Role of Polymer Matrix in Polymer/Silver Complexes for Structure, Interactions, and Facilitated Olefin Transport

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ABSTRACT: The role of the polymer matrix in facilitated olefin transport through polymer/silver salt complex membranes was investigated, particularly its influence on the structure and interactions of polymer/silver salt complexes and hence on the interactions of silver ions with olefin molecules. This role was assessed for complexes of silver salts with polymeric ligands containing three different carbonyl groups, specifically, amide, ketone, and ester groups. It was found that the threshold concentration of silver salt for facilitated olefin transport depends on the polymeric ligand and has the following order: amide > ketone > ester. This dependence of the threshold concentration on the polymeric ligand is explained in terms of the differences between the comparative strengths of the interactions of silver ions with the different carbonyl oxygens and that of silver ions with olefin molecules. It is concluded that when the former interaction is stronger than the latter, the threshold concentration for facilitated olefin transport is high, and when the former interaction is weaker than the latter, the threshold concentration for facilitated olefin transport is low. These interactions were characterized experimentally using differential scanning calorimetry, X-ray photoelectron spectroscopy, and FT-IR and Raman spectroscopy.

Introduction

The separation of olefin/paraffin mixtures is very important in the petrochemical industry. At present, it is mostly carried out by cryogenic distillation processes that require enormous capital investment and have high operational costs. The difficulty of separating olefins and paraffins in mixtures such as propylene/propane and ethylene/ethane, which have very similar boiling points, means that expenditure on the separation process is approximately 75% of the total olefin production cost. Other technologies such as membrane separation or reactive absorption have received much attention for both economic and environmental reasons.[1−6]

Facilitated transport has been receiving tremendous attention as a potential energy-saving separation technology because it can simultaneously improve both the permeability and selectivity of a membrane.[7−11] Various types of facilitated transport membrane such as supported liquid membranes or ion-exchange membranes have been investigated for use in olefin/paraffin separation.[12−17] However, these membranes often exhibit critical problems in industrial applications, mainly due to operational instabilities caused by evaporation of the liquid media.

Recently, polymer/silver salt complex membranes have been identified as the most promising alternative because they exhibit remarkably high performance in the separation of olefin/paraffin mixtures in the solid state.[18−28] Upon incorporation of $AgBF_4$ into poly(2-ethyl-2-oxazoline) (POZ) or into poly(*N*-vinylpyrrolidone) (PVP) at a concentration of [C═O]:[Ag] = 1:1, the propylene permeance and the ideal separation factor of propylene over propane were found to increase remarkably, from 0.05 to 45 GPU [1 GPU = 1.0×10^{-6} cm^3 (STP)/(cm^2 s cmHg)] and from nearly 1 to 15 000, respectively.[18] This extremely high separation performance results from the high loading of silver ions into the polymer matrix and their fast and reversible complexation with olefin molecules.[18]

In a series of previous studies, we obtained results that shed light on the mechanism of facilitated olefin transport through silver polymer electrolyte membranes.[19−22] The gas transport properties of these membranes were found to be sensitive both to the interaction of the olefin molecules with the polymer electrolytes and to structural changes in the polymer electrolytes themselves; the changes in transport behavior with changes in the structures of the polymer electrolytes were found to be associated with (1) the coordination number of the silver cation along with transient cross-links, (2) the length of the bond between the silver ion and its anion, and (3) the size of the anion.[19] It was additionally found that $AgBF_4$ polymer electrolytes have strong silver cation/carbonyl oxygen interactions and weak silver cation/anion interactions and hence exhibit more effective silver cation complexation of propylene molecules, resulting in higher propylene solubility.[20] All silver salts are completely dissolved into free ions in an olefin environment, resulting in complexes of the silver cations with the olefin molecules, suggesting that olefin molecules are good ligands for silver salts.[21] From these experimental findings, a new mechanism for the complexation reaction between propylene and silver salts in silver polymer electrolytes was proposed. The existence of a threshold concentration was attributed to the following observations:[22] (1) the most favorable coordination number for silver ions in polymer electrolytes in a propylene environment is 3, and (2) the interactions between silver ions and carbonyl oxygens are marginally stronger than those between silver ions and olefin molecules. It was thus proposed that a silver ion can act as an olefin carrier only when it has vacant coor-

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dination sites, i.e., when the number of carbonyl oxygens coordinated to the silver ion is less than 3.

