Novel Composite Membranes Comprising Silver Salts Physically Dispersed in Poly(ethylene-*co*-propylene) for the Separation of Propylene/Propane

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Abstract: Novel composite membranes, which delivered high separation performance for propylene/propane mixtures, were developed by coating inert poly(ethylene-*co*-propylene) rubber (EPR) onto a porous polyester substrate, followed by the physical distribution of $AgBF_4$. Scanning electron microscopy-wavelength dispersive spectrometer (SEM-WDS) revealed that silver salts were uniformly distributed in the EPR layer. The physical dispersion of the silver salts in the inert polymer matrix, without specific interaction, was characterized by FT-IR and FT-Raman spectroscopy. The high separation performance was presumed to stem from the *in-situ* dissolution of crystalline silver ionic aggregates into free silver ions, which acted as an active propylene carrier within a propylene environment, leading to facilitated propylene transport through the membranes. The membranes were functional at all silver loading levels, exhibiting an unusually low threshold carrier concentration (less than 0.06 of silver weight fraction). The separation properties of these membranes, i.e. the mixed gas selectivity of propylene/propane ~55 and mixed gas permeance ~7 GPU, were stable for several days.

Keywords: silver, inert membrane, poly(ethylene-*co*-propylene), propylene, facilitated transport.

Introduction

The recovery of olefin from olefin/paraffin mixtures in petrochemical industry is of pivotal importance. Since the separation of olefin/paraffin has been usually performed by energy-intensive cryogenic distillation processes, an alternative energy-saving process is demanding, e.g. adsorption, absorption and membranes.[1-3] Among them, facilitated transport membranes containing silver ions as olefin carrier showed a possible alternative to the distillation by exhibiting high permselectivity in the separation performance. Initially, the development of facilitated transport membranes were based on immobilized liquid membranes, solvent-swollen membranes or ion exchanged membranes.[4-6] However, the types of membranes suffer from the loss of the liquid solvent and carrier, the limits of the operation temperature and the membrane thickness because they are operated with liquid solvent-vapor saturated feed and permeate streams. Thus, the development of liquid-free facilitated transport membranes in the solid state is desirable.[7-10]

Recently, the facilitated transport membranes utilizing silver polymer electrolytes, which are composed of low lattice silver salts such as $AgBF_4$, $AgClO_4$, $AgSbF_6$, or $AgCF_3SO_3$ dissolved in polymer solvent such as poly(2-ethyl-2-oxazoline) (POZ),[11-14] poly(N-vinyl pyrrolidone) (PVP),[15,16] poly(ethylene oxide) (PEO),[17,18] poly(methacrylate) (PMA),[19,20] poly(vinyl methyl ketone) (PVMK)[20] or nylon-12/tetramethylene oxide block copolymer (PA12-PTMO)[21] showed extremely high separation performance of olefin/paraffin mixtures in solid state. The propylene permeance through the 1 : 1 POZ/$AgBF_4$ membrane was as high as 45 GPU (1 GPU = 10^{-6} cm^3 (STP)/(cm^2 s cmHg)) at a propylene pressure of 138 kPa, while the propane permeance was extremely

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low as 0.003 GPU. Thus, the ideal separation factor of propylene over propane was more than 15,000, but the mixed gas selectivity is around 50 due to propylene-induced plasticization of membranes.[14,20]

The basis for the separation is the fast and reversible olefin complexation with silver ions dissolved in polymer solvent, leading to the facilitated olefin transport across the membranes. Thus, the facilitated transport property is strongly dependent on the dissolution behavior of silver salt into polymer matrix. For example, it has been found that free silver ions are the most active olefin carrier among various ionic constituents including ion pairs and higher-order ionic aggregates.[13] To allow easier dissociation of silver salt, the polar polymers containing amide, ester, ketone or ether have been in common use.[11-21]

Recently we have made a very important observation by *in-situ* FT-Raman spectroscopy that all ionic constituents of silver salt are completely dissolved into free ions under olefin environment, implying that olefin molecules can be directly used as a ligand for the silver salts.[13] We also found the free silver ions are the most effective olefin carrier among ion pairs and higher order ionic aggregates. Based on this experimental finding, novel inert composite membranes consisting of silver salt physically dispersed in poly(dimethyl siloxane) (PDMS) matrix have been previously reported.[22] This type of membranes provides less susceptibility to the loss of carrier, i.e. the formation of silver ions to silver nanoparticles, thereby giving more stable separation performance against time. It may be because the polar polymer matrices containing heteroatom such as N or O play a role as reducing agent for silver salts,[23-27] but inert polymers do not.

