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Feature Article

Silver Polymer Electrolyte Membranes for Facilitated Olefin Transport: Carrier Properties, Transport Mechanism and Separation Performance

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Abstract: Facilitated transport membranes for the separation of olefin/paraffin mixtures have long been of interest in separation membrane science because olefins, such as propylene and ethylene, which are important chemicals in petrochemical industries, are currently separated by energy-intensive cryogenic distillation processes. Recently, solid polymer electrolyte membranes containing silver ions have demonstrated remarkable performance in the separation of olefin/paraffin mixtures in the solid state and, thus, they can be considered as alternatives to cryogenic distillation. Here, we review recent progress, and critical issues affecting in the use of facilitated olefin transport membranes; in particular, we provide a general overview with reference to carrier properties, transport mechanisms, and separation performance.

Keywords: facilitated transport, membrane, olefin, polymer electrolyte, silver.

Introduction

The separation of gas mixtures via polymeric membranes has emerged into a commercial unit operation from late 1970s. Although many polymeric materials have been utilized for gas separation membranes, they suffer from low separation performance. In particular, polymeric membranes have usually exhibited the tradeoff relation between permeability and selectivity of specific gas pairs.¹⁻³ For example, polymer

membranes with relatively high permeability are mostly less selective and *vice versa*. To overcome this critical drawback in polymeric membranes, numerous researches have been carried out during last decades. One such a way is to elucidate the relationship between the molecular structure and gas transport properties and thereby to improve the transport properties: structure-properties relationship approach.⁴⁻⁶ Molecular sieve membrane is another way to improve the permeability and selectivity simultaneously.^{7,8} The facilitated transport is also considered to be an alternative approach to overcome the trade-off behavior of conventional polymeric membranes because it can improve the permeability and

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selectivity simultaneously.⁹⁻¹¹

The gas permeation through the polymeric membranes follows the solution-diffusion mechanism, i.e. Fickian transport, driven by a chemical potential gradient between upstream and downstream faces of a membrane. In facilitated transport, however, carrier mediated transport occurs in addition to a normal Fickian transport owing to the reversible reaction of the carrier with a specific solute, and thus separation efficiency can be improved remarkably. Schematic of facilitated transport of solute molecule through the membrane with fixed site carriers is presented in Figure 1.

Olefins such as ethylene or propylene are the most important feedstock in petrochemical industries and their separation from olefin/paraffin gas mixtures have been currently carried out by cryogenic distillation processes. Since it needs high capital investment and enormous operation cost, alternative energy-saving separation technology is demanding. Membrane separation technology has been proposed as a possible alternative to distillation due to low cost and simple operation. However, the separation of olefin/paraffin mixtures via conventional polymeric membranes has not been very effective because of the indiscernible physico-chemical properties of olefins and paraffins such as molecular size and solubility.²

Facilitated olefin transport membranes have been considered as an alternative to the distillation for olefin/paraffin separation. Initially, the development of facilitated transport membranes are based on immobilized liquid membranes, solvent-swollen membranes or ion exchanged membranes.¹²⁻¹⁶ However, the commercial application of liquid membranes is limited because they are operated with liquid solvent-vapor saturated feed and permeate streams. Thus, many problems

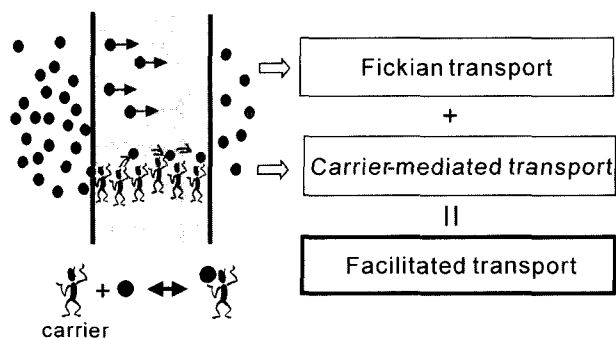


Figure 1. Schematics of facilitated transport through solid membrane with fixed site carriers.

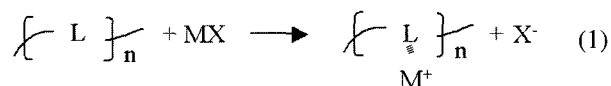
are encountered; the loss of the liquid solvent and carrier, the limits of the operation temperature and the membrane thickness. Therefore, the development of liquid-free facilitated transport membranes in the solid state is desirable.

The main objective of this feature article is to provide the reader with a general overview of the present knowledge of facilitated transport membranes in solid state with reference to carrier properties, transport mechanism, membrane performances.

Carrier Properties

In facilitated transport membranes, a carrier should reversibly reacts with a specific solute. In the case of olefin/paraffin separation, transition metal ions such as silver or copper ions dissolved in a polymeric matrix have been used as an olefin carrier because they reversibly react with olefin compound, resulting in facilitated olefin transport.¹⁷⁻³⁵ In the following section, the properties of silver polymer electrolytes as olefin carrier will be reviewed, highlighting the formation and the structures of silver polymer electrolytes and their interaction with olefins.

Formation of Polymer Electrolytes. In order to dissolve metal salts into metal ions, a polymer solvent having appropriate ligands (L) to coordinatively interact with metal ions is necessary.¹⁷ Formation process of polymer electrolytes can be schematically written as eq. (1):



where L denotes a polymeric repeating unit, and M and X are a metal ion and its counteranion, respectively. Thermodynamically, complex formation via eq. (1) involves the dissociation of salts into ions (requiring lattice energy) and solvation of ions into polymer solvent (releasing solvation energy). The dissolution process involves the dissociation step associated with the lattice energy of salts and the solvation step associated with the solvation energy of ions in polymer solvents. Therefore, the lattice energy is one important criterion in forming polymer electrolytes and in determining the ionic constituents of the complex and consequently, most chemical and physical properties of polymer electrolytes.

Dissociation energies of transition metal salts were calculated theoretically using the density functional theory of B3LYP level with 6-311+G(d,p) and 6-311+G(2df,p) basis

Table I. Lattice Energies of Metal Salts (kJ/mol)³⁶

	F	Cl ⁻	NO ₃ ⁻	SCN ⁻	CF ₃ SO ₃ ⁻	ClO ₄ ⁻	BF ₄ ⁻
Ag ⁺	928	859	794	796	695	677	680
Cu ⁺	1008	926	859	870	761	759	733

sets.³⁶ The effective core potential of LANL2DZ and SDD on transition metals for 6-311+G(d,p) and 6-311+G(2df,p) calculations, respectively, were employed. The lattice energies are then obtained from the linear relationship between the dissociation and lattice energies and the results are shown in Table I.³⁶ It is found that 1) the lattice energies of metal salts become smaller with the size of the anion bigger and 2) the lattice energies of silver compounds is lower than those of copper compounds.