According to previous research,[20,23,28] facilitated olefin transport is strongly dependent upon the properties of the anionic constituents of the silver salts. Large and weakly electronegative anions such as BF_4^-, $CF_3SO_3^-$, and ClO_4^- form silver salts with low lattice energies[29] that are good olefin carriers and so enable facilitated olefin transport. On the other hand, small and highly electronegative anions such as F^-, Cl^-, and NO_3^- form silver salts with high lattice energies,[29] hindering olefin−silver complexation, and so do not exhibit facilitated olefin transport. However, there has been little systematic research into the role of the polymer matrix in the formation of olefin/silver cation complexes and in facilitated olefin transport in general.

Polymer matrices with carbonyl oxygens have usually been used in polymer/silver salt complex membranes in order to dissolve the silver salt. In this study we investigated the influence of the polymer matrix on the structural properties of polymer/silver salt complex membranes as well as on their facilitated olefin transport. Polymers with three kinds of carbonyl group, i.e., the ester groups in poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA), the ketone groups in poly(vinyl methyl ketone) (PVMK), and the amide groups in poly(2-ethyl-2-oxazoline) (POZ) and poly(*N*-vinylpyrrolidone) (PVP), were studied.

Experimental Section

The polymers PMMA ($M_w = 3.5 \times 10^5$), PBMA ($M_w = 3.37 \times 10^5$), PVMK ($M_w = 5 \times 10^5$), and POZ ($M_w = 5 \times 10^5$) and the silver salts silver tetrafluoroborate ($AgBF_4$, 98%) and silver trifluoromethanesulfonate (AgTF, $AgCF_3SO_3$, >99%) were purchased from Aldrich Chemical Co. PVP ($M_w = 1 \times 10^6$) was purchased from Polysciences. All chemicals were used as received. The silver salts were dissolved in 20 wt % polymer solution in methanol (for POZ and PVP) or tetrahydrofuran (for PMMA, PBMA, and PVMK). The amounts of added salt were determined in order to obtain the desired mole fractions of silver salt. The solution was then cast on a Teflon-glass plate and dried under nitrogen. The resulting films were further dried in a vacuum oven for 2 days at room temperature to remove residual solvent.

IR measurements were performed on a Mattson Galaxy 6030 spectrometer; 64−200 scans were signal-averaged at a resolution of 2 cm^{-1}. Raman spectra for the polymer/silver salt complexes were recorded at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman. 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 pressure cell equipped with CaF_2 windows. A Perkin-Elmer DSC-7 was used to measure the glass transition temperatures of the complexes at a heating rate of 20 °C/min in an N_2 environment. X-ray photoelectron spectroscopy (XPS) was carried out 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 in order to minimize surface contamination.

Gas permeation experiments were carried out using a constant pressure/variable volume method. For the gas permeation test, the polymer solution was coated onto a microporous polysulfone substrate (Seahan Industries Inc., Seoul, Korea) or a polyester substrate (Whatman, 0.1 μm) using an RK control coater. After evaporation of the 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 mixed gas (a 50:50 vol % propylene/propane mixture) separation performance of the membranes was evaluated by gas chromatography (Hewlett-Packard G1530A) equipped with a TCD detector. The stage cut (θ), i.e., the ratio of permeate to feed flow rates, was always less than 2%. The unit of gas permeance is GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cmHg).

