Role of Transient Cross-Links for Transport Properties in Silver−Polymer Electrolytes

Jong Hak Kim,[†,‡] Byoung Ryul Min,[‡] Chang Kon Kim,[†] Jongok Won,*[,†] and Yong Soo Kang*[,†]

Center for Facilitated Transport Membranes, Korea Institute of Science & Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea, and Department of Chemical Engineering, Yonsei University, Seoul 120-749, South Korea

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ABSTRACT: The interaction of the silver cation of $AgClO_4$ with carbonyl oxygen in poly(2-ethyl-2-oxazoline) (POZ) was found to be similar to that of $AgBF_4$ by infrared and Raman spectroscopic results. The two silver salts are similar in molecular size and lattice energy. However, the two silver−polymer electrolytes showed remarkably different gas transport properties. The POZ:$AgClO_4$ membrane showed very low gas permeance compared with the POZ:$AgBF_4$ at the 1:1 [C═O]:[Ag] mole ratio. The difference in the transport properties has been attributed mostly to the changes in chain mobility upon both the formation of transient cross-links by silver cations and the dangling of the heavy anions on the main chain. The changes in chain mobility were characterized by the glass transition temperature and the intersegmental *d* spacing. The extent of the transient cross-links seems to be strongly associated with the coordination number of the silver cation; the silver cation in $AgClO_4$ has a higher coordination number than that in $AgBF_4$. The structure difference for the two systems was also confirmed by the difference in the bond length between the cation and anion calculated from ab initio methods, despite the very similar lattice energies for two salts. Thus, the gas transport properties were successfully used to monitor the role of the transient cross-link as well as of the neighboring counteranion on the structure and physical properties of polymer electrolytes.

Introduction

Transient cross-links of polymer electrolytes, in which metal salts are dissolved in a polymeric solvent, are formed from the coordinative interaction of polymer chains with metal cations or metal cation−anion−cation bridges.[1] For the polymer electrolytes containing Li^+ ions, it is generally believed that Li^+ ions form both interchain and intrachain cross-links through transient coordinative Li−O bonds.[2,3] A large number of studies have been made on transient cross-links by Li^+ ions to elucidate the ionic transport mechanism in lithium polymer electrolytes. It has thus been found that the transient cross-links reduce the mobility of polymeric chains and consequently increase the glass transition temperature. They also reduce the mobility of charge-carrying ionic species and thereby cause a decrease in the ionic conductivity.[4] However, there are few reports about the effects of transient cross-links on the gas transport properties through solid polymer electrolyte membranes.

Polymer electrolytes containing silver ions are of particular interest for their potential application to separation of olefin/paraffin mixture[5−8] because the silver cation reversibly reacts with olefin to make silver−olefin complexes.[9,10] When either silver tetrafluoroborate ($AgBF_4$) or silver triflate ($AgCF_3SO_3$) is dissolved in one of the following three polymers—poly(ethylene oxide) (PEO), poly(2-ethyl-2-oxazoline) (POZ), and poly(vinylpyrrolidone) (PVP)—the silver cation is active for olefin complexation, resulting in facilitated olefin transport. The polymer matrix studied from POZ and PVP has relatively less effect on the olefin facilitated transport property than the counteranion of the silver ion.[5,6] Both the coordination numbers of the silver ion of $AgBF_4$ and that of $AgCF_3SO_3$ with the carbonyl oxygen of POZ and PVP are close to unity, showing high solubility of silver ions in the POZ and PVP matrices.[11]

Table 1. Gas Permeance and Selectivity through Polymer Electrolyte Films of 50:50 (vol %) Ethylene:Ethane Mixture Gas at 25 °C[a]

system	total permeance (GPU)	selectivity (C_2H_4/C_2H_6)
POZ:$AgClO_4$	0.3	103.4
POZ:$AgBF_4$	14.1	98.1

[a] The mole ratio of carbonyl oxygen to silver ion was fixed at 1:1. Δp = 275.6 kPa, Θ < 0.02, 1 GPU = 1 × 10^{-6} cm^3 (STP)/(cm^2 s cmHg).

