

Selective Coordination of Silver Ions to Poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) and its Influence on Morphology and Facilitated Olefin Transport

Dong Hoon Lee and Yong Soo Kang*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

Jong Hak Kim

Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

Sang Wook Kang

School of Chemical & Biological Engineering, Seoul National University, Seoul 151-744, Korea

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Abstract: The π -complex membranes of poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS) of two silver salts of AgBF₄ and AgCF₃SO₃ were prepared and tested for the separation of the propylene/propane mixtures. The Fourier-transform infrared (FT-IR) spectra of these complexes showed that the silver salts were dissolved in SEBS up to a silver mole fraction of 0.14, due to π -complexation between the aromatic C=C bonds of styrene blocks and silver ions. Above this solubility limit, ion pairs and high-order ionic aggregates began to form, so that silver salts were distributed unselectively in both the EB and PS blocks. The domain size of the PS blocks was enlarged up to this critical concentration with increasing silver concentration without structural transitions, as confirmed by small angle x-ray scattering (SAXS). These structural properties of the SEBS/silver salt complexes may explain the lower separation properties for propylene/propane mixtures compared to poly(styrene-*b*-butadiene-*b*-styrene)(SBS)/silver salt complex membranes.

Keywords: silver, facilitated transport, membrane, block copolymer, small angle x-ray scattering (SAXS).

Introduction

Olefins such as ethylene and propylene are one of the most important products in the petrochemical industry. To obtain olefins, the separation of hydrocarbons must be carried out, which is currently performed by low temperature distillation processes. Although distillation is reliable, it requires enormous amounts of energy, has high operating costs and necessitates a large capital investment. Thus, the development of an alternative separation technology, e.g. membranes, with cost effectiveness and low energy consumption, is necessary. Unfortunately, the separation of olefin/paraffin mixtures through conventional polymeric membranes is not very effective due to the similar physicochemical properties between the olefin and paraffin.¹

Silver ions have been known to react reversibly with olefin molecules.² Because of the reversible interactions of silver ions with olefins, silver ions can act as olefin carriers in polymeric membranes, resulting in facilitated olefin transport. Paraffins, however are unable to form these complexes

with silver ions, and thus the facilitated olefin transport results in high separation performance for olefin/paraffin mixtures.^{3,4} Numerous investigations have been conducted for olefin/paraffin separations using various types of facilitated transport membranes, i.e. supported liquid membranes or ion-exchange membranes.⁵⁻⁷

Among such membranes, solid polymer electrolytes consisting of silver ions dissolved in a polymer solvent have recently attracted much interest for olefin/paraffin separation due to their remarkable separation performance in the solid state.⁸⁻²⁰ Polymers such as poly(2-ethyl-2-oxazoline) (POZ), poly(ethylene oxide) (PEO) and poly(vinyl pyrrolidone) (PVP) which contain polar groups in their chains have been used as a polymer matrix to dissolve the silver salts with low lattice energy such as AgBF₄, AgClO₄ and AgCF₃SO₃ for facilitated olefin transport membranes.

Previously we have reported a novel type of π -complex membranes comprised of silver salt dissolved in poly(styrene-*b*-butadiene-*b*-styrene) (SBS) block copolymers for the use of facilitated olefin transport.²¹ Facilitated olefin transport was not observable up to a silver mole fraction of 0.14, a threshold concentration, above which transport increased

*Corresponding Author. E-mail: kangys@hanyang.ac.kr

almost linearly with respect to the silver salt concentration. This was because the silver ions selectively coordinate with the C=C bonds of PB blocks up to a silver mole fraction of 0.14, and that the coordinative interaction of the silver ions with aliphatic C=C was stronger than that with aromatic C=C.

In this work, we investigated the selective interactions and morphological changes of the π -complexes of poly(styrene-*b*-poly(ethylene-*co*-butylene)-*b*-styrene) (SEBS) block copolymer with silver salt. Facilitated olefin transport through the SEBS/silver salt complex membranes are also reported and compared with SBS/silver salt complex membranes. The differences of their separation properties were elucidated in terms of ionic interactions as well as the structural changes of the block copolymer complexes.