The solvation energy is associated with the coordinative interaction between the metal cation and polar groups in polymer backbone. For examples, polar oxygen atoms in ether, amide, ester, and ketone groups readily coordinate to metal cations, resulting in dissolution of metal salts in a polar polymer matrix. Polar polymers such as poly(2-ethyl-2-oxazoline) (POZ),¹⁸⁻²² poly(*N*-vinyl pyrrolidone) (PVP),²³⁻²⁵ poly(ethylene oxide) (PEO),^{26,27} poly(vinyl methyl ketone) (PVMK),^{31,32} poly(methacrylates) (PMA),^{32,33} cellulose acetate (CA)³⁵ are a good solvent to dissolve metal salts having low lattice energy by the coordinative interaction between silver ion and polar groups in polymers. The coordinative interaction between silver ion and polar groups in polymers is readily investigated by infrared and Raman spectroscopy. In the complexes of POZ or PVP with AgBF₄, the coordinative interaction was confirmed by the band shift in carbonyl stretching to a lower wavenumber as shown in Figure 2.¹⁷ The uncomplexed, free carbonyl band from pure POZ was observed at 1641 cm⁻¹, which shifted to a new position at 1596 cm⁻¹ (for PVP, from 1671 to 1630 cm⁻¹). Therefore it is concluded that silver salts are dissolved in polymer solvent to become free ions because of the coordinative interaction between the silver cation and carbonyl oxygens.

Structure of Silver Polymer Electrolytes. When silver salts are incorporated into a polymer matrix to form polymer electrolytes, their structure and properties will be changed mainly due to the coordinative interaction between the silver cation and carbonyl oxygens. For example, the intersegmental distance, glass transition temperature and gas permeability change with the silver concentration.

The intersegmental distance of the polymer electrolytes was investigated by wide angle x-ray scattering (WAXS). The WAXS spectra of POZ and POZ complexes with AgCF₃SO₃ showed two broad amorphous peaks and their corresponding intersegmental distances or d-spacings were obtained from the Bragg's law as shown in Figure 3,³⁷ where the first peak at lower 2θ was assigned to the interchain distance and the second at higher 2θ to the distance associated with the pendant groups coordinated by silver cations. Interestingly, the interchain distance decreased with the silver salt concentration at low silver salt concentrations, reached a minimum and started to increase afterwards, whereas the distance from the second peak decreased monotonically with the silver salt concentration. At the low silver salt concentration regime (up to a silver mole fraction of 0.25), the silver cation

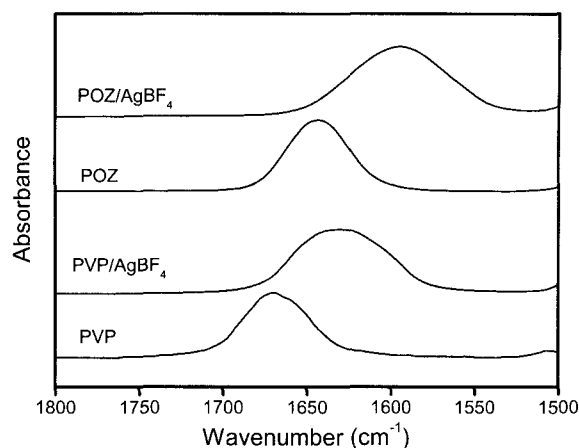


Figure 2. FT-IR spectra of pure polymer and polymer electrolytes containing AgBF₄ at [C=O]:[Ag]=1:1.¹⁷

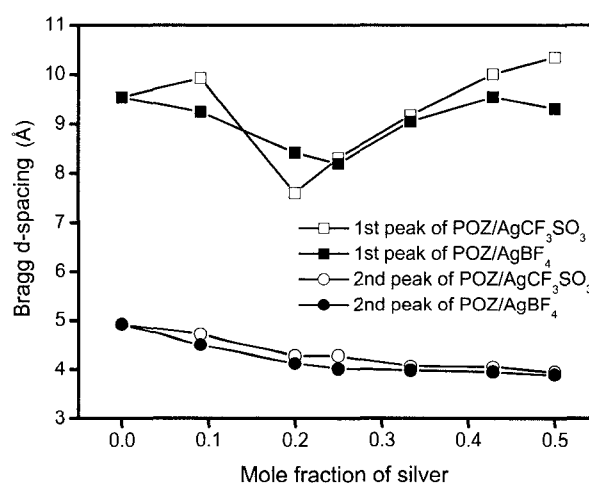


Figure 3. Bragg d-spacing of POZ complexes with AgCF₃SO₃ and AgBF₄ as a function of silver concentration.³⁷

plays a transient cross-linker by the coordinative interaction and pulls the chains, resulting in the decrease in the interchain distance.¹⁹ However, at high silver salt concentrations, the free anion concentration becomes high and their electrostatic repulsion becomes stronger, pushing the polymer chains apart.^{38,39} When the repulsion force by the anions is higher than the attractive "pulling-in" one by the silver cations coordination, the interchain distance would be increased.³⁷⁻³⁹ However, the monotonic decrease in the distance from the second peak appears to be due to the coordinative interaction of silver cations with carbonyl oxygens.

Glass transition temperature (T_g) can also monitor the structure of polymer electrolytes. The T_g values of POZ/silver salt were measured using differential scanning calorimetry (DSC) and shown in Figure 4. Each plot exhibits the same general feature of increasing T_g with increasing salt contents, reaches a broad maximum, followed by a slight decrease.

This trend is in a good agreement with an extended configurational entropy theory as follows.^{40,41}

$$\ln \frac{T_{g12}}{T_{g1}} = \beta \left[\left(1 - \gamma_{com} \ln \left(\frac{z-1}{e} \right) \right) \left(\frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right) - \frac{\phi_2}{r_2 v m} \frac{4}{3} A_{diss} I^{3/2} \tau(I^{1/2}) \right] \quad (2)$$

where $\beta = zR/M_{1u}\Delta C_{pp}$. R , M_{1u} and ΔC_{pp} are the gas constant, the molecular weight of the repeat unit and the isobaric specific heat jump of the polymer, respectively. z is the lattice coordination number. γ_{com} is a proportionality constant representing the complexation interaction between polymer and salt.⁴⁰ $\tau(x) = \frac{3}{x} \left[\ln(1+x) - x + \frac{x^2}{2} \right]$ and $I = \frac{1}{2} m v |z_M z_X|$. m is a solute molality (mol/kg polymer). $V = (v_M + v_X)$; v_M and v_X are the number of M and X ions, respectively) is the number of ions per salt. I is the ionic strength and z_M and z_X are the valences of the M and X ions, respectively. A_{diss} is the Debye-Hückel coefficient, representing the strength of the interaction between cation and anion.⁴¹ The increase in T_g upon addition of metal salts is primarily attributed to both the transient cross-links of polymer segments and the dangling of metal salts on the chain. The solid lines in Figure 4 were obtained from eq. (2) with the interaction parameters γ_{com} of 1.10, 0.98, 0.92, and 0.87 and A_{diss} of 0.16, 0.10, 0.21 and 0.27 for POZ/AgClO₄, POZ/AgBF₄, POZ/AgCF₃SO₃, and POZ/AgNO₃ complexes, respectively. Therefore, it is suggested that the strength of polymer-salt interaction is ordered as follows; AgClO₄ > AgBF₄ > AgCF₃SO₃ > AgNO₃. On the other hand, the strength of cation-anion interaction exhibits the reverse order. The ionic interactions of POZ/silver complexes determined by T_g variation agree with the results from experimental spectroscopy as well as from theoretical *ab initio* calculation.²⁰