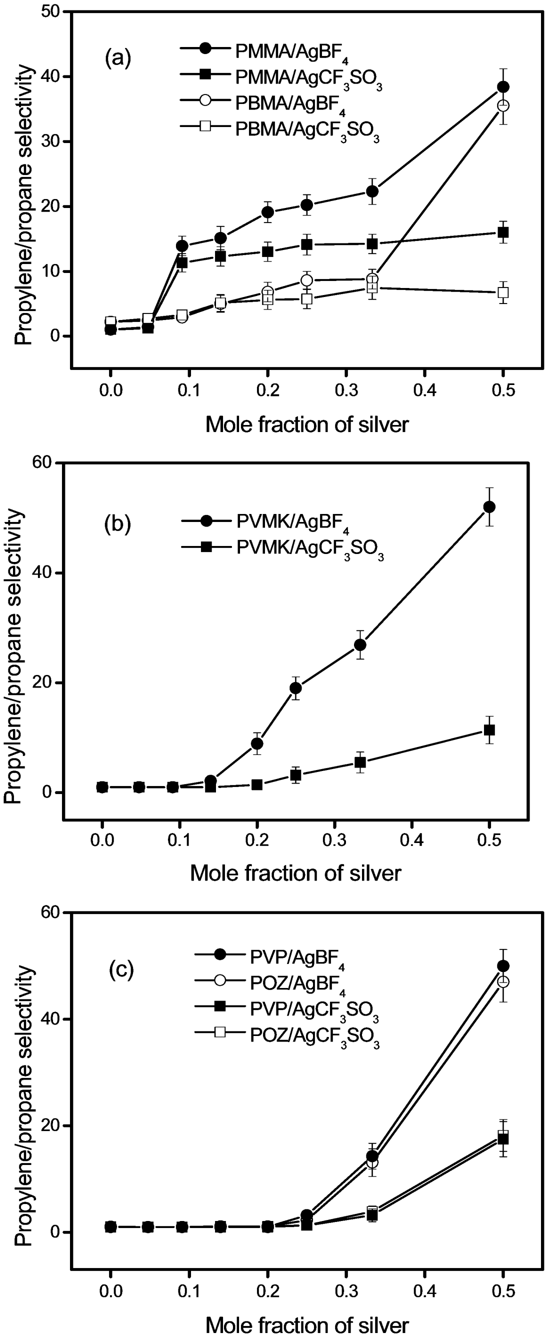

Figure 1. Selectivity of propylene/propane through polymer/silver salt complex membranes as a function of the silver salt concentration: (a) ester ligands, (b) ketone ligands, and (c) amide ligands.

Results and Discussion

Facilitated Olefin Transport. The separation of propylene/propane mixtures using polymer/silver salt complex membranes was evaluated for three kinds of electron-donating carbonyl oxygen ligands: ester, ketone, and amide groups. The separation performance was found to strongly depend on the characteristics of the ligand as well as on the nature of the anion of the silver salt. Figure 1 shows the selectivity of propylene

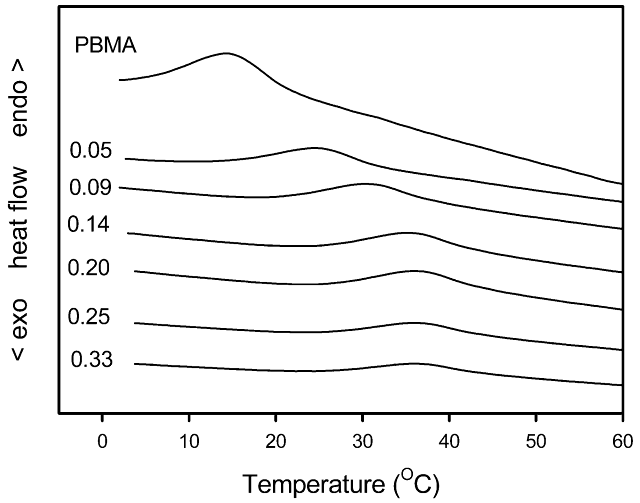

Figure 2. DSC thermograms of PBMA/$AgCF_3SO_3$ complexes for various mole fractions of silver salt.

