the results of siloxane-containing polyimides[22].

Fig. 2 shows the DSC thermograms for the blend polymers with the ratio of Si-PI/PVP. To define the phase separation of a polymer blend, DSC is the most conventionally used to determine  $T_g$  or two  $T_g$ s. A single  $T_g$  is the criterion for the miscibility of a polymer blend. On the other hand, an immiscible polymer blend exhibits more than one  $T_g$ [29]. As shown in the figure, the  $T_g$  of the Si-PI/PVP polymer blends were significantly upper-shifted with decreasing the amount of PVP. In the literatures[30,31], PVP has a  $T_g$  in the range of 126-174°C while those of Si-PI was observed at 221°C due to the aromatic imide domain. From these results, it was concluded that Si-PI and PVP formed the homogeneously mixed polymer blends. However, we deduced that PVP formed the micro-phase separation domain in Si-PI even though the hydrophobic Si-PI and the hydrophilic PVP were homogeneously mixed. Therefore, the effect of the micro-phase separated PVP domains on the properties of porous carbon structures during the pyrolysis is studied with the N<sub>2</sub> adsorption isotherms and their gas separation properties.



**Fig. 3.** N<sub>2</sub> gas adsorption isotherms of C-SiO<sub>2</sub> membranes pyrolyzed at 550°C as a function of amount of PVP CSi550-P0.

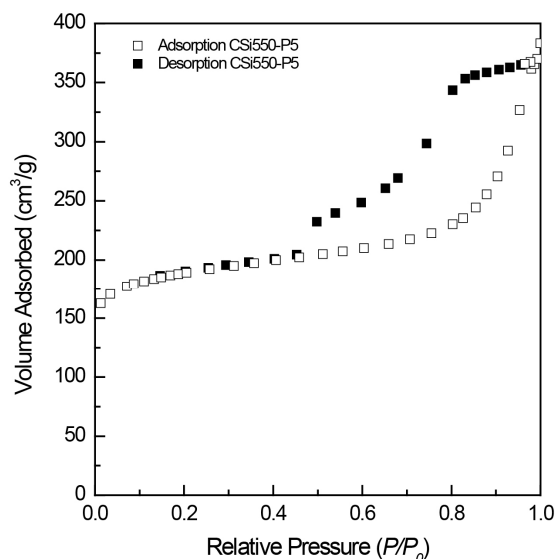


**Fig. 4.** N<sub>2</sub> gas adsorption isotherms of C-SiO<sub>2</sub> membranes pyrolyzed at 550°C as a function of amount of PVP CSi550-P2.

### 3.2. Nitrogen adsorption isotherms

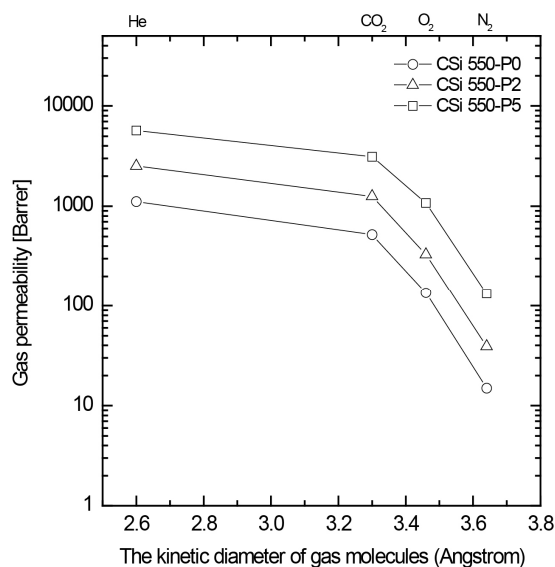
Gas adsorption isotherm is one of the most widely used techniques to characterize porous carbon structures[32]. A knowledge of adsorption mechanisms in different sizes of porosity is necessary to explain the shapes of isotherms. The isotherm shapes are divided into six major classes according to IUPAC classification. One of the physical adsorption according to IUPAC classification, type I isotherm is given by the microporous materials having pores no wider than ~2 nm whereas type IV isotherm is related with the mesoporous materials with pores in the range 2-50 nm. As shown in Fig. 3, Fig. 4, and Fig. 5, the C-SiO<sub>2</sub> membrane derived from sample SiPI-P0 precursor showed the type I isotherm. On the other hand, the isotherm shapes of the C-SiO<sub>2</sub> membranes prepared by pyrolysis of samples SiPI-P2 and SiPI-P5 precursors were changed to the type IV isotherm shapes with increasing content of PVP.