Paraffins such as propane do not have any specific interaction with silver ions and thus permeate only via Fickian transport. The permeance behavior of propane is therefore strongly associated with the structure of the polymer electrolyte. Figure 5 shows the propane permeance through pure POZ and PVP and their complexes with AgCF₃SO₃ at 25 °C.²¹ The propane permeances of the POZ and PVP systems decrease rapidly up to the silver mole fraction of 0.25, after which they decrease very slowly before reaching an almost constant value. The decrease in the propane permeance also confirms that the polymer electrolyte membranes become densified due to the coordinative interaction between the silver ion-carbonyl oxygen.

Olefin Solubility in Membranes. Olefin is dissolved to a great extent in polymer electrolytes containing silver salts because of the silver-olefin complex formation. When small molecules are in contact with metal-polymer complexes, they will be dissolved in two modes: a normal dissolution mode in the matrix and an immobilization mode by a reversible

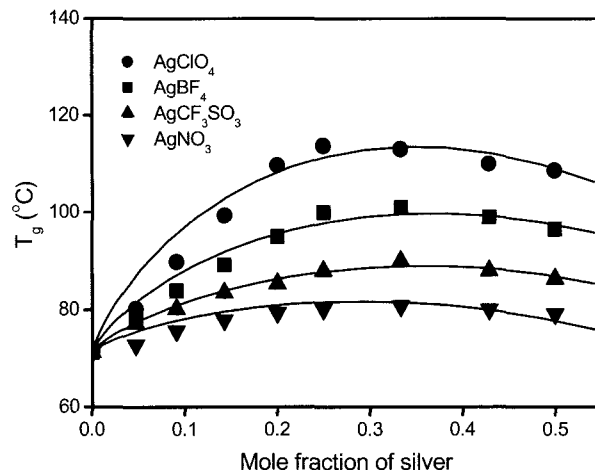


Figure 4. Variations of glass transition temperatures for POZ complexes with silver salts as a function of silver concentration.⁴¹

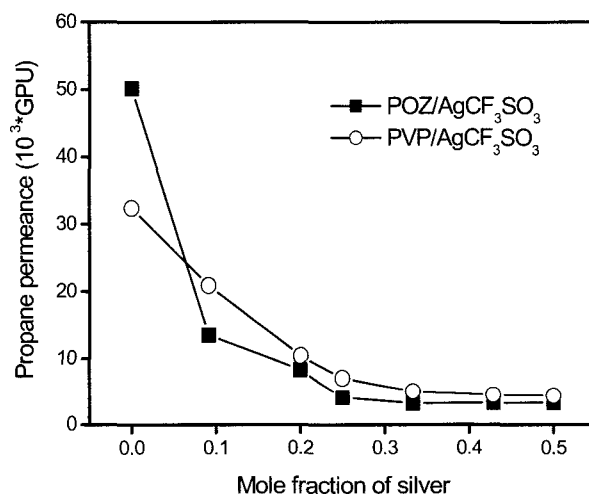


Figure 5. Permeance of propane through polymer electrolyte membranes containing AgCF₃SO₃ as a function of silver concentration.²¹

chemical reaction with carriers. The dissolution mode is commonly expressed by the Henry's law for simple gases except for soluble gases such as carbon dioxide. The mathematical expression of the reversible immobilization mode is identical to that of the Langmuir adsorption isotherm for a simple gas in a porous media. The total solubility is the summation of the both contributions for the dissolution mode by the Henry's law and for the immobilization mode by the Langmuir mode: the dual mode sorption. At equilibrium, the total solubility of solute A becomes:^{42,43}

$$C = k_D p_2 + \frac{C_c' K p_2}{1 + K p_2} \quad (3)$$

where C is the concentration of the solute gas A in the membrane, p_2 is the applied gas pressure, k_D is the solubility coefficient of the gas A for Henry's law, K is the gas binding equilibrium constant, and C_c' is the saturated amount of the gas A reversibly bound to the carriers B .

The propylene solubilities in silver polymer electrolytes (POZ/silver salt) were measured using the pressure decay method and were plotted against propylene pressure as shown in Figure 6.^{18,21} The mole ratios of carbonyl oxygen to silver ion were fixed at one and two, i.e. $[C=O]:[Ag] = 1:1$ and $2:1$. The experimental results indicate that the propylene solubility in silver polymer electrolytes is tremendously increased compared to that in pure POZ because of the immobilization of propylene into silver cations. The propylene solubility in pure POZ increased linearly with propylene pressure, demonstrating that the hole-filling/or Langmuir mode is hardly apparent. Thus, the solubility of propylene in POZ can be readily described by a simple Henry's mode ($C = k_D P_o$). The curves of the propylene solubility in silver polymer electrolytes become concave to the ordinate with increasing silver concentration, indicating the presence of the second mode sorption. The second mode sorption is evidently

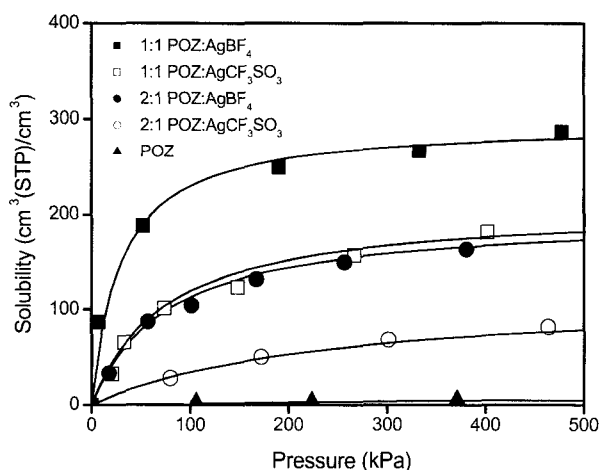


Figure 6. Solubility of propylene in pure POZ and POZ/silver electrolytes against propylene pressure at 25 °C.^{18,21}

Table II. Dual Sorption Parameters in Correlation of Propylene Solubility in POZ/silver Electrolytes at 25 °C¹⁶

Membranes	$k_D \times 10^5$ (cm ³ (STP)/cm ³ cmHg)	$K \times 10^3$ (1/cmHg)	$C_c' \times 10^3$ (mol/cm ³)
1:1 POZ/AgBF ₄	15.54	45.44	13.24
1:1 POZ/AgCF ₃ SO ₃	13.35	17.32	8.15
2:1 POZ/AgBF ₄	13.21	16.90	8.07
2:1 POZ/AgCF ₃ SO ₃	3.54	5.44	5.24
Pure POZ	3.29	.	.

due to the interaction between silver ions and propylene molecules and can be described by a simple Langmuir model. Thus, the propylene solubility in silver polymer electrolytes was analyzed using the dual sorption model of eq. (3) and their parameters are listed in Table II. As expected, the ordinary dissolution term is very small whereas the Langmuirian term is very large. This suggests that the total solubility depends mostly on the immobilization of propylene by the reversible chemical reaction between propylene and silver cation.

