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Revelation of Facilitated Olefin Transport through Silver-Polymer Complex Membranes Using Anion Complexation

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ABSTRACT: Polymer complex membranes containing $AgNO_3$ dissolved in a polymeric solvent do not exhibit facilitated olefin transport *in the solid state* due to strong interaction between the silver ion and its counteranion. However, we successfully made $AgNO_3$ as an active olefin carrier upon incorporation of positively charged polypyrrole (PPy) into a polymer solvent such as poly(*N*-vinylpyrrolidone) (PVP) or poly(2-ethyl-2-oxazoline) (POZ). Upon addition of positively charged PPy into polymer/$AgNO_3$ complex membranes, the interaction of the silver cation with the nitrate anion was weakened because of nitrate anion complexation by positively charged PPy. This was confirmed by FT-IR and X-ray photoelectron spectroscopy. The enhanced carrier activity of $AgNO_3$ in PVP or POZ with PPy is attributable to complexation of NO_3^- with positively charged PPy, which led to a weak interaction between Ag^+ and NO_3^-.

Introduction

Low molecular weight olefins, such as ethylene and propylene are important feedstocks with wide uses in production of polymers, acids, alcohols, esters, and ethers. Olefins are mainly produced by cryogenic distillation of olefin/paraffin mixtures. Because cryogenic distillation has a significant disadvantage that it requires intensive energy consumption, the development of an alternative energy-saving separation process has been in high demand.[1−6]

Facilitated transport has been receiving tremendous attention as a potential energy-saving separation technology, because it can simultaneously improve the permeability and selectivity of a membrane.[7−11] These two factors are commonly in conflict for ordinary polymeric membrane materials. Facilitated transport is defined as a transport phenomenon in a membrane with carriers by means of coupled diffusion and reaction. In this the carrier forms a reversible complex with a specific component, thereby increasing the transport rate of the component relative to others. Various types of facilitated transport membranes such as supported liquid membranes or ion exchange membranes have been investigated for olefin/paraffin separation.[12−17] However, these membranes often exhibit critical problems for industrial applications mainly due to operational instability caused by evaporation of the liquid media.

Recently solid silver−polymer complex membranes have been developed by dissolving silver salts of low lattice energy in a polymer matrix via coordination bond, and they are successfully used as facilitated olefin transport membranes in the solid state.[18−32] Silver−polymer complex membranes containing $AgBF_4$ or $AgCF_3SO_3$ dissolved either in poly(2-ethyl-2-oxazoline) (POZ), in poly(*N*-vinylpyrrolidone) (PVP) or in poly(ethylene oxide) (PEO) exhibit facilitated olefin transport, resulting in high olefin separation performance from its mixture with paraffin.[18−24] For example, a thin composite membrane comprising $AgBF_4$ dissolved in POZ or PVP is approximately 15 000 times more permeable to propylene than propane in pure gas permeation because of the reversible complexation between the silver ion and propylene; the facilitated propylene transport. However, polymer complex membranes containing $AgNO_3$ do not show the facilitated olefin transport *in the solid state*.[23−27] Such a difference in the facilitated olefin transport seems to be ascribed to the difference in the interaction between silver ion and its counteranions.

The reversible complexation of olefin with silver ion determines the facilitated olefin transport, which directly depends on the interactions of the silver with its counteranion and with polymer.[27] A silver ion interacts weakly with an anion of large size and low lattice energy such as BF_4^-, $CF_3SO_3^-$, or ClO_4^-,[28] readily interacts with olefin to make reversible olefin−silver complexes, and becomes a good olefin carrier for facilitated olefin transport. On the other hand, small-sized and highly electronegative anions having high lattice energies such as F^-, Cl^- or NO_3^- hinder the silver−olefin complexation due to the strong electrostatic interaction between the silver ion and small-sized anions, resulting in no facilitated olefin transport.[28] Thus, it is anticipated that the silver−polymer complex membranes containing $AgNO_3$ can show the facilitated olefin transport when the interaction of Ag^+ with NO_3^- is properly controlled by anion complexation.