According to the nitrogen adsorption isotherms, type I isotherms are related with the microporous solids having a small external area. The very steep region at low  $P/P_0$  is due to the filling of very narrow pores and the limiting uptake is dependent on the accessible mi-



**Fig. 5.** N<sub>2</sub> gas adsorption isotherms of C-SiO<sub>2</sub> membranes pyrolyzed at 550°C as a function of amount of PVP CSi550-P5.

cropore volume[33]. Therefore, the C-SiO<sub>2</sub> membrane derived from sample SiPI-P0 precursor might have the microporous carbon structures. However, the C-SiO<sub>2</sub> membranes prepared by pyrolysis of Si-PI containing PVP showed type IV isotherms possessing a significant hysteresis loop with increasing the amount of PVP,



**Fig. 6.** Gas permeabilities of C-SiO<sub>2</sub> membranes pyrolyzed at 550°C as a function of PVP concentration in Si-PI.

which is associated with mesoporous materials. That is, the mesoporous carbon structures were created by the thermal decomposition of phase separated PVP domain during the pyrolysis. Interestingly, we did not observe the type IV isotherms showing a hysteresis loop in the carbon molecular sieve (CMS) membranes derived from polyimide containing PVP in our previous study [26]. Carbon membranes from PI/PVP showed the typical type I isotherm.

As compared with the N<sub>2</sub> adsorption isotherms of the CMS membranes derived from PI/PVP and the C-SiO<sub>2</sub> membranes derived from Si-PI/PVP, the properties of porous carbon structures were mainly affected by the phase separation behaviors between two polymers. In the literature, the miscibility of polymers is determined by the interaction between different polymers[34]. The miscibility of PVP and Si-PI decreased due to the hydrophobic nature of PMDA-PDMS segments even though two polymers were homogeneously mixed. That is, the phase separated PVP domain was mixed with Si-PI, and also the larger phase separated domain size of PVP was formed in Si-PI than the phase separation domain of PVP in polyimide. In addition, the larger phase separation PVP was affected by the incremental PVP contents. Therefore, the C-SiO<sub>2</sub>

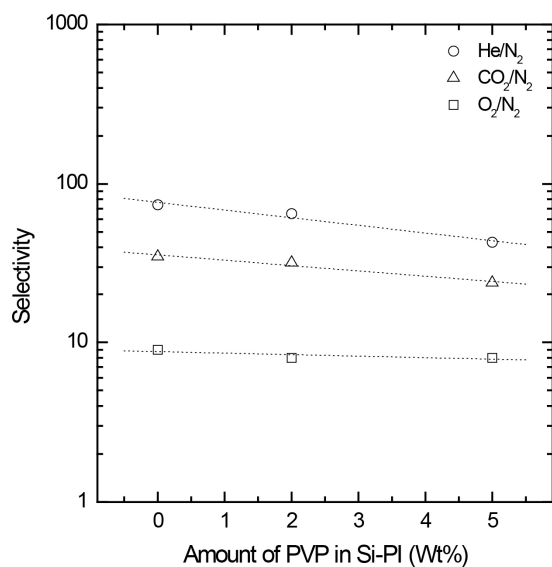
membranes derived from Si-PI/PVP polymer blends obtained the mesoporous carbon structures caused by the thermal decomposition of PVP as confirmed by the nitrogen adsorption isotherm results. The relationship between the characteristics of N<sub>2</sub> adsorption isotherms and the gas permeation results of the C-SiO<sub>2</sub> membranes is described with detailed explanation in the next section.

### 3.3. Molecular sieving properties

Until now, we characterized the porous structures of the C-SiO<sub>2</sub> membranes prepared by the pyrolysis of blend polymers containing the thermal labile polymer using N<sub>2</sub> adsorption isotherms. Basically, the thermal labile polymer, PVP acted as a pore-forming agent in the CMS membranes during the pyrolysis even though the porous carbon structures were influenced by the miscibility of two blending polymers. In the next section, the results of gas permeation performances and separation properties of C-SiO<sub>2</sub> membranes prepared with the ratio of Si-PI/PVP and the pyrolysis conditions, such as the final pyrolysis temperature and the isothermal time are described.

