Measurement and Analysis of Propylene Solubility in Polymer Electrolytes Containing Silver Salts

Seong Uk Hong, Chang Kon Kim, and Yong Soo Kang*

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

Received April 26, 2000

ABSTRACT: The propylene solubilities were measured in solid polymer electrolyte films comprising $AgBF_4$ or $AgCF_3SO_3$ dissolved in poly(2-ethyl-2-oxazoline) (POZ) or poly(*N*-vinylpyrrolidone) (PVP). The propylene solubility for 1:1 POZ:$AgBF_4$ membrane is almost 25-fold higher than that for pure POZ and further is nearly 2-fold higher than that for 1:1 POZ:$AgCF_3SO_3$ membrane. The solubility difference between $AgBF_4$ and $AgCF_3SO_3$ polymer electrolytes was interpreted in terms of the anion size and the lattice energy of salts, the interaction intensity of metal ion with polymer chains, and the bond length between the silver ion and the closest anion atom calculated by the ab initio method. As a result, it was found that the solubility was better correlated with the bond length than other parameters.

1. Introduction

Polymer electrolytes have been extensively studied in the past 20 years because of their potential applications in high-energy density batteries and fuel cells, etc.[1] Among these studies, most of them were about complexes between alkaline metal salts and polyethers,[2−5] but few studies have been conducted on polymer−salt complexes containing silver ions.[6−12] Polymer electrolytes containing silver ions are of particular interest owing to their potential application to facilitated transport membranes for separating unsaturated hydrocarbons from gas stream.[8−12]

Recently, we have reported facilitated transport of propylene through silver polymer electrolytes made of silver salts of $AgBF_4$ or $AgCF_3SO_3$ dissolved in poly(2-ethyl-2-oxazoline) (POZ) or poly(*N*-vinylpyrrolidone) (PVP).[11] The shift in the carbonyl absorption band of the infrared and Raman spectra of POZ and PVP with the silver salts confirmed complex formation via coordinative interaction between silver ions and carbonyl oxygens. Further, it was found that the coordination number of silver ion with carbonyl oxygen of POZ and PVP is close to unity, demonstrating unusually high solubility of silver ions in the POZ and PVP matrices. It has been well-known that silver ions can reversibly react with olefin molecules to make silver−olefin complexes.[13,14] Because of such silver−olefin complex formation, propylene is expected be dissolved to a great extent in polymer electrolytes containing silver salts.

In this study, propylene solubility in these silver polymer electrolytes was measured using the pressure decay method. The solubility data were then interpreted in terms of the anion size and the lattice energy of salts, the interaction intensity of metal ion with polymer chains, and the bond length between the silver ion and the closest anion atom.

2. Experimental Section

2.1. Sample Preparation. Poly(2-ethyl-2-oxazoline) (POZ) (MW: 500 000) and poly(*N*-vinylpyrrolidone) (PVP) (MW: 1 000 000) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Polysciences, Inc. (Los Angeles, CA), respectively. $AgBF_4$ (98%) and $AgCF_3SO_3$ (99+%) were purchased from Aldrich Chemical Co. All chemicals were used as received. Appropriate amounts of silver salts were dissolved in 20 wt % polymer solutions in water. The polymer electrolyte solution was cast on a glass plate and dried under a nitrogen environment. The cast film was finally dried overnight in a vacuum at room temperature to remove residual water.

2.2. Olefin Solubility Measurements. Solubility of propylene in solid polymer electrolytes (SPE) was measured using a barometric (pressure-decay) sorption apparatus at 25 °C. The system temperature was controlled to ±0.1 °C with a heating element. Samples with 1:1 mole ratio of carbonyl oxygen to silver ion were used. Initially, a SPE film was placed in the sample chamber and evacuated for more than 12 h. Propylene gas was then introduced into the chamber and allowed to equilibrate. Once the chamber pressure remained constant, additional gas was introduced and again allowed to achieve equilibrium. In this incremental manner, propylene solubility as a function of gas pressure was determined and expressed as cm^3 (STP) of propylene uptake per unit volume of SPE.