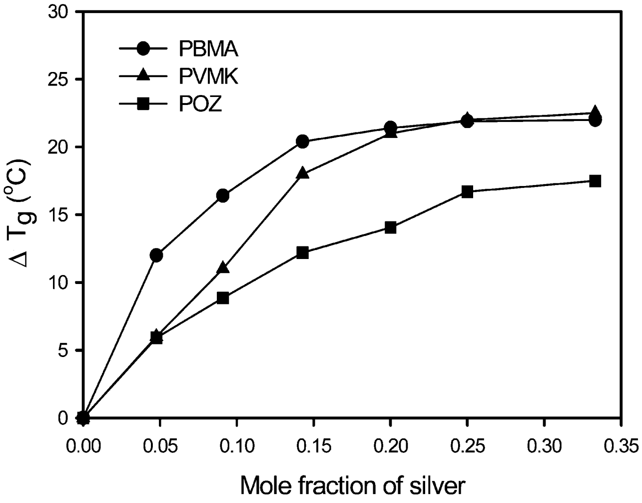

Figure 3. Variations of ΔT_g for polymer complexes with $AgCF_3SO_3$ as a function of silver salt concentration.

over propane as a function of the silver salt concentration. The PMMA and PBMA membranes (i.e., those with ester groups) exhibit a low onset silver salt concentration (a silver mole fraction of 0.09) for facilitated olefin transport, whereas the POZ and PVP membranes (i.e., those with amide groups) exhibit a higher onset concentration (a silver mole fraction of 0.25). PVMK membranes (with ketone groups) exhibit an intermediate onset concentration (a silver mole fraction of 0.14). In summary, the onset concentration for facilitated propylene transport is relatively low for ester ligands, medium for ketone ligands, and high for amide ligands. It was also found that the effect of using different polymer matrices on transport properties is negligible if these polymers have the same ligands. In other words, PBMA has nearly the same onset concentration as PMMA and POZ has nearly the same onset concentration as PVP. Further, the separation performance of a membrane containing $AgBF_4$ was found to be always higher than a membrane containing $AgCF_3SO_3$ for a given polymer matrix. The dependence of facilitated propylene transport on the nature of the polymeric ligand is discussed below in relation to the structural properties of the polymer/silver salt complexes and the relative strengths of the interactions of silver ions with polymeric ligands and those with the counteranions.

Structural Changes in the Polymer Matrices Due to Silver Salt Incorporation. Previously, we demonstrated that facilitated transport using polymer/silver salt complexes is strongly dependent on the structural properties of the polymer such as the chain rigidity and the free volume.[19,22] The glass transition temperatures of PBMA/$AgCF_3SO_3$ complexes with various mole fractions of silver salt were obtained from DSC thermograms (see Figure 2) as a measure of the chain rigidity. The value of T_g initially increases with increasing silver salt concentration and then remains invariant above a certain concentration, which is a common feature of polymer/metal salt complexes.[30−34] The variations of T_g and ΔT_g (= $T_{g,\text{complex}} - T_{g,\text{polymer}}$) for the three polymer/$AgCF_3SO_3$ complexes with silver salt concentration are compared in Figure 3. It is seen that both the initial rate of increase with respect to composition and the composition at which an invariant value is reached are dependent on the polymer matrix. Compared to POZ complexes, PBMA complexes have a higher initial rate of increase and a lower silver salt concentration at which an invariant T_g is reached. The complexes of PVMK exhibit behavior intermediate between those of PBMA and POZ. We have previously determined that the variation of ΔT_g with silver salt concentration depends on the intensity of the interaction of the silver ion with the ligand and thus on the transient cross-links by silver ions,[19,22] which is consistent with the results presented here.

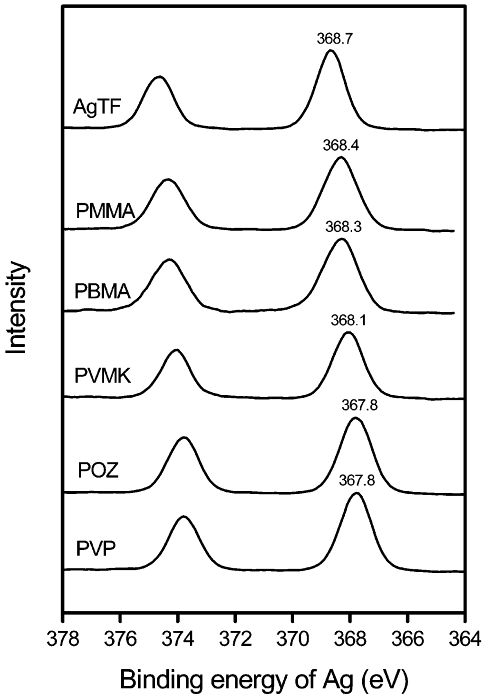

Figure 4. Ag $3d_{5/2}$ XPS spectra of pure $AgCF_3SO_3$ and various polymer/$AgCF_3SO_3$ complexes at a silver mole fraction of 0.33.