Anion of silver salts also plays an important role in determining olefin solubility and consequently the facilitated olefin transport. For example, the propylene solubility in polymer electrolytes containing AgBF₄ is always higher than that containing AgCF₃SO₃ for two compositions as shown in Figure 6. The former is almost two fold higher compared to the latter, demonstrating the dependence of the propylene solubility on the type of the anion. The influence of anion properties on olefin solubility in PEO/silver salt films has been also reported.²⁷ PEO/AgBF₄ and PEO/AgCF₃SO₃ sorb 8.5 and 1.76 g of propylene per 100 g of polymer electrolyte, respectively, at 30 °C and 70 cmHg pressure. In contrast, PEO/AgNO₃ only sorbs 0.52 g of propylene per 100 g of polymer electrolyte. Therefore, anion characteristics are an important factor in determining olefin solubility.

Reversible Interaction. The reversible olefin coordination to silver ions in solid polymer electrolytes was investigated using FTIR and UV spectroscopy.^{31,35} A series of IR spectra in Figure 7 demonstrate the solid-state interaction of AgBF₄ with PVMK and the reversible olefin coordination to silver ions dissolved in the solid PVMK/AgBF₄ films.³¹

When the sample (2:1 PVMK/AgBF₄) was exposed to 207 kPa of propylene and then purged with N₂, a new IR

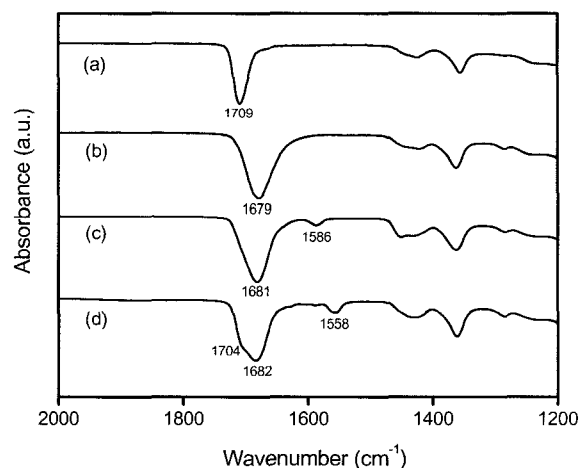


Figure 7. FT-IR spectra for the solid state interactions of AgBF₄ with PVMK and olefins: (a) PVMK, (b) 2:1 PVMK/AgBF₄, (c) propylene-coordinated membrane, and (d) 1,3-butadiene-coordinated membrane.³¹

absorption peak at 1586 cm⁻¹ appeared (Figure 7(c)). This new peak represents the C=C stretching vibration of coordinated propylene (ν₁ and ν₂ of C=C in free propylene are 1665 and 1640 cm⁻¹, respectively). It is interesting to notice that the peak at 1586 cm⁻¹ remains even after outgassing at 10⁻⁵ torr for 4 h at room temperature. However, the exposure of the propylene-coordinated membrane to 1,3-butadiene of 207 kPa and subsequent treatment with N₂ gives a new peak at 1558 cm⁻¹ with the concomitant disappearance of the peak at 1586 cm⁻¹ (Figure 7(d)). The peak at 1558 cm⁻¹ can be assigned to the C=C stretching of the coordinated 1,3-butadiene. The peak at 1558 cm⁻¹ is again replaced by the peak at 1586 cm⁻¹ with the introduction of propylene into the gas cell containing 1,3-butadiene-coordinated PVMK/AgBF₄ membrane. These results strongly indicate that the coordinated olefins are rather rigidly held to silver ions, but they are rapidly exchanged by other olefins. The rapid exchange reaction seems to be a major reason for facilitated olefin transport. The same reversible olefin coordination behavior was also observed by UV spectroscopy.^{31,35}

Transport Mechanism

Role of Ionic Constituents. The complexation mechanism of facilitated olefin transport in silver polymer electrolyte membranes has been elucidated.²³ According to FT-Raman spectra of PVP/AgCF₃SO₃ complexes, only free anions at 1032 cm⁻¹ are present up to the silver mole fraction of 0.33 ([C=O]:[Ag] = 2:1), and ion pairs at 1038 cm⁻¹ start to form at 0.5 ([C=O]:[Ag] = 1:1), followed by higher-order ionic aggregates at 1048 cm⁻¹ above 0.75 ([C=O]:[Ag] = 1:2). At the silver mole fractions above 0.25, the propylene permeance increased almost linearly with the total silver concentration, unexpectedly, regardless of the silver ionic constituents. It was also found that all the silver constituents including ion pairs and higher-order ionic aggregates were completely

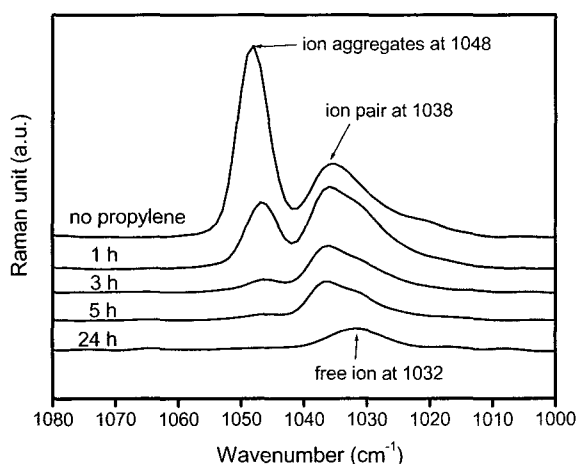
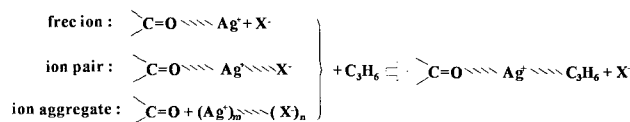