2.3. DSC Experiments. Glass transition temperatures of POZ films containing silver salts were measured under a dry nitrogen environment using a Perkin-Elmer DSC 7 calorimeter. The heating rate was 20 °C/min. Samples of POZ complexed with $AgBF_4$ or $AgCF_3SO_3$ were prepared with carbonyl oxygen-to-silver ratios of 20:1, 10:1, 6:1, 5:1, 4:1, and 3:1.

3. Results and Discussion

The propylene solubilities in SPE films were measured using the pressure decay method at 25 °C and were plotted against propylene pressure as shown in Figure 1. The mole ratio of carbonyl oxygen to silver ion was 1:1. The olefin solubility in the POZ or PVP alone was very low (for example, the propylene solubility in the POZ film at 136 kPa was only 9 cm^3 (STP)/cm^3). The propylene solubility in the $AgBF_4$ membranes is almost 25 times higher than that in pure POZ at 136 kPa. This implies that the overall solubility seems to be mostly associated with the complexation of olefin with silver ions. The experimental results indicate that the propylene solubility in SPE films containing $AgBF_4$ is always higher than that containing $AgCF_3SO_3$ for both polymers. The former is almost 2-fold increased

---

* To whom correspondence should be addressed. Tel +82-2-958.6862; Fax +82-2-958-6869; E-mail yskang@kist.re.kr.

10.1021/ma000735o CCC: $19.00

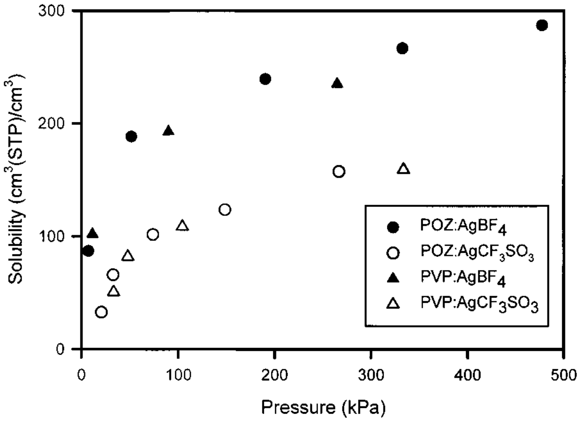

Figure 1. Solubility of propylene in solid polymer electrolyte films at 25 °C.

compared to the latter. The propylene solubilities in poly(ethylene oxide):$AgBF_4$ and poly(ethylene oxide): $AgCF_3SO_3$ membranes were reported to be 8.5 and 1.76 g of propylene per 100 g of polymer electrolyte, respectively, at 35 °C and 700 Torr.[10] This also shows that the propylene solubility in $AgBF_4$ polymer electrolytes is much higher than that in $AgCF_3SO_3$ ones.

Polymer electrolytes are composed of metal salts dissolved in polymer solvents. When metal salts are dissolved in polymer solvents, the salts are first dissociated into their ions (dissociation), which were subsequently solvated in polymeric solvents (solvation). The dissolution process involves the dissociation step associated with the lattice energy of salts and the solvation step with the solvation energy of ions in polymer solvents. Therefore, the properties of polymer electrolytes, in particular their complexation with olefin molecules, strongly depend on the lattice and solvation characteristics, which dictate the type of the ionic constituents of salts in polymer electrolytes: free ion, ion pair, and ion aggregate. The type of the ionic constituents can be fairly well represented by the distance between cation and anion.

The effect of the anion size on silver ion–olefin complexation in chloroform solution was first investigated with Fourier transform infrared (FTIR) spectroscopy by Sunderrajan et al.[10] The silver salts with the larger BF_4^- (0.232 nm) and $CF_3SO_3^-$ (0.256 nm) anions have a much stronger tendency to form complexes with olefins than those with the smaller anions such as NO_3^- (0.189 nm) and $CF_3CO_2^-$ (0.156 nm). They concluded that the tendency of silver salts to form complexes in solution was most strongly correlated with anion size and was not well-correlated with measures of anion-donor electron density or softness parameter.[10] However, we found experimentally that the propylene solubility in SPE films containing $AgBF_4$ is higher than that containing $AgCF_3SO_3$ although the size of $CF_3SO_3^-$ (0.256 nm) is larger than that of BF_4^- (0.232 nm).[15] This represents that the anion size influences the propylene solubility to some extent but not crucially.

