Novel Carbon Molecular Sieve Membranes Derived from Poly(phenylene oxide) and Its Derivatives for Gas Separation

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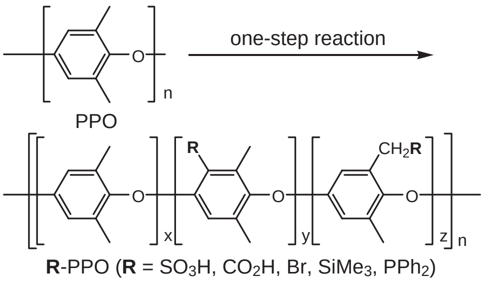
We succeeded in fabricating new carbon molecular sieve (CMS) membranes as hollow fibers using poly(phenylene oxide) (PPO) and its functionalized derivatives (R-PPO). Gas transport properties were measured for He, H_2, CO_2, O_2, and N_2. PPO CMS membranes exhibited higher performances than those of polymeric precursors. The highest performance was attained by trimethylsilyl-PPO (TMSPPO) CMS membrane pyrolyzed at 923 K, of which O_2 permeability was 125 Barrer and O_2/N_2 permselectivity was 10.0 at 298 K.

Membrane technologies have recently emerged as a promising gas separation processes especially for H_2 and O_2 production. Carbon molecular sieve (CMS) membranes have quite attractive characteristic such as excellent shape selectivity, high hydrophobicity, heat resistance, and high corrosion resistance.[1] Lately, numerous precursors have been used to form CMS membranes, such as polyimide, polyacrylonitrile, phenolic resin, poly(furfuryl alcohol), poly(vinylidene chloride), cellulose, and others. Most of reported CMS membranes are related to polyimides due to these high thermal stabilities and excellent gas separation performances, however, they cost too high and their commercial availabilities are very limited.[1,2]

Poly(phenylene oxide) (PPO) is one of the versatile commercial polymers utilized as engineering plastics and is much cheaper than polyimide. In addition, PPO has the highest gas permeability among other aromatic polymers and is easily modified with functional groups to achieve more favorable material for gas separation.[3] In this report, we aimed to prepare the CMS hollow fiber membranes derived not only from poly(2,6-dimethyl-1,4-phenylene oxide) but also its functionalized derivatives (R-PPO), and the gas transport properties of these membranes are studied. PPO derivatives were synthesized in one-step reactions as shown in Scheme 1. For functional groups (R) with various features, we chose SO_3H (SPPO), CO_2H (CPPO), Br (BrPPO), $SiMe_3$ (TMSPPO), and PPh_2 (PPhPPO) in this work.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was purchased from Aldrich Chemicals. Syntheses of PPO derivatives were carried out according to the literatures.[4] The hollow fiber polymeric precursor membranes were fabricated with the coagulation method. For example, a 20 wt % PPO solution in chloroform was immersed into an ethanol bath as a coagulating agent then dried in air at room temperature. In the similar way, polymeric precursor membranes of functionalized PPO were obtained. These hollow fiber membranes have symmetric structure in SEM observation.



R-PPO (**R** = SO_3H, CO_2H, Br, $SiMe_3$, PPh_2)

Scheme 1. Syntheses of functionalized PPO derivatives.

Carbon membranes were obtained through the pyrolysis of PPO and R-PPO polymeric membranes at 823–1023 K for 2 h under vacuum by a heating rate of 10 K·min^{-1}. Before carbonization process the membranes were preoxidized in air at 553 K for 45 min. The detail of membrane fabrication was described in elsewhere.[5]

Gas permeability (He, H_2, CO_2, O_2, and N_2) was measured at 298 K with a high-vacuum time-lag method under the pressure difference of 1 atm. Both the feed and permeate sides of the membrane cell were evacuated ($<10^{-5}$ Torr) prior to each measurement. Permselectivity was defined in the present study as the ideal separation factor, which is the ratio of permeability of chosen gas over that of N_2.

Figure 1 gives the effect of pyrolysis temperature for PPO membrane on permeability and permselectivity at 298 K together with its polymeric precursor. The obtained PPO carbon mem-

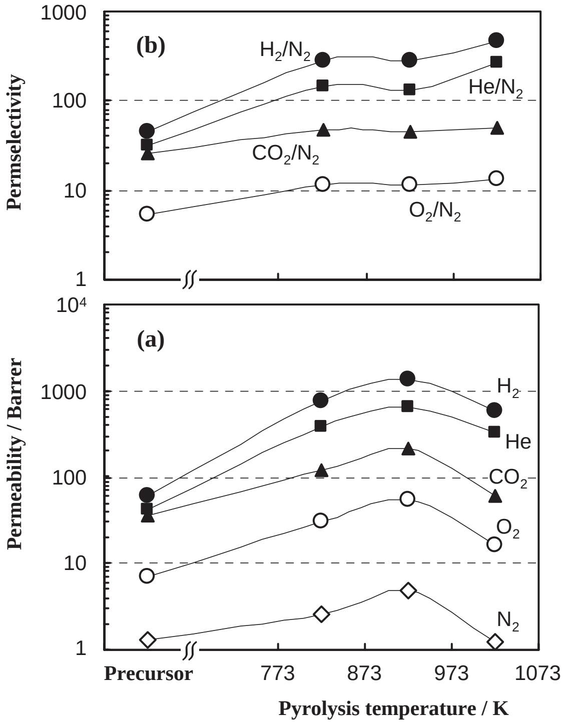


Figure 1. Influence of pyrolysis temperature on: (a) permeability; and (b) permselectivity at 298 K for PPO membranes.

