

Notes

Long-Term Separation Performance of Phthalate Polymer/Silver Salt Complex Membranes for Olefin/Paraffin Separation

Sang Wook Kang^{1,2}, Jong Hak Kim¹, Kookheon Char², and Yong Soo Kang^{1,*}

¹Center for Facilitated Transport Membranes, Korea Institute of Science and Technology P. O. Box 131, Cheongryang, Seoul 130-650, Korea

²School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-744, Korea

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Introduction

Silver ions have been known to react reversibly with olefin molecules to make silver-olefin complexes.¹ Due to reversible and specific interaction of silver ions with olefins, silver ions can act as olefin carriers, resulting in facilitated olefin transport. Many investigations have been reported on olefin/paraffin separations by various types of facilitated transport membranes.²⁻⁴ Solid polymer electrolyte membranes containing silver ions are of particular interest for their high separation performance for olefin/paraffin mixture.^{5,6} For example, when either silver tetrafluoroborate (AgBF_4) or silver triflate (AgCF_3SO_3) is dissolved in a polar polymer such as poly(ethylene oxide) (PEO), poly(2-ethyl-2-oxazoline) (POZ) or poly(vinylpyrrolidone) (PVP), the silver cations are active for olefin complexation, resulting in facilitated olefin transport.

However, polymer membranes containing silver salts exhibit some disadvantages to limit their industrial applications. One of the major drawback observed in such membranes is the gradual decrease in membrane performance with time, possibly due to the reduction of silver ions to silver nanoparticles.^{7,8}

Recently, we have reported that the strong coordination between the phthalic structure and silver ion prevents the reduction of silver ions to silver nanoparticles.⁹ However it is not clear whether the phthalic group in polymer is the

only parameter in determining the long-term stability of facilitated olefin transport membranes. Thus, in this study, two phthalic polymers with different chemical structures are used as polymer matrix and their complexes with AgBF_4 are characterized in terms of long-term membrane stability mostly by FT-IR and TEM analysis.

Experimental

Poly(ethylene phthalate) (PEP) ($M_w = 19,500$ g/mole) was synthesized by condensation reaction of phthalic anhydride with ethylene glycol as reported previously.¹⁰ Poly[trimethylolpropane/di(propylene glycol)-*alt*-adipic acid/phthalic anhydride] (PTDP) and silver tetrafluoroborate (AgBF_4 , 98%) were purchased from Aldrich Chemical Co.

PTDP/ AgBF_4 membranes were prepared by dissolving AgBF_4 in methanol solution containing 20 wt% PTDP. PEP/ AgBF_4 membranes were prepared by dissolving AgBF_4 in THF solution containing 20 wt% of PEP. The solutions were coated onto a polyester membrane support with a average pore diameter of $0.1 \mu\text{m}$ (Whatman) using a RK Control Coater (Model 101, Control Coater RK Print-Coat instruments LTD, UK). The amounts of AgBF_4 added into the polymer matrix were determined depending on the mole ratio of the silver ion to the monomeric unit of polymer. The membranes were dried in a light-protected convection oven under nitrogen for 1 h, and dried completely in a vacuum oven for 2 day at room temperature. The thickness of the top polymer electrolyte layer was ca. $1 \mu\text{m}$, as determined by scanning electron microscopy. Gas flow rates represented by gas permeance were determined by mass flow controller. The unit of the gas permeance is GPU, where $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \text{ s cmHg})$. The mixed gas (50:50 vol% of propylene:propane mixture) separation properties of the membranes were quantified using a gas chromatography (Hewlett-Packard G1530A, MA) equipped with a TCD detector and a unibead 2S 60/80 packed column.

IR measurement was performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64-200 scans were signal-averaged at a resolution of 4 cm^{-1} . Transmission electron micrographs (TEM) were obtained from a Philips CM30 microscope operating at 300 kV to observe silver nanoparticles, resulting from the reduction of silver ions. Membranes for TEM were prepared by casting a methanol solution of PTDP (10 wt%) containing AgBF_4 and by casting a THF solution of PEP (10 wt%) containing AgBF_4 on a glass plate and dried for 2 h in a light-protected convection oven at room temperature under nitrogen. After completely dried, the membranes were dissolved in methanol and THF, respectively, and then a drop of this colloidal silver dispersion was placed onto a standard copper grid.