Positively charged polypyrrole (PPy) is doped with sulfuric acid (H_2SO_4) to interact electrostatistically with nitrate anion.[33−35] Therefore, the interaction intensity of Ag^+ with NO_3^- can be manipulated by the anion complexation with positively charged PPy. On the basis of the anion complexation, we are successful in making

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$AgNO_3$ as an active olefin carrier for facilitated olefin transport. The separation performance of propylene/propane mixtures was first evaluated through polymer/$AgNO_3$ complex membranes with and without PPy. Then the interactions of silver ion with carbonyl oxygens of polymer matrix and with propylene were characterized by FT-IR and X-ray photoelectron spectroscopy (XPS) to elucidate the physical principles of facilitated olefin transport.

Experimental Section

Poly(2-ethyl-2-oxazoline) (POZ) ($M_w = 5 \times 10^5$ g/mol) and all silver salts, including silver nitrate ($AgNO_3$, 99.9%), silver tetrafluoroborate ($AgBF_4$, 98%), and silver triflate ($AgCF_3SO_3$, 99+%) were purchased from Aldrich Chemical Co. Poly(*N*-vinylpyrrolidone) (PVP) ($M_w = 1 \times 10^6$) was supplied by Polyscience Inc. A 5 wt % solution of polypyrrole (PPy) doped with surfuric acid in water was purchased from Aldrich. All chemicals were used without further purification. Polymer solutions were prepared by dissolving the predetermined amounts of PVP and PPy to make 20 wt % polymers in water. After the solution was stirred for an hour, silver nitrate was added to maintain the mole ratio of [C=O]:[Ag] = 1:1 for preparing the casting solution. The homogeneous solution was then cast on a silicone wafer and dried at room temperature under N_2 environment. The films were further dried in a vacuum oven for 2 days at room temperature. IR measurements were performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64−200 scans were signal-averaged at a resolution of 2 cm^{-1}. IR spectroscopic characterization was performed using a pressure cell equipped with CaF_2 window. For the gas permeation test, the casting solution was coated onto an asymmetric microporous polysulfone substrate (Seahan Industries Inc., Seoul, Korea) using a RK control coater. After evaporation of solvent in a convection oven at room temperature under nitrogen, the membrane was dried completely in a vacuum oven for 2 days at room temperature. The thickness of the top coated layer was ca. 1 μm and the pressure difference was 276 kPa. Mixed gas (50:50 vol % of propylene/propane mixture) separation properties of the membranes were measured by bubble flow meter and gas chromatography (Hewlett-Packard G1530A, MA) equipped with a TCD detector. AFM measurement was carried out using scanning probe microscope (Nanoscope IIIa, Digital Instruments) operating in tapping mode. XPS was measured using a VG Scientific ESCALAB 220 spectrometer equipped with a hemispherical energy analyzer. The nonmonochromatized Al Kα X-ray source ($h\nu = 1486.6$ eV) was operated at 12.5 kV and 16 mA. Before data acquisition, the samples were degassed for 3 h at 298 K under a pressure of about 1.0×10^{-9} Torr to minimize the surface contamination.

Results and Discussion

The permeation test through PVP/$AgNO_3$ membranes containing PPy was carried out using the 50:50 propylene:propane gas mixtures. The gas transport properties were plotted against PPy concentration as shown in Figure 1, where the Py stands for the repeating unit of PPy. The mole ratio of the carbonyl oxygen to the silver ion was fixed at 1. PVP/$AgNO_3$ membranes without PPy exhibited extremely low gas permeation and inseparable property of propylene/propane mixtures; mixed gas permeance is ca. 0.1 GPU (1 GPU = 1 $\times 10^{-6}$ cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$) and the selectivity of propylene/propane is nearly unity. Both the propylene permeance and the selectivity increased gradually with increasing amount of PPy, while the propane permeance continuously decreases from 0.136 to 0.016 GPU. Propane is unable to form complexes with silver ions and permeates only through Fickian transport. The reduced propane permeance could be due to the barrier effect of PPy.