In this research, we have found that the transport of ethylene was significantly retarded through the POZ:$AgClO_4$ polymer electolyte membrane compared to that through the POZ:$AgBF_4$, whereas both silver−polymer electrolytes showed somewhat similar selectivity on the ethylene/ethane separation as listed in Table 1. Although $AgClO_4$ and $AgBF_4$ salts have similar anion sizes, 2.36 and 2.32 Å, and comparable lattice energies, 677 and 680 kJ/mol, respectively,[12] their transport properties are significantly different. The distinct transport property is interpreted here by the structure of silver−polymer electrolytes. The structure of polymer electrolytes depends on the dissolution behavior of a metal salt in polymer matrix.[13−15] Therefore, the information on the interactions of silver ions with matrix polymer provides insights into structural changes when their complexes are formed and also into transport properties. Raman and IR spectroscopy are employed to investigate the interactions of silver ions with matrix polymers and to characterize their stoichiometry and

† Korea Institute of Science & Technology.
‡ Yonsei University.
* To whom correspondence should be addressed. Tel +82-2-958-5362; Fax +82-2-958-6869; E-mail yskang@kist.re.kr.

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the coordination number of the silver cation with the carbonyl oxygen of POZ. Measurement of glass transition temperature and *d* spacing of polymer electrolytes will also help to elucidate the structure of silver−polymer electrolytes. In addition, the electronic structure of silver−polymer electrolytes is calculated by ab initio methods to confirm the interaction of silver salts with polymers. Thus, the relationship between the characteristics of polymer electrolytes and the transport properties has been investigated.

Experimental Section

Poly(2-ethyl-2-oxazoline) (POZ) ($M_w = 5 \times 10^5$), silver tetrafluoroborate ($AgBF_4$, 99.99+%), and silver perchlorate ($AgClO_4$, 99.9%) were purchased from Aldrich Chemical Co. and were used without further purification. The appropriate amounts of POZ and silver salts were dissolved in acetonitrile (99%, Aldrich Chemical Co.). The solution was then cast on a Teflon-attached glass plate and dried under a N_2 environment. The film was further dried in a vacuum oven for at least 2 days at room temperature. Mixed gas (50:50 vol % of ethylene/ethane mixture) separation properties of the films were 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%. IR spectra were obtained with a Mattson Galaxy 6030 spectrometer; 64−200 scans were signal-averaged at a resolution of 1 cm^{-1}. Raman spectra for POZ:Ag salt electrolytes were recorded at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman at a resolution of 1 cm^{-1}. This experimental apparatus includes a neodymium-doped yttrium aluminum garnet (Nd^{3+}:YAG) laser operating at 1.064 μm. Spectroscopic characterization was performed using a homemade pressure cell equipped with CaF_2 windows. A Perkin-Elmer DSC-7 was used to measure glass transition temperatures of POZ:Ag salt electrolytes at a heating rate of 20 °C/min under a N_2 environment. A wide-angle X-ray diffractometer with Cu Kα radiation was utilized to determine the value of the intersegmental *d* spacing in silver−polymer electrolytes at a scanning speed of 10°/min.

Results and Discussion

FT-IR and Raman spectroscopic experiments demonstrated that silver salts of $AgBF_4$ are dissolved in polymer matrices (POZ) because of the coordinative interaction of silver ions and carbonyl oxygens.[11] The uncomplexed carbonyl band was evident up to the 2:1 POZ:$AgBF_4$ but disappeared completely at the 1:1 POZ:$AgBF_4$.[11] The results suggest that the coordination number of the silver ion with the carbonyl oxygen of POZ is close to unity, implying unusually high solubility of silver ions in the POZ matrix. In the case of POZ:$AgClO_4$ complexes, similar IR spectra in the carbonyl stretching region were obtained. The intensity of a "free" carbonyl stretching band at 1641 cm^{-1} decreased with increasing silver salt content. A new band at 1595 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 with the silver ion. The bands of POZ:$AgClO_4$ systems were deconvoluted into a free C═O band (1641 cm^{-1}) and a complexed C═O stretching band (1595 cm^{-1}). The uncomplexed free C═O band is apparent up to 5:1 POZ:$AgClO_4$ but disappears at the 3:1 POZ:$AgClO_4$ complex. For a range of [C═O]:[Ag] from 3:1 to 1:1, this indicates that all the carbonyl groups are coordinatively bonded with silver cations and that only coordinated carbonyl groups are apparent. This is one distinctive difference with the POZ:$AgBF_4$ complex where the free carbonyl bands completely have disappeared at concentration above 1:1. These results suggest that the coordination number of the silver cation is higher in the POZ:$AgClO_4$ complex than in the POZ:$AgBF_4$ and changes with the amount of silver in the POZ:$AgClO_4$ complex.