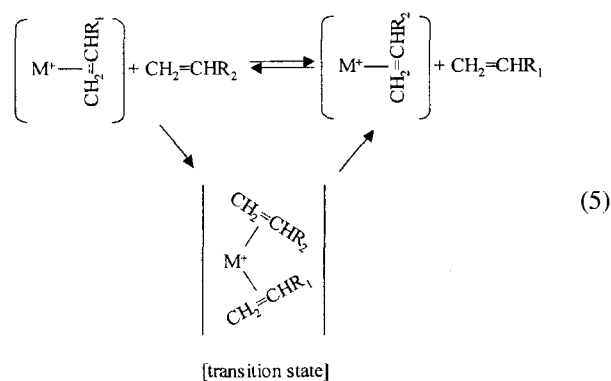
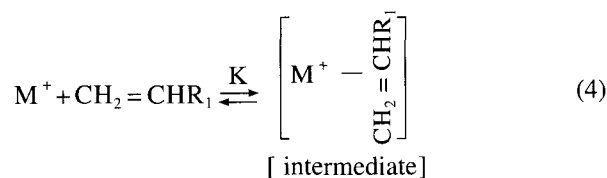
Figure 8. Time evolution Raman spectra for ν_s(SO₃) mode in 1:3 PVP/AgCF₃SO₃ absorbing propylene at 275.6 kPa.²³

redissolved into free anions under the propylene environment, as shown in Figure 8.²³ It strongly represents that propylene is a good ligand for the silver cation to make complexes of silver cation with propylene. On these experimental findings, a new mechanism for the complexation reaction between propylene and silver salt in silver polymer electrolytes was proposed as follows.



The new mechanism is consistent with the linearity between the propylene permeance and the total silver concentration regardless of the kind of the silver constituents. Therefore, the facilitated propylene transport through silver polymer electrolytes may be associated mainly with silver cation weakly coordinated with both carbonyl oxygen and propylene.

Two Step Reaction. The characterization of polymer electrolytes containing silver ion and their interaction with olefin led us to propose a new mechanism on the interaction between silver ion carrier and olefin molecules as in eqs. (4) and (5).⁴⁴ Facilitated olefin transport is likely to occur with two-step reactions. The first step (4) is the apparently irreversible and slow process to form silver-olefin complexes as an intermediate; the second reaction (5) is the rapid and reversible olefin exchange reaction which appears to be a key step in determining facilitated olefin transport.



where R₁ and R₂ represent either hydrogen atom or alkyl group.

Threshold Concentration. The existence of the threshold concentration is commonly observed in solid-state facilitated transport membranes.^{21,26,32} In facilitated olefin transport

through silver polymer electrolytes, the threshold concentration was observed at a silver mole fraction of approximately 0.25 for AgBF_4 or AgCF_3SO_3 dissolved in POZ or PVP (i.e. $[\text{C}=\text{O}]:[\text{Ag}] = 3:1$), below which facilitated transport was not observed.²¹ However, both the propylene permeance and the selectivity of propylene/propane increased nearly linearly with the silver concentration at silver concentrations above the threshold concentration as shown in Figure 9. The threshold concentration is found to be strongly associated with the coordination behavior of the silver ion by both carbonyl oxygens and olefin molecules.²¹

The coordination number of the silver ion, m , by carbonyl oxygens ($\text{C}=\text{O}$) can be obtained simply by the concentration ratio of the complexed carbonyl oxygen to the concentration of both the free silver ion and the ion pair from IR and Raman spectra.¹⁷ The coordination number of the silver ion, n , by olefin molecules is obtained from the concentration ratio of propylene molecules coordinated to silver ions (C_c) to the concentration of both the free silver ion and the ion

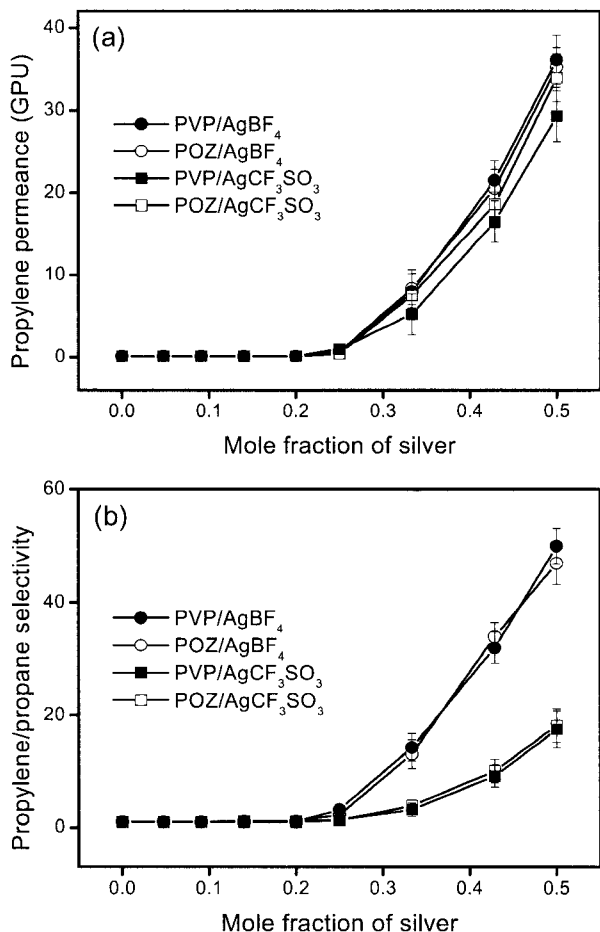
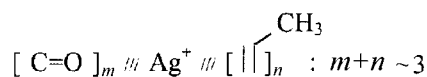


Figure 9. Separation performance of (a) propylene permeance and (b) the selectivity of propylene/propane through polymer electrolyte membranes as a function of the silver concentration at 23 °C.^{21,32}

pair.²¹ The coordination numbers of silver ions in POZ/ AgCF_3SO_3 are plotted against the mole fraction of silver salt as shown in Figure 10.²¹ It is clear from the figure that m decreases exponentially with the silver concentration whereas n increases slightly. Surprisingly, the total coordination number, $(m+n)$, becomes nearly invariant and is around 3. This result strongly suggests that the most favorable coordination number of the silver ion dissolved in a polymer matrix under propylene environment is ~ 3 .



Furthermore, it was found from IR spectra^{20,23} and theoretical calculations²¹ that the interaction of silver ion with carbonyl oxygen of POZ is slightly stronger than that with olefin molecules. Therefore, the relationship between the threshold concentration and the most probable coordination number of silver ion can be deduced from the favorable coordination number and difference in the interactions.

