특별강연 1

올레핀 촉진 수송 분리를 위한 유기 박막

원 종옥, 차 봉준, 박 정옥, 박 용순, 강 용수
촉진수송 분리막 연구단, 한국 과학 기술 연구원

Organic Thin Films for Facilitated Olefin Transport

Jongok Won, Bong Jun Cha, Jeong Ok Park, Yong Soon Park,
Yong Soo Kang
Center for Facilitated Transport Membranes, Korea Institute of Science and Technology

1. Introduction

Facilitated transport membranes containing silver-polymer electrolyte as a olefin carrier have been extensively studied for the separation of olefin/paraffin mixtures[1-3]. In the facilitated transport of olefins, silver ions confined to the membrane medium form reversible complexes with olefin molecules[4]. Because of the reversible and specific interaction of silver ions with olefin molecules, silver ions can act as olefin carriers for facilitated transport in the membrane and then lead a carrier-mediated transport in addition to a normal Fickian transport. Paraffins are unable to form complexes with silver ions and permeate only through Fickian transport. This results in high olefin/paraffin separation.

Gas permeation can be improved through the preparation of a composite membrane, where a thin dense toplayer is supported by a porous sublayer. The thickness of toplayer determines the efficiency of the permeationm and the typical thickness of the toplayer obtained from coating processes was an order of micrometer. Alternative processes that reduce the toplayer thickness are desirable. In this respect, the preparation of thin layered composite membranes for the olefin facilitated transport has been studied in this laboratory[2].

In here thin layers using amine-terminated Starburst (PAMAM) dendrimers that are covalently attached to the plasma-modified surface of polydimethylsiloxane (PDMS) membranes were prepared. The product layers are densely functionalized and easily modified. The coupling of the surface of dendrimers and functional polymer electrolytes leads to covalently attached polymer electrolyte layers. Such dendrimer composite membranes are complexed with $AgBF_4$ and their gas transport behavior of propylene/propane is investigated.

2. Experimental Section

Materials. Fourth-generation amine-terminated poly(amidoamine) (PAMAM) dendrimer of 10% in methanol (D), silver tetrafluoroborate ($AgBF_4$, 99.0%), 2-ethyl-2-oxazoline, methyl-p-toluenesulfonate, succinic ahnydride, 1,3-dicyclohexylcarboimide, 4-dimethylaminopyridine, N-hydroxysuccinimide were purchased from Aldrich and used as received. Maleic anhydride (MAH; Junsei) and methanol (Merch, RPA) were purchased. Polydimethylsiloxane (PDMS; model # SSPM100) membrane as a support was purchased from Specialty Silicone Products, Inc. (NY).

PDMS-Air-Dendrimer (PDMS-Air-D) composite membranes: Plasma treatment was carried out using a R300A radio-frequency generator (Autoelectric, Seoul), operating at 13.56 MHz and setting at 50W. The PDMS samples were soaked in a boiling methanol at 65°C for 3 hrs in the flask equipped with a reflux apparatus, then sonicated for 1hr, washed in pure methanol and deionized water several times and dried in vacuum for 2 days. The PDMS membrane was glow-discharged in air for 1 min under the pressure of 0.02 torr. After drying, all substrates were used for the composite layer formation immediately. Different range of dendrimers was cast on plasma-modified PDMS membranes by solution deposition-evaporation. After drying at room temperature, samples were immediately annealed in 120°C oven for 1hr to induce the reaction of dendrimer with PDMS surface. All samples then were washed repeatedly with pure methanol several times and dried. Different amounts of $AgBF_4$ (1.6×10^{-6} - 1.6×10^{-5} moles/cm^2)

dendrimer contains a reduced amount of oxygen (20%) and a certain amount of nitrogen (11.8%). The reduction of atom % of oxygen is due to the formation of chemical bond between the dendrimer and the carboxyl group on the surface of PDMS membranes. Similar behavior was shown for the PDMS-MAH-D composite membranes.