In this study, we extend the range of inert composite membranes, in which silver salts are physically dispersed in inert polymer matrices. This is especially useful for the pairs in which polymers do not make homogeneous mixture with silver salt solution. Poly(ethylene-*co*-propylene) rubber (EPR) was used as an inert polymer matrix, because it does not contain any functional group and is known to be a high gas permeable material.[28] The membrane structures and performance for facilitated olefin transport of novel composite membranes are reported.

Experimental

Poly(ethylene-*co*-propylene) rubber (EPR, M_w = 170,000) and silver tetrafluoroborate (AgBF$_4$, 98%) were purchased from Aldrich Chemical Co. All chemicals were used without further purification. EPR solutions were prepared by dissolving 3 wt% EPR in toluene (+99%, Aldrich). The solution was then coated onto a porous polyester membrane substrate (Whatman, 0.1 μm) using a RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments LTD, UK). After drying solvent, the silver salt solutions in

ethanol were carefully spread onto the EPR-coated polyester membranes. The resulting membranes were dried in an N$_2$ environment and then further dried in a vacuum oven for two days at room temperature.

The permeation experiments were carried out using the constant pressure/variable volume method. Mixed gas (50 : 50 vol% of propylene/propane mixture) separation performance of the membranes was evaluated by gas chromatography (Hewlett Packard G1530A, MA) equipped with a TCD detector. The stage cut (θ), the ratio of permeate to feed flow rates, was always less than 2%. The unit of gas permeance is GPU, where 1 GPU = 1 × 10⁻⁶ cm³ (STP)/cm² s cmHg).

Raman spectra were collected for the membranes at room temperature using Perkin Elmer System 2000 NIR FT-Raman. This experimental apparatus includes a neodymium-doped yttrium aluminum garnet (NdYAG) laser operating at 1064 nm. IR measurements were performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64-200 scans were signal-averaged at a resolution 2 cm⁻¹. Raman and IR Spectroscopic characterization was performed using a pressure cell equipped with quartz and CaF$_2$ windows, respectively. The distribution of silver atoms for cross-section of the prepared membrane was characterized by the scanning electron microscopy-wavelength dispersive spectrometer (SEM-WDS, JEOL JXA-8600).

Results and Discussion

Preparation procedure of inert composite membranes in which silver salts are physically dispersed in polymer matrix is provided in Figure 1. This approach is of especial use for immiscible systems of polymer and silver salt in a common solvent, offering great versatility for various combinations of polymer/metal salt. Two important features are addressed here. First, the polymers should be swollen by silver solution for facile penetration of silver salts and uniform distribution throughout the polymers. Second, the low T_g of polymers such as EPR is preferred, because flexible chains
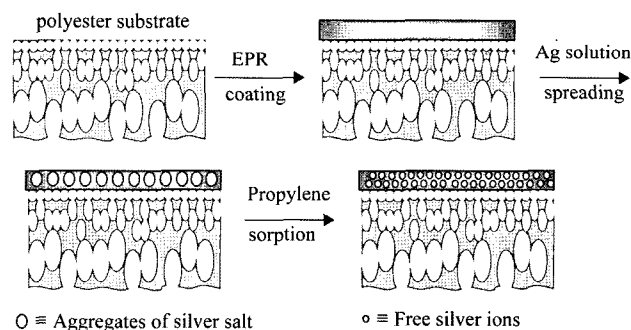