When $m \geq 3$, silver ions may not be able to interact with surrounding olefin molecules, implying that the silver ion does not act as an olefin carrier. However, when $m < 3$, the coordination sites of the silver ion are not completely occupied by carbonyl oxygen and thus vacant sites are available for olefin coordination. Therefore, silver ions can act as an olefin carrier only when $m < 3$, in other words, the threshold concentration of the mole fraction of the silver salts is 0.25 ($[\text{C}=\text{O}]:[\text{Ag}] = 3:1$), which is consistent with Figure 9.

$$[\text{C}=\text{O}]_m // \text{Ag}^+ \begin{cases} \text{when } m < 3 : \text{active olefin carrier} \\ \text{when } m \geq 3 : \text{inactive} \end{cases}$$

This is the first report on the importance of the coordination

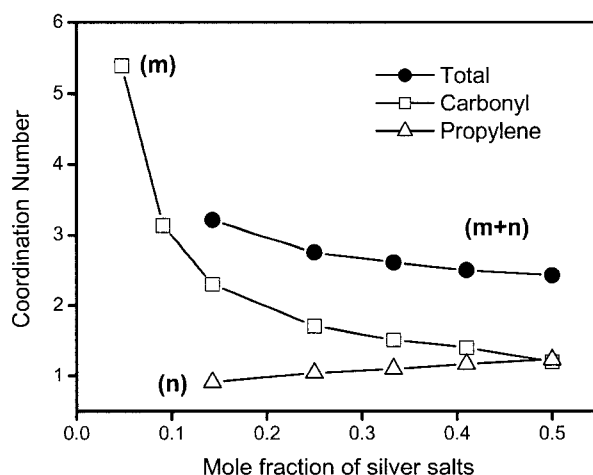


Figure 10. Coordination numbers of silver ion by carbonyl oxygen and propylene in POZ/ AgCF_3SO_3 as a function of the silver salt concentration.²¹

behavior of metal ion in determining the activity of silver ion as olefin carrier, and the presence of the threshold concentration for facilitated transport membranes in solid state. It was further found that the threshold concentration for facilitated olefin transport was strongly dependent on the kind of polymer ligand, i.e. the relative strength of the interactions of silver ion with the carbonyl oxygen and with olefin.³² The threshold concentration is high when the former interaction is slightly stronger than the latter, and is low when the latter is stronger than the former.

Membrane Performance

Separation Property. Composite membranes are prepared by coating silver polymer electrolyte solution onto an asymmetric porous support. Permeation experiments were carried out using pure dry propylene and propane gases through four different solid membranes (two silver salts (AgBF_4 and AgCF_3SO_3) and two polymer solvents (POZ and PVP)).¹⁸ The mole ratio of carbonyl oxygen to silver ion was fixed at 1 in the polymer-salt complexes: $[\text{C}=\text{O}]:[\text{Ag}] = 1:1$. The permeances of propylene and propane through the membranes are shown as a function of feed pressure in Figure 11. The polymer membranes containing AgBF_4 in POZ or PVP gave the propylene permeance about 45 GPU (1 GPU = $1 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ sec}^{-1} \text{ cmHg}^{-1}$) at 140 kPa whereas the propylene permeance through membranes made of pure POZ and PVP was approximately 0.05 GPU. This result shows more than three orders of magnitude increase in terms of the propylene permeance and clearly demonstrates the facilitated transport of propylene due to the presence of silver ion. Meanwhile the propane permeance was extremely low as 0.003 GPU. Thus, the ideal separation factor of propylene over propane was approximately 15,000. This fact implies that polymer-silver salt complexes could be successfully used

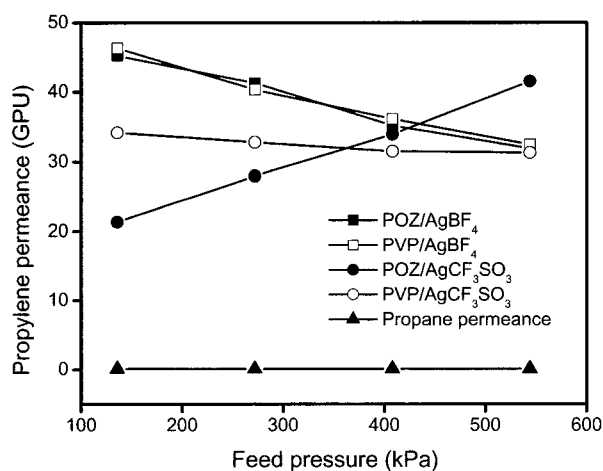


Figure 11. Permeances of propylene and propane through silver polymer electrolyte membranes (at $[\text{C}=\text{O}]:[\text{Ag}]=1:1$) as a function of feed pressure.¹⁸

as a facilitated transport membrane material for separation of olefin/paraffin mixtures.

Kang *et al.*^{45,46} proposed a concentration fluctuation model to explain facilitated transport behavior in the solid state.

$$\frac{\bar{P}_f}{\bar{P}_0} = 1 + \left(\frac{p_d}{p}\right) \sqrt{n^2 + \left\{ \frac{2\pi k_2 L^2 [B]_0 \ln(1 + Kp)}{P_0 p} \right\}^2} \quad (6)$$

where \bar{P}_f and \bar{P}_0 are the permeabilities of facilitated transport membrane and the membrane matrix without carrier, respectively. p_d is pressure fluctuation due to the reversible reaction, $n = N[B]_0(\pi r^2 L)$ where N is the Avogadro number, L is membrane thickness and r is the permeant radius. k_2 and K are the backward reaction rate constant and the equilibrium constant of the carrier-solute reaction, respectively.

According to the concentration fluctuation model, \bar{P}_f decreases with increasing feed pressure (p), which is one intrinsic drawback of the facilitated transport.⁴⁷⁻⁴⁹ Our experimental results were also consistent with the theoretical predictions of the concentration fluctuation model except for the POZ/ AgCF_3SO_3 system. Although the propylene permeances decreased with increasing feed pressure for most systems investigated, they were still high even at high feed pressures. Such high permeance may arise predominantly from the high concentration of the propylene carriers, silver ions.

The effect of silver salt concentration on propylene permeance was also investigated. Figure 9(a) shows the propylene permeance through POZ/silver and PVP/silver composite membranes with increasing amount of silver salt. The feed pressure was 413.5 kPa. As shown in this figure, there is no significant improvement of the propylene permeance through POZ/silver and PVP/silver until the mole fraction of silver salt reached 0.25. However, the permeance increased up to 35 GPU with increasing silver ion content. This dependence of the carrier concentration is consistent with eq. (6). The propylene permeance of POZ and PVP containing AgBF_4 or AgCF_3SO_3 shows similar trends with increasing silver salt contents. The mixed-gas separation properties of polymer electrolyte membranes were also evaluated in order to obtain the actual selectivity, as shown in Figure 9(b). The actual selectivities were determined by the ratio of mole fractions of the gas components in the permeate stream to those in the feed one. The facilitating effect of the silver ions increases with increasing mole fraction of silver salt. The anion of the silver salt has a significant effect on the facilitated transport while there is no significant dependence of polymer matrix, POZ or PVP at this experimental condition. The polymer electrolyte membranes containing AgBF_4 showed greater separation properties than those containing AgCF_3SO_3 .