Experimental

Materials. Poly(styrene-*b*-poly(ethylene-*co*-butylene)-*b*-styrene) (SEBS) block copolymer (28 wt% PS), silver tetrafluoroborate (AgBF_4 , 98%), and silver trifluoromethanesulfonate (AgCF_3SO_3 , 99+%) were purchased from Aldrich Chemical Co. The polymer and silver salts were used without further purification.

Membrane Preparation and Permeance Measurements. Polymer solutions were prepared by dissolving 10 wt% SEBS in tetrahydrofuran (THF, 99+%, Aldrich) with stirring at room temperature. After complete dissolution, a predetermined amount of silver salt was added to each solution depending on the desired mole fraction of silver salt. The solutions were then coated onto a polyester membrane substrate (Whatman, 0.1 μm) using an RK Control Coater (Model 101, Control Coater RK Print-Coat instruments LTD, UK). The solvent was evaporated in a light-protected convection oven at room temperature under a stream of nitrogen, and then the membranes were dried completely in a vacuum oven for two days at room temperature. The thickness of the top polymer electrolyte layer was approximately 1 μm , as determined by scanning electron microscopy (SEM). Permeation tests were performed in a stainless steel separation module as described elsewhere.⁸⁻¹⁰ The flow rate of the mixed gas and sweep gas (helium) were controlled using mass flow controllers. The gas flow rates represented by gas permeance were determined using a soap bubble flow meter. The unit of the gas permeance is GPU, where 1 GPU = $1 \times 10^{-6} \text{ cm}^3 \text{ (STP)}/(\text{cm}^2 \text{ s cmHg})$. Mixed gas (50:50 vol% of propylene: propane mixture) separation properties of the membranes were evaluated by a gas chromatograph (Hewlett Packard) equipped with a TCD and a unibead 2S 60/80 packed column.

Characterization. The solutions were cast onto Teflon-attached glass plates and dried under an N_2 environment. The films were further dried in a vacuum oven for two days at room temperature. Infrared (IR) measurements were per-

formed on a 6030 Mattson Galaxy Series FT-IR spectrometer; and 64–200 scans were signal-averaged at a resolution of 2 cm^{-1} . Raman spectra were collected for SEBS/silver salts films at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman at a resolution of 1 cm^{-1} . This experimental apparatus included a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at 1,064 nm. Spectroscopic characterization was performed using a pressure cell equipped with CaF_2 windows. Small angle X-ray scattering (SAXS) measurements were performed at the 4C1 SAXS beam line at the Pohang Accelerator Laboratory (PAL) in Korea. A double crystal monochromator with an energy resolution ($\Delta E/E$) of about 1% was used to obtain photon numbers with a wavelength of $\lambda=1.6 \text{ \AA}$.

Results and Discussion

Coordination Interactions between Silver Ions and SEBS.

The FT-IR spectra for π -complexation between C=C bonds and silver ions in SEBS/ AgCF_3SO_3 complexes are provided in Figure 1. The free C=C stretching bands of pristine SEBS appeared at 1602 and 1582 cm^{-1} , which are ascribed to the free aromatic C=C stretching in styrene. Upon the incorporation of the silver salt, these peaks became broad and the main peak shifted to 1597 cm^{-1} . This is presumably due to the loosened C=C double bond strength by the coordinative interaction between the silver cation and C=C of styrene. Further increases of the silver concentration to more than 0.2 mole fraction did not lead to any significant changes of the C=C peak, implying there was no large change of the coordinative interactions in the complexes.

