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Wide-Angle X-ray Scattering Studies on the Structural Properties of Polymer Electrolytes Containing Silver Ions

Sangwook Choi, Jong Hak Kim, and Yong Soo Kang*

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

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ABSTRACT: Wide-angle X-ray scattering (WAXS) has been used to study the structural properties of polymer electrolytes containing silver ions. The WAXS spectra of pure poly(2-ethyl-2-oxazoline) (POZ) and poly(vinylpyrrolidone) (PVP) showed two broad amorphous peaks. The first of these peaks was assigned to the interchain distance, and the second peak was assigned to the distance between the pendant groups of the polymer chains. When silver salts such as $AgBF_4$, $AgCF_3SO_3$, or $AgClO_4$ were introduced into the polymer matrices, their silver ions coordinated with the carbonyl oxygens on the pendant groups to form polymer/silver salt complexes. In the case of the PVP/silver salt complexes, the first peak shifted to lower angle and became narrower with increasing silver concentration, indicative of an increase in the interchain distance and ordering. In contrast, the position of the second peak remained almost constant. For the POZ/silver salt complexes, however, the positions of both peaks shifted to higher scattering angle with increasing silver concentration until the mole ratio of carbonyl oxygen to silver reached about 3:1. Further increase of the concentration caused the first peak to shift to lower angle while the second peak remained almost constant, which is similar to the behavior of the PVP/Ag salt complexes. The difference in the behavior of the PVP/Ag and POZ/Ag salt complexes may arise from different strengths of the transient cross-links formed by silver cations with the pendant groups of POZ and PVP. The Bragg *d* spacing results calculated from the second peak indicate that the silver ions coordinate more strongly with the pendant groups in the POZ/$AgClO_4$ complex than in the POZ/$AgCF_3SO_3$ and POZ/$AgBF_4$ complexes. It is worth noting that the Bragg *d* spacings for the POZ/silver and PVP/silver salt complexes were very different at low silver concentrations but approach almost the same value at high silver concentrations (e.g., at a mole ratio of [C=O]:[Ag] = 1:1). These findings are consistent with our previous results on facilitated olefin transport and glass transition temperature behavior in silver polymer electrolyte membranes. We therefore conclude that the facilitated olefin transport and glass transition temperature behavior in polymer electrolytes are strongly related to the structural change that occurs upon coordination of silver cations with the carbonyl oxygens of the polymeric chains.

Introduction

Polymer electrolytes have generated considerable research interest because of their applications in devices such as solid-state batteries, fuel cells, and electrochemical displays.[1−3] Recently, polymer electrolytes containing silver salts have been shown to be potential materials for constructing facilitated transport membranes for the separation of olefin/paraffin mixtures.[4−13] In these facilitated transport membranes, silver ions confined to the polymer chains form reversible silver−olefin complexes that act as olefin carriers, which leads to carrier-mediated transport in addition to the normal Fickian transport. Kang et al. studied the structure and facilitated transport properties of complexes of silver ions with poly(2-ethyl-2-oxazoline) (POZ) or poly(vinylpyrrolidone) (PVP).[7−13] The propylene permeance through the 1:1 POZ/$AgBF_4$ complex was as high as 45 GPU (1 GPU = 10^{-6} cm^3 (STP)/(cm^2 s cmHg)) at a propylene pressure of 138 kPa, whereas the propane permeance was as low as 0.003 GPU. Thus, the ideal separation factor of propylene over propane is greater than 15 000 using this complex. The high propylene permeance is attributed mainly to the extraordinarily high loading of silver salts in the POZ or PVP matrix; the coordination number of the silver ion with the carbonyl oxygen of POZ and PVP is close to unity, indicating a high solubility of silver ions in the POZ and PVP matrices.[9] The propylene permeance strongly depends on the silver concentration and is associated with the structure of the polymer electrolytes.