Table 1. Gas permeabilities and permselectivities at 298 K for PPO polymeric and carbon molecular sirve (CMS) membranes

Precursor	Permeabilities for polymeric membranes (Barrer[a])					Permselectivities for polymeric membranes			
	PHe	PH_2	PCO_2	PO_2	PN_2	$\alpha He/N_2$	$\alpha H_2/N_2$	$\alpha CO_2/N_2$	$\alpha O_2/N_2$
PPO	42	60	35	7.1	1.3	32	45	26.3	5.3
SPPO	24.6	20.8	6.9	1.5	0.23	108	92	30.5	6.5
CPPO	30.9	37.0	28	5.1	0.87	35	42	31.8	5.9
BrPPO	60.4	95.1	102	16.9	3.7	16	26	27.6	4.6
TMSPPO	94.8	136	107	24.4	5.4	18	25	19.9	4.5
PPhPPO	24.7	32.0	19.4	3.7	0.72	34	44	26.8	5.2

Precursor	Permeabilities for CMS membranes[b] (Barrer[a])					Permselectivities for CMS membranes[b]			
	PHe	PH_2	PCO_2	PO_2	PN_2	$\alpha He/N_2$	$\alpha H_2/N_2$	$\alpha CO_2/N_2$	$\alpha O_2/N_2$
PPO	635	1355	218	55	4.8	133	283	45.5	11.4
SPPO	504	1069	134	40	2.9	175	371	46.5	14.0
CPPO	353	778	225	47	4.9	72	158	45.6	9.6
BrPPO	799	972	109	27	2.4	334	407	45.8	11.5
TMSPPO	743	1843	529	125	12.4	60	148	42.5	10.0
PPhPPO	150	283	64	14	1.2	125	237	53.7	11.7

[a] 1 Barrer = 1×10^{-10} $cm^3(STP) \cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$. [b] Pyrolyzed under vacuum for 2 h at 923 K.

branes showed the superior performances in both permeabilities and permselectivities to that of the polymeric precursor due to molecular sieving effect. It is well known that the micropores with sharp pore distribution are generated after the pyrolysis in carbon membranes, which contribute toward increasing the permeability and the permselectivity.[1,2]

The gas permeability reached a maximum when pyrolyzed at 923 K, and then decreased at higher temperature. On the other hand, the permselectivity was nearly the same at this pyrolysis temperature. As a result, the pyrolysis at 923 K provided the best performance from a view of permeability-permselectivity combination.

The gas transport properties for PPO polymeric and PPO CMS membranes with various functional groups pyrolyzed at 923 K are summarized in Table 1. Every PPO CMS membrane displayed superior performance in both permeability and permselectivity compared with that of its polymeric precursor. For smaller gas permeation such as He and H_2, PPO CMS membranes with sulfonic acid group (SPPO) and bromine group (BrPPO) yield higher permselectivities compared with unmodified membrane. The introduction of trimethylsilyl group (TMSPPO) enhanced the permeabilities for all gases tested, along with decreasing the permselectivities. However, the differences in CO_2/N_2 and O_2/N_2 permselectivities between PPO and TMSPPO CMS membranes are small, overall yields were increased in TMSPPO CMS membrane. We assumed that the functional groups affect the membrane structures after the heat treatment owing to these decomposition behaviors. From CO_2 adsorption, it is revealed that TMSPPO CMS membrane had larger micropore volume than that of PPO CMS membrane, which is considered to increase the diffusivity of TMSPPO CMS membrane to give higher permeability.

Figure 2 shows the relations between O_2 permeability and O_2/N_2 permselectivity at 298 K for PPO CMS membranes pyrolyzed at 923 K, together with reported CMS membranes derived from polyimides.[2b] CMS membranes prepared from PPO derivatives had properties above the upper bound of conventional polymeric membranes reported by Robeson;[6] including PPO polymeric precursors. The highest performance was attained by TMSPPO CMS membrane, of which O_2 permeability was 125 Barrer and O_2/N_2 permselectivity was 10.0 at 298 K. These results indicate that CMS membranes based on PPO derivatives have as high performances as that of CMS membrane derived from polyimide.

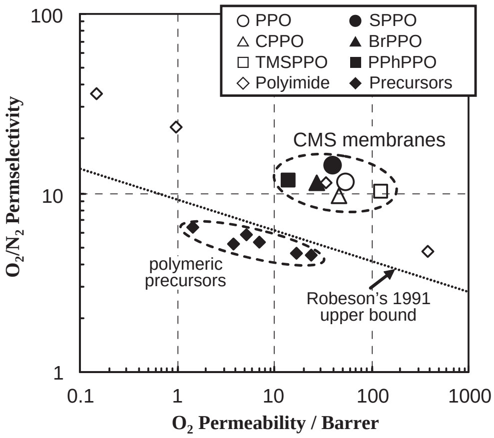


Figure 2. Relations between O_2 permeability and O_2/N_2 permselectivity at 298 K for PPO CMS membranes pyrolyzed at 923 K compared to these polymeric precursors.

In conclusion, CMS membrane derived from PPO was prepared for the first time and we found that modified PPO CMS membranes exhibited excellent performances for gas separation. We also succeeded in preparing the asymmetric CMS membrane, which is promising alternative precursor as unsupported CMS membrane for commercial application.

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