#### 3.3.1. Effect of thermal labile polymer

To study the gas permeation performance of the C-SiO<sub>2</sub> membranes derived from blend polymers with the ratio of Si-PI/PVP, the gas permeabilities through the C-SiO<sub>2</sub> membranes were measured using pure single gases, such as He, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> at 25°C. Fig. 6 shows gas permeabilities and Fig. 7 shows selectivities of the C-SiO<sub>2</sub> membranes prepared by the pyrolysis of samples SiPI-P0, SiPI-P2, and SiPI-P5 precursors at 550°C. As shown in Fig. 6, all of the C-SiO<sub>2</sub> membranes showed that their permeabilities increased with the order of gas molecular size [He (2.6 Å) > CO<sub>2</sub> (3.3 Å) > O<sub>2</sub> (3.46 Å) > N<sub>2</sub> (3.64 Å)]. In general, the permeabilities of small gas molecules through the microporous CMS membranes are basically determined by the kinetic diameters of gas molecules. That is, the gas transport mechanism through the C-SiO<sub>2</sub> membranes derived from Si-PI/PVP precursors followed the



**Fig. 7.** Gas selectivities of C-SiO<sub>2</sub> membranes pyrolyzed at 550°C as a function of PVP concentration in Si-PI.

molecular sieving mechanism.

The main objective of this study was to study the effect of the thermal labile polymer on the gas permeation performances of the C-SiO<sub>2</sub> membranes. To achieve this purpose, we introduced the PVP in the Si-PI with the amount of 2 and 5% by weight. From the results, all of the gas permeabilities through the C-SiO<sub>2</sub> membranes increased remarkably with incremental PVP contents. These gas permeation results are well explained with the results of N<sub>2</sub> adsorption experiments as introduced above. The isotherm of sample CSi550-P5 illustrates that the adsorption rapidly increased at  $P/P_0 > 0.8$  and shows the hysteresis during the desorption process, which indicates that a number of ink-bottle-like pores are formed by the thermal decomposition of PVP during the pyrolysis. Furthermore, the C-SiO<sub>2</sub> membranes showed the higher surface area with the incremental PVP contents in the order: 96.48 m<sup>2</sup>/g (sample CSi550-P0) < 113.59 m<sup>2</sup>/g (sample CSi550-P2) < 136.04 m<sup>2</sup>/g (sample CSi550-P5). Also, the total pore volume increased in the order: 0.353 cm<sup>3</sup>/g (sample CSi550-P0) < 0.365 cm<sup>3</sup>/g (sample CSi550-P2) < 0.513 cm<sup>3</sup>/g (sample CSi550-P5). In our previous study[26], we also confirmed that the gas permeabilities through the CMS membranes derived from

PI/PVP increased with the higher PVP contents.

The selectivities of all of the C-SiO<sub>2</sub> membranes are shown in Fig. 7 as a function of PVP contents in Si-PI. The He/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, and O<sub>2</sub>/N<sub>2</sub> selectivities of the C-SiO<sub>2</sub> membranes derived from Si-PI/PVP decreased with increasing the contents of PVP. In particular, the O<sub>2</sub> permeabilities of the C-SiO<sub>2</sub> membranes increased from 135 to 1080 Barrer and the O<sub>2</sub>/N<sub>2</sub> selectivities decreased from 9 to 8 with the increasing ratio of Si-PI/PVP.

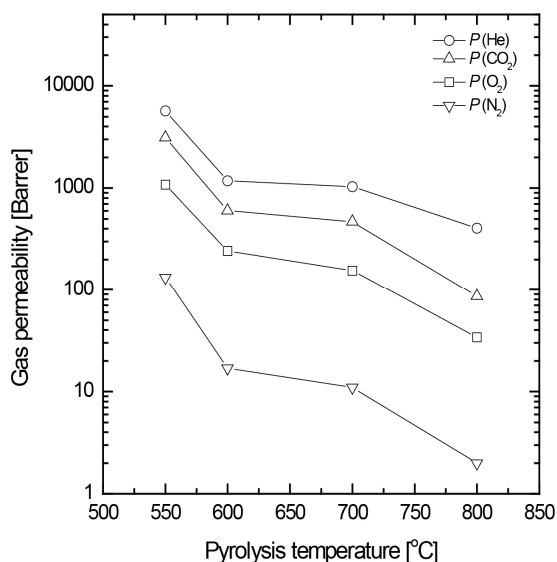
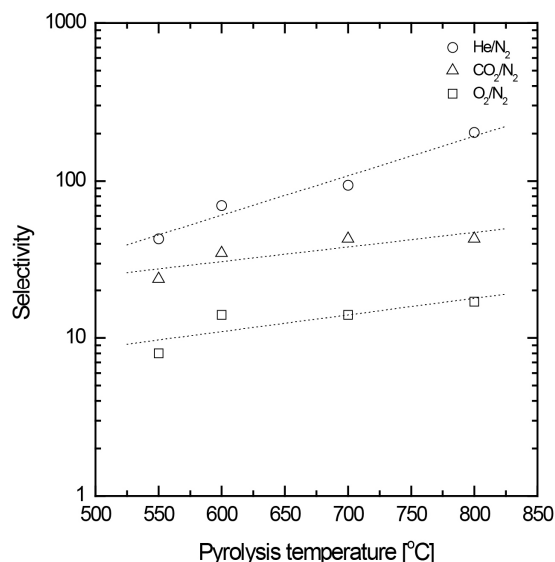
### 3.3.2. Effect of pyrolysis temperature