The IR spectra of composite membranes also change with increasing loading amount of the dendrimer. The band for carboxyl groups is observed at 1730cm^{-1} for plasma treated PDMS membranes in air. This band disappears after addition of the dendrimer, and new bands for amides at 1649 and 1551 cm^{-1} appear as shown in Figure 1.

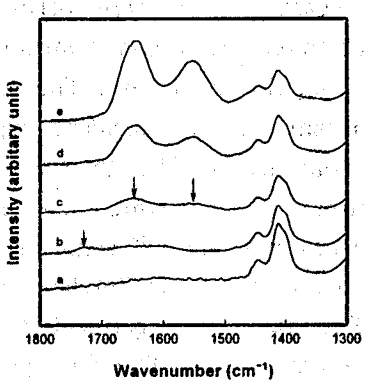

Figure 1. ATR FT-IR spectra of PDMS composite membranes. Spectra are shown for membranes of (a) nascent PDMS, (b) plasma treated PDMS (c) PDMS-AIR-D membranes deposited with 3.1 x 10^{-11}, (d) 3.1 x 10^{-10}, and (e) 3.1 x 10^{-9} moles/cm^{2} of dendrimers.

PDMS-MAH-D composite membranes show similar trends. Bands for anhydride groups are observed at 1858 and 1782 cm^{-1} for PDMS-MAH membranes. They are decreased after the addition of dendrimer, and new bands for amides at 1640 and 1550 cm^{-1} appear. The latter gradually increase their intensity with increasing concentration of the dendrimer.

The gas transport properties of a nascent PDMS membrane and composite membranes are summarized in Table 1. All membranes show no selectivity of propylene over propane. As shown in the table, the gas permeability decreased significantly with the existence of dendrimer on PDMS-AIR or PDMS-MAH membranes implying the barrier property of the dendrimer.

Table 1. Gas permeabilities of PDMS composite membranes

Membrames	Propylene	Propane	Selectivity
Nascent PDMS	13430	13850	0.97
PDMS-AIR-D	7500	6890	1.09
PDMS-MAH	2150	2130	1.01
PDMS-MAH-D	720	690	1.04
PDMS-AIR-D-POZ	6970	7606	0.92

The effect of silver salt concentration on propylene permeability was investigated. The propylene permeabilities through the composite membranes with increasing loading amount of $AgBF_4$ are shown in Table 2.

Table 2. Gas Permeance of PDMS composite membranes with silver salt.

$AgBF_4$ ($\times 10^{-6}$mole/cm^2)	PDMS-AIR-D			PDMS-MAH-D		
	propylene	propane	selectivity	propylene	propane	selectivity
1.6	10980	10110	1.08	2220	901	2.46
3.1	8890	8860	1.00	2150	-	-
16	9460	8160	1.16	4410	-	-

As shown in the table, the propylene permeabilities through PDMS-AIR-D membranes were hardly changed with salt concentration. By comparison, the propylene permeabilities through PDMS-MAH-D membranes increased from 720 up to 4400 barrer with increasing silver ion content. Meanwhile, the propane permeability through the membrane was unmeasurably small (less than 10 barrer). The ideal separation factor for propylene/propane, defined as the permeability ratio of propylene over propane, is more than 440 at high silver concentration[6].

Although PDMS-AIR-D-POZ composite membranes showed reasonable facilitated transport behavior with the coordination of silver salt, the performance was not high enough. It was thought that the low performance of this composite membrane is because of low loading of POZ in this process.

4. Summary

Thin dendrimer layer on polymer membrane was prepared and characterized by XPS and ATR FT-IR spectroscopy. The dendrimer layer reduced the gas permeability significantly, demonstrating its barrier property. For PDMS-MAH-D membranes, the propylene permeability and its ideal separation factor over propane increased from ca. 720 to 4400 barrer and from ca. 1 to 440, respectively, with increasing silver salt concentration. This excellent performance predominantly was attributed to the reversible interaction of propylene with silver ions incorporated on maleic anhydride layer.

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5. Reference

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6. We assumed that the permeability of propane is 10 barrer since it was not detected being below the practical lower limit of the bubble flow meter.