Recently, Kim at al. calculated theoretically lattice energies for metal salts using the density functional theory.[16] They first calculated dissociation energies of metal salts and then calculated the lattice energies using the linear relationship between the dissociation and the lattice energies. According to them, the lattice energies for silver salts increase as follows: $AgBF_4$ (667 kJ/mol) < $AgCF_3SO_3$ (716 kJ/mol) < $AgNO_3$ (773 kJ/mol). This indicates that the interaction of silver ion with BF_4^- is weaker than that with $CF_3SO_3^-$ and consequently that the complexation of Ag^+ with olefin molecules may be stronger in the $AgBF_4$ membrane than that in the $AgCF_3SO_3$ membrane, resulting in higher propylene solubility in SPE films containing $AgBF_4$. This is consistent with experimental data. However, the lattice energy is defined as energy necessary for dissociation of a salt into ions and does not consider the solvation effect in polymer solvents, which is more important than the lattice energy in many cases.[17] Therefore, it seems to be difficult to relate the lattice energy with complexation process directly.

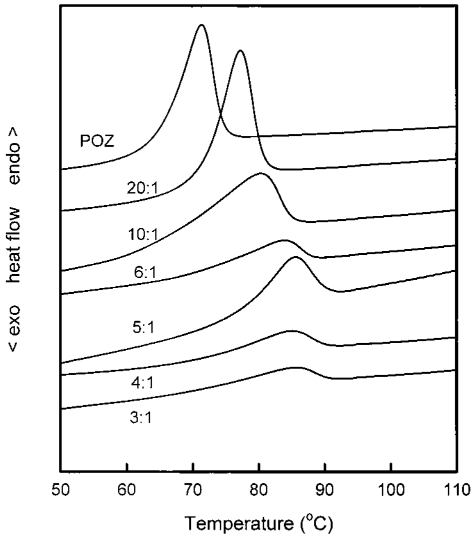

Figure 2. DSC thermograms for POZ:$AgCF_3SO_3$ systems with varying mole ratio of carbonyl oxygen to silver ion.

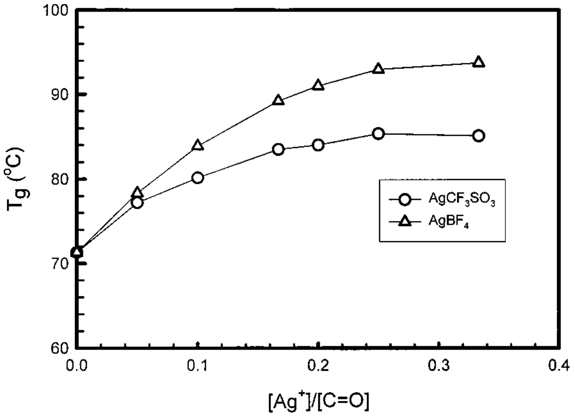

Figure 3. Variations of glass transition temperatures as a function of salt concentration for POZ with $AgBF_4$ and with $AgCF_3SO_3$.

The solvation process is also important in determining the propylene solubility, which is strongly influenced by the interaction energy of silver ions with polymer matrix. The interaction between carbonyl oxygens of the polymer matrix and silver ions for both silver salts has been investigated spectroscopically earlier.[12] However, we were not able to measure the difference in the strength of the interaction of carbonyl oxygen with silver ion in $AgBF_4$ and $AgCF_3SO_3$ membranes quantitatively using the spectroscopic method. One method to quantify this interaction is to study glass transition temperatures (T_g) of SPE films. When silver cations interact with polar groups of polymer chains, T_g of the polymer matrix will be increased owing to the decreased mobility of