Polymer electrolytes comprise metal salts dissolved in a polymeric solvent. Their structure therefore depends on the polymer and metal salt as well as the interactions between these species. When metal salts are incorporated into a polymer matrix that has polar ligands such as carbonyls, amides, and esters, the metal cation coordinatively interacts with these ligands. When the metal cation coordinates with more than two ligands, it acts as a cross-linker, resulting in the formation of transient cross-links.[1−3] When the transient cross-links form through coordinative bonds, changes occur in the Bragg *d* spacing and chain mobility, and consequently the glass transition temperature is altered. These changes eventually influence the transport behavior of small molecules.[14−20] Recent neutron diffraction experiments showed the contraction and ordering of polymer chains when $LiClO_4$ was introduced into a poly(propylene oxide) (PPO) matrix.[21]

Wide-angle X-ray scattering (WAXS) is a powerful technique for characterizing the *d* spacing of polymeric materials. It is well-known that polymers containing pendant groups such as polystyrene and poly(2,6-diphenyl-1,4-phenylene oxide) (PDPPO) have two amorphous WAXS peaks.[22,23] These peaks are assigned to the interchain distance and the distance between pendant groups, and their structure can be visualized using the "super chain" model. In the present study we found that

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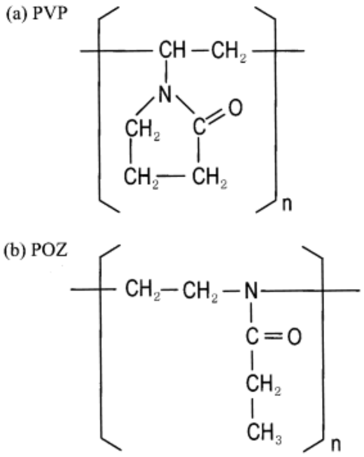

Figure 1. Chemical structures of (a) PVP and (b) POZ.

POZ and PVP with pendant amide groups also show two WAXS peaks. The way in which these peaks shift upon incorporation of silver salts differs between POZ and PVP. For polyether/salt complexes, the change in polymer electrolyte structure with salt concentration has been considered to be primarily due to the formation of cross-links at points where the cation coordinates to ether oxygens in the backbone polyether chain. An interesting characteristic of POZ/Ag and PVP/Ag salt systems is that changes can occur in both the interchain distance and the distance between the pendant groups, associated with the formation of transient cross-links as the Ag ions coordinate to the carbonyl oxygens in the pendant groups. The strength of the transient cross-links depends on the metal−polymer interactions in the POZ/Ag and PVP/Ag salt complexes, which can be characterized by the change in the glass transition temperature upon addition of the salt.

In this paper, wide-angle X-ray scattering (WAXS) was used to study the structural properties of polymer electrolytes containing various silver salts. We also investigated the effect of the different salts on transport properties and the glass transition temperature.

Experimental Section

Polymer electrolyte membranes were prepared using silver salts and polymer solvents. Poly(2-ethyl-2-oxazoline) (POZ) (M_w = 500 000) and poly(vinylpyrrolidone) (PVP) (M_w = 1 000 000) were purchased from Aldrich Chemical Co. and Polyscience, Inc., respectively. The chemical structures of PVP and POZ are shown in Figure 1. Silver tetrafluoroborate ($AgBF_4$), silver triflate ($AgCF_3SO_3$), and silver perchlolate ($AgClO_4$) were purchased from Aldrich Chemical Co. All chemicals were used as received. Samples were prepared for the WAXS, glass transition temperature, and mixed gas permeance measurements by dissolving the appropriate linear polymer and silver salt in methanol and then allowing the solution to evaporate in a Teflon Petri dish to form a thin film. The film was then dried in a vacuum to remove any remaining methanol. The mole ratio of silver to carbonyl oxygen in polymer varied from a concentration of [C=O]:[Ag] = 10:1 to 1:1 ([C=O]:[Ag] being the mole ratio of carbonyl oxygen to silver).

Wide-angle X-ray scattering experiments were carried out on a Siemens Hi-Star area detector with Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV and 45 mA at the National Instrumentation Center for Environment Management (NICEM) in Seoul National University, South Korea. Two-dimensional data were circularly averaged to produce $I(2\theta)$ vs 2θ plots, where $I(2\theta)$ is the scattered intensity and 2θ is the scattering angle. The 2θ range was from 3° to 30°, and the sample-to-detector distance was 6.1 cm.