In CMS membranes, the gas permeabilities and separation properties are mainly depended on the pyrolysis conditions, such as pyrolysis temperature[11,15,35,36], heating rate[11], isothermal time[9], and pyrolysis atmosphere[9,11] because the pore size, pore size distribution, and bulk density of porous carbon structures are determined by the pyrolysis conditions. In the present study, we fabricated the C-SiO<sub>2</sub> membranes derived from sample SiPI-P5 with the final pyrolysis temperature from 550 to 800°C under argon flow and measured their gas permeabilities. As shown in Fig. 8 and Fig. 9, all of the gas permeabilities of the C-SiO<sub>2</sub> membranes decreased with increasing pyrolysis temperature while the selectivities increased. In the literatures [11,35,36], the pyrolysis temperature determined the permselectivities of carbon molecular sieve membranes due to the enhanced compactness of the turbostratic carbon structure and the reduction of effective pore sizes, which brought about the lower permeabilities and the higher selectivities.

The permeability ( $P = DS$ ) of non-porous polymeric membrane and CMS membrane is determined by the diffusion coefficient ( $D$ ) and the solubility coefficient ( $S$ ), and the permselectivity ( $\alpha = P_A/P_B$ ) is terms of the diffusion selectivity ( $D_A/D_B$ ) and the solubility selectivity ( $S_A/S_B$ ). In the CMS membranes, the diffusion coefficient is a main determining factor for their permeation performances. The O<sub>2</sub> and N<sub>2</sub> diffusion coefficients and the O<sub>2</sub>/N<sub>2</sub> diffusion selectivities of the C-SiO<sub>2</sub> membranes prepared by varying the pyrolysis

**Table 1.** Diffusion Coefficients of O<sub>2</sub> and N<sub>2</sub> through C-SiO<sub>2</sub> Membranes Derived from SiPI-P5 at 25°C and Diffusivity Selectivity of O<sub>2</sub>/N<sub>2</sub> as a Function of Pyrolysis Temperature

Sample Code	Diffusivity (10 <sup>-10</sup> cm <sup>2</sup> /s)		<i>D</i> (O <sub>2</sub> /N <sub>2</sub> )	<i>S</i> (O <sub>2</sub> /N <sub>2</sub> )	<i>P</i> (O <sub>2</sub> /N <sub>2</sub> )
	<i>D</i> (O <sub>2</sub> )	<i>D</i> (N <sub>2</sub> )			
CSi550-P5	2790	416	6.7	1.2	8
CSi600-P5	312	41.1	7.6	1.8	14
CSi700-P5	91.6	9.64	9.5	1.5	14
CSi800-P5	62.8	4.80	13.1	1.3	17

**Fig. 8.** Gas permeabilities of C-SiO<sub>2</sub> membranes derived from SiPI-P5 precursor as a function of pyrolysis temperature.**Fig. 9.** Gas selectivities of C-SiO<sub>2</sub> membranes derived from SiPI-P5 precursor as a function of pyrolysis temperature.

temperature are listed in Table 1. The diffusion coefficient ( $D = L^2/6\theta$ ) can be estimated from the membrane thickness ( $L$ ) and the time lag ( $\theta$ ) of a transient permeation measurement. As listed in the table, the O<sub>2</sub>/N<sub>2</sub> permselectivities through C-SiO<sub>2</sub> membranes particularly prepared by the higher pyrolysis temperature were mainly determined by the diffusion selectivities. In the meantime their solubility selectivities were the range of 1.2-1.8 which was the general trend of CMS membranes. These results are consistent with the reduction of effective pore sizes at higher pyrolysis temperature.