Figure 1. Scheme of preparation procedure of novel inert composite membranes comprising a nonporous EPR/AgBF$_4$ films coated onto a porous polyester membrane substrate.
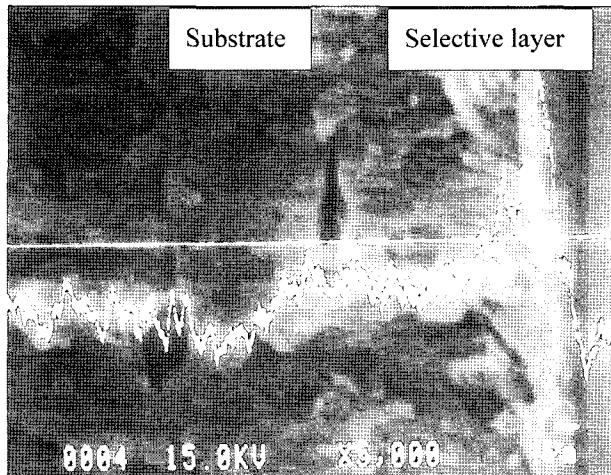
Figure 2. SEM-WDX cross-sectional image of composite membrane comprising a nonporous EPR/AgBF$_4$ films coated onto a porous polyester membrane substrate.

introduce high mobility of polymer matrix, thereby allowing homogenous distribution of salt. *In-situ* dissolution of silver ionic aggregates into free ions under propylene environment has been previously observed by FT-Raman spectroscopy[13] and wide angle x-ray scattering (WAXS).[22]

Figure 2 shows the SEM-WDS photograph of the cross-section of membrane consisting of EPR/AgBF$_4$ top layer and polyester bottom substrate layer. The white solid line denotes the distribution of silver atom across the membrane. The concentration of silver salt was 0.62 of the weight fraction of AgBF$_4$ in EPR/AgBF$_4$. The thickness of the top selective layer is approximately 1-2 μm. It is also found that the silver salts are mostly distributed in top EPR nonporous layer, supporting the plausible scheme of membrane preparation in Figure 1.
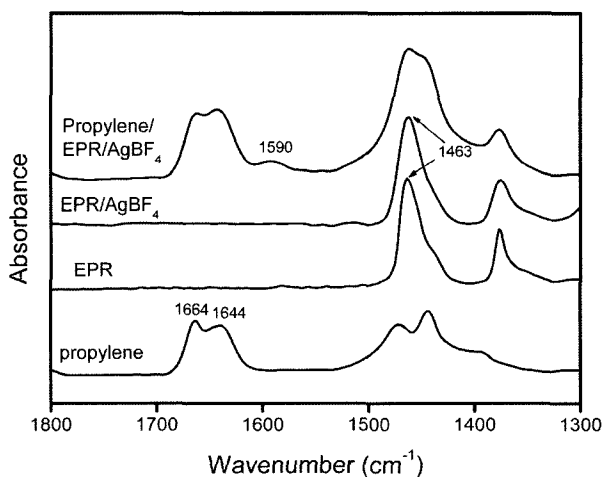
Due to the poor electron donating ability of EPR, silver salts are expected to be dispersed physically in EPR matrix without specific interaction upon incorporation of silver salt. Figure 3 shows the FT-IR spectra of pure propylene, EPR, EPR/AgBF$_4$, and propylene-coordinated EPR/AgBF$_4$. The spectrum of pure propylene exhibits two characteristic peaks of C=C stretching vibration at 1664 and 1644 cm^{-1}. The spectrum of pure EPR shows sharp peak at 1463 cm^{-1} attributable to the CH$_2$ bending mode. Upon the incorporation of AgBF$_4$ into EPR at 0.62 weight fraction of silver salt, the spectrum in the region of CH$_2$ bending mode is hardly changed, representing no specific interaction between silver salt and EPR. When the EPR/AgBF$_4$ membrane was exposed to propylene of 413.5 kPa for 30 min, a new shoulder peak at 1590 cm^{-1} was observed. This peak can be assigned to the coordinated C=C of propylene with silver ion by π-complexation.[12] The shift to a lower wavenumber (1664, 1644 cm^{-1} => 1590 cm^{-1}) may result from the loosened double bond interaction in propylene by the coordination. The spectroscopic results clearly represent that silver salts physically dispersed in EPR interact with propylene molecules, implying they can be used as propylene carrier in the membranes.