*e-mail: yskang@kist.re.kr

Results and Discussion

Two polymers of poly[trimethylolpropane/di(propylene glycol)-*alt*-adipic acid/phthalic anhydride] (PTDP), and poly(ethylene phthalate) (PEP) as phthalate polymer were selected and their chemical structures are presented in Scheme I. PTDP contains various functional groups of aliphatic ester, ether, hydroxyl and phthalate.

Polymers containing electron donor group can dissolve silver salts via coordination bonds to form polymer electrolyses. Thus, the selected polymers are expected to coordinate to silver ions. It is expected that PEP containing only phthalates as a functional group have the chelating interaction between two carbonyl groups and a silver ion, whereas PTDP does various coordinative interactions between various oxygens and silver ion.

Silver ions in polymer electrolytes are labile to be reduced to silver nanoparticles photo-chemically^{7,8} or under the pres-

ence of a reducing agent. However we reported that the reduction of silver ions could be significantly prevented due to the strong coordination between the phthalates and silver ion.⁹ PTDP contains various functional groups besides phthalates, which expect to involve in reduction of silver ions. Silver ions in PTDP are expected to be mostly coordinated to phthalate oxygens because the interaction of silver ions with phthalate oxygens is approximately 2-fold stronger than that with single carbonyl oxygen.⁹ Thus, PTDP membranes are expected to have rather good long-term stability of separation performance.

The long-term experiments have been carried out to support the above assumption and the results are shown in Figures 1 and 2. The mixed gas selectivity of propylene/propane and the total permeance for the PEP/AgBF₄ membrane remain nearly constant throughout the experiments for up to 140 hrs. On the other hand, the mixed gas selectivity and the permeance for PTDP/AgBF₄ membrane continuously

Polymers Type	Chemical Structure
Poly[trimethylolpropane/di(propylene glycol)- <i>alt</i> -adipic acid/phthalic anhydride] (PTDP)	
Poly(ethylene phthalate) (PEP)	

Scheme I. Phthalic polymers selected for study and their chemical structure.

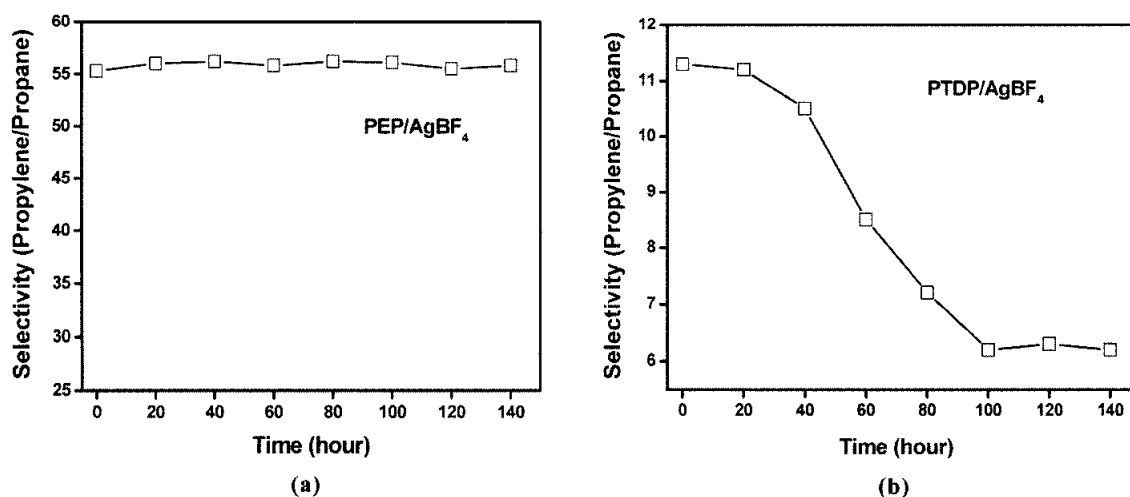


Figure 1. Mixed-gas selectivity of propylene/propane as a function of time for (a) 1:1 PEP/AgBF₄ and (b) 1:1 PTDP/AgBF₄ membranes.

decrease with time and reach a minimum after approximately 100 hrs.