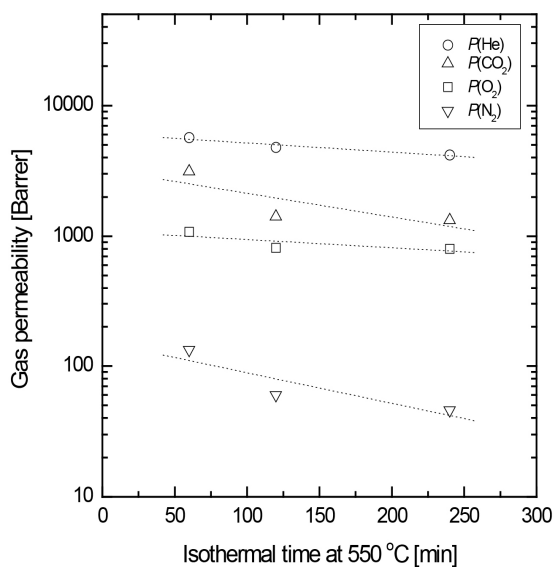
### 3.3.3. Effect of isothermal time

One of the pyrolysis conditions, the isothermal time (soaking time) was varied to prepare C-SiO<sub>2</sub> mem-

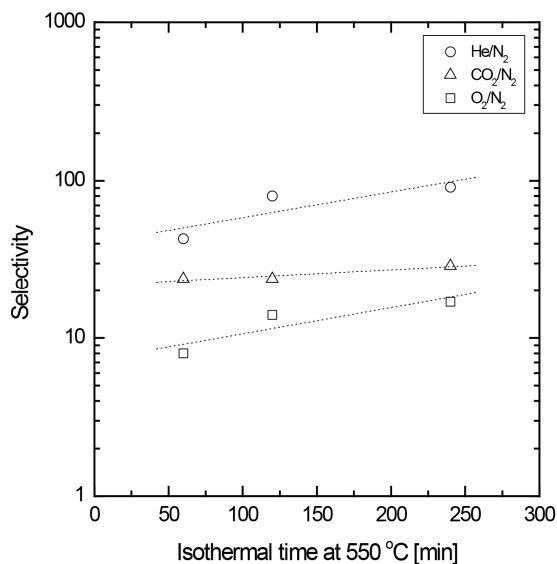
branes derived from sample SiPI-P5 from 60 to 240 min at 550°C and measured their permeation performances. Koros *et al.*[36] reported on the effect of isothermal time on the permeabilities and selectivities of CMS membranes. In particular, the reduction of isothermal time effectively affected the improved permeability while the selectivity was maintained.

Fig. 10 and Fig. 11 show the results of permeabilities and selectivities of the C-SiO<sub>2</sub> membranes prepared with the incremental isothermal time of 60, 120, and 240 min at 550°C, respectively. The permeabilities of all the gas molecules through the C-SiO<sub>2</sub> membranes decreased with increasing the isothermal time while their selectivities increased. This result coincided with the Koros' report. Among the gas separation properties of the C-SiO<sub>2</sub> membranes, the O<sub>2</sub>/N<sub>2</sub> se-





**Fig. 10.** Gas permeabilities of C-SiO<sub>2</sub> membranes derived from sample SiPI-P5 as a function of isothermal time at 550°C.

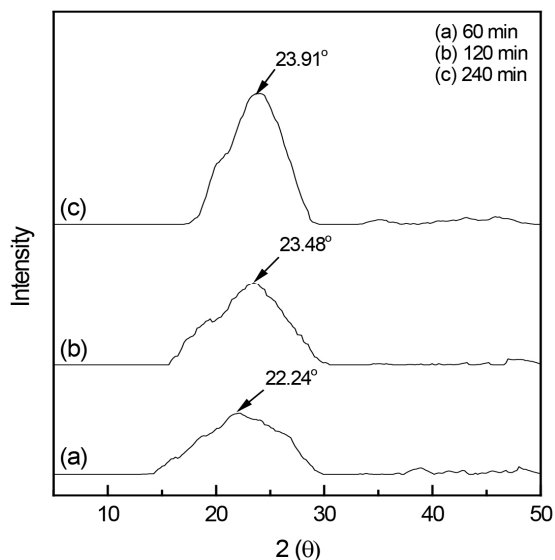


**Fig. 11.** Gas selectivities of C-SiO<sub>2</sub> membranes derived from sample SiPI-P5 as a function of isothermal time at 550°C.

lectivity of the C-SiO<sub>2</sub> membrane prepared with the isothermal time of 240 min is 110% higher than those of the C-SiO<sub>2</sub> membranes prepared with the isothermal time of 60 min while the permeability is 26% lower. In this study, very high separation factors of the C-SiO<sub>2</sub> membranes can be achieved by the varying iso-