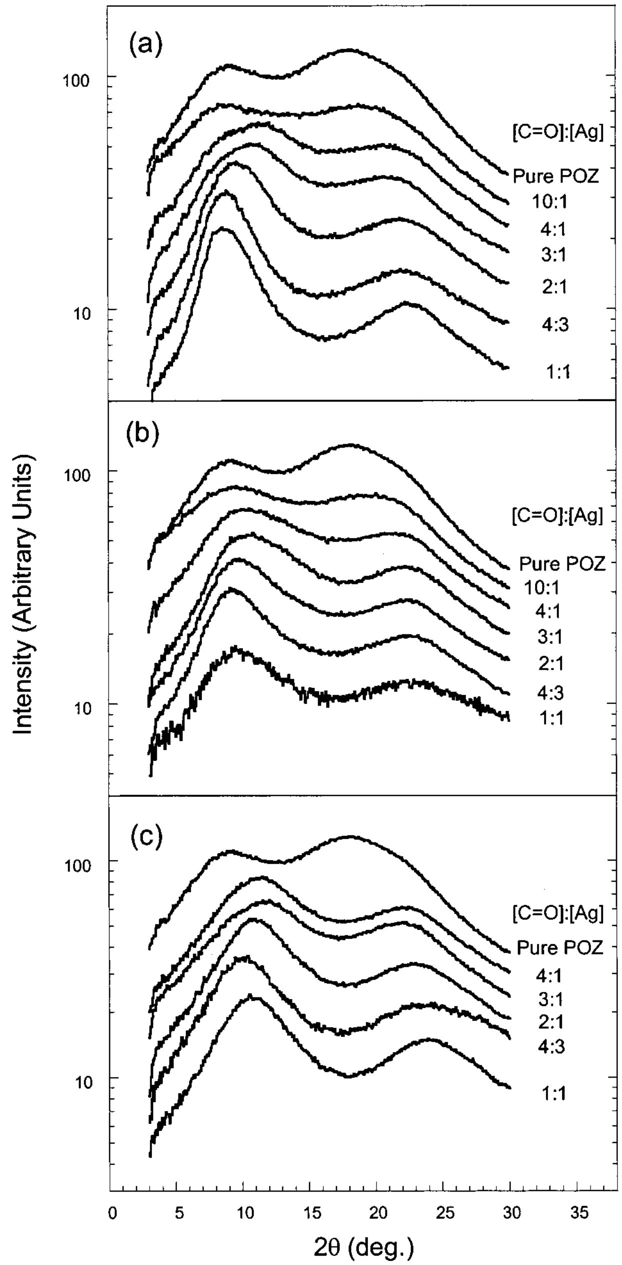

Figure 2. WAXS data of $I(2\theta)$ vs 2θ as a function of silver concentration: (a) POZ/$AgCF_3SO_3$; (b) POZ/$AgBF_4$; (c) POZ/$AgClO_4$.

A Perkin-Elmer DSC-7 was used to measure the glass transition temperature of the POZ/Ag salt complexes at a heating rate of 20 °C/min under a N_2 environment. The mixed gas (50:50 vol % of propylene/propane 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 rate, was always less than 2%.

Results and Discussion

Structure of POZ and POZ/Silver Salt Complexes. WAXS data for the POZ/$AgCF_3SO_3$, POZ/$AgBF_4$, and POZ/$AgClO_4$ complexes as a function of salt concentration are shown in Figure 2a−c. Pure POZ gives rise to an $I(2\theta)$ vs 2θ plot with two broad amorphous peaks. In previous work, two peaks have been observed in X-ray diffraction experiments on poly(2,6-diphenyl-1,4-phenylene oxide) (PDPPO) and polystyrene (PS) containing pendant groups.[22,23] According to Mitchell and Windle,[22] the X-ray scattering of polystyrene beyond

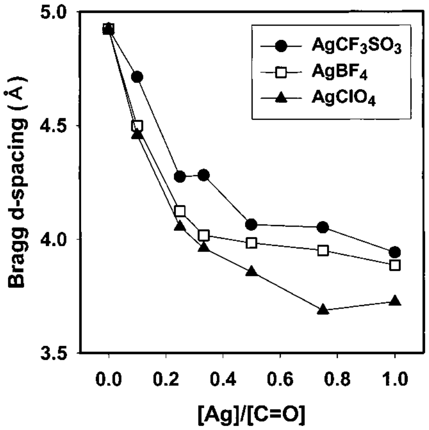

Figure 3. Comparison of the Bragg *d* spacings calculated from the position of the second peak in the $I(2\theta)$ vs 2θ plot for POZ/$AgCF_3SO_3$, POZ/$AgBF_4$, and POZ/$AgClO_4$.