Dissolution of Silver Salt. The dissolution behavior of silver salts in SEBS via π -complexation was investigated by monitoring the SO_3^- anion vibrational mode for the SEBS/ AgCF_3SO_3 complexes with various silver mole fractions. The FT-Raman spectra of SEBS complexes with AgCF_3SO_3

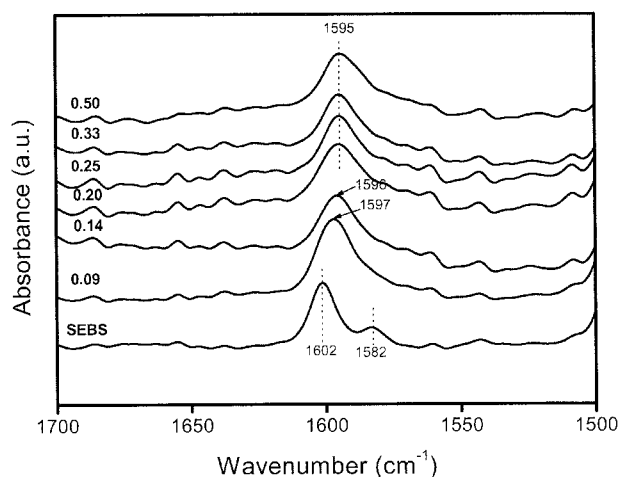


Figure 1. FT-IR spectra of neat SEBS and SEBS/ AgCF_3SO_3 complexes with various mole fractions of silver salt.

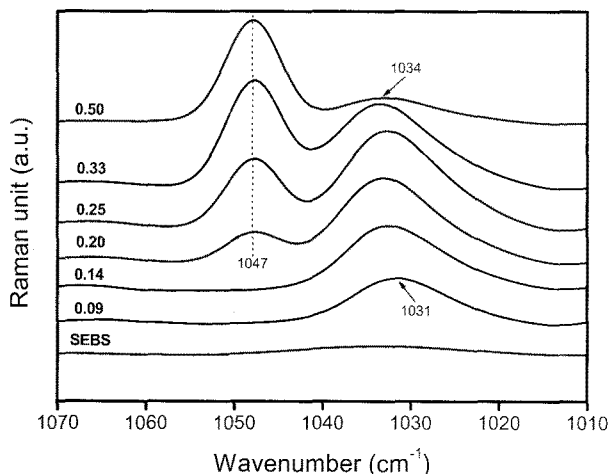


Figure 2. FT-Raman spectra of neat SEBS and SEBS/AgCF₃SO₃ complexes with various mole fractions of silver salt.

were obtained for silver salt mole fractions from 0.09 to 0.50 (Figure 2). It has been reported that the anion stretching bands of SO₃⁻ at 1031, 1037 and 1047 cm⁻¹ are assigned to free ions, ion pairs and higher-order ionic aggregates.^{15,22} Up to a silver mole fraction of 0.14, only the free ions of SO₃⁻ were present. However, when silver concentration was increased further, the main band shifted to 1034 cm⁻¹, and a new peak appeared at 1047 cm⁻¹. The former was attributed to the coexistence of free ions at 1031 cm⁻¹ and ion pairs at 1037 cm⁻¹, and the latter was assigned to higher order ionic aggregates. These FT-Raman spectra represent that silver salts had dissolved to form silver ions up to a mole fraction of 0.14 silver due to π -complexation between the C=C of PS domains and silver ions, above which, silver was present in the form of ion pairs and higher order ionic aggregates.

Structural Change of SEBS/Silver Complexes. To investigate the nano-structural changes of the SEBS block copolymer upon the incorporation of a silver salt, SAXS profiles were obtained for the SEBS/silver salt complexes and are shown in Figure 3. It has been well established that the structure of the block copolymer can be determined from the q values at the intensity maxima, e.g. 1, 2, 3, 4... for a lamellar structure, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$... for a cylindrical structure, and 1, $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{5}$... for a spherical structure.²³⁻²⁷ The neat SEBS block copolymer cast from 10 wt% of SEBS in the THF solution showed a lamellar morphology ($q_1:q_2=1:2$), even though the volume concentration of PS (25 vol% PS) might produce hexagonally packed cylinder morphology. The unusual morphology may arise from the differences of relative interaction strength of THF with PS and EB. Since the interaction of THF/PS pair is stronger than that of THF/EB, THF will be trapped in PS domains for a longer period of time and thus the volume ratio of PS to EB domains might be increased by the amounts of trapped THF. At the end of solvent evaporation, the residual