The coordinative interaction of silver ion with carbonyl oxygens in PEP and PTDP was investigated by FT-IR spectroscopy as shown in Figure 3. Figure 3(a) shows that pure PEP exhibits a free C=O peak with strong intensity at 1729 cm^{-1} and two weak C=C peaks of aromatic rings at around 1600 cm^{-1} . Interestingly, when the silver concentration increases (up to a mole ratio of [phthalate]:[Ag⁺]=1:1), the

intensity of free C=O peak at 1729 cm^{-1} decreases and the new C=O peak at 1629 cm^{-1} becomes dominant. In other words, the free carbonyl peak at 1729 cm^{-1} shifts to a lower wavenumber at 1629 cm^{-1} upon the increase of the silver concentration, indicating strong chelating bonds of phthalate group with silver ions. The shift to a lower wavenumber is attributable to the loosened C=O bond interaction by the electron donation of oxygens to silver ions. However, in the case of PTDP/silver complex, the peak intensity of the coor-

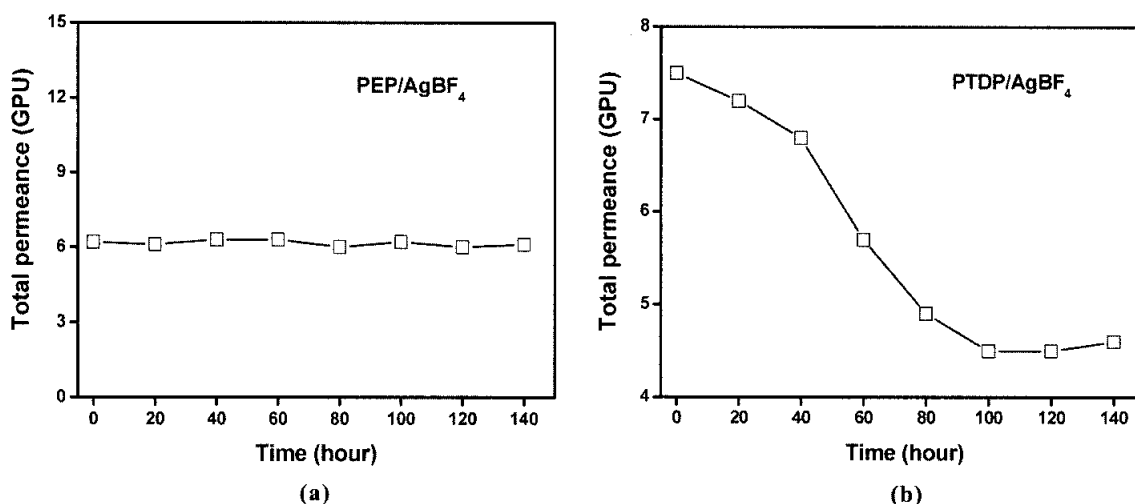


Figure 2. Mixed-gas permeance as a function of time for (a) 1:1 PEP/AgBF₄ and (b) 1:1 PTDP/AgBF₄ membranes.

