

특별강연 I

은-고분자 전해질막을 이용한 올레핀/파라핀 분리

김중학

*한국과학기술연구원 촉진수송분리막연구단

Polymer Electrolyte Membranes and Their Application to Olefin/Paraffin Separation

Jong Hak Kim

Center for Facilitated Transport Membranes, KIST

Introduction

Olefins such as ethylene and propylene are the most important feedstock for chemical and petrochemical industries. Approximately 35 and 20 million tons of ethylene and propylene, respectively, are produced in Korea annually, which are the 4th in the worldwide olefin production. Olefins are currently produced by a cryogenic distillation, which is highly energy-intensive because of the necessary low temperature and high pressure operating conditions. Consequently, there is an enormous economic incentive to develop alternative separation processes with lower energy consumption.

Membrane technology offers an intriguing alternative to cryogenic distillation. However, the separation of olefin/paraffin mixtures using conventional polymeric membranes has not been effective because of their indiscernible transport properties such as molecular size and solubility. Facilitated transport membrane is an alternative approach to conventional polymer membranes for olefin/paraffin separation. Most facilitated transport membranes investigated so far were either using supported liquid membranes or ion exchange membranes such as Nafion containing silver ion carrier together with water [1-3]. However,

evaporation of liquid media in such liquid membranes gives a serious drawback and problems for practical applications. Therefore, development of solvent-free solid state facilitated transport membranes has been longed for [4-9].

Experimental

Poly (2-ethyl-2-oxazoline) (POZ) and all silver salts including silver tetrafluoroborate (AgBF_4), silver percholate (AgClO_4), silver triflate (AgCF_3SO_3) and silver nitrate (AgNO_3) were purchased from Aldrich Chemical Co. and poly(N-vinyl pyrrolidone) (PVP) from Polysciences. All chemicals were used as received. The silver salts were dissolved in 20 wt% polymer solution in methanol the amount of added salt was chosen so as to achieve the desired mole ratio of $[\text{C}=\text{O}]:[\text{Ag}]$. The solution was then cast on a teflon-glass plate and dried under nitrogen. The resulting films were further dried in a vacuum oven for two days at room temperature to remove residual solvent.

Results and discussion

The propylene permeances through POZ/ and PVP/silver salts membranes are plotted as a function of the concentration of silver salt in Figure 1 [4]. There is no significant improvement of the propylene permeance until the mole ratio of silver to carbonyl reaches approximately 0.25. However, the propylene permeance increases up to almost 40 GPU with increasing silver ion content, while the propane permeance is reduced to as low as 0.003 GPU. Thus, the ideal separation factor of propylene over propane is approximately 10,000 [8]. The improved separation permeance may arise predominantly from the high concentration of the silver ion, and the fast reversible complexation reaction between silver ion and olefin molecule. The threshold concentration is found to be strongly associated with the coordination behavior of the silver ion by both carbonyl oxygens and olefin molecules [8].

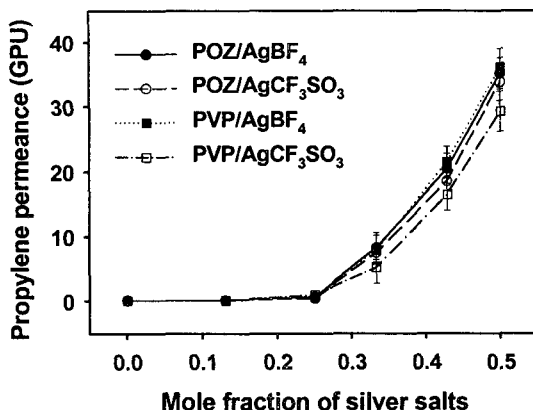


Figure 1. Propylene permeance for polymer electrolyte membranes as a function of the silver concentration at 23°C, $\Delta p=413.5$ kPa. 1 GPU = $1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ sec cmHg}$ [4].

The coordination number of the silver ion, m , by carbonyl oxygens can be obtained simply by the concentration ratio of the complexed carbonyl oxygen to the silver ion from IR and Raman spectra. The coordination number of the silver ion, n , by olefin molecules is obtained from the concentration ratio of propylene molecules coordinated to silver ions to the silver ion concentration. The coordination numbers of silver ions in POZ/AgCF₃SO₃ are plotted against the mole fraction of silver salt as shown in Figure 2. It is clear from the figure that m decreases exponentially with the silver concentration whereas n increases slightly. Surprisingly, the total coordination number, $(m+n)$, becomes nearly invariant and is around 3. This result strongly suggests that the most favorable coordination number of the silver ion dissolved in polymer matrix under propylene environment is "3". It was also found from IR spectra and theoretical calculations that the interaction of silver ion with carbonyl oxygen of POZ is slightly stronger than that with olefin molecules. Therefore, the relationship between the threshold concentration

and the most probable coordination number of silver ion can be deduced from two facts of the favorable coordination number and of the difference in the interactions. When $m \geq 3$, silver ions may not be able to interact with surrounding olefin molecules, implying that the silver ion does not act as an olefin carrier. However, when $m < 3$, the coordination sites of the silver ion are not completely occupied by carbonyl oxygen and thus vacant sites are available for olefin coordination. Therefore, it is concluded that silver ions can act as an olefin carrier only when $m < 3$, in other words, the threshold concentration of the mole fraction of the silver salts is 0.25 ($=1/(1+3)$).