The separation performance of facilitated transport membranes consisting of polymer-silver salts complexes for propylene/propane mixtures was improved several orders of magnitude compared with that of conventional polymeric

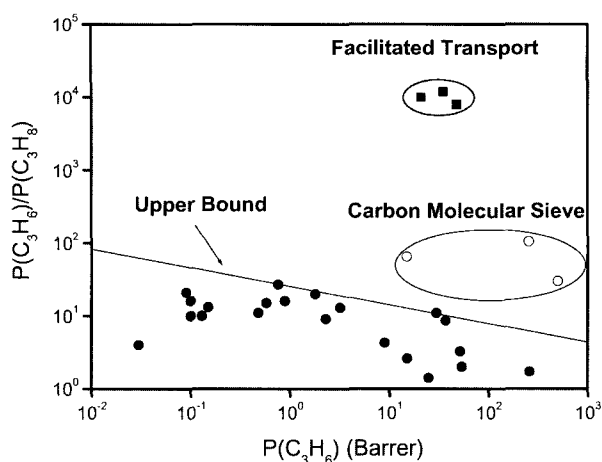


Figure 12. Relationship between propylene permeability and its ideal separation factor over propane. The data of facilitated transport membranes are from References #18, #21 and #26. The data of conventional polymers and carbon molecular sieve membranes are from Reference #2.

membranes² such as polyimides, polysulfone, poly(phenylene oxide), ethyl cellulose, poly(dimethyl siloxane), etc. as shown in Figure 12. The propylene permeance reaches more than 45 GPU (1 GPU = 1.0×10^{-6} cm³(STP)/cm² sec cmHg) and the ideal separation factor of propylene over propane is extremely high at several thousands. This represents that more than 99% pure propylene can be obtained by only a single pass through the facilitated transport membrane when the propylene concentration of the feed was 50%.

Long-term Stability. Despite the high separation performance of the facilitated olefin transport membranes in solid state, a pending question for industrial applications is the stabilization of carriers. They frequently suffer from a lack of long-term stability because the separation performance of the membrane decreases with time mainly due to the deactivation of the carrier. For example, the polymer electrolyte membranes consisting of AgBF₄ dissolved in POZ, PVP or PEO containing oxygen atom show the slightly continuous decrease in separation performance.^{50,51} This is possibly due to the reduction of silver ions to silver nanoparticles during the separation process, because polymers such as PEO, POZ or PVP used as a polymer solvent in the solid polymer electrolytes also plays a role as a reducing agent for the silver salts.^{22,50-53}

It has been recently reported that plasticizers such as dialkyl and diaryl phthalates are highly effective to prolong the carrier activity of the free silver ion, thereby increasing the performance of the dry polymer electrolyte membranes, as shown in Figure 13.^{50,51} Stability enhancement is attributed to the fact that the silver ions are more strongly held by the phthalate groups to form chelating bonds and consequently their reduction reaction to metal is mostly prevented.

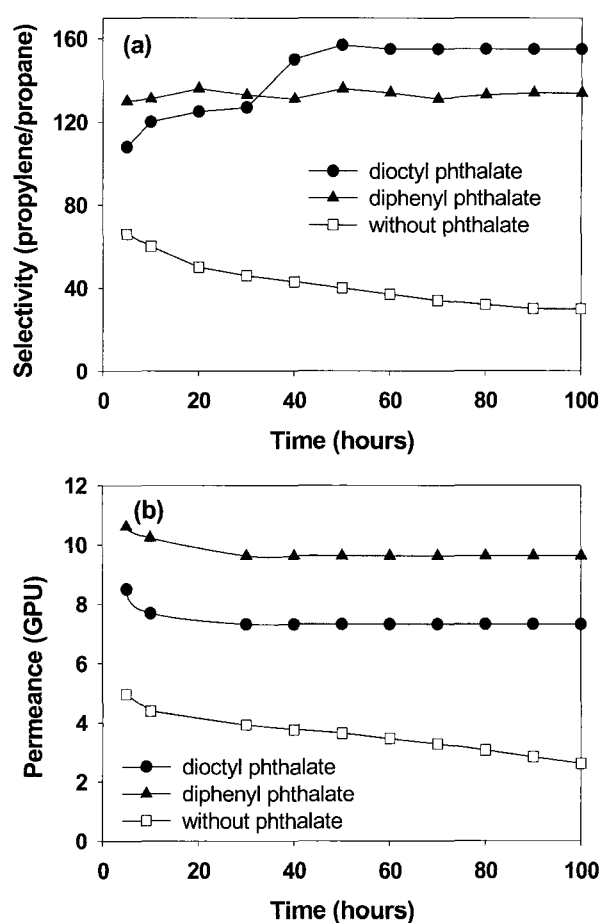


Figure 13. Mixed gas selectivity and permeance of PVP/AgBF₄ membranes containing with and without phthalate as a function of time (a) selectivity and (b) permeance.^{50,51}

Conclusions

In this feature article, the recent developments on the facilitated olefin transport membranes in the solid state have been described, in particular with the reference to the carrier properties, transport mechanism, and membrane separation performances. The polymer electrolyte membranes consisting of silver ions dissolved in a polar polymer containing ligands show the selective olefin transport, resulting in the facilitated olefin transport and consequently high separation performances for olefin/paraffin mixtures. For example, the solid polymer electrolyte membranes comprising AgBF₄ dissolved in POZ or PVP give the propylene permeance up to about 45 GPU and the ideal selectivity of propylene/propane ca. 15,000, which are several orders of the magnitude higher than those of conventional polymeric membranes.

In mechanistic studies, the coordination behavior of silver ion with polymer ligands as well as olefins mostly determines the activity of the olefin carrier, the facilitated transport and the structure of the polymer electrolytes. The free silver ion

among three ionic species including free ion, ion pair and aggregate is found to be the most active olefin carrier. The reaction mechanism of the silver ion with olefin is suggested to have two-step reaction: the complexation and exchange steps. The exchange step is found to be critically important in determining facilitated transport, which is only observable in facilitated transport membranes but not commonly. However, the separation performance of the silver polymer electrolyte membranes decreases with time mostly due to the deactivation of the carrier by the reduction of silver ions to silver nanoparticles. Thus, the carrier activity should be maintained for a prolonged time for practical applications by preventing the reduction of silver ion to silver nanoparticles and the reaction with sulfur compounds or with acetylene. Nevertheless polymer/metal complexes, i.e. silver polymer electrolyte membranes are expected to be a promising candidate as a new separation material for olefin/paraffin mixtures.