When metal salts are incorporated in polymeric matrice, three ionic constituents such as free ions, contact ion pairs and higher-order ion aggregates are present depending on the interaction strength between metal ions and polymers. For example, free ions are more likely to be formed when the interaction of metal ions with polymers is strong, and thereby the interaction with counteranions becomes weak. The FT-Raman spectra of ERP/AgBF$_4$ composites were measured to investigate the dissolution behavior silver salt and characterize the ionic constituents. Figure 4 presents the Raman spectra of the ν_1 symmetric stretching mode of BF$_4^-$ anion. Irrespective of silver concentration, the position of

Figure 3. FT-IR spectra of pure propylene, EPR, EPR/AgBF$_4$, and propylene-coordinated EPR/AgBF$_4$.
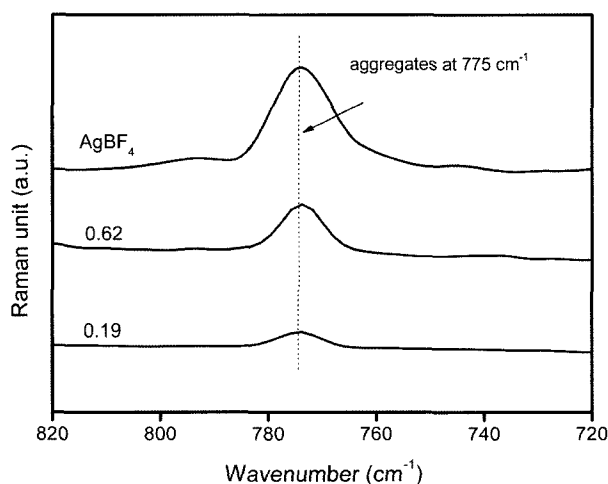

Figure 4. FT-Raman of AgBF$_4$ and EPR/AgBF$_4$ membranes with different weight fractions of salt.
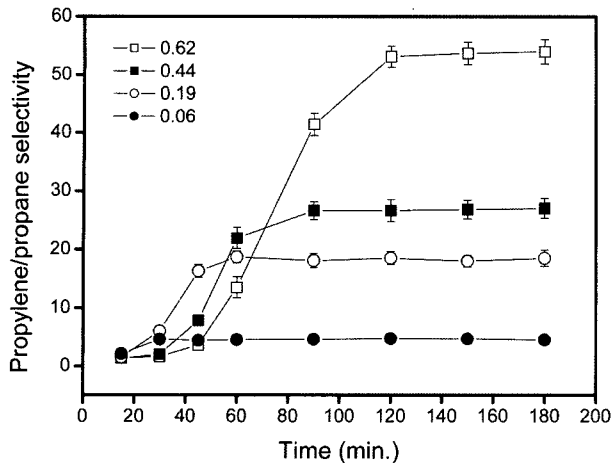
Figure 5. The selectivity of propylene/propane through EPR/AgBF₄ membranes as a function of time with different concentration of AgBF₄.
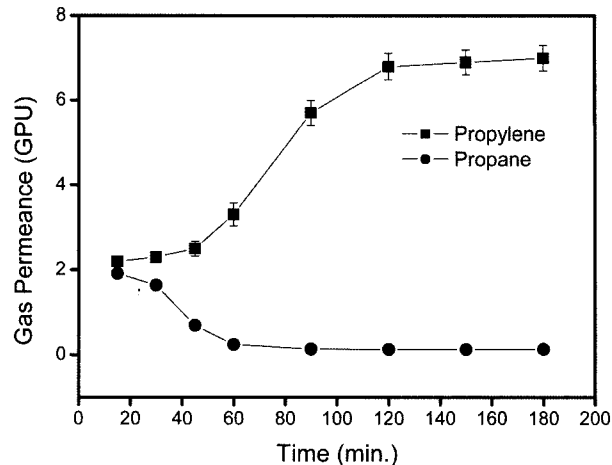

Figure 6. Gas permeances of propylene and propane through EPR/AgBF₄ membrane with 0.62 of silver weight fraction as a function of time.

strong peak at 775 cm⁻¹ in the composites, which is attributed to the ionic aggregates of BF_4^- anion remains invariant.[12,29] The spectrum of pure AgBF₄ was also included in the graph to confirm the ionic state of silver salt as ionic aggregates.