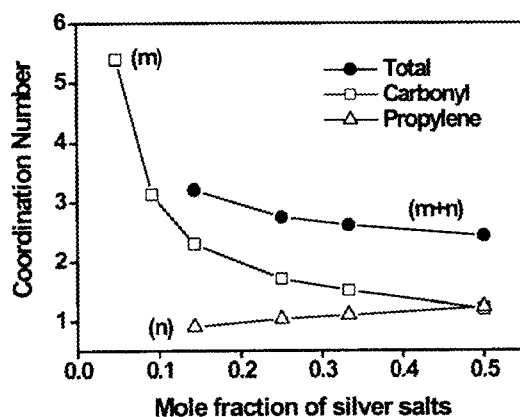


Figure 2. Coordination numbers of silver ion by carbonyl oxygen and propylene in POZ/AgCF₃SO₃ as a function of the silver salt concentration [8].

Silver ion constituents may possibly change in the propylene environment [6]. Thus, the time evolution Raman spectra of the δ_s (SO_3^-) symmetric stretching band for the 1:3 PVP/AgCF₃SO₃ at propylene pressure of 275.6 kPa were obtained in Figure 3. The 1:3 PVP/AgCF₃SO₃ membrane before a propylene contact has nearly 0.0 % of free ions, 42.7 % of ion pairs and 57.3 % of ion aggregates according to the deconvolution of the peaks. When propylene molecules contact

with polymer electrolytes, they will be dissolved by coordination to silver ions. As the contact time of propylene with polymer electrolytes was increased, the band intensities of both ion aggregates at 1048 cm^{-1} and ion pairs at 1038 cm^{-1} gradually decreased whereas a new shoulder peak around at 1032 cm^{-1} was apparent and became prominent with time, implying the regeneration of free SO_3^- ions. Interestingly, after 24 hours, the only band associated with the free SO_3^- ion was observed, indicating that ion aggregates and ion pairs were not present. This notable observation clearly represents that propylene can be a good ligand for the silver ion dissolved in the polymer matrices and can coordinate to the silver ions of ion aggregates and ion pairs, resulting in redissolution into free anions. The redissolution of ion aggregates and ion pairs in PVP/AgCF₃SO₃ electrolytes under the propylene environment is possible because the coordination sites of the silver ion can possibly be occupied by π -electrons of propylenes and consequently weaken the interaction of the silver cation with its counter anion.

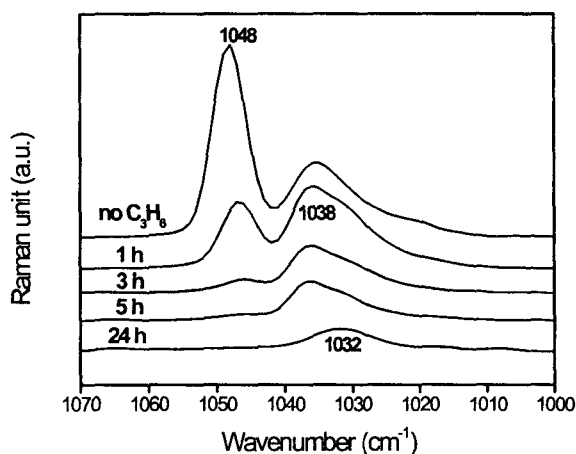
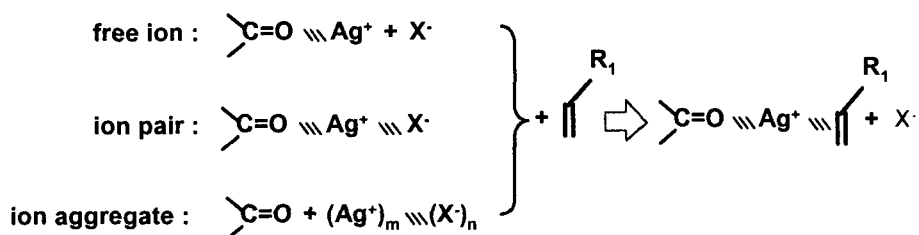


Figure 3. Time evolution Raman spectra for δ_s (SO_3^-) mode in 1:3 PVP/AgCF₃SO₃ absorbing propylene (40 psig) [6].

From the results of FTIR and Raman spectra in PVP/AgCF₃SO₃ electrolytes upon absorbing propylene, it was found that 1) ion pairs and ion aggregates in the silver polymer electrolytes are converted into spectroscopically free anions under the propylene environment and 2) the coordinative bond between the silver ion and carbonyl oxygen maintains but becomes weakened upon propylene sorption. A possible mechanism of the complexation between propylene and silver polymer electrolytes is proposed as follows.



Therefore, the linear relationship between the propylene permeance and the total silver concentration regardless of the kind of the silver constituents could be explained by the new complexation mechanism proposed in this research [6].

References

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