Pyrolytic Carbon Membranes Containing Silica Derived from Siloxane-Containing Copolyimides: Role of Siloxane Domain on Gas Permeation Properties

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1. Introduction

Membrane-based separation science and technology has seen a great upswing in the past few decades, especially in the field of gas separation. Commercial markets for gas separation have made eye-opening progress, in that the performance of membrane materials has improved, exceeding the existing upper bounds for separating gas pairs such as H_2/N_2, He/N_2, O_2/N_2, and CO_2/N_2. In particular, inorganic membrane such as zeolites, sol-gel, and molecular sieving carbon or nanoporous carbon offer significant potential advantages over conventional polymeric membranes [1-4]. A significant advantage of the inorganic membranes is that they can perform the separation of small molecules under harsh conditions such as elevated temperature and pressure. Simultaneously, to achieve a desirable and practical flux and selectivity, the microporous inorganic membranes need to have a molecular sieving capability rendered by micropores with dimensions near the sizes of the permeating gas molecules.

In our previous study[5,6], a new class of pyrolytic carbon membranes containing silica ($C-SiO_2$) has been prepared by the pyrolysis copolyimides containing of two phases and characterized. The $C-SiO_2$ membranes exhibited an outstanding molecular sieving capability, together with a high gas permeability. Furthermore, the gas permeation behavior of the $C-SiO_2$ membrane was very similar to that of the precursor. In this study, the role of siloxane phase in the precursor was investigated on the gas permeation properties of the $C-SiO_2$ membrane. Thus, siloxane-containing copolyimides were prepared at various siloxane contents and chain lengths, and were carbonized under an inert

atmosphere.

2. Experimental Section

2.1 Materials

Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were obtained from Tokyo Kasei Co., Inc., Tokyo, Japan, and used without further purification. Aminopropyl poly(dimethyl siloxane) (PDMS) was kindly donated by Shinetsu., Inc., Tokyo Japan, and used after being dried in a vacuum oven at 90°C. Table 1 shows detailed information about the PDMS in this study.

Table 1. Characteristics of Aminopropyl-Terminated PDMS Oligomers Used in This Study

Sample	M_n(g/mol)[a]	n[b]	T_g (°C)[c]
PDMS 9	900	10	−122
PDMS 16	1600	14−15	−123

[a]Determined by GPC. [b]Average number of siloxane repeat units in the oligomers. [c]Determined by DSC with a heating rate of 5°C/min

2.2 Membrane Preparation

The carbon membranes containing silica fabricated in this work were prepared by the pyrolysis of imide-siloxane copolymers with different PDMS compositions (content and molecular weight). Before each pyrolysis trail, the free-standing poly(imide siloxane) (PIS) films were rinsed with deionized water and stored at 120°C under a vacuum oven until any residual solvent and dust was completely eliminated. After these pretreatments, the PIS films were than pyrolyzed at 600°C, 800°C, and 1000°C in a muffle furnace equipped with an automatic temperature controller.

2.3. Molecular Probe Study

The permeability coefficient for a permanent gas is determined by multiplying the permeation rate by the membrane thickness and can be

expressed by

$$P = dp/dt(VT_0L/p_0T\Delta pA)$$

(1)

where P is the permeability represented in Barrer; dp/dt is the rate of the pressure rise under the steady state; $V(\text{cm}^3)$ is the downstream volume; $L(\text{cm})$ is the membrane thickness; $\Delta P(\text{cmHg})$ is the pressure difference between the two sides; $T(\text{K})$ is the measurement temperature; $A(\text{cm}^2)$ s the effective area of the membrane; and p_0 and T_0 are the standard pressure and temperature, respectively. Permselectivity as defined in this study is the ratio of permeability of the selected gases to that of nitrogen.

3. Results and Discussion

As listed in Table 2, the gas permeability increased with volume fraction of siloxane in the precursor, indicating that the characteristic skeleton of the two phases might be considerably conserved even after the pyrolysis. Indeed, the rigid imide domain composed of the aromatic backbone and the flexible siloxane domain performed the roles of organic molecular sieve and percolator, respectively. After the transition from the organic to the inorganic phase by the heat treatment, the imide and siloxane domains were gradually changed into a carbon-rich phase with crosslinked voids of amorphous regions and the interlayer spacing of graphite-like or highly ordered microcrystalline carbon and a silica rich phase with a sparse carbon clusters.

Table 2. Gas Permeation Results for $C-SiO_2$ Membranes at 25°C

Precursor	Pyrolysis Temp ($^\circ$C)	Permeability (Barrer)				Selectivity to N_2		
		He	CO_2	O_2	N_2	He/N_2	CO_2/N_2	O_2/N_2
PIS I	600	315	21	7.6	0.33	955	62	23
PIS II	600	1250	84	30	1.35	1033	62	22
PIS III	600	610	386	111	18	34	21	6.2

Table 3 illustrate the O_2 permeability vs. O_2/N_2 selectivity of carbon

membranes containing silica derived from random and block PIS at a same siloxane content. As shown in Figure 1, the morphological changes in the PISs led to different gas transport behaviors (permeability and permselectivity) of the final pyrolytic $C-SiO_2$ membrane.

Table 3. Gas Permeation Results for $C-SiO_2$ Membranes at $25^\circ C$

Precursor	Pyrolysis Temp ($^\circ$C)	Permeability (Barrer)				Selectivity to N_2		
		He	CO_2	O_2	N_2	He/N_2	CO_2/N_2	O_2/N_2
r-PIS	800	1107	26	19.3	0.6	1845	43.3	32
b-PIS	800	1449	155	55.8	3.9	371.5	39.7	14.3

Table 4 summarizes the gas permeation results of $C-SiO_2$ membranes derived from PIS having different siloxane chain length (M_n = 900 and 1600) at the same siloxane content (30 wt%).

Table 4. Gas Permeation Results for $C-SiO_2$ Membranes at $25^\circ C$

Precursor	Pyrolysis Temp ($^\circ$C)	Permeability (Barrer)					Selectivity to N_2			
		H_2	He	CO_2	O_2	N_2	H_2/N_2	He/N_2	CO_2/N_2	O_2/N_2
PIS9	600	–	610	386	111	18	–	34	21	6.2
PIS16	600	12598	7319	2526	595	69	182	105	36.5	8.6

4. References

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