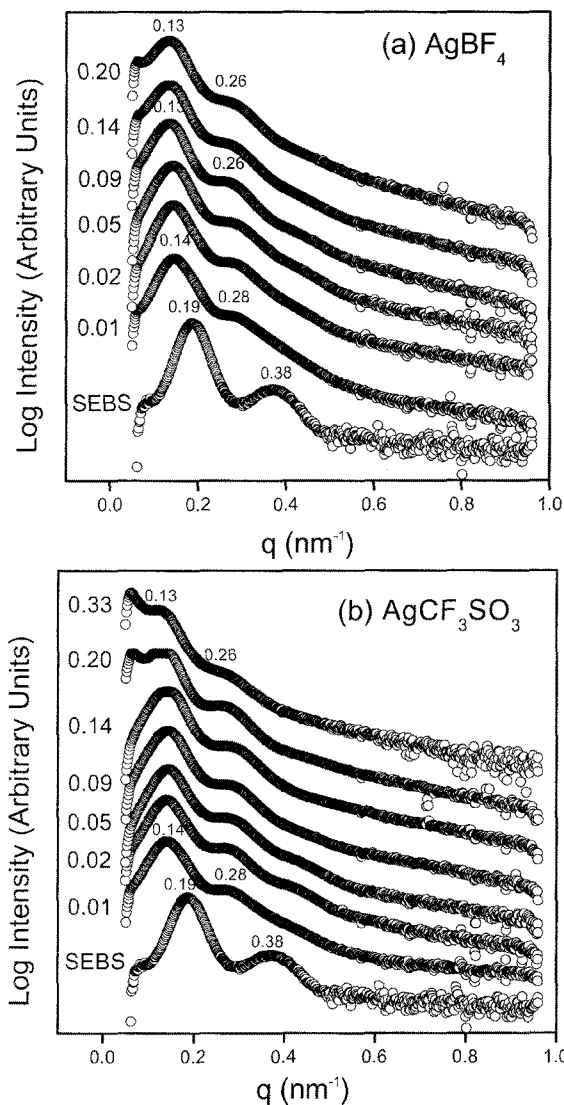


Figure 3. SAXS spectra of (a) SEBS/AgBF₄ and (b) SEBS/AgCF₃SO₃ complexes with various mole fractions of silver salt.

THF behaves like a plasticizer only to the domain of PS. Thus, such an effect of THF on the domain of PS results in the lamellar structure of the SEBS membrane. It is also to be noted that all of the membranes in this study were not annealed to permit structural refinement, because the high temperature annealing (>70 °C) results in a rapid reduction of the silver ions to silver nanoparticles, and a loss of the olefin carrier activity.²⁸

Interestingly, the morphologies of the complex membranes were significantly altered upon the incorporation of silver salt into the SEBS block copolymer, primarily due to the relative volume change of each block by both the addition of silver salts and the coordinative interaction between the silver ions and the C=C bonds. Upon the addition of silver salt up to 0.2, both peaks shifted to a lower q value with

