

The Structural Transitions of π -Complexes of Poly(styrene-*b*-butadiene-*b*-styrene) Block Copolymers with Silver Salts and Their Relation to Facilitated Olefin Transport

Dong Hoon Lee^a, Jong Hak Kim^a, Jongok Won^b, Yong Soo Kang^{a,*}

^a Center for Facilitated Transport Membranes, Korea Institute of Science and Technology,
South Korea

^b Department of Applied Chemistry, Sejong University, Seoul 143-747, South Korea

Introduction

Olefins are the most important feedstock in the petrochemical industry and thus the separation of olefin/paraffin mixtures is crucial to that industry. At present, this separation is mostly carried out using cryogenic distillation processes that require enormous capital investment and have high operational costs. Because this process requires high capital investment and consumes enormous energy, other separation technologies such as membrane separation and reactive absorption have received much attention for both economic and environmental reasons.¹⁻⁴

Polymers containing unsaturated or aromatic C=C bonds can also dissolve silver salts because of the formation of π -complexes between C=C bonds and silver ions. Poly(styrene-*b*-butadiene-*b*-styrene) (SBS) block copolymer is especially appropriate to this purpose because it contains both aliphatic and aromatic C=C bonds, and additionally would offer an extra degree of freedom in tailoring nano-structural properties of polymer/metal salt complexes. To our knowledge, no previous report has addressed the π -complexes of transition metal salts with block copolymers containing C=C bonds. In this study, we have fabricated π -complex membranes consisting of silver salts and SBS block copolymers (30 wt% PS) for use in facilitated olefin transport, and investigated the effects on facilitated transport of the nano-structural transitions of the complexes.

Results and Discussion

Gas separation experiments were carried out using propylene/propane gas mixtures and SBS π -complex membranes containing AgBF₄ and AgCF₃SO₃. The separation performances of the membranes are presented as a function of silver concentration in Figure 1. There is no significant improvement in the selectivity of the membranes up to a silver mole fraction of

0.14, i.e., this is a threshold concentration above which the selectivity increases in proportion to the concentration of the silver salt, reaching approximately 80 for SBS/AgBF₄ and 15 for SBS/AgCF₃SO₃ at a silver mole fraction of 0.5. The significance of this threshold concentration is elucidated in this paper in terms of both the coordination behavior of silver ions with the C=C bonds of the SBS block copolymer and the structural transitions of the π -complex membranes. It should also be noted that 1) the mixed gas selectivity through SBS block copolymer complex membranes is higher than that through other homopolymer complex membranes such as PEO, POZ, PVP, poly(vinyl methyl ketone) (PVMK), poly(methyl methacrylate) or poly(butyl methacrylate),⁵⁻¹⁰ and 2) the SBS block copolymer complex membranes containing AgBF₄ exhibit a better separation performance than those containing AgCF₃SO₃.

The FT-IR spectra of the SBS/silver salt complexes are presented in Figure 2. The uncomplexed, free C=C stretching of neat SBS produces peaks at 1641, 1602 and 1582 cm⁻¹. The peak at 1641 cm⁻¹ is due to uncomplexed aliphatic C=C stretching in PB, whereas the other peaks are due to uncomplexed aromatic C=C stretching in PS. The coordination behavior of C=C bonds with silver ions in SBS/AgCF₃SO₃ complexes can be elucidated. The intensity of the uncomplexed aliphatic C=C stretching band at 1641 cm⁻¹ diminishes rapidly with increases in the silver concentration, whereas that for uncomplexed aromatic C=C stretching remains almost unchanged up to a silver mole fraction of 0.14. At higher silver concentrations, a shift of the aromatic C=C stretching band of PS from 1602 to 1596 cm⁻¹ is evident. These results suggest that silver ions at first preferentially coordinate with the aliphatic C=C bonds of PB blocks upon incorporation of the silver salt in SBS, implying that the coordination interaction between silver ions and the aliphatic C=C bonds of PB is stronger than that between silver ions and the aromatic C=C bonds of PS. Another interesting point to note is that the silver mole fraction of 0.14 corresponds approximately to the threshold concentration for facilitated olefin transport through the SBS/Ag salt complex membranes.

To investigate the nano-structural changes in the SBS block copolymer that occur upon incorporation of a silver salt, SAXS profiles were obtained for the SBS/silver salt complexes and are shown in Figure 3. The SAXS profiles show that the SBS block copolymer has a bicontinuous hexagonally packed cylinder morphology, as indicated by the presence of maxima at positions corresponding to ratios of $1:\sqrt{3}:\sqrt{4}$. The SAXS profiles are significantly changed by the incorporation of a silver salt into the SBS block copolymer. For low salt concentrations in the range 0.01 to 0.09, there is no second peak in the SAXS spectrum, indicating a transition from the bicontinuous hexagonally packed cylinder structure to a disordered micellar structure (i.e., an order-disorder transition). When the salt

concentration is increased up to a silver mole fraction of 0.14, a lamellar morphology with a 1:2 ratio of the intensities of the first and second peaks was observed (i.e. a disorder-order transition), but with positions shifted to lower q values. Interestingly, this composition is coincident with the composition at which silver ions coordinate with PS blocks and thus at which facilitated olefin transport starts to occur.