Interactions of the Polymeric Ligands with Silver Ions. The Ag $3d_{5/2}$ regions of the XPS spectra of polymer/silver salt complexes are very sensitive to the chemical environment around the silver ions, particularly to the electron-donating ability of the polymeric ligand and to the strength of the interaction between the silver ion and the polymeric ligand. Figure 4 shows the Ag $3d_{5/2}$ regions of the XPS spectra of pure $AgCF_3SO_3$ and of the polymer/$AgCF_3SO_3$ complexes. The Ag $3d_{5/2}$ spectrum of pure $AgCF_3SO_3$ exhibits a single peak at 368.7 eV. However, the dissolution of a silver salt in a polymer matrix with carbonyl oxygen groups results in a decrease in the silver salt binding energy, presumably due to the coordination of the silver ions with the carbonyl oxygens. Thus, the electron-donating ability of each polymeric ligand can be estimated from the magnitude of the peak shift that occurs when the silver salt is dissolved in the polymer matrix.[20] The Ag $3d_{5/2}$ peak positions in the XPS spectra of the polymer/$AgCF_3SO_3$ complexes shown in Figure 4 imply that the extent of peak shift (i.e., toward a lower silver binding energy) has the following sequence: POZ, PVP > PVMK > PMMA, PBMA. It is therefore concluded that (1) the electron-donating ability of the ligands has the order amide > ketone > ester and (2) the strength of the interaction between the ligand and silver ion has the same order.

Dissolution of Silver Salts. The electron-donating ability of a polymeric ligand with respect to a given silver salt determines the identity of the ionic constituents of the polymer/silver salt complex (i.e., free ions, ion pairs, and higher-order aggregates) because it has a direct bearing on the strength of the interactions of the silver ions with the polymeric ligands and with the counteranions. For instance, free ions are more likely to form on dissolution of a silver salt in a polymer solvent when the electron-donating ability of the polymeric ligand is high and thus the interaction between the silver ion and the anion is weakened. Assessing the strength of these interactions is therefore important for the characterization of the ionic constituents and consequently for understanding the interaction between silver ions and olefin molecules. The FT-Raman spectra of polymer complexes with $AgCF_3SO_3$ were obtained as a function of the silver mole fraction. Figure 5 shows the Raman spectra of the ν_1 symmetric stretching vibration of SO_3^- for the complexes with (a) PMMA, (b) PVMK, and (c) PVP. According to previous research,[35-37] the bands for the $\nu_s(SO_3^-)$ stretching mode at 1032, 1036, and 1048 cm^{-1} in the complexes are due to free ions, ion pairs, and higher-order ionic aggregates, respectively. For the PMMA/$AgCF_3SO_3$ complex, free ions are present up to a silver mole fraction of 0.09. When the silver mole fraction is increased above 0.09, the main band shifts to a higher wavenumber and becomes asymmetric, demonstrating the presence of ion pairs. The higher-order ionic aggregates start to appear at a silver mole fraction of 0.5. However, for the PVP/$AgCF_3SO_3$ complex, free ions are present up to a silver mole fraction of 0.33, above which ion pairs start to form; ionic aggregates start to appear at a silver mole fraction of 0.67. The PVMK/$AgCF_3SO_3$ complexes exhibit behavior that is intermediate between the behavior of PMMA and PVP complexes. Then, since ion pairs are more likely to be formed in the presence of the polymers in the order PMMA > PVMK > PVP, the strength of the interaction of the silver ion with the polymeric ligand has the reverse order. Thus, the ability of the ligands to donate electrons to the silver salts has the order amide > ketone > ester, which is consistent with the XPS results.

