

**Poly(vinylpyrrolidone-co-vinylacetate)/은염 전해질의
올레핀 촉진수송과 배위결합 연구**

주승환, 장정식, 원종욱**, 김종학*, 강용수*

서울대학교 응용화학부 고분자재료연구실

* 한국과학기술연구원 촉진수송분리막연구단

** 세종대학교 응용화학

**Facilitated Olefin Transport and Coordinative
Interactions for
Poly(vinylpyrrolidone-co-vinylacetate)/silver salt
Electrolyte Membranes**

Seung Hwan Joo, Jyongsik Jang, Jongok Won**, Jong Hak Kim*,
and Yong Soo Kang*

School of Chemical Engineering and Institute of Chemical Processes,
Seoul National University

* Center for Facilitated Transport Membranes, KIST, Seoul

** Department of Applied Chemistry, Sejong University, Seoul

Introduction

Separation of olefin/paraffin gas mixtures is one of the most energy intensive processes in petrochemical industries because it is performed mainly by cryogenic distillations. Membrane processes using the concept of facilitated transport have been considered to be an intriguing alternative to the cryogenic distillation. In particular, solid polymer electrolyte membranes comprising silver salts have offered a promise as a highly efficient membrane for olefin/paraffin separation [1-5]. In spite of the extensive research on facilitated olefin transport phenomena in

the polymer/silver complex membranes, the relationship between the structure of macromolecular ligand and facilitated transport has been insufficiently explored. Thus the study on ligand structure of polymer matrix is investigated in this study. Among various polymer matrices containing carbonyl oxygen, three different poly(N-vinylpyrrolidone-vinyl-acetate) (PVP-co-PVAc), (PVP:PVAc=30:70, 50:50, 70:30) have been chosen, because two functional groups (amide and ester) are included in this copolymer for complexation with the silver ions.

Experimental

Poly(N-vinylpyrrolidone-vinyl-acetate) (PVP-co-PVAc) was purchased from Polysciences, Inc. Silver tetrafluoroborate (AgBF_4) and silver trifluoromethanesulfonate (silver Triflate, AgCF_3SO_3) were purchased from Aldrich Chemical Co. All chemicals were used as received. The silver salts were dissolved in 20 wt% polymer solution in IPA; the amount of added salt was chosen so as to achieve the desired mole fraction of silver salt. The solution was then cast on a polyester membrane and dried under nitrogen. The resulting membranes were further dried in a vacuum oven for two days at room temperature to remove residual solvent.

Results and discussion

PVP-co-PVAc has two kinds of functional groups of carbonyl oxygen, i.e. amide and ester, and thus there are two possible coordination sites in the copolymer. The mixed-gas separation properties of polymer electrolyte membranes were evaluated in order to obtain the actual selectivity. As shown in Figure 1, the facilitating effect of the silver ions increases with increasing mole fraction of silver salt. Especially the selectivity is enhanced when the amount of PVP is higher. Through this phenomenon, we could expect that the amide group is more effective than the ester group for facilitated olefin transport. To obtain more information on the different olefin solubilities in the PVP-co-PVAc/silver salt complexes, FT-IR were measured. Figure 2 presents the in-situ FT-IR spectra of the copolymer membranes

containing AgBF_4 with and without propylene sorption. As shown in this figure, the copolymer exhibits two strong C=O peaks; one at 1736 cm^{-1} and the other at 1678 cm^{-1} are assigned to ester C=O in PVAc and amide C=O in PVP respectively. In amide group of PVP, a resonance effect occurs when the unpaired electrons of nitrogen atom conjugate with C=O group, resulting in increased single bond character and consequently lower wavenumber in the spectra. Upon adding AgBF_4 , the C=O peak shifted to 1691 cm^{-1} and 1627 cm^{-1} respectively, due to the silver coordination with C=O in polymer. Intriguing feature is the different coordination behavior in ester oxygen and amide oxygen of the copolymer. At low silver concentration, e.g. silver mole fraction is 0.14, the ester C=O still remains as free C=O whereas amide C=O nearly almost are complexed with silver ions. Moreover, the peak shift of C=O in the complexes is more intense in amide C=O ($\Delta f=50$) than ester C=O ($\Delta f=44$). Therefore, it is clearly demonstrated that the coordination of silver ions with amide C=O is more favorable than that with ester C=O and the interaction in the former is much stronger than the latter.

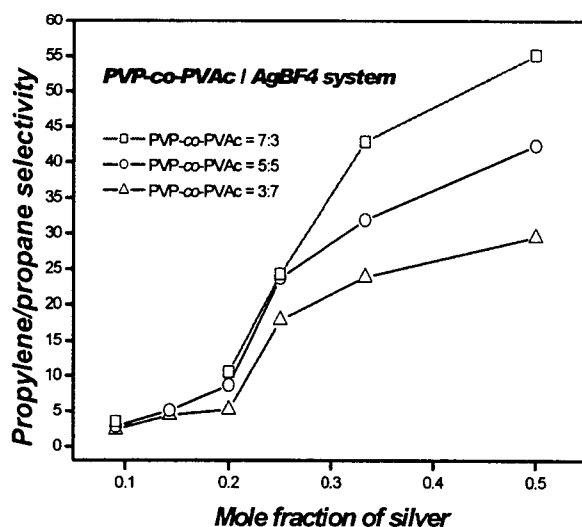


Fig. 1 Mixed-gas selectivity for PVP-co-PVAc/AgBF₄ membranes as a

function of silver mole fraction.

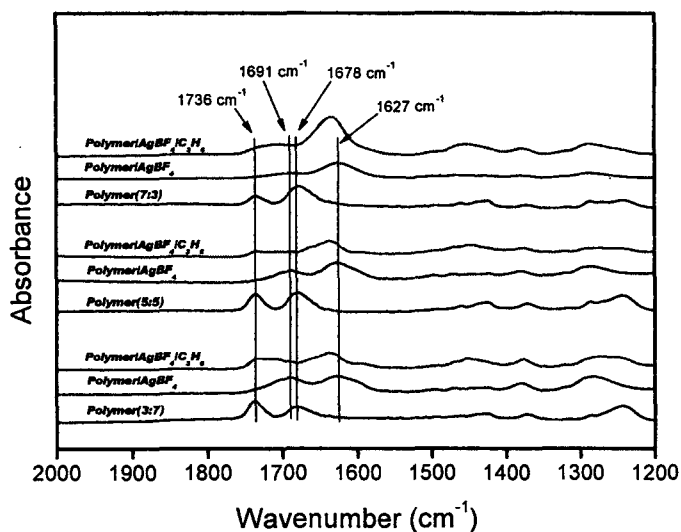


Fig. 2 The FT-IR spectra of poly(vinylpyrrolidone-co-vinylacetate) membranes

References

1. Hong, S. U.; Jin, J. H.; Won, J.; Kang, Y. S. *Adv. Mater.* 2000, 12, 968.
2. Kim, J. H.; Min, B. R.; Kim, C. K.; Won, J.; Kang, Y. S. *J. Phys. Chem. B.* 2002, 106, 2786
3. Kim, J. H.; Min, B. R.; Won, J.; Kang, Y. S. *Chem. Eur. J.* 2002, 8, 650.
4. Kim, J. H.; Min, B. R.; Kim, C. K.; Won, J.; Kang, Y. S. *Macromolecules* 2001, 34, 6052.
5. Kim, H. S.; Ryu, J. H.; Kim, H.; Ahn, B. S.; Kang, Y. S. *Chem. Commun.* 2000, 1261.