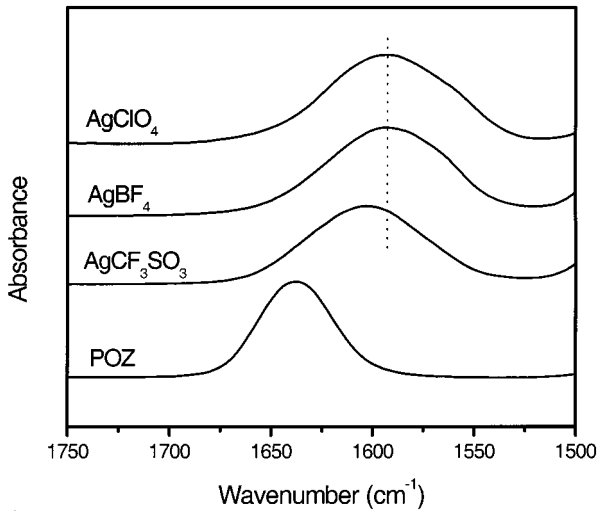

Figure 1. FT-IR spectra of POZ complexes with $AgClO_4$, $AgBF_4$, and $AgCF_3SO_3$ at 1:1 [C═O]:[Ag] mole ratio.

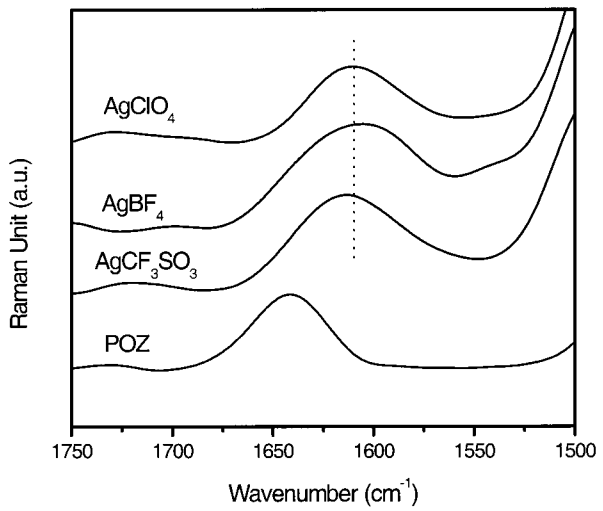

Figure 2. FT-Raman spectra of POZ complexes with $AgClO_4$, $AgBF_4$, and $AgCF_3SO_3$ at 1:1 [C═O]:[Ag] mole ratio.

Figure 1 compares the IR spectra of pure POZ with POZ:silver complexes of $AgBF_4$, $AgClO_4$, and $AgCF_3SO_3$ at 1:1 [C═O]:[Ag] mole ratio. The IR spectrum of the POZ:$AgClO_4$ in the C═O stretching region is almost identical to that of the POZ:$AgBF_4$ complex, implying the comparable interaction of the silver ion with the polymer matrix. On the other hand, the strength of the coordination interaction between the silver cation and the POZ matrix in POZ:$AgCF_3SO_3$ is estimated to be lower than that in either POZ:$AgBF_4$ or POZ:$AgClO_4$, because the band shift of C═O to a lower wavelength is less in POZ:$AgCF_3SO_3$ than in the others. Raman spectroscopy also supports the similar peak shift of the C═O band in POZ:$AgBF_4$ and POZ:$AgClO_4$ systems, as shown in Figure 2. These results corroborate the fact that either $AgClO_4$ or $AgBF_4$ is dissolved in the polymer solvent, POZ, due to the coordination interaction of silver ions with carbonyl oxygens. It was also found that the interaction between the C═O and silver ion in POZ:$AgBF_4$ is similar to that in POZ:$AgClO_4$.