Strengths of the Interactions of Silver Ions with Polymeric Ligands and Propylene. The strengths of the interactions of silver ions with the carbonyl oxygens of polymeric ligands and with propylene molecules were studied using FT-IR spectroscopy. The FT-IR spectra of the pure polymers, the polymer/$AgBF_4$ complexes, and the propylene-coordinated polymer/$AgBF_4$ complexes are shown in Figure 6. The positions of the free carbonyl bands of the three polymers have the following order: PMMA (1729 cm^{-1}) > PVMK (1710 cm^{-1}) > PVP (1671 cm^{-1}).

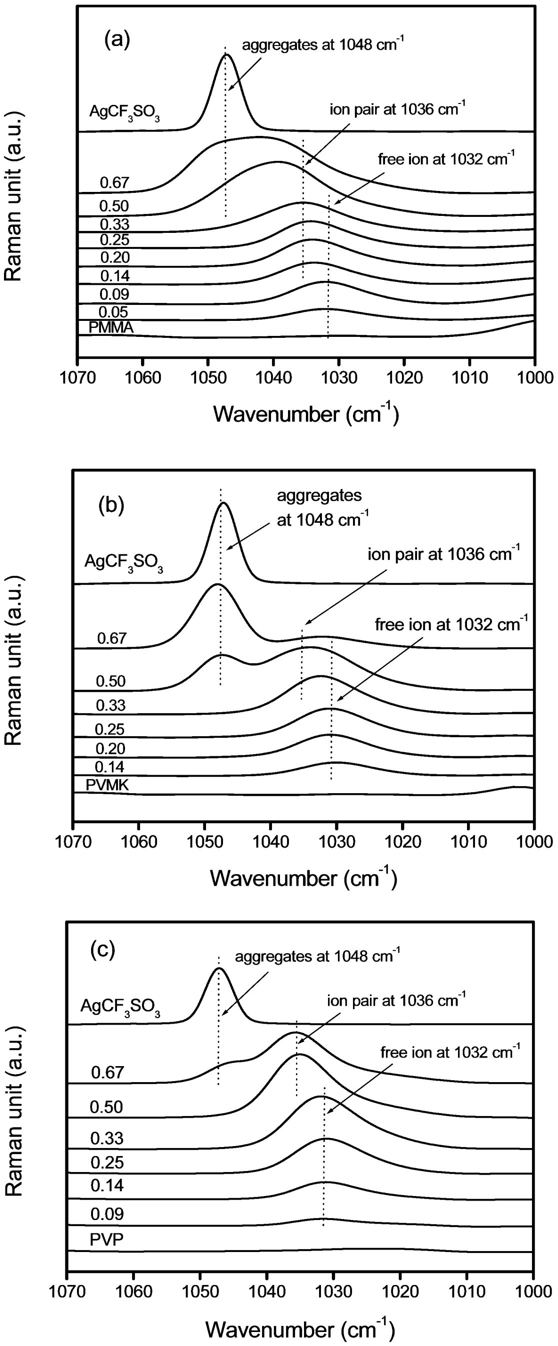

Figure 5. FT-Raman spectra of polymer/$AgCF_3SO_3$ complexes as a function of silver mole fraction: (a) PMMA, (b) PVMK, and (c) PVP.

When silver salts are dissolved in a polymer matrix and the silver ions coordinate with the polymer's carbonyl oxygens, the free C=O peak shifts to lower wavenumber. When the polymer/silver salt complexes were exposed to 50 psig of propylene for 30 min and successively purged with nitrogen for less than 1 s, a new shoulder peak appears at 1590 cm^{-1}, corresponding to the C=C stretching vibration of a propylene molecule coordinated to a silver ion. The free C=C stretching vibrations of pure propylene appear at 1665 and 1640 cm^{-1}. Upon sorption of propylene into PMMA/$AgBF_4$ complexes, the intensity of the complexed C=O band is