Figure 5 shows the selectivity change of propylene/propane through the EPR/AgBF₄ membranes with different concentrations of silver salt as a function of permeation time. At initial time of permeation experiment, the membranes exhibit low separation performance, i.e. the selectivity of propylene/propane is around 1.0. However, as the permeation time increases, the selectivities increase gradually and finally reach the steady-state value. This behavior of separation properties is unusual, which can be explained as follows. Initially the silver salts are dispersed physically in EPR matrix as higher-order ionic aggregates, inactive olefin carrier, and thus the selectivity of propylene/propane is very low. As the permeation time increases, however, the ionic aggregates are dissolved gradually via propylene coordination to silver ion and converted to free silver ions, active olefin carrier, resulting in the enhancement of facilitated propylene transport.[22] The time to reach equilibrium state strongly depends on the concentration of the silver salt. At high concentrations of silver salt, the concentrations of corresponding ionic aggregates are high, because silver salts are present mainly as ion aggregates. Thus it takes longer to reach equilibrium time to dissociate ionic aggregates into free ions at high concentrations of silver salt. It should be also noted that the high separation performance (selectivity ~55) of EPR/AgBF₄ membranes with 0.62 of the weight fraction of salt is achieved.

The normalized gas permeances of corresponding propylene and propane through EPR/AgBF₄ membrane with 0.62 of silver weight fraction are presented in Figure 6. Initially,

the value of propylene permeance is not greatly different from that of propane, representing lower selective property of the membrane. However, the permeance of propylene increases gradually with increasing time of permeation experiment and reaches an equilibrium value finally after ca. 2 h. This time may be associated with the time to dissociate silver ionic aggregates into free ions, similar to the behavior of the selectivity of propylene/propane. Meanwhile the permeance of propane through the membrane is decreased continuously with an increase in operation time. After equilibrium time is reached, therefore, the membrane of EPR/AgBF₄ could be successfully used as facilitated transport membrane material for the separation of propylene/propane mixtures. This result strongly represents that the polymer
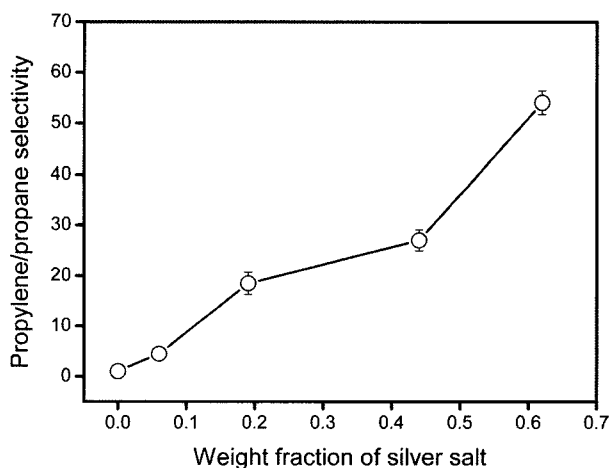

Figure 7. The selectivity of propylene/propane through EPR/AgBF₄ membranes as a function of the weight fraction of silver salt.

without functional group can be utilized as polymer matrix by directly using olefin molecule as ligand to dissolve silver salt.

Figure 7 presents the selectivity of propylene/propane through EPR/AgBF$_4$ membranes at steady state as a function of silver concentration. It is a very intriguing result that the facilitated propylene transport occurs in proportion to the concentration of silver salt, not showing any threshold concentration. The membranes consisting of the polymer matrices containing function groups have commonly showed the threshold concentration. In general, the membranes with lower interactions between polymers and silver ions exhibit lower onset concentration of silver salt.[20] Likewise, EPR/AgBF$_4$ system hardly has interactions between polymer and silver ions, because EPR has no functional group to coordinate with silver ions. Thus silver ions even in the low concentrations of silver salt can interact with propylene molecule via forming π-complex, thereby playing an effective role as propylene carrier.

Conclusions

The novel composite membranes have been prepared by a simple, flexible process, i.e. the coating of inert EPR polymer matrix onto polyester substrate, followed by homogenous distribution of AgBF$_4$. The membranes consist of silver salt physically dispersed in inert polymer matrices without specific interaction. The separation performances clearly present that the novel composites were successfully applied to the facilitated transport membranes for the separation of propylene/propane. The high performance comes from the in-situ dissociation of silver ionic aggregates into free ions as active olefin carrier by π-complexation of propylene molecules with silver ions. This approach presumably eliminates the need for the polymer matrice containing functional groups and provides the routes to overcome the reduction problem of silver ions to silver metal particles.

Long-term stability of the facilitated transport membranes is also of pivotal importance for a practical application. A pending problem is to maintain the stability of silver ions as an olefin carrier. Thus our groups are currently investigating the development of a new, alternative olefin carrier for the use of solid-state olefin transport membranes.

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