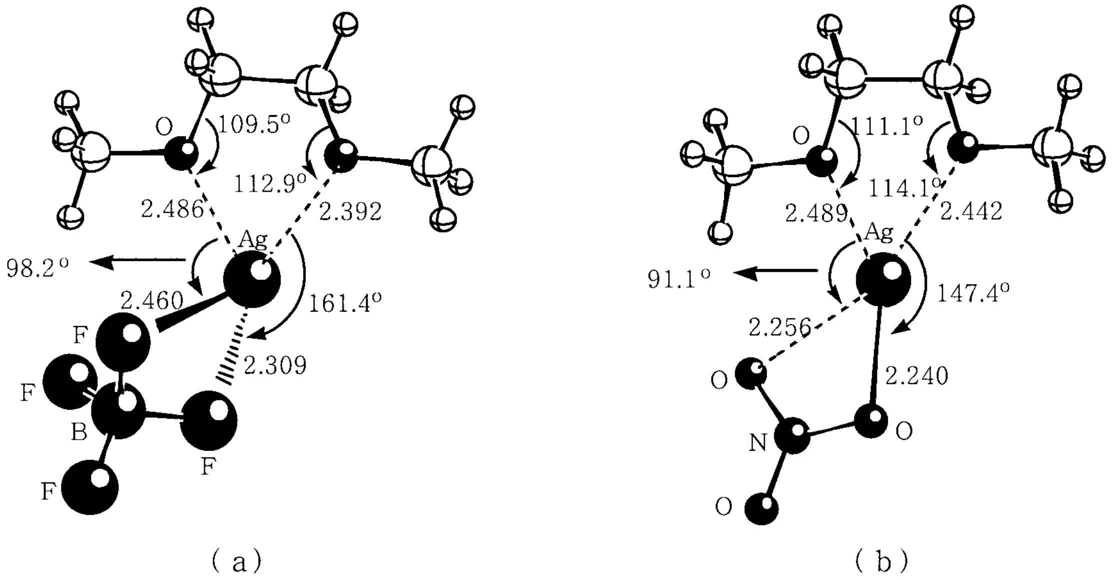

Figure 4. Structures of complexes of (a) 1,2-dimethoxyethane with $AgBF_4$ and (b) 1,2-dimethoxyethane with $AgNO_3$, where 1,2-dimethoxyethane is a model compound of poly(ethylene oxide).

polymer chains.[18] Therefore, glass transition temperatures of POZ containing $AgBF_4$ and $AgCF_3SO_3$ were measured using DSC. Figure 2 shows DSC heating curves of the POZ:$AgCF_3SO_3$ system with various salt concentrations. As shown in Figure 2, the glass transition temperature increases with increasing salt content as expected.[19] Both systems show pronounced variations, which are qualitatively similar for both salts, in the temperature range over which the glass transition occurs. Each plot exhibits the same general features of increasing T_g with increasing salt contents; i.e., T_g first increases and then remains invariant above a certain salt content, indicating the limiting value of salt solubility in polymer solvent.[17] The increase in T_g is more pronounced in $AgBF_4$ than that in $AgCF_3SO_3$. This result indicates that the complexation intensity of the polymer matrix with $AgBF_4$ is stronger than that with $AgCF_3SO_3$ ones. Then we would expect that the propylene solubility in $AgCF_3SO_3$ polymer electrolytes is higher than that in $AgBF_4$ ones. This is not consistent with our experimental findings.

As mentioned previously, the type of ionic constituents of salts in polymer electrolytes is very important in determining their various physical properties. Metal salts may exist as free ions, contact ion pairs, or higher ion aggregates in polymer electrolytes. One way to characterize the ionic contituents is the distance between cation and anion or the bond length between the cation and the closest anion atom (silver to oxygen for $AgCF_3SO_3$ and $AgNO_3$, silver to fluorine for $AgBF_4$) in SPE films. The bond length between the silver ion and the closest anion atom is influenced by the relative strength of interactions of silver ions with anions and with polymer matrix as well as steric effect. The longer the bond length, the smaller the interaction of silver cations with anions (lower lattice energy) and the higher with the polymer chains (higher T_g). Therefore, the long bond length helps olefin molecules to approach to their silver coordination sites easily and consequently results in the high propylene solubility.