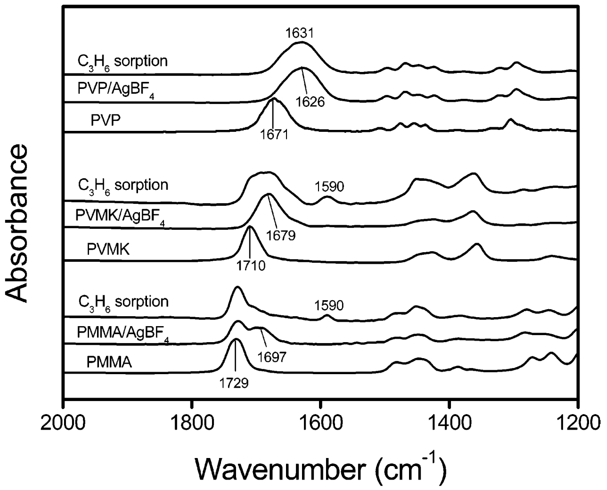

Figure 6. FT-IR spectra of pure polymer, the polymer/AgBF$_4$ complexes, and the propylene-coordinated polymer/AgBF$_4$ complexes at a silver mole fraction of 0.33.

significantly reduced, and there is a concomitant increase in the intensity of the free C═O band, which shows that the coordination of silver ions by ester oxygens is mostly replaced by coordination with propylene molecules, and thus coordinated C═O is converted to free C═O. This suggests that the bonds between silver ions and the C═O groups of PMMA are weaker than the bonds between silver ions and olefin molecules.

Contrary to the behavior of the PMMA/AgBF$_4$ complexes, in the PVP/AgBF$_4$ complex the band position of the C═O groups coordinated with silver ions moves to slightly higher wavenumber after propylene sorption, specifically from 1626 to 1631 cm^{-1}. This shift of the C═O band might be explained by the fact that silver ions coordinated with carbonyl oxygens also interact with the π-electrons of propylene molecules, and hence the double-bond character of C═O is only partially recovered. This incomplete recovery to the band position found for free carbonyl (1671 cm^{-1}) implies that the silver ions maintain coordination with both carbonyl oxygens and propylene. The change in the C═O band in PVMK/AgBF$_4$ upon propylene sorption is intermediate between the changes observed for PMMA and PVP. Therefore, the strengths of the interactions of the silver ion with the various ligands can be tentatively specified as follows: amide ≥ C═C ≈ ketone > ester.

Role of the Polymer Matrix in Facilitated Transport. As shown in Figure 1, facilitated propylene transport is strongly dependent upon the ligand species; facilitated transport commences at a low concentration of silver salt for ester ligands whereas it commences at a higher concentration for amide ligands. For complexes containing amide ligands, all silver ions at low silver salt concentrations (below a silver mole fraction of 0.25) are coordinated with carbonyl oxygens, and the interaction of silver ions with amide oxygens is slightly stronger than that with olefin. Under these circumstances olefin molecules are unlikely to form complexes with silver ions, and thus silver ions at low silver salt concentrations are not active as olefin carriers. However, for complexes containing ester ligands, the interaction of the silver ions with ester oxygens is weaker than that with propylene. Thus, silver ions even at low silver concentrations can bind with propylene molecule to form π-complexes and play active roles as propylene carriers, resulting in a low onset silver salt concentration in polymers with ester groups for facilitated propylene transport.

Conclusion

The role of the polymer matrix in facilitated olefin transport through polymer/silver salt complex membranes was investigated. The membranes containing ester ligands (i.e., PMMA and PBMA) exhibited low threshold silver salt concentrations (a silver mole fraction of 0.09) for facilitated olefin transport, whereas those containing amide ligands (i.e., POZ and PVP) exhibited higher threshold concentrations (a silver mole fraction of 0.25). The membrane containing ketone ligands (i.e., PVMK) yielded an intermediate threshold concentration (a silver mole fraction of 0.14). The differences between the threshold concentrations for facilitated olefin transport were ascribed here to the relative strengths of the interactions of silver ions with the different polymeric ligands and with olefin molecules. The threshold concentration is high when the former interaction is stronger than the latter and is low when the latter is stronger than the former. XPS, FT-Raman, and FT-IR spectroscopy clearly show that the strengths of the interactions of silver ions with the various ligands have the following order: amide ≥ C═C ≈ ketone > ester.

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