일반강연 A-4

은-고분자 전해질막을 이용한 올레핀 촉진수송 및 구조적 변화

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Facilitated Olefin Transport and Structural Properties of Silver Polymer Electrolyte Membranes

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Introduction

Polymer electrolytes containing silver ions are of particular interests for their potential application to separate olefin/paraffin mixture using the reversible silver-olefin complexes as a carrier for a facilitated transport [1-2]. Silver salts such as $AgBF_4$, $AgCF_3SO_3$ dissolved in polymers such as poly(ethylene oxide) (PEO), poly (2-ethyl-2-oxazoline) (POZ) or poly (vinyl pyrrolidone) (PVP) are active for olefin complexation [3-10]. In this study, we have found that the transport of ethylene was significantly retarded in the POZ/$AgClO_4$ complex film compared to the one in the POZ/$AgBF_4$, whereas both silver polymer electrolytes showed somewhat similar selectivity on the ethylene/ethane separation. Although $AgClO_4$ and

$AgBF_4$ salts have similar anion sizes, 2.36 and 2.32Å, and comparable lattice energies, 677 and 680 kJ/mol, respectively, their transport properties are significantly different. Such distinct transport property will be interpreted here by the structure of silver polymer electrolytes.

Experimental

Poly (2-ethyl-2-oxazoline) (POZ), $AgBF_4$ and $AgClO_4$ were purchased from Aldrich Chemical Co. and were used without further purification. The appropriated amounts of POZ and silver salts were dissolved in acetonitrile. The solution was then cast on a teflon-attached glass plate and dried under N_2 environment. The films were further driedin a vacuum oven for at least two days at room temperature.

Results and discussion

Figure 1 presents the IR spectra in the carbonyl stretching region for pure POZ and POZ/$AgClO_4$ complexes with various mole ratios of [C=O]:[Ag]. The intensity of a "free" carbonyl stretching band at 1641 cm^{-1} decreased with increasing silver salt content whereas a new band at 1598 cm^{-1} was observed upon addition of $AgClO_4$, and its intensity grew with increasing silver concentration. This new band is attributable to the carbonyl group coordinated to silver ions. The bands of POZ/$AgClO_4$ systems were deconvoluted into a free C=O band (1641cm^{-1}) and a complexed C=O stretching band (1598cm^{-1}). The uncomplexed free C=O band is apparent up to 5:1 POZ/$AgClO_4$, but disappear at the 3:1 POZ/$AgClO_4$ complex. This suggests that for a range of [C=O]:[Ag] from 3:1 to 1:1, all the carbonyl groups are coordinatively bonded with silver cations. For the concentrations above 3:1, only coordinated carboxyl groups are apparent. This is one distinctive difference with POZ/$AgBF_4$ complex where the free carbonyl bands completely disappeared at concentration above 1:1. These results suggest us that the coordination number of the silver cations would be

higher in the POZ/$AgClO_4$ complex than in the POZ/$AgBF_4$ and would be changed with the amount of silver in the POZ/$AgClO_4$ complex.

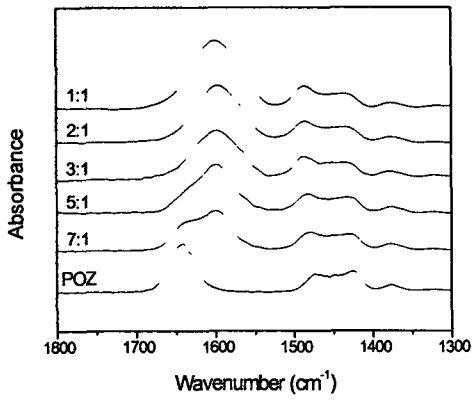

Figure 1. FT-IR spectra of pure POZ and POZ/$AgClO_4$ complexes of various [C=O]:[Ag] mole ratios.