Since the dissolution behavior of salts in polymer matrices affects the physical properties of polymer

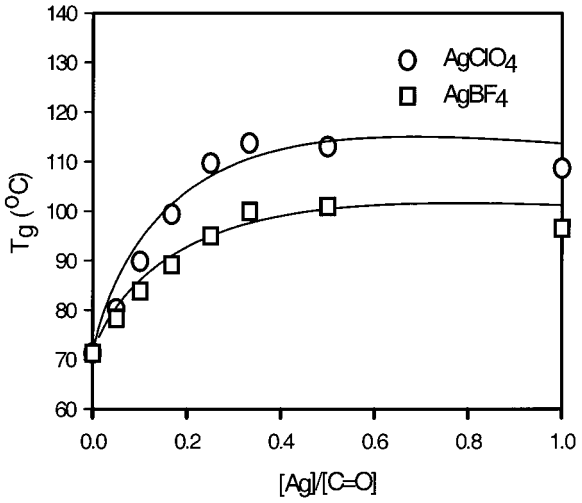

Figure 3. Glass transition temperatures with increasing silver concentration in POZ electrolytes containing $AgClO_4$ and $AgBF_4$. The lines are calculated from eq 1.[19]

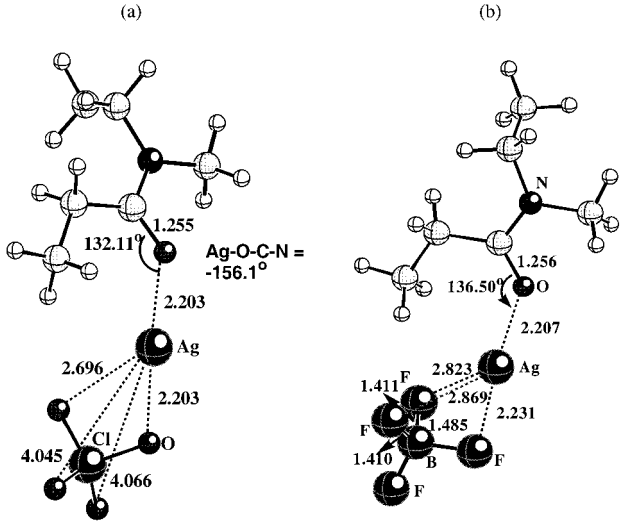

Figure 4. Structures of complexes of *N*-methyl-*N*-ethylpropionamide with (a) with $AgClO_4$ and (b) with $AgBF_4$, where *N*-methyl-*N*-ethylpropionamide is the model compound of poly(2-ethyl-2-oxazoline).

electrolytes,[13−15] the ionic constituents such as free ions, contact ion pairs, and ion aggregates on polymer electrolytes were investigated by monitoring the anion mode. The Raman spectra of the POZ complexes with $AgBF_4$ and $AgClO_4$ were recorded in the concentration range from 7:1 to 1:1 mole ratios of [C═O]:[Ag]. The Raman spectra of the ν_1 symmetric stretching mode of the BF_4^- anion[16] at 765 cm^{-1} and of the ClO_4^- anion[17] at 930 cm^{-1} are attributed to the free anion modes and remain invariant when the silver concentration is increased up to the 1:1 mole ratio. Therefore, the free ions will be dominant ionic constituents in POZ:$AgBF_4$ as well as in POZ:$AgClO_4$ up to the 1:1 mole ratio.