**Table 2.** Average *d*-spacing Values of C-SiO<sub>2</sub> Membranes Pyrolyzed with Isothermal Time Conditions at 550°C

Isothermal Time (min)	<i>d</i> -spacing (Å)
60	4.0
120	3.8
240	3.7



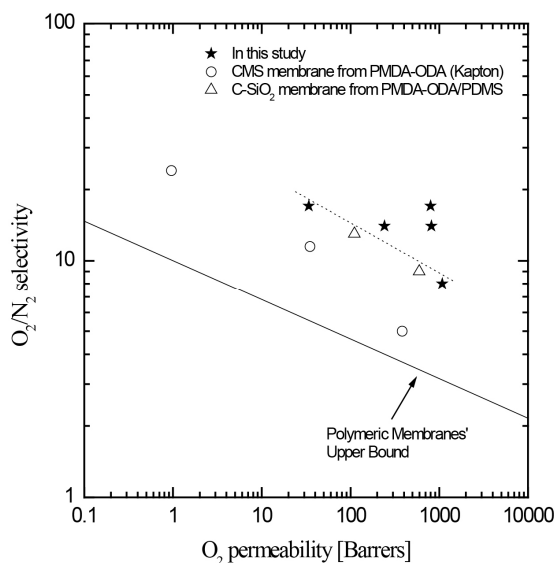
**Fig. 12.** WAXD patterns of C-SiO<sub>2</sub> membranes derived from SiPI-P5 as a function of isothermal time at 550°C.

thermal time conditions.

The relationship between the permeation results and the porous C-SiO<sub>2</sub> membranes was studied by calculating average *d*-spacing values using WAXD patterns. In general, WAXD is used to measure the difference in interlayer spacing between carbon materials[37]. The average *d*-spacing values of the C-SiO<sub>2</sub> membranes were calculated from the Bragg equation as follows:

$$n\lambda = 2d\sin\theta \quad (2)$$

where *d* is the *d*-spacing value,  $\theta$  the diffraction angle,  $\lambda$  the X-ray wavelength, and *n* an integral number. As shown in Fig. 12, broad peaks of the C-SiO<sub>2</sub> membranes were observed at  $2\theta = 22.24$ ,  $23.48$ , and  $23.91^\circ$  with an incremental isothermal time. As listed in Table 2, the calculated average *d*-spacing



**Fig. 13.**  $O_2$  permeabilities vs  $O_2/N_2$  selectivities of C-SiO<sub>2</sub> membranes derived from polyvinylpyrrolidone containing poly(imide siloxane).

values of the C-SiO<sub>2</sub> membranes decreased with increasing the isothermal time. From the WAXD patterns, the separation factors of the C-SiO<sub>2</sub> membranes were reasonably explained with the average *d*-spacing values. That is, the constructed initial porous carbon structures derived from polymer blends shrank under the isothermal condition. Therefore, the carbon layers were stacked densely, which led to the reduced pore size between the carbon layers. Consequently, the C-SiO<sub>2</sub> membranes prepared under the isothermal conditions showed the higher selectivities and reduced permeabilities.

Fig. 13 shows performances of the C-SiO<sub>2</sub> membranes prepared by the thermal labile polymer and the pyrolysis conditions as compared with other carbon membranes derived from the PMDA/ODA-based polyimide precursors. From the results, the performances of the C-SiO<sub>2</sub> membranes derived from Si-PI/PVP precursors located upper right position as compared with other CMS membranes. In particular, the C-SiO<sub>2</sub> membranes showed the similar slope with the upper bound of polymeric membranes between the  $O_2$  permeabilities and the  $O_2/N_2$  selectivities with the pyrolysis temperature in this study. Park *et al.*[17] also reported that

the slope of the upper bound between the permeability and the selectivity of CMS membrane was depended on the final pyrolysis temperature if the same precursors were used. Consequently, the C-SiO<sub>2</sub> membranes derived from Si-PI containing PVP showed the  $O_2$  permeabilities of 30-1,080 Barrer and the  $O_2/N_2$  selectivities of 8-17 in this study depending a pyrolysis temperature and isothermal time.