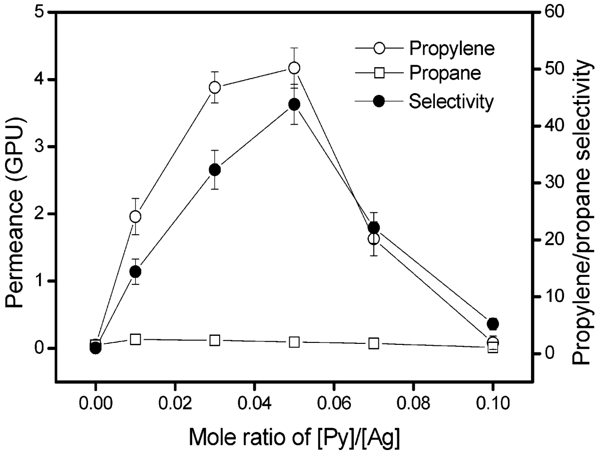


Figure 1. Effect of PPy on the gas permeance and the selectivity of propylene/propane for 1:1 PVP/$AgNO_3$ membranes.

Meanwhile, the propylene permeance increased with the PPy concentration up to a mole ratio of Py to Ag^+ of 0.05. The enhanced propylene transport may be explained by the favorable reversible complexation of propylene with silver ions. This is possible because of the weakened interaction of Ag^+ and NO_3^- compensated by the electrostatic interaction between the positively charged PPy and NO_3^- anion. This result obviously represents that PPy plays an essential role in the reversible complexation between the silver ion and propylene. It is worth noting that the gas permeance and the selectivity intriguingly decreased with the PPy concentration above a mole ratio of Py to Ag^+ of 0.05. This may be considered to be caused by the heterogeneity or defect formation due to the miscibility limitation between three components including two polymers and the silver salt.

The topographical and phase images of PVP/$AgNO_3$ membranes without and with two concentrations of PPy are shown in Figure 2. PVP/$AgNO_3$ complex membranes with and without the mole ratio of Py to Ag^+ of 0.05 exhibit continuous and homogeneous phase, but that with a mole ratio of 0.1 exhibits the phase-separated microdomain structure. Thus, the segregation between the components would deteriorate the optimum environment for propylene−silver complex formation.

The separation performance through POZ/$AgNO_3$ membranes, instead of PVP, containing various concentrations of PPy was also measured (data not shown here). Similar results were obtained for this. Both the propylene permeance and the selectivity of propylene/propane simultaneously increase with increasing concentration of PPy up to a mole ratio of 0.05 but above that decrease, as with the PVP/$AgNO_3$/PPy membranes.

The microstructural change of the PVP/$AgNO_3$ complex by the addition of PPy was investigated spectroscopically. FT-IR spectra for pure PVP and PVP/$AgNO_3$ complex with and without PPy are shown in Figure 3. The mole ratio of [Py]/[Ag^+] was fixed at 0.05, which is the optimum composition of PVP/$AgNO_3$/PPy complexes for the facilitated propylene transport. When PPy was added to pure PVP, the shape and position of C=O stretching band at 1660 cm^{-1} was invariant, indicating the negligible specific interaction between C=O of PVP and PPy. Upon incorporation of $AgNO_3$ into PVP, the C=O stretching band shifted from 1660 to 1638 cm^{-1}, presumably due to the C=O double bond loosened by the coordinative interaction between the silver ion and