From the results of IR and Raman spectroscopic measurements, the interactions between the silver ion and the polymer matrix in POZ:$AgClO_4$ electrolytes are similar to those in POZ:$AgBF_4$. However, a significant difference in gas permeance was observed. Therefore, the difference in the gas permeance between these two systems will be investigated as follows.

The values of the glass transition temperature (T_g) in the complexes of POZ with $AgClO_4$ and $AgBF_4$ for various mole ratios of [C═O]:[Ag] are presented in Figure 3. T_g of the pure POZ film was 343 K. In the presence of Ag salts, the values of T_g in both systems increase gradually, indicating the restricted chain mobility of POZ. T_g reached the maximum with an increasing amount of silver salts while it decreased slightly thereafter, which is a common observation in the solid polymer electrolytes.[18−20] The increase in T_g upon addition of metal salts is primarily attributable to both the transient cross-link of polymer segmental chains and the dangling of metal salts on the main chain. The extent of the increase in T_g with increasing silver salt concentration is greater for POZ:$AgClO_4$ than for POZ:$AgBF_4$, displaying a significant structural difference between them. The configurational entropy theory for glass transition temperatures of polymer−salt complexes explains the increase in T_g with the amount of metal salts as follows:[19]

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = \beta_1\left[\left(\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right)\left(1 - \gamma_{12}\ln\left(\frac{z-1}{e}\right)\right)\right] \quad (1)$$

where T_{g12} and T_{g1} are the glass transition temperatures of the polymer electrolyte and the matrix polymer, respectively. ϕ_i and r_i are the volume fraction and the degree of polymerization for the component i, respectively. Here $r_2 = 1$. $\beta_1 = zR/M\Delta C_p$ where z (=12) is the lattice coordination number, R the gas constant, M the molecular weight of the repeating unit of the polymer, and ΔC_p the isobaric specific heat of polymer. γ_{12} is a proportionality constant representing the interaction between the polymer and salt.

The solid lines in Figure 3 were obtained from eq 1 with the interaction parameter γ_{12} of 1.07 and 0.95 for the POZ:$AgClO_4$ and POZ:$AgBF_4$ systems, respectively. The high γ_{12} represents a strong interaction of a metal salt with a polymer ligand. This represents that ClO_4^- groups are more strongly dangled in the main chain than BF_4^- groups because the interaction between Ag^+ and carbonyl oxygen was found to be almost similar as described previously.

To support this hypothesis, the bond lengths of the complex of *N*-methyl-*N*-ethylpropionamide/silver salt were calculated using the density functional theory of the Becke3LYP. *N*-Methyl-*N*-ethylpropionamide was used as a model compound of POZ. The theoretical electronic structure demonstrates that the bond lengths between the silver cation and the anions are shorter in the POZ:$AgClO_4$ system than in the POZ:$AgBF_4$ as shown in Figure 4: 2.696 and 2.203 Å for the Ag−O bond and 2.869, 2.823, and 2.231 Å for the Ag−F bond. This verifies that ClO_4^- groups are more tightly attached on the main chain than BF_4^- groups. If this is the case, the intersegmental d spacing of the POZ:$AgClO_4$ system will be smaller than that of the POZ:$AgBF_4$.[21]

The wide-angle X-ray diffraction technique was also employed to determine the intersegmental d spacing in silver−polymer electrolytes. The value of the d spacing was calculated using Bragg's equation $d = \lambda/2 \sin\theta$ with θ of the peak maximum. The values of the d spacing in the POZ complexes with $AgBF_4$ and $AgClO_4$ for various mole ratios are plotted in Figure 5. The d spacing of the pure POZ film is 4.54 Å, and it decreases gradually with the silver salt concentration in the both polymer electrolytes. The d spacing of the POZ:$AgClO_4$ is smaller