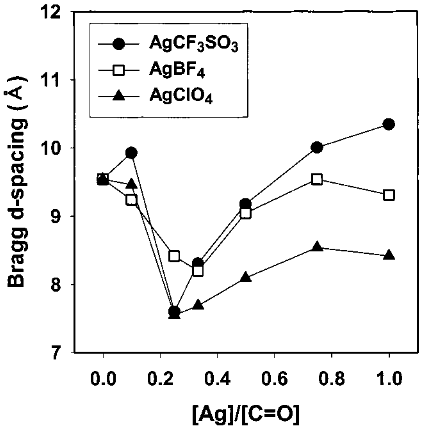

Figure 4. Comparison of the Bragg *d* spacings calculated from the position of the first peak in the $I(2\theta)$ vs 2θ plot for POZ/$AgCF_3SO_3$, POZ/$AgBF_4$, and POZ/$AgClO_4$.

$q = 1.0$ Å^{-1} is very similar to that of benzene and styrene. However, on polymerization of styrene, a peak appears at $q = 0.75$ Å^{-1}, which is completely absent for the styrene monomer. Mitchell and Windle proposed the “superchain” model for PS, in which the phenyl groups segregate on a molecular scale to form stacks and the polymer chains behave as if they were flexible superchains. According to the superchain model, the first peak is due to the intermolecular distance between the polymer chains, and the second peak arises from the inter-phenyl distance. Aguilar-Vega and Paul studied the relationship between the structure and gas transport properties in PDPPO and poly(1,4-phenylene sulfide) (PPS).[23] PDPPO gave two peaks in the WAXS plot of $I(2\theta)$ vs 2θ, whereas PPS, which has no pendant group, showed only a single peak that can be attributed to the distance between polymer chains. According to Lovell and Windle,[24] poly(methyl methacrylate) (PMMA) also shows two WAXS peaks. They argue that the peak at $q = 0.95$ Å^{-1} is due to the intermolecular distance, whereas the peak at $q = 1.2$ Å^{-1} represents correlations in the positions of the side groups because the neighboring side groups in PMMA are closely associated.

Since POZ has a pendant group, it is expected to give two peaks in the $I(2\theta)$ vs 2θ plot. This behavior is observed in Figure 2a–c. The *d* spacing was estimated from the two peaks using the Bragg relation.[25,26] The distance between pendant groups and the interchain distance between polymer chains are shown in Figures 3 and 4, respectively. For pure POZ, the interchain distance between polymer chains is 9.5 Å (calculated from the first peak) and the distance between pendant groups is 4.9 Å (calculated from the second peak).

For the POZ/Ag salt complexes, both the interchain distance and the distance between pendant groups decrease with increasing salt concentration until the mole ratio of carbonyl oxygen to silver reaches about 3:1. A decrease in the distance between pendant groups with increasing salt concentration is expected, because the silver ions coordinate to the carbonyl oxygens of the pendant groups, forming transient cross-links between the polymer chains. The decrease in the interchain distance at concentrations lower than [C=O]:[Ag] = 3:1 can be explained by the fact that the increase in the strength of the transient cross-links between pendant groups causes polymer chain contraction.

As the concentration was raised above [C=O]:[Ag] = 3:1, the interchain distance for the POZ/$AgCF_3SO_3$ complex increased while the distance between pendant groups decreased monotonically. This result can be interpreted in terms of past results for the PPO/$LiClO_4$ complex. In this complex, the ClO_4^- anions are weakly solvated and located among the polymer chains, which causes chain expansion as the polymer chains are pushed apart by the large anions.[20,21,27] According to X-ray and neutron diffraction studies,[21] it has been suggested that the Li^+ in the PPO/$LiClO_4$ complex has a pulling-together effect because Li^+ forms cross-links between the polymer chains, whereas ClO_4^- pushes the polymer chains apart. The increase of the interchain distance at concentrations above [C=O]:[Ag] = 3:1 seen in our work (Figure 4) may be attributed to the expansion of the POZ chains as more anions accumulate among the polymer chains. Furthermore, it is worth noting that the change in the distance between pendant groups shown in Figure 3 is much smaller than the change in interchain distance, particularly at concentrations above [C=O]:[Ag] = 3:1.