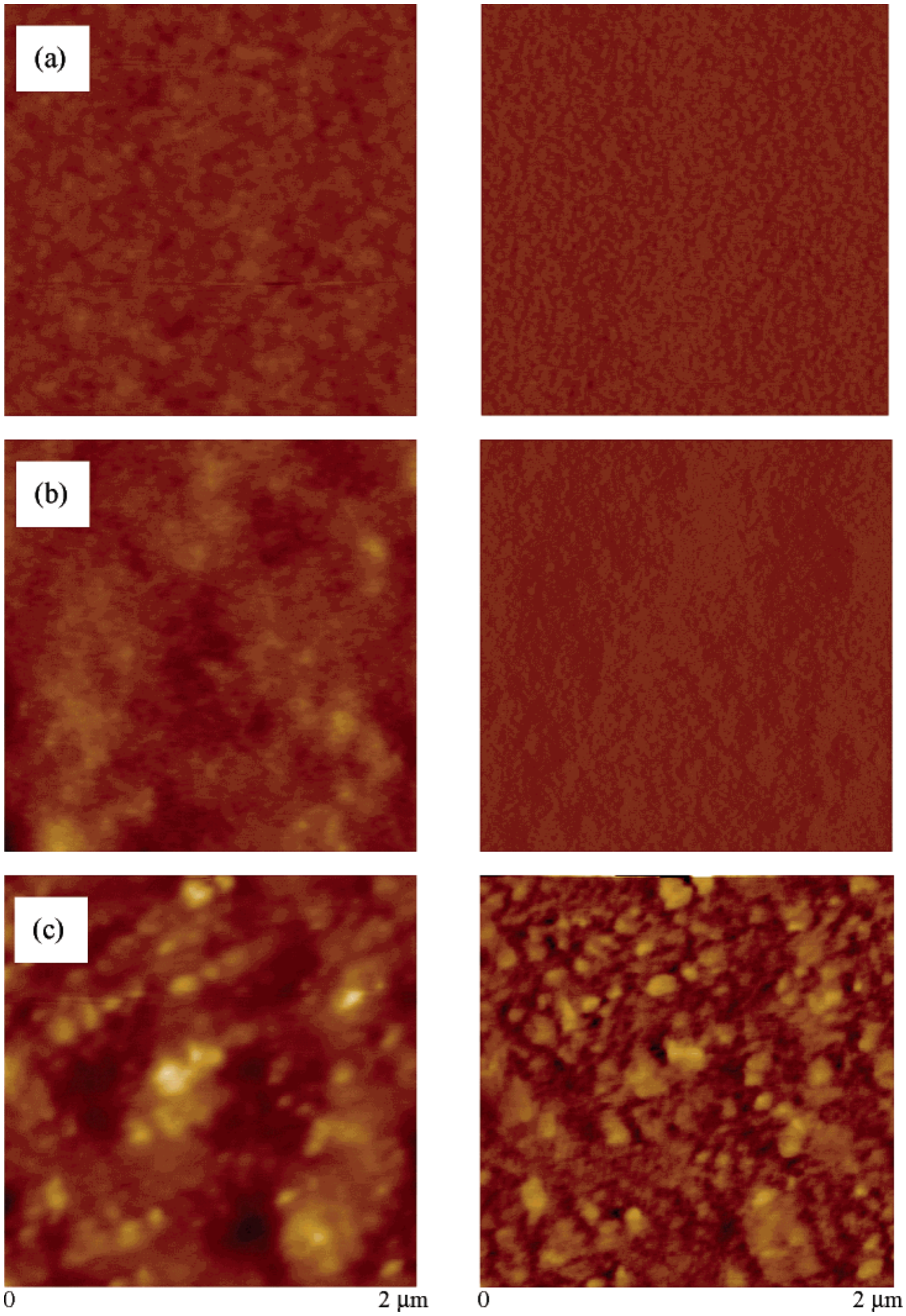


Figure 2. AFM images of (a) 1:1 PVP/$AgNO_3$, (b) 1:1:0.05 PVP/$AgNO_3$/PPy, and (c) 1:1:0.1 PVP/$AgNO_3$/PPy membranes. Left and right are topographical and phase images, respectively.

the carbonyl oxygen of PVP. The further shift of the C═O stretching band from 1638 to 1633 cm^{-1} was observed when PPy was added in the PVP/$AgNO_3$ complex. Such changes in the C═O bond strength may result from the fact that the nitrate anions are pulled up from the silver ions by the positive charge of PPy resulting in the anion complexation and thereby making the interaction between silver cation and the counteranion weak.