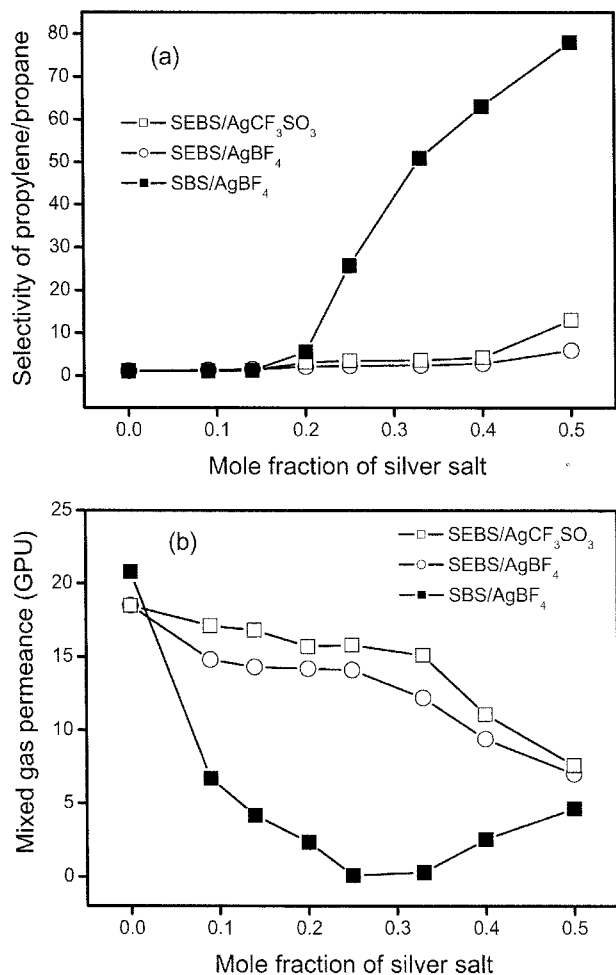


Figure 4. Separation performance of (a) mixed gas selectivity of propylene/propane and (b) total gas permeance through SEBS/AgBF₄, SEBS/AgCF₃SO₃ and SBS/AgBF₄ membranes with various mole fractions of silver salt.

the same ratio of $q_1:q_2=1:2$, indicating a lamellar structure was maintained for both systems. This structural change is probably due to the preferential dissolution of silver salts in PS domains rather than EB domains, resulting in the expansion of PS domains. A further increase in the silver concentration did not greatly change the SAXS spectra for the complexes, indicating the structure persists in the SEBS/silver salt complex membranes.

Facilitated Propylene Transport. Gas separation experiments were carried out using propylene/propane mixtures and SEBS π -complex membranes containing AgBF₄ and AgCF₃SO₃. The separation performances of the membranes are presented as a function of silver concentration in Figure 4. The selectivity of propylene/propane and mixed gas total permeance of SBS/AgBF₄ complex membranes are also included in the figure to compare their separation properties. SBS block copolymer was interesting because it contains both aliphatic and aromatic C=C bonds to interact with

silver ions, and additionally would offer an extra degree of freedom in tailoring nano-structural morphologies of the membranes. As a result, we have found that the facilitated olefin transport is barely observable in the PB membranes whereas it is remarkable in the PS membranes.²¹ The selectivity behavior between SBS and PS complexes is very similar to each other, suggesting that the transport behavior through the SBS complex membranes is mostly controlled by that through the PS domains in SBS membranes. In other words, the high selectivity of the SBS membranes is strongly associated with the facilitated olefin transport through the PS domains in the SBS membranes. Thus, the selectivity through the SBS/AgBF₄ membranes proportionally increased with an increase of silver concentration when the mole fraction of silver salt was more than 0.14. However, there was no significant improvement in the selectivity of the SEBS/silver salt membranes up to a silver mole fraction of 0.5.

These lower separation performances of SEBS/silver salt complex membranes can be elucidated in terms of the morphological properties of the membranes, as revealed by SAXS analysis. At low silver salt concentrations, i.e. lower than a silver mole fraction of 0.14, the silver salts preferentially interacted with the C=C bonds of styrene and thus were mostly located in the styrene domains. At high silver salt concentrations, i.e. above this solubility limit (0.5 mole fraction of silver salt), silver salts were unselectively distributed in both two domains. However, the silver concentrations in styrene domains was higher than that in the EB domains, producing no overall uniform distribution of silver salt in the membranes and consequently less activity of silver ions as an olefin carrier. It should be noted that the concentrations of silver ions in PS domains are still higher than those in EB domains. A schematic illustration of the structural changes of SEBS/silver salt complex membranes with increasing silver concentration is provided in Figure 5.