The peaks for the POZ/Ag salt complexes become narrower with increasing salt concentration. For the 1:1 POZ/$AgCF_3SO_3$ complex, the peak in Figure 2a becomes very sharp compared to that for pure POZ, indicating ordering of the polymer chains. The ordering of polymer chains in polymer electrolytes induced by cations has been previously reported in thermodynamic, neutron diffraction, and Raman studies of ion solvation and association.[20,21,28] Thermodynamic analysis of the ion association equilibrium in the polymer/salt complexes showed that ion association is accompanied by a large entropy increase, indicating an increase in the configurational freedom of the polymer chains. This implies that ion dissociation and linking with polymer chains have strong ordering effects on the system as the configurational freedom of the polymer chains decreases.

Glass Transition Temperature of POZ/Ag Salt Complexes. The glass transition temperatures (T_g) of the POZ/Ag salt complexes are presented as a function of salt concentration in Figure 5. The value of T_g for the pure POZ film was 343 K. The configurational entropy theory for the glass transition temperature of polymer–salt complexes well predicts the increase in T_g with the amount of metal salt as follows:[11]

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

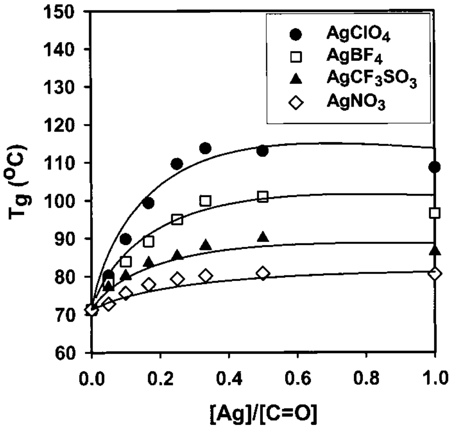

Figure 5. Glass transition temperatures with increasing salt concentration for POZ/$AgCF_3SO_3$, POZ/$AgBF_4$, POZ/$AgClO_4$, and POZ/$AgNO_3$.

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 is the gas constant, M is the molecular weight of the repeating unit of the polymer, and ΔC_p is the isobaric specific heat of the polymer. γ_{12} is a proportionality constant representing the interaction between the polymer and salt. The solid lines in Figure 5 were obtained from eq 1 using interaction parameters (γ_{12}) of 1.07, 0.95, 0.86, and 0.8 for the POZ/$AgClO_4$, POZ/$AgBF_4$, POZ/$AgCF_3SO_3$, and POZ/$AgNO_3$ complexes, respectively. A higher value of γ_{12} represents a stronger interaction between the metal salt and polymer ligands. As shown in Figure 5, the value of T_g for the POZ/Ag salt complexes increases initially with increasing the salt concentration and reaches a broad maximum near 3:1. The dependence of the interchain distance on the mole ratio of carbonyl oxygen to silver, shown in Figure 4, suggests that the polymer chain mobility decreases due to interchain contraction until the mole ratio reaches about 3:1, after which the chain mobility increases because the interchain distance increases. As a result, the value of T_g for the POZ/Ag salt complexes is expected to increase at low salt concentrations up to a maximum at around [C=O]:[Ag] = 3:1, which is exactly the behavior observed in Figure 5. The smaller increase in T_g observed in Figure 5 for the POZ/$AgNO_3$ complex might result from the lower polymer–silver interaction and higher cation–anion interaction that has been previously verified for this system by FT-IR and Raman spectroscopy.[30]

Comparison of the Interactions of Carbonyl Oxygens with Silver Ions. The extent to which the distance between pendant groups decreases on addition of salt follows the trend $AgCF_3SO_3 < AgBF_4 < AgClO_4$ (see Figure 3). The same trend is seen in the glass transition temperature results in Figure 5, which show that the extent of the increase in T_g follows the order $AgCF_3SO_3 < AgBF_4 < AgClO_4$. This implies that the strength of the interaction between the carbonyl oxygen and silver ion is the lowest for POZ/$AgCF_3SO_3$ and the highest for POZ/$AgClO_4$, within the experimental range considered.

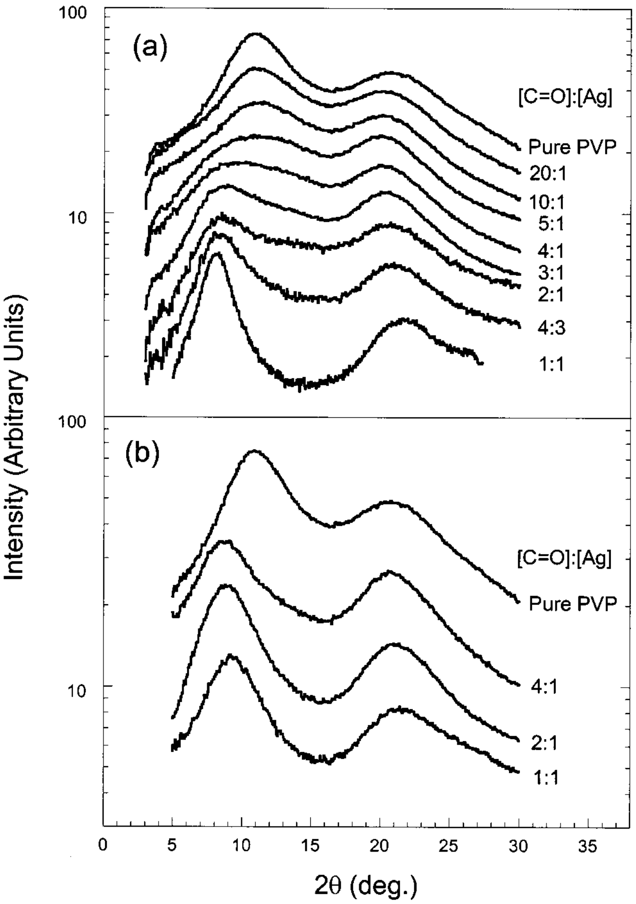

Figure 6. WAXS data of $I(2\theta)$ vs 2θ as a function of silver concentration: (a) PVP/$AgCF_3SO_3$; (b) PVP/$AgBF_4$.

Relationship between Structure and Transport Properties. Polymer electrolyte membranes containing silver salts have been investigated for their potential application to the separation of olefin/paraffin mixtures, as described in the Introduction section. The propylene permeance of POZ/$AgBF_4$ and POZ/$AgCF_3SO_3$ membranes has been found to increase significantly with increasing salt concentration at concentrations above [C=O]:[Ag] = 3:1, whereas these materials did not exhibit facilitated olefin transport behavior at concentrations below [C=O]:[Ag] = 3:1.[8] It was also found that the propylene permeances for 1:1 POZ/$AgBF_4$ and 1:1 POZ/$AgCF_3SO_3$ membranes were almost the same, but the selectivity of POZ/$AgBF_4$ was larger than that of POZ/$AgCF_3SO_3$.

Propylene permeance obviously depends strongly on the structure of the polymer electrolyte. However, propane permeance is more directly related to the structural change that occurs upon incorporation of the silver salt, because propane does not interact with the silver ions. For this reason, measurements were made of the propane permeance through the polymer electrolyte membranes. The propane permeances of the POZ/$AgCF_3SO_3$, POZ/$AgBF_4$, and POZ/$AgClO_4$ membranes with [C=O]:[Ag] = 1:1 were 0.508, 0.316, and 0.007 GPU, respectively. The high permeance of the POZ/$AgCF_3SO_3$ membrane may be associated with the larger free volume in this system, as indicated by its large interchain distance shown in Figure 4.

In summary, the structural change that occurs on incorporation of silver salts into POZ was evident in the propane permeance of the polymer electrolytes. This change in structure will also affect the facilitated propylene permeance.

Structure of PVP and PVP/Ag Salt Complexes. Since PVP also has a pendant group, two peaks ap-

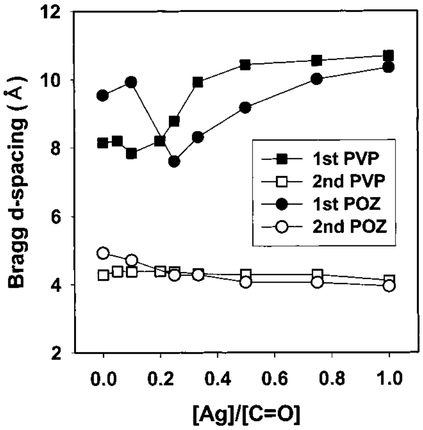

Figure 7. Comparison of the Bragg *d* spacings calculated from the position of both peaks in the *I*(2*θ*) vs 2*θ* plot for PVP/$AgCF_3SO_3$ and POZ/$AgCF_3SO_3$.

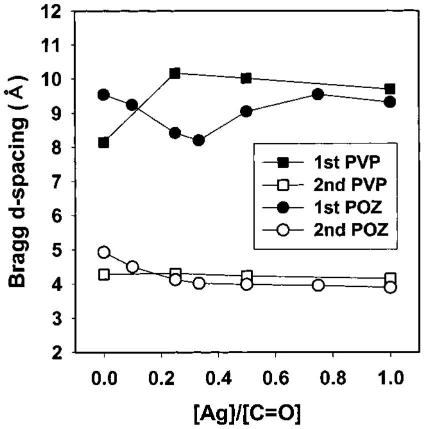

Figure 8. Comparison of the Bragg *d* spacing calculated from the position of both peaks in the *I*(2*θ*) vs 2*θ* plot for PVP/$AgBF_4$ and POZ/$AgBF_4$.

peared in the *I*(2*θ*) vs 2*θ* plot, as shown in Figure 6. The interchain distance between polymer chains and the distance between pendant groups were 8.1 and 4.3 Å, respectively. As the salt concentration increased, the first peak shifted considerably to lower angle while the position of the second peak remained almost unchanged. This implies that the extent to which the anions push the polymer chains apart increases with increasing salt concentration. The distance between pendant groups is expected to decrease with increasing salt concentration, owing to the formation of transient cross-links. However, the difference in the position change of the second peak between the PVP/silver and POZ/silver salt complexes appears to be due to the different silver−polymer interactions in these systems. The silver−polymer interaction is weaker in the PVP/silver salt complexes than the POZ/silver salt complexes, possibly due to the greater steric hindrance of the large pendant group of PVP in comparison to the more flexible POZ pendant group. The narrower first and second peaks for the PVP/$AgCF_3SO_3$ at high silver concentrations seen in Figure 6 are indicative of a more ordered structure of polymer chains and pendant groups compared to pure PVP.

Effect of Polymer Matrix on the Structural Change. The Bragg *d* spacings for POZ and PVP doped with $AgCF_3SO_3$ or $AgBF_4$ are compared in Figures 7 and 8. The interchain distance and the distance between pendant groups of the PVP/silver and POZ/silver salt complexes approach similar values at high salt concentrations, suggesting similar structures in these systems. This result is consistent with previous reports, which showed that the facilitated transport properties of polymer electrolyte membranes containing silver ions were independent of the polymer matrix at high concentrations of silver salt.[8]

Conclusions

The WAXS spectra of both POZ and PVP showed two broad amorphous peaks, where the first peak was assigned to the interchain distance and the second to the distance between the pendant groups of the polymer chains. The shift in these peaks upon incorporation of silver salt into the polymer matrix differed between POZ and PVP. The general trend observed was the contraction of the polymer chains as the strength of the interaction between the pendant groups increased due to the coordination of the silver ions to the carbonyl oxygens in the pendant group of the polymer chains. When the distance between the pendant groups was almost constant, the interchain distance increased. The polymer chains showed a considerably ordered structure at the highest salt concentration studied ([C=O]:[Ag] = 1:1). The decrease in the distance between pendant groups seems to be due to the formation of transient cross-links associated with the coordination interaction of silver ions with carbonyl oxygens, whereas the increase in the interchain distance is possibly due to the anions pushing the polymer chains apart. The extent of the decrease in the distance between the pendant groups, calculated from the second peak, was in the order $AgCF_3SO_3 < AgBF_4 < AgClO_4$. This behavior, which reflects the interactions between the silver ions and carbonyl oxygens in the different polymer electrolytes, is consistent with the trends both in the glass transition temperature and in the propane permeability.

The *d* spacings of the POZ/silver and PVP/silver salt systems approach a similar value at high silver concentrations. This is a key factor in explaining why the facilitated transport properties in the POZ/silver and PVP/silver salt systems are almost identical at the silver concentration of [Ag]:[C=O] = 1:1. Therefore, the transport properties of both propane and propylene through POZ/Ag and PVP/Ag salt complex membranes were found to strongly depend on the structural change of the polymer matrix upon incorporation of the silver salt.

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