The change of the chemical environment around silver ions in polymer/silver complexes with and without PPy was observed by XPS. Figure 4 shows the Ag $3d_{5/2}$ regions of XPS spectra for $AgNO_3$, PVP/$AgNO_3$, and PVP/$AgNO_3$/PPy complexes. The Ag $3d_{5/2}$ spectrum of pure $AgNO_3$ shows a peak at 371.7 eV, which is higher than the corresponding value (369.2 eV) of $AgBF_4$,[32] the most effective olefin carrier.[25−27] The higher value of silver binding energy in $AgNO_3$ is attributed to the stronger interaction between Ag^+ and NO_3^- ion, compared to that in $AgBF_4$. The dissolution of $AgNO_3$ in PVP matrix induce a decrease in silver binding energy from 371.7 to 368.7 eV due to the coordination of the silver ion by the carbonyl oxygen ligands in PVP. When PPy was added to the PVP/$AgNO_3$ complex, the Ag $3d_{5/2}$ peak shifted further to a lower binding energy of 368.4 eV, attributable to the fact that the pulling up of nitrate anions by the positive charge of PPy; i.e., the anion complexation renders the interaction between silver cation and counteranion weaker.

The complexation of propylene with silver cation in PVP/$AgNO_3$ complexes with and without PPy was also investigated by IR spectroscopy. When the 1:1:0.05 PVP/

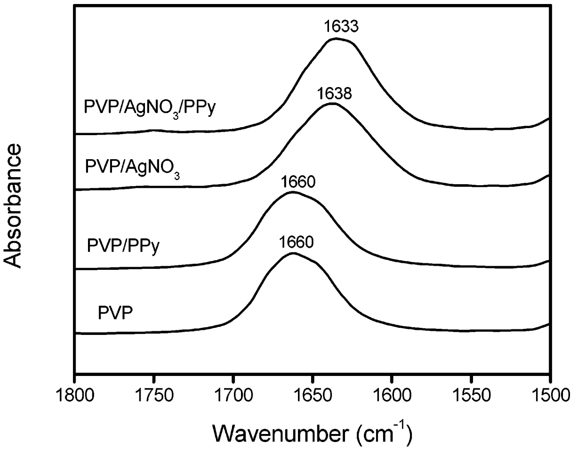


Figure 3. FT-IR spectra of PVP, PPy/PVP, 1:1 PVP/$AgNO_3$ and 1:1:0.05 PVP/$AgNO_3$/PPy complexes.

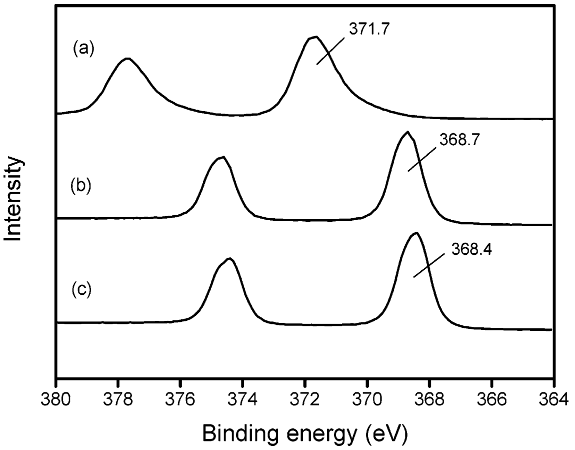


Figure 4. Ag $3d_{5/2}$ XPS spectra of (a) $AgNO_3$, (b) 1:1 PVP/$AgNO_3$, and (c) 1:1:0.05 PVP/$AgNO_3$/PPy complexes.