Separation experiments have been performed using different silver salts such as AgClO₄ and AgNO₃. As a result, the membranes containing AgNO₃ did not show facilitated propylene transport through the membranes. The membranes containing AgClO₄ exhibited the similar separation

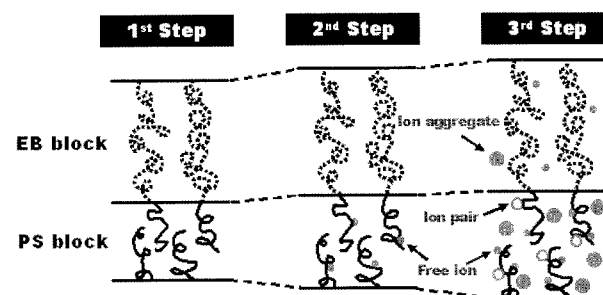


Figure 5. Schematic illustration of the structural changes of SEBS/silver salt complex membranes with an increase of silver concentration.

properties with AgBF_4 and AgCF_3SO_3 . The facilitated propylene transport is seemingly associated with the value of lattice energy of salt. According to the theoretical calculation based on density functional theory, the lattice energy of silver salts is arranged in the order:²⁸ AgBF_4 (680 kJ/mol) \approx AgClO_4 (677) < AgCF_3SO_3 (695) < AgNO_3 (794). A large value of lattice energy represents a strong interaction between silver cations and counteranions, and vice versa. Thus poor facilitated transport through the membranes containing AgNO_3 can be attributed to its higher lattice energy than other salts by around 100 kJ/mol. It demonstrates that interaction of π -complexation between propylene and AgNO_3 is not strong enough to dissociate AgNO_3 . It is also important to see that there is no significant effect of the kind of silver salt among AgBF_4 , AgClO_4 and AgCF_3SO_3 in separating propylene/propane mixtures through SEBS membranes. This result again represent that the morphological properties of membranes are more important than the coordinative interaction strength of silver ions with polymeric matrix in the SEBS membranes.

The mixed gas permeances through SEBS/silver salt complex membranes continuously decreased by increasing silver salt concentration, presumably resulting from the structural compaction of the membranes through the incorporation of salt. In the case of SBS membranes, silver ions interact with both PS domains and PB domains. However, silver ions interact with only PS domains in the SEBS membranes. The structural compaction of SBS membranes would be more significant than SEBS membranes, which results in lower gas permeance in the former than in the latter. It has previously been found that the coordination of silver ions to the ligands of a polymer matrix causes the polymer chains to become more rigid or compact because of transient crosslinks between chains, resulting in higher packing density of the polymer and higher glass transition temperature.¹⁰ As a result, the behavior of gas permeance through the SBS/ AgBF_4 membranes was quite different from that of the SEBS membranes and exhibited two distinct regimes at a limit of a silver mole fraction around 0.25. At the low salt concentration regime, the facilitated olefin transport and the structural compaction effect occurred simultaneously, but the latter was dominant, resulting in less apparent facilitated transport through the membranes. At higher silver concentrations, however, the effect of facilitated propylene transport by the olefin carrier activity of a large amount of silver ions would become dominant compared to that of structural compaction, leading to a gradual, linear increase in the propylene permeance.

Conclusions

Silver salts were selectively dissolved in SEBS block copolymer through the formation of π -complex between aromatic C=C bonds and silver ions. According to the FT-IR and FT-

Raman spectra, silver salts were preferentially coordinated with the C=C bonds of styrene as the form of free ions up to a silver mole fraction of 0.14, above which they were dispersed in the form of both ion pairs and higher order ionic aggregates. Upon the incorporation of silver salt, an extension of the PS domain was observed without a structural transition of the SEBS complex membranes. The SEBS complex membranes exhibited lower separation properties for propylene/propane mixtures than SBS membranes, possibly due to the preferential, selective confinement of silver salt in the former.