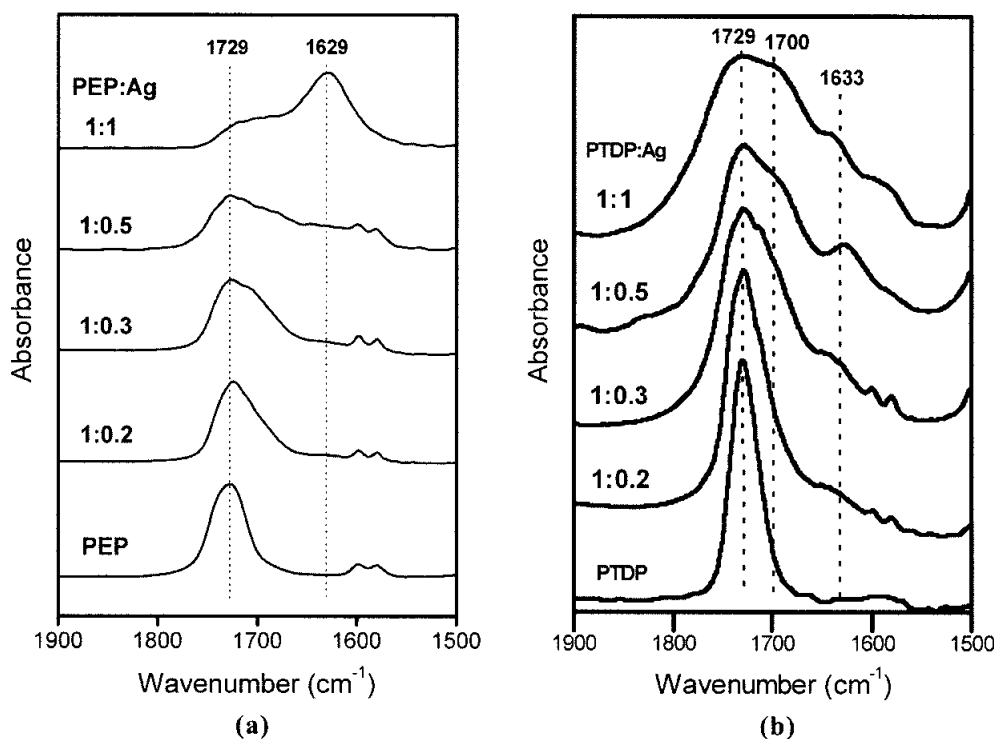


Figure 3. FT-IR spectra of (a) pure PEP and PEP/AgBF₄ membrane with different mole ratios of silver to the monomeric unit of PEP and (b) pure PTDP and PTDP/AgBF₄ membrane with different mole ratios of silver to the monomeric unit of PTDP.

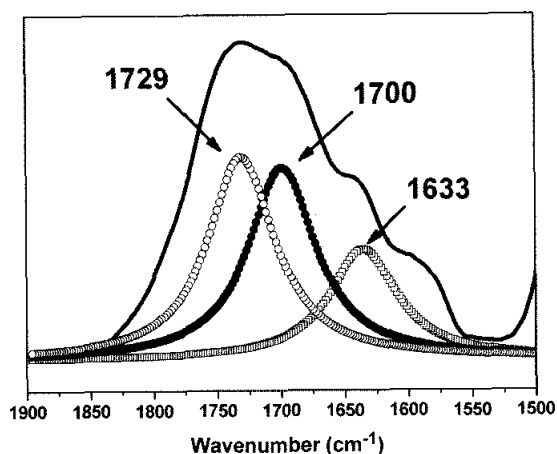


Figure 4. Deconvoluted FT-IR spectra for 1:1 PTDP:AgBF₄ as complexes. Open circles and open squares are for the free C=O stretching and for the complexed C=O stretching of phthalate oxygens with silver ions in PTDP, respectively. Filled circles are for the complexed C=O stretching of aliphatic carbonyl oxygen with silver ion.

inated phthalate group at 1633 cm⁻¹ is not that strong. Instead, the free C=O peak at 1729 cm⁻¹ and the peak at 1700 cm⁻¹ assignable to the coordinated ester oxygen are prominent. It is estimated from the deconvoluted spectra that the fraction of the coordinated aliphatic carbonyl oxygen increases from 0 to 37% upon the addition of silver salt up to 1 molar ratio, and the fraction of the coordinated phthalate oxygen from 0 to 21% as shown in Figure 4. Consequently, the FT-IR data suggest that the silver ions are coordinated by both aliphatic carbonyl oxygen and phthalate oxygens.

This result represents that the silver ions are unexpectedly coordinated to both aliphatic ester carbonyl oxygen and phthalate oxygens in PTDP/silver complex in spite of the much stronger silver interaction with the latter. Thus, the deterioration of performance in the long-term stability experiment for PTDP/AgBF₄ membrane may be originated from the silver coordination with various oxygens besides phthalate.