$AgNO_3$/PPy complex was exposed to propylene at 551 kPa for 1 h and subsequently purged with N_2, the C=O band shifted from 1633 to 1640 cm^{-1} and a new shoulder band at 1586 cm^{-1} appeared, as seen in Figure 5a. This new shoulder peak represents the C=C stretching vibration of propylene coordinated to silver ion (ν_1 and ν_2 of C=C in free propylene are 1665 and 1640 cm^{-1}, respectively). The frequency shift of the C=O band from 1633 to 1640 cm^{-1} upon propylene sorption indicates that the interaction between silver ions and carbonyl oxygens becomes weaker by the coordination of propylene to silver ions. This result strongly represents that the propylene molecules compete with the carbonyl oxygens of PVP for the coordination sites of the silver ion. On the other hand, no different spectra were observed in PVP/$AgNO_3$ without PPy between before and after propylene sorption, implying negligible specific complexation of propylene with silver ion as shown in Figure 5b.

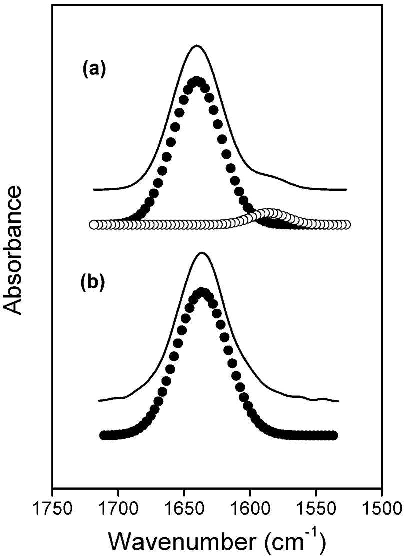


Figure 5. Deconvoluted FT-IR spectra of 1:1 PVP/$AgNO_3$ complexes after propylene sorption (a) with and (b) without PPy. Filled circles are for the C=O stretching of PVP, and open circles are for the C=C stretching of propylene complexed with silver ions.

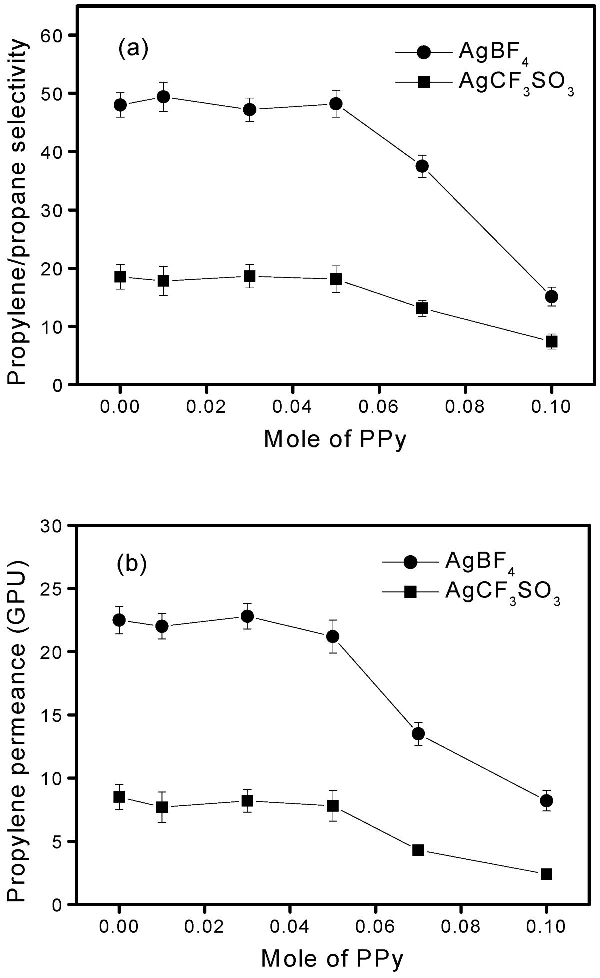
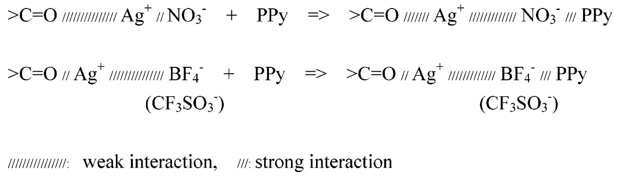


Figure 6. Effect of PPy on (a) the selectivity of propylene/propane and (b) the propylene permeance for 1:1 PVP/Ag salt membranes.