#### 4. Conclusions

In this study, the C-SiO<sub>2</sub> membranes were prepared by pyrolyzing Si-PI/PVP polymer blends and by varying the ratio of Si-PI/PVP and the pyrolysis conditions. The characteristics of porous carbon structures derived from polymer blends was investigated using nitrogen adsorption isotherms. While the C-SiO<sub>2</sub> membranes derived from Si-PI showed the typical type I isotherm according to IUPAC classifications, the C-SiO<sub>2</sub> membranes with the higher content of PVP showed the type IV isotherm with the hysteresis loop. It is believed that the phase separated domain of the thermal labile polymer PVP in Si-PI affected the microporous carbon structures containing mesopores. From the molecular sieving properties of the C-SiO<sub>2</sub> membranes, the gas permeabilities increased with the content of PVP in Si-PI while their selectivities decreased. In addition, the performances of the C-SiO<sub>2</sub> membranes were significantly related with the pyrolysis conditions, such as the final pyrolysis temperature and the isothermal time. In particular, the C-SiO<sub>2</sub> membranes pyrolyzed at 550°C with the incremental isothermal times showed the 110% enhanced  $O_2/N_2$  selectivity while the  $O_2$  permeability was reduced by about 26%.

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## Reference

1. H. Suda and K. Haraya, "Carbon molecular sieve membranes: preparation, characterization, and gas permeation properties", *ACS Symposium Series*, 744: Membrane Formation and Modification, pp. 295, Washington, USA (2000).
2. A. Singh and W. J. Koros, "Significance of entropic selectivity for advanced gas separation membranes", *Ind. Eng. Chem. Res.*, **35**, 1231 (1996).
3. H. B. Park and Y. M. Lee, "Pyrolytic carbon-silica membrane: a promising membrane materials for improved gas separation", *J. Membr. Sci.*, **213**, 263 (2003).
4. A. Singh and W. J. Koros, "Pyrolytic carbon membranes for air separations", *Membr. J.*, **7**, 15 (1997).
5. Y. M. Lee, H. B. Park, and I. Y. Suh, "Preparation and applications of carbon molecular sieve membranes for gas separation", *Membr. J.*, **11**, 1 (2001).
6. C. W. Jones and W. J. Koros, "Carbon molecular sieve gas separation membranes. I. Preparation and characterization based on polyimide precursors", *Carbon*, **32**, 1419 (1994).
7. H. Suda and K. Haraya, "Molecular sieving effect of carbonized Kapton polyimide membrane", *J. Chem. Soc. Chem. Commun.*, **11**, 1179 (1995).
8. J. Hayashi, M. Yamamoto, K. Kusakabe, and S. Morooka, "Simultaneous improvement of permeance and permselectivity of 3,3',4,4'-biphenyltetracarboxylic dianhydride-4,4'-oxydianiline polyimide membrane by carbonization", *Ind. Eng. Chem. Res.*, **34**, 4364 (1995).
9. J. Hayashi, H. Mizuta, M. Yamanoto, K. Kusakabe, and S. Morooka, "Effect of oxidation on gas permeation of carbon molecular sieving membranes based on BPDA-pp'ODA polyimide", *Ind. Eng. Chem. Sci.*, **36**, 2134 (1997).
10. H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata, and S. Yoshitomi, "Carbon molecular sieve films from polyimide", *Carbon*, **30**, 305 (1992).
11. C. G. Vincent and W. J. Koros, "Effect of polyimide pyrolysis conditions on carbon molecular sieve membrane properties", *Ind. Eng. Chem. Res.*, **35**, 2999 (1996).
12. S. Wang, M. Zeng, and Z. Wang, "Asymmetric molecular sieve carbon membranes", *J. Membr. Sci.*, **109**, 267 (1996).
13. F. K. Katsaros, T. A. Steriotis, A. K. Stubos, A. Mitropoulos, N. K. Kanellopoulos, and S. Tennison, "High pressure gas permeability of microporous carbon membranes", *Microporous Mater.*, **8**, 171 (1997).
14. Y. D. Cheng and R. T. Yang, "Preparation of carbon molecular sieve membrane and diffusion of binary mixtures in the membrane", *Ind. Eng. Chem. Res.*, **33**, 3146 (1994).
15. Y. K. Kim, H. B. Park, and Y. M. Lee, "The gas separation properties of carbon molecular sieve membranes derived from polyimides having carboxylic acid groups", *J. Membr. Sci.*, **235**, 139 (2004).
16. S. J. Jeong, J. H. Lim, S. H. Han, H. C. Koh, and S. Y. Ha, "Study on the gas separation of carbon molecular sieve (CMS) membrane for recovering the perfluorocompound gases from the electronics industry", *Membr. J.*, **26**, 220 (2016).
17. H. B. Park, Y. K. Kim, J. M. Lee, S. Y. Lee, and Y. M. Lee, "Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes", *J. Membr. Sci.*, **229**, 117 (2004).
18. W. Zhou, M. Yoshino, H. Kita, and K. Okamoto, "Carbon molecular sieve membranes derived from phenolic resin with a pendant sulfonic acid group", *Ind. Eng. Chem. Res.*, **40**, 4801 (2001).
19. A. F. Ismail and L. I. B. David, "A review on the latest development of carbon membranes for gas separation", *J. Membr. Sci.*, **193**, 1 (2001).
20. J. Ozaki, N. Endo, W. Ohizumi, K. Igarashi, M. Nakahara, and A. Oya, "Novel preparation method for the production of mesoporous carbon fiber