The effect of the functional groups on the formation of

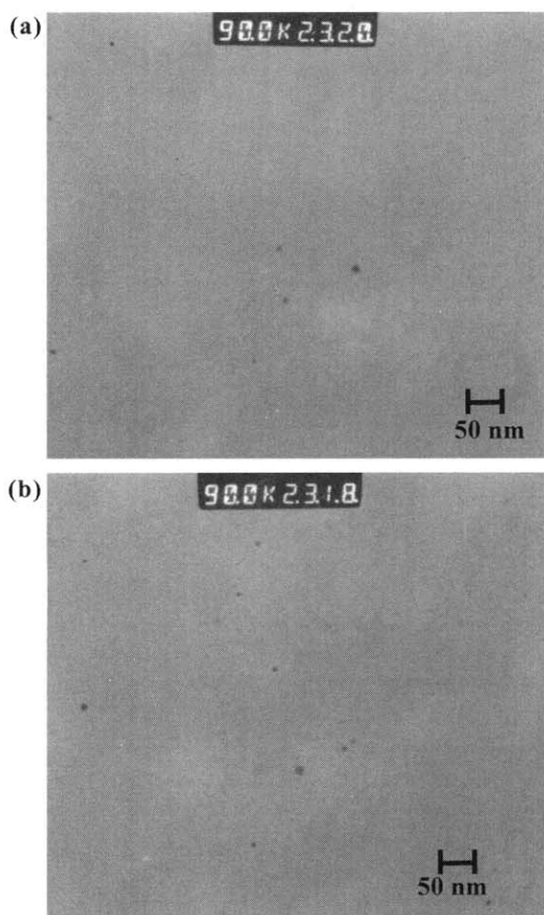


Figure 5. Transmission electron micrographs of PEP/AgBF₄ membrane (a) just after preparation and (b) after one week of preparation.

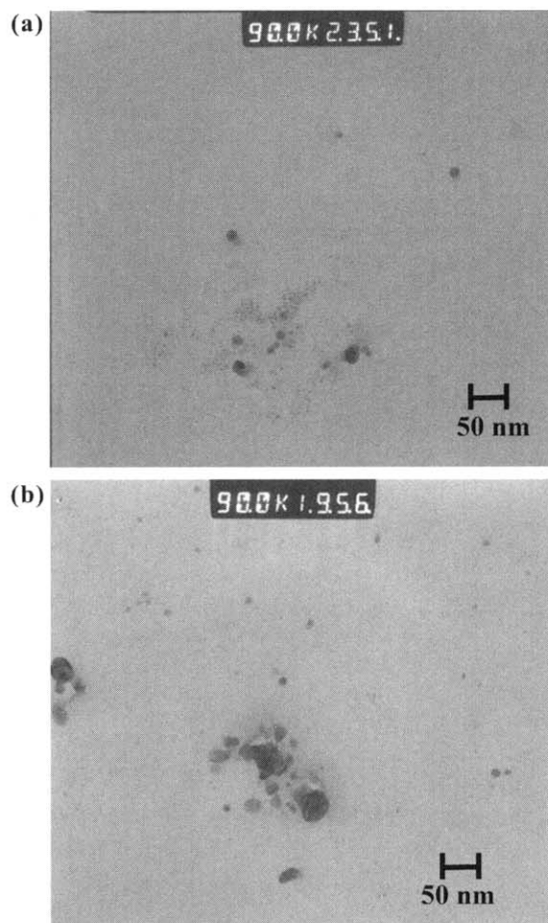


Figure 6. Transmission electron micrographs of PTDP/AgBF₄ membrane (a) just after preparation and (b) after one week of preparation.

silver nanoparticles in the phthalate polymer/AgBF₄ membrane was investigated using TEM analysis. The TEM micrograph of the 1:1 PEP/AgBF₄ membrane taken just after preparation shows the presence of a small number of silver nanoparticles of approximately 5 nm in size (Figure 5(a)). The TEM micrograph of the same membrane after one week shows a similar number and size of silver nanoparticles (Figure 5(b)). However, the TEM micrograph of the 1:1 PTDP/AgBF₄ taken after one week of preparation shows both bigger size and leager number of silver nanoparticles, as shown in Figure 6. This result indicates that silver ions coordinated to aliphatic carbonyl group are readily converted into the silver nanoparticles to lose its olefin complexing ability, resulting in poor long-term separation performance.

Conclusions

The membrane performance and long-term stability have been investigated for two kinds of polymer/silver salt complex membranes containing phthalate groups. The PEP/AgBF₄ membranes containing only phthalates exhibited much better long-term stability than PTDP/AgBF₄ membranes having aliphatic ester, ether and hydroxyl groups beside phthalates. Therefore, it is concluded that the critical parameter in determining the long-term separation performance in silver polymer electrolyte membranes is the exclusive presence of phthalate groups.

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