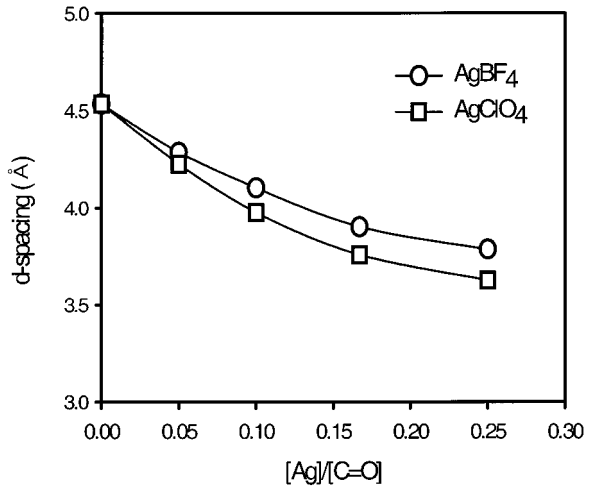

Figure 5. *d* spacing of POZ electrolytes containing $AgClO_4$ and $AgBF_4$ with increasing silver concentration.

than that of the POZ:$AgBF_4$ at a fixed amount of silver salt in POZ, which is consistent with the change in the glass transition temperature.

Another important fact is that the ClO_4^- group (ionic weight: 99.5) is heavier than the BF_4^- (ionic weight: 86.8). Therefore, the main chain mobility will be reduced more in the POZ:$AgClO_4$ system than in the POZ:$AgBF_4$.

As shown in Figures 3 and 5, the increase in T_g and the decrease in the *d* spacing in the POZ:$AgClO_4$ complexes are larger than those in POZ:$AgBF_4$. Two significant factors are considered to affect the structure of the polymer electrolyte. The first is transient cross-links created by the coordination bond between the C═O and silver ion. Metal cations, coordinated with electron donor groups of polymers such as C═O, are believed to act as a cross-linker and thereby alter the dynamics of polymer electrolytes.[21] The transient cross-link makes the glass transition temperature higher and the *d* spacing smaller as demonstrated previously. The extent of the cross-link is higher in the POZ:$AgClO_4$ than in the POZ:$AgBF_4$ complex because the former has a higher coordination number than the latter. Consequently, low gas permeances were obtained through the POZ:$AgClO_4$ complex compared to that through the POZ:$AgBF_4$. The second is the effect of counteranion, which appears to be located close to the silver ion. The two salts of $AgClO_4$ and $AgBF_4$ are similar in size and lattice energy, but the former is heavier and more strongly dangled to the main chain than the latter, as evidenced by the theoretical electronic structure. Therefore, the ClO_4^- group will hinder the main chain mobility more effectively than the BF_4^- group, resulting in higher T_g and lower *d* spacing of the POZ:$AgClO_4$ complex than those of the POZ:$AgBF_4$.

In summary, the transient cross-links as well as the strongly dangled heavy counteranions restrict the polymer chain mobility in the POZ:$AgClO_4$ much more than in the POZ:$AgBF_4$. Consequently, the former gives an extremely lower gas permeance than the latter.

Conclusions

Infrared and Raman spectroscopic results demonstrated that the interactions of the silver cation with carbonyl oxygen in both the POZ:$AgClO_4$ and the POZ:$AgBF_4$ systems are similar to each other. However, the former exhibits much lower gas permeance than the latter although the two silver salts are similar in size and lattice energy. Interestingly, it was found that the coordination number of the silver cation in the POZ:$AgClO_4$ is higher than that in the POZ:$AgBF_4$ system. The difference in transport behavior between the two systems may be explained by the differences in (1) the extent of transient cross-links associated with the coordination number of silver cation, (2) the bond length between the silver cation and anion, and (3) the weight of the dangling anion on the polymeric chain. Such differences have been characterized by the changes in the glass transition temperature and the *d* spacing as well as by the electronic structure theoretically calculated by ab initio methods. The transient cross-links by silver cations in the POZ:Ag complexes induce the increase in the glass transition temperature owing to the reduced chain mobility and also the decrease in the intersegmental *d* spacing. The difference in the bond length between the cation and anion for the two polymer electrolyte systems seems to be strongly related with the difference in the interaction of the cation with anion as supported by the difference in the interaction parameter γ_{12} value.

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