Conclusion

Silver salts are dissolved in SBS block copolymers by the formation of π -complexes between C=C bonds and silver ions. The complex membranes exhibit excellent performance in the separation of olefin/paraffin mixtures (mixed gas selectivity ≈ 80) due to facilitated olefin transport. According to the FT-IR spectra of these systems, silver ions predominantly coordinate with the C=C bonds of PB blocks, and to a lesser extent with the aromatic C=C bonds of PS blocks. Upon incorporation of the silver salt, the bicontinuous hexagonally packed cylinder morphology of the SBS block copolymer changes to a disordered structure at low silver concentrations (up to a silver mole fraction of 0.05), but a lamellar structure and enlarged domain size of PS blocks arise at high silver concentrations (above a silver mole fraction of 0.14). Interestingly, the threshold concentration (a silver mole fraction of 0.14) for facilitated olefin transport is nearly coincident with the composition at which the silver ions coordinate with the aromatic C=C bonds of PS blocks and thus at which transitions of the complexes' structures from disordered to lamellar start to occur.

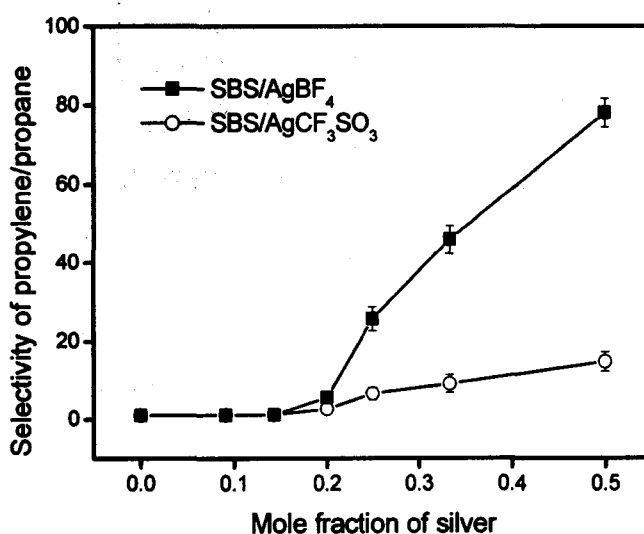


Figure 1. The propylene/propane mixed gas selectivity of SBS block copolymer complexes with silver salts as a function of silver mole fraction.

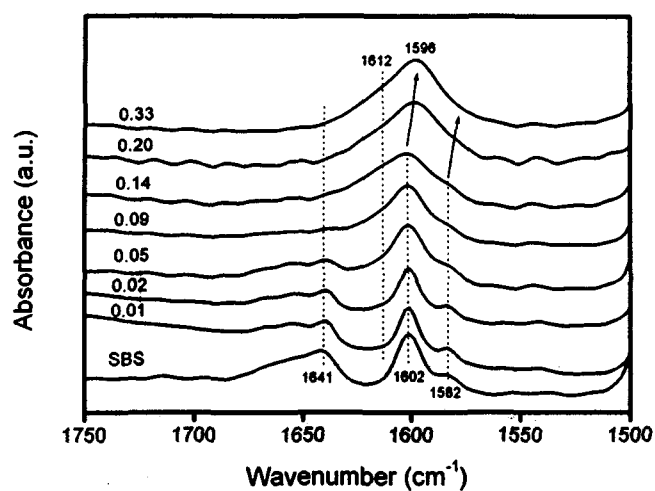


Figure 2. FT-IR spectra of SBS/AgCF₃SO₃ complexes with various silver salt mole fractions.

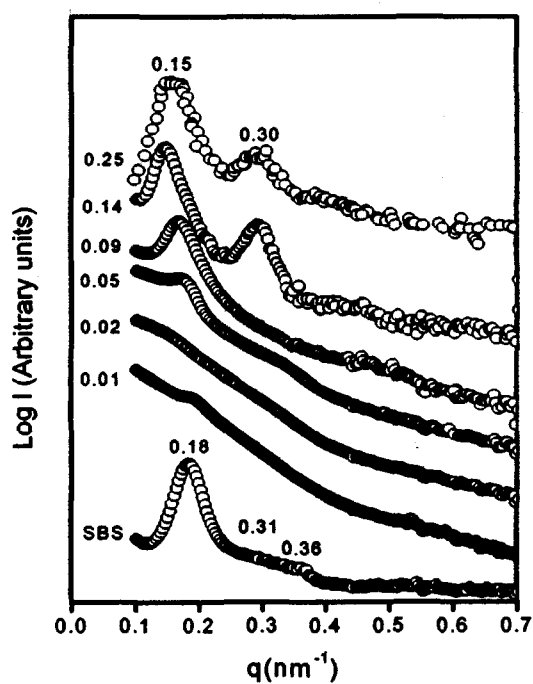


Figure 3. SAXS spectra of SBS/AgCF₃SO₃ complexes with various silver salt mole fractions.

Acknowledgments

The authors gratefully acknowledge the financial support of the Ministry of Science and Technology of Korea through the Creative Research Initiatives Program.

References

1. Safarik, D. J.; Eldridge, R. B. *Ind. Eng. Chem. Res.* **1998**, *37*, 2571.
2. Huang, H. Y.; Padin, J.; Yang, R. T. *J. Phys. Chem. B.* **1999**, *103*, 3206.
3. Padin, J.; Yang, R. T.; Munson, C. L. *Ind. Eng. Chem. Res.* **1999**, *38*, 3614.
4. Zhu, W.; Kapteijn, F.; Moulijn, J. A. *Chem. Commun.* **1999**, 2453.
5. Zalewska, A.; Stygar, J.; Ciszewska, E.; Wiktorko, M.; Wieczorek, W. *J. Phys. Chem. B.* **2001**, *105*, 5847.
6. Hong, S. U.; Jin, J. H.; Won, J.; Kang, Y. S. *Adv. Mater.* **2000**, *12*, 968.
7. Pinnau, I.; Toy, L. G.; Casillas, C. *U. S. Patent* 5,670,051, 1997.
8. Kim, J. H.; Min, B. R