To support this hypothesis, the bond length in 1,2-dimethoxyethane/silver salt films was calculated using the density functional theory of the Becke3LYP method with the 6-31+G(d) basis set for nonmetallic elements and the effective core potential of the LANL2DZ basis set for silver cation. 1,2-Dimethoxyethane was used as a model compound of poly(ethylene oxide). To obtain the energetics in polymer medium, the dielectric constant (ϵ) was assumed to be 5, and the isodensity polarized continuum solvation (IPCM) method with an isodensity level of 0.001 au was used. The structures of complexes containing (a) $AgBF_4$ and (b) $AgNO_3$ are illustrated in Figure 4. The complex (a) was sp^3-hybrid type because the Ag^+ cation bonded to both the monomer and anion. This structure could be rationalized from the fact that the silver cation has a coordination number of 4 using vacant 5s- and 5p-orbitals, since the electron configuration of silver cation is [core]$4s^2 4p^6 4d^{10}$. The theoretical calculation demonstrates that the bond length between the silver ion and the closest anion atom in the more propylene soluble PEO:$AgBF_4$ film (2.309 Å) is larger than that in the less propylene-soluble PEO:$AgNO_3$ film (2.240 Å). Thus, the bond length appears to be a good measure to interpret the propylene solubility in silver polymer electrolytes. EXAFS (extended X-ray absorption fine structure) is a technique to measure the bond length directly[20] and will be studied further in our lab.

4. Conclusions

It has been observed that the propylene solubility in facilitated transport membranes of silver polymer electrolytes influences to a large extent the propylene permeance. The enhanced solubility of propylene in silver polymer electrolyte membranes resulted from the complexation of propylene with silver ions. The solubility was better correlated with the bond length between the cation and the closest anion atom than other parameters such as anion size and interaction intensity of silver with polymer chains. It was thus suggested that the bond length might be an important factor in controlling the solubility of propylene in silver polymer electrolytes. The bond length depends on the relative strength of interactions of silver ions with anions as well as with polymer matrix. However, further studies are necessary to generalize this finding.

Acknowledgment. The authors gratefully acknowledge financial support from the Ministry of Science and

Technology of Korea through the Creative Research Initiatives Program.

References and Notes

(1) Bruce, P. G.; Vincent, C. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3187 and references therein.
(2) Armand, M. B. *Solid State Ionics* **1983**, *9–10*, 745.
(3) Gray, F. M. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 1441.
(4) Ferry, A.; Jacobsson, P.; Stevens, J. R. *J. Phys. Chem.* **1996**, *100*, 12574.
(5) Cameron, G. G.; Ingram, M. D.; Sorrie, G. A. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3345.
(6) Rao, S. S.; Rao, U. V. S. *Mater. Sci. Lett.* **1994**, *13*, 1771.
(7) Reddy, M. J.; Rao, S. S.; Laxminarsaiah, E.; Rao, U. V. S. *Solid State Ionics* **1995**, *80*, 93.
(8) Sunderrajan, S.; Pinnau, I.; Freeman, B. D. *Polym. Mater. Sci. Eng.* **1997**, *77* (*2*), 267.
(9) Pinnau, I.; Toy, L. G.; Sunderrajan, S.; Freeman, B. D. *Polym. Mater. Sci. Eng.* **1997**, *77* (*2*), 269.
(10) Sunderrajan, S.; Freeman, B. D.; Hall, C. K. *Ind. Eng. Chem. Res.* **1999**, *38*, 4051.
(11) Hong, S. U.; Jin, J. H.; Won, J.; Kang, Y. S. *Adv. Mater.* **2000**, *12*, 968.
(12) Jin, J. H.; Hong, S. U.; Won, J.; Kang, Y. S. *Macromolecules* **2000**, *33*, 4932.
(13) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.
(14) Beverwijk, C. D.; van der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. *Organomet. Chem. Rev. A* **1970**, *5*, 215.
(15) Gray, F. M. In *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH: New York, 1991.
(16) Kim, C. K.; Won, J.; Kim, H. S.; Kang, Y. S.; Li, H. G.; Kim, C. K. *J. Comput. Chem.*, submitted.
(17) Angell, C. A.; Liu, C.; Sanchez, E. *Nature* **1993**, *362*, 137.
(18) Besnaer, S.; Prud'homme, J. *Macromolecules* **1989**, *22*, 3029.
(19) Kim, J. Y.; Hong, S. U.; Won, J.; Kang, Y. S. *Macromolecules* **2000**, *33*, 3161.
(20) Antino, M. R.; Tsou, D. T. *Ind. Eng. Chem. Res.* **1993**, *32*, 273.

MA000735O