The bond length in complexes of silver salts/ N-methyl-N-ethyl-propionamide was calculated using the density functional theory of the Becke3LYP. N-methyl-N-ethyl-propionamide was used as a model compound of POZ. The theoretical calculation demonstrates that the bond lengths between the silver cation and the anions are shorter in the POZ/$AgClO_4$ system than the POZ/$AgBF_4$ as shown in Figure 2: 2.696 and 2.203Å for Ag-O bond; and 2.869, 2.823 and 2.231Å for Ag-F bond. This confirmed the stronger interaction in the POZ/$AgClO_4$ system than the POZ/$AgBF_4$ although the lattice energies and the molecular sizes of two salts are very similar together. This also supports that ClO_4 groups are more tightly attached on the main chain than BF_4 groups. Another important fact is that ClO_4 group (ionic weight: 99.5) is heavier than BF_4 (ionic weight: 86.8). Therefore, the main chain mobility would be reduced more in POZ/$AgClO_4$ system than POZ/$AgBF_4$. If this is the case, the d-spacing

of the POZ/$AgClO_4$ system would be smaller than that the POZ/$AgBF_4$.

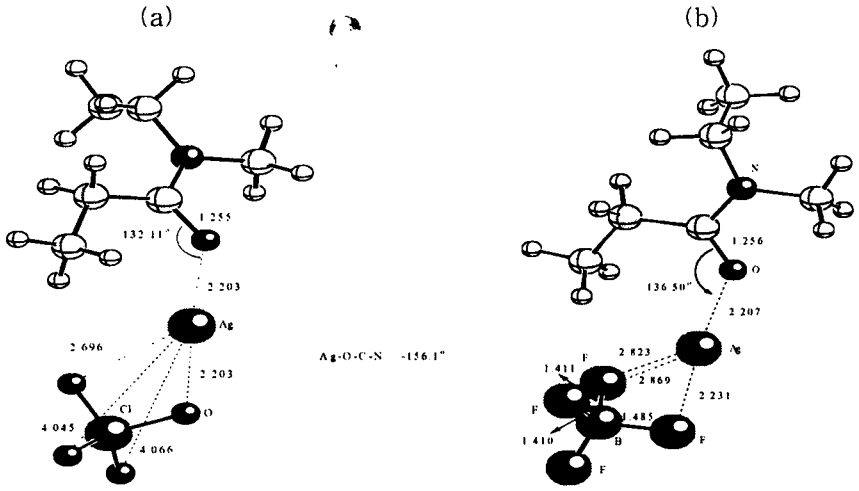

Figure 2. Structure of complexes of N-methyl-N-ethyl-propionamide with (a) $AgClO_4$ and (b) with $AgBF_4$.

References

1. Hartley, F. R. *Chem. Rev.* 1973, 73, 163.
2. Ho, W. S.; Doyle, G.; Savage, D. W.; Pruett, R. L. *Ind. Eng. Chem. Res.* 1988, 27, 334.
3. Hong, S. U.; Jin, J. H.; Won, J.; Kang, Y. S. *Adv. Mater.* 2000, 12, 968.
4. Yoon, Y.; Won, J.; Kang, Y. S. *Macromolecules* 2000, 33, 3185.
5. Choi, S.; Kim, J. H.; Kang, Y. S. *Marcomolecules*, 2001, 34, 9087.
6. Kim, J. H.; Min, B. R.; Kim, C. K.; Won, J.; Kang, Y. S. *J. Phys. Chem. B.* 2002, 106, 27.
7. Kim, C. K.; Won, J.; Kim, H. S.; Kang, Y. S.; Li, H. G.; Kim, C. K. *J. Comput. Chem.* 2001, 22(8), 827.
8. Kim, J. H.; Min, B. R.; Won, J.; Kang, Y. S. *Chem. Eur. J.* 2002, 8, 650.
9. Kim, J. H.; Min, B. R.; Kim, C. K.; Won, J.; Kang, Y. S. *Macromolecules* 2001, 34, 6052.
10. Kim, J. H.; Min, B. R.; Kim, C. K.; Won, J.; Kang, Y. S. *Macromolecules*, 2002, 35, 5250.