- from a polymer blend”, *Carbon*, **35**, 1031 (1997).
21. H. Hatori, T. Kobayashi, Y. Hanzawa, Y. Yamada, Y. Iimura, T. Kimura, and M. Shiraishi, “Mesoporous carbon membranes from polyimide blended with poly(ethylene glycol)”, *J. Appl. Polym. Sci.*, **79**, 836 (2001).
  22. H. B. Park, I. Y. Suh, and Y. M. Lee, “Novel pyrolytic carbon membranes containing silica: preparation and characterization”, *Chem. Mater.*, **14**, 3034 (2002).
  23. H. B. Park, D. W. Han, and Y. M. Lee, “Effect of a UV/Ozone treatment on siloxane-containing copolyimides: Surface modification and gas transport characteristics”, *Chem. Mater.*, **15**, 2346 (2003).
  24. H. B. Park and Y. M. Lee, “High permeability, high selectivity carbon-silica membranes for gas separation”, *Membr. J.*, **12**, 107 (2002).
  25. Y. K. Kim, H. B. Park, and Y. M. Lee, “Carbon molecular sieve membranes derived from thermally labile polymer containing blend polymers and their gas separation properties”, *J. Membr. Sci.*, **243**, 9 (2004).
  26. J. H. Kim, M. S. Whang, and C. K. Kim, “Novel miscible blends composed of poly(ether sulfone) and poly(1-vinylpyrrolidone-co-styrene) copolymers and their interaction energies”, *Macromolecules*, **37**, 2287 (2004).
  27. H. B. Park, C. H. Jung, Y. K. Kim, S. Y. Nam, S. Y. Lee, and Y. M. Lee, “Pyrolytic carbon membranes containing silica derived from poly(imide siloxane): The effect of siloxane chain length on gas transport behavior and a study on the separation of mixed gases”, *J. Membr. Sci.*, **235**, 87 (2004).
  28. J. M. Lee, M. G. Lee, S. J. Kim, H. C. Koh, and S. Y. Nam, “Characterization of gas permeation properties of polyimide copolymer membranes”, *Membr. J.*, **25**, 223 (2015).
  29. S. W. Kuo and F. C. Chang, “Miscibility and hydrogen bonding in blends of poly(vinylphenol-co-methyl methacrylate) with poly(ethylene oxide)”, *Macromolecules*, **34**, 4089 (2001).
  30. J. R. Fried, “Polymer science and technology”, Prentice-Hall International Inc., London (1995).
  31. H. B. Park, “Membrane materials for gas and vapor separation derived from siloxane containing copolymers”, Ph. D Dissertation, Univ. of Hanyang, Seoul (2001).
  32. J. W. Patrick, “Porosity in carbons: Characterization and applications”, Edward Arnold, London (1995).
  33. K. S. W. Sing, “The use of gas adsorption for the characterization of porous solids”, *Colloids Surf.*, **38**, 113 (1989).
  34. M. Yamazaki, M. Kayama, K. Ikeda, T. Alii, and S. Ichihara, “Nanostructured carbonaceous material with continuous pores obtained from reaction-induced phase separation of miscible polymer blends”, *Carbon*, **42**, 1641 (2004).
  35. A. S. Ghosal and W. J. Koros, “Air separation properties of flat sheet homogeneous pyrolytic carbon membranes”, *J. Membr. Sci.*, **174**, 177 (2000).
  36. D. Q. Vu, W. J. Koros, and S. J. Miller, “High pressure CO<sub>2</sub>/CH<sub>4</sub> separation using carbon molecular sieve hollow fiber membranes”, *Ind. Eng. Chem. Res.*, **41**, 367 (2002).
  37. D. Q. Vu, W. J. Koros, and S. J. Miller, “Mixed matrix membranes using carbon molecular sieves. I. Preparation and experimental results”, *J. Membr. Sci.*, **211**, 311 (2003).