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References

- (1) L. M. Robeson, *J. Membr. Sci.*, **62**, 165 (1991).
- (2) R. L. Burns and W. J. Koros, *J. Membr. Sci.*, **211**, 299 (2003).
- (3) B. D. Freeman, *Macromolecules*, **32**, 375 (1999).
- (4) I. W. Kim, K. J. Lee, J. Y. Jho, H. C. Park, J. Won, Y. S. Kang, M. D. Guiver, G. P. Robertson, and Y. Dai, *Macromolecules*, **34**, 2908 (2001).
- (5) Y. Dai, M. D. Guiver, G. P. Robertson, Y. S. Kang, and K. J. Lee, *Macromolecules*, **36**, 6807 (2003).
- (6) Y. P. Yampolskii, A. P. Korikov, V. P. Shantarovich, K. Nagai, B. D. Freeman, T. Masuda, M. Teraguchi, and G. Kwak, *Macromolecules*, **34**, 1788 (2001).
- (7) H.-K. Jeong, J. Krohn, K. Sujaoti, and M. Tsapatsis, *J. Am. Chem. Soc.*, **124**, 12966 (2002).
- (8) H. B. Park, I. Y. Suh, and Y. M. Lee, *Chem. Mater.*, **14**, 3034 (2002).
- (9) A. Figoli, W. F. C. Sager, and M. H. V. Mulder, *J. Membr. Sci.*, **181**, 97 (2001).
- (10) H. Nishide and E. Tsuchida, in *Polymers for Gas Separation*, N. Toshima, Ed., Wiley, NY, 1992, Vol. 6, p. 183.
- (11) J. D. Way and R. D. Noble, *Facilitated Transport*, in *Membrane Handbook*, W. S. Ho and S. S. Sirkar, Eds., Van Nostrand, New York, 1992.
- (12) W. S. Ho and D. C. Dalrymple, *J. Membr. Sci.*, **91**, 13 (1994).
- (13) J. S. Yang and G. H. Hsiue, *J. Membr. Sci.*, **138**, 203 (1998).
- (14) S. Bai, S. Sridhar, and A. A. Khan, *J. Membr. Sci.*, **147**, 131 (1998).
- (15) T. Yamaguchi, H. Kurita, and S. Nakao, *J. Phys. Chem. B.*, **103**, 1831 (1999).
- (16) P. Klausener and D. Woermann, *J. Membr. Sci.*, **168**, 17 (2000).
- (17) J. Jin, S. U. Hong, J. Won, and Y. S. Kang, *Macromolecules*, **33**, 4932 (2000).
- (18) S. U. Hong, J. H. Jin, J. Won, and Y. S. Kang, *Adv. Mater.*, **12**, 968 (2000).
- (19) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *Macromolecules*, **34**, 6052 (2001).
- (20) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *J. Phys. Chem. B.*, **106**, 2786 (2002).
- (21) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *Macromolecules*, **35**, 5250 (2002).
- (22) J. H. Kim, B. R. Min, H. S. Kim, J. Won, and Y. S. Kang, *J. Membr. Sci.*, **212**, 283 (2003).
- (23) J. H. Kim, B. R. Min, J. Won, and Y. S. Kang, *Chem. Eur. J.*, **8**, 650 (2002).
- (24) J. H. Kim, B. R. Min, J. Won, and Y. S. Kang, *Macromolecules*, **36**, 4577 (2003).
- (25) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *J. Polym. Sci., B: Polym. Phys.*, **40**, 1813 (2002).
- (26) I. Pinnau and L. G. Toy, *J. Membr. Sci.*, **184**, 39 (2001).
- (27) S. Sunderrajan, B. D. Freeman, C. K. Hall, and I. Pinnau, *J. Membr. Sci.*, **182**, 1 (2001).
- (28) J. H. Kim, B. R. Min, J. Won, C. K. Kim, and Y. S. Kang, *J. Polym. Sci., B: Polym. Phys.*, **42**, 621 (2004).
- (29) T. C. Merkel, Z. He, A. Morisato, and I. Pinnau, *Chem. Commun.*, 1596 (2003).
- (30) J. H. Kim, B. R. Min, K. B. Lee, J. Won, and Y. S. Kang, *Chem. Commun.*, 2732 (2002).
- (31) H. S. Kim, J. H. Ryu, H. Kim, B. S. Ahn, and Y. S. Kang, *Chem. Commun.*, 1261 (2000).
- (32) J. H. Kim, B. R. Min, J. Won, S. H. Joo, H. S. Kim, and Y. S. Kang, *Macromolecules*, **36**, 6183 (2003).
- (33) J. H. Kim, S. H. Joo, C. K. Kim, J. Won, and Y. S. Kang, *Macromol. Res.*, **11**, 375 (2003).
- (34) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *J. Polym. Sci., B: Polym. Phys.*, **42**, 232 (2004).
- (35) J. H. Ryu, H. Lee, Y. J. Kim, Y. S. Kang, and H. S. Kim, *Chem. Eur. J.*, **7**, 1525 (2001).
- (36) C. K. Kim, J. Won, H. S. Kim, Y. S. Kang, H. G. Li, and C. K. Kim, *J. Comput. Chem.*, **22**, 827 (2001).
- (37) S. Choi, J. H. Kim, and Y. S. Kang, *Macromolecules*, **34**, 9087 (2001).
- (38) S. Schantz, *J. Chem. Phys.*, **94**, 6296 (1991).
- (39) P. Carlsson, B. Mattsson, J. Swenson, L. Borjesson, L. M. Torell, R. L. McGreevy, and W. S. Howells, *Electrochim. Acta*, **40**, 2077 (1997).
- (40) J. Y. Kim, S. U. Hong, J. Won, and Y. S. Kang, *Macromolecules*, **33**, 3161 (2000).
- (41) J. H. Kim, B. R. Min, J. Won, and Y. S. Kang, *J. Phys. Chem. B.*, **107**, 5901 (2003).
- (42) H. Nishide, H. Kawakami, S. Toda, E. Tsuchida, and Y. Kamiya, *Macromolecules*, **24**, 5851 (1991).
- (43) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Macromolecules*, **20**, 417 (1987).
- (44) C. K. Kim, C. K. Kim, B.-S. Lee, J. Won, H. S. Kim, and Y. S. Kang, *J. Phys. Chem. A.*, **105**, 9024 (2001).
- (45) Y. S. Kang, J. M. Hong, U. Y. Kim, and J. Jang, *J. Membr. Sci.*, **109**, 149 (1996).
- (46) S. U. Hong, J. Won, H. C. Park, and Y. S. Kang, *J. Membr. Sci.*, **163**, 103 (1999).

- (47) H. Nishide, H. Kawakami, Y. Sasame, K. Ishiwata, and E. Tsuchida, *J. Polym. Sci., A: Polym. Chem.*, **30**, 77 (1992).
- (48) H. Nishide, T. Suzuki, H. Kawakami, and E. Tsuchida, *J. Phys. Chem.*, **98**, 5084 (1994).
- (49) H. Nishide, Y. Tsukahara, and E. Tsuchida, *J. Phys. Chem. B.*, **102**, 8766 (1998).
- (50) B. Jose, J. H. Ryu, B. G. Lee, H. Lee, Y. S. Kang, and H. S. Kim, *Chem. Commun.*, 2046 (2001).
- (51) B. Jose, J. H. Ryu, Y. J. Kim, H. Kim, Y. S. Kang, S. D. Lee, and H. S. Kim, *Chem. Mater.*, **14**, 2134 (2002).
- (52) J. H. Kim, B. R. Min, J. Won, and Y. S. Kang, *J. Membr. Sci.*, **227**, 197 (2003).
- (53) J. Won, Y. Yoon, and Y. S. Kang, *Macromol. Res.*, **10**, 80 (2002).