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References

- (1) R. L. Burns and W. J. Koros, *J. Membr. Sci.*, **211**, 299 (2003).
- (2) J. P. C. M. Van Dongen and C. D. M. Beverwijk, *J. Organomet. Chem.*, **51**, C36 (1973).
- (3) H. Y. Huang, J. Padin, and R. T. Yang, *J. Phys. Chem. B*, **103**, 3206 (1999).
- (4) D. J. Safarik and R. B. Eldridge, *Ind. Eng. Chem. Res.*, **37**, 2571 (1998).
- (5) W. S. Ho and D. C. Dalrtnple, *J. Membr. Sci.*, **91**, 13 (1994).
- (6) J. S. Yang and G. H. Hsiue, *J. Membr. Sci.*, **111**, 17 (1996).
- (7) D. S. Manley, D. L. Williamson, R. D. Noble, and C. A. Koval, *Chem. Mater.*, **8**, 2595 (1996).
- (8) S. W. Kang, K. Char, J. H. Kim, and Y. S. Kang, *Macromol. Res.*, **15**, 167 (2007).
- (9) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *Macromolecules*, **34**, 6052 (2001).
- (10) J. H. Kim, B. R. Min, C. K. Kim, J. Won, and Y. S. Kang, *Macromolecules*, **35**, 5250 (2002).
- (11) J. H. Kim, B. R. Min, Y. W. Kim, S. W. Kang, J. Won, and Y. S. Kang, *Macromol. Res.*, **15**, 343 (2007).
- (12) S. Sunderrajan, B. D. Freeman, C. K. Hall, and I. Pinnau, *J. Membr. Sci.*, **182**, 1 (2001).
- (13) I. Pinnau and L. G. Toy, *J. Membr. Sci.*, **184**, 39 (2001).
- (14) T. C. Merkel, Z. He, A. Morisato, and I. Pinnau, *Chem. Commun.*, 1596 (2003).
- (15) J. H. Kim, B. R. Min, J. Won, and Y. S. Kang, *Chem. Eur. J.*, **8**, 650 (2002).
- (16) C. H. Jung, G. W. Kim, S. H. Han, and Y. M. Lee, *Macromol. Res.*, **15**, 565 (2007).
- (17) J. H. Kim, B. R. Min, and Y. S. Kang, *Macromolecules*, **39**, 1297 (2006).
- (18) S. H. Kim, J. H. Ryu, H. Kim, B. S. Ahn, and Y. S. Kang, *Chem. Commun.*, 1261 (2000).
- (19) J. H. Kim, B. R. Min, K. B. Lee, J. Won, and Y. S. Kang, *Chem. Commun.*, 2732 (2002).
- (20) J. H. Kim, B. R. Min, J. Won, S. H. Joo, H. S. Kim, and Y. S.

- Kang, *Macromolecules*, **36**, 6183 (2003).
- (21) J. H. Kim, D. H. Lee, J. Won, H. Jinnai, and Y. S. Kang, *J. Membr. Sci.*, **281**, 369 (2006).
- (22) B. L. Papke, M. A. Ratner, and D. F. Shriver, *J. Electrochem. Soc.*, **129**, 1434 (1982).
- (23) S. Rosselli, A.-D. Ramminger, T. Wagner, B. Silier, S. Wiegand, W. Haubler, G. Lieser, V. Scheumann, and S. Hoger, *Angew. Chem. Int. Ed.*, **40**, 3138 (2001).
- (24) M. A. Hillmyer, P. M. Lipic, D. A. Hajduk, K. Almdal, and F. S. Bates, *J. Am. Chem. Soc.*, **119**, 2749 (1997).
- (25) S. Sakurai, S. Aida, S. Okamoto, T. Ono, K. Imaizumi, and S. Nomura, *Macromolecules*, **34**, 3672 (2001).
- (26) H. S. Lee, A. Roy, A. S. Badami, and J. E. McGrath, *Macromol. Res.*, **15**, 160 (2007).
- (27) D. H. Kim and S. C. Kim, *Macromol. Res.*, **16**, 457 (2008).
- (28) C. K. Kim, J. Won, H. S. Kim, Y. S. Kang, H. G. Li, and C. K. Kim, *J. Comp. Chem.*, **22**, 827 (2001).