The positively charged PPy is doped with sulfuric acid (H_2SO_4). To investigate the possible effect of the anion (SO_4^{2-}) on transport properties, the PVP/$AgNO_3$ membrane containing sulfuric acid was prepared. The elemental analysis of PPy doped with surfuric acid reveals that the mole ratio of surfuric acid to Py is 0.032. So, the PVP/$AgNO_3$ membrane containing the same amount of sulfuric acid was prepared and tested for the separation of propylene/propane gas mixtures. The mixed gas permeance is below 0.1 GPU, and the selectivity is nearly unity, clearly indicating that the presence of sulfuric acid is hardly effective in controlling the facilitated olefin transport.

The separation performance of olefin/paraffin mixtures was also evaluated through polymer/$AgBF_4$ and

Scheme 1



polymer/$AgCF_3SO_3$ complex membranes containing positively charged PPy to investigate the effect of counteranion of salts. The mixed gas permeance and the selectivity through the membranes as a function of PPy concentration are plotted and shown in Figure 6. As seen, the presence of PPy hardly improves the separation performance in the membranes that exhibited the facilitated olefin transport originally. In addition, the permeance and the selectivity simultaneously decreased at PPy concentrations above a mole ratio of Py to silver of 0.05, possibly due to the miscibility limitation between the components. This is similar to the results of polymer/$AgNO_3$ membranes containing PPy. It is very characteristic that PPy plays an effective role only in the polymer/$AgNO_3$ membranes but not in $AgBF_4$ and $AgCF_3SO_3$ membranes.

In brief, the effects of PPy on the coordinative interaction in polymer/silver complexes are schematically illustrated in Scheme 1. Polymer/$AgNO_3$ complex exhibits the weak interaction of polymer/silver ion and strong one of silver ion/anion. Upon addition of PPy in the polymer/$AgNO_3$ complex, the interaction of silver ion/anion becomes weaker and that of polymer/silver ion gets stronger, as evidenced by FT-IR and XPS. Thus, the activity of silver ion as olefin carrier increases with the PPy concentration, resulting in facilitated olefin transport. However, in the cases of the weak interaction of silver ion/anion such as polymer/$AgBF_4$ or polymer/$AgCF_3SO_3$ complexes,[18,27] PPy is hardly effective in the further enhancement of the facilitated olefin transport.

Conclusions

The addition of PPy into polymer/$AgNO_3$ complex membranes induced changes in the chemical environment of the silver ions, resulting in the facilitated propylene transport. The propylene permeance and the mixed gas selectivity of propylene/propane increased from ca. 0.1 to 4 GPU and about 1 to 40, respectively, when a 0.05 mole ratio of [Py]/[Ag] was added to the PVP/$AgNO_3$ or POZ/$AgNO_3$ complex membranes. This enhanced separation performance may be attributed predominantly to the pulling up of NO_3^- anions from Ag^+ by the complexation of NO_3^- with positively charged Py unit, as confirmed by FT-IR and XPS.

As far as we know, it is the first research to observe the facilitated olefin transport for $AgNO_3$-based polymer membranes in the solid state. We showed that the activity of silver ion could be greatly enhanced if the interaction of silver ion with counteranion is weakened sufficiently. The separation performance for PVP/$AgNO_3$/PPy membrane was not notably higher than other simple systems, e.g. PVP/$AgBF_4$ or POZ/$AgBF_4$ membranes. However, we could manipulate the competitive ionic interaction strength by giving a secondary source of positively charged PPy, thus providing a route to improve silver ion activity in silver polymer electrolytes. Thus, we believe that this work provides a significant contribution to the development of silver polymer electrolyte membranes for facilitated transport, as well as shedding new light on the complexation structure of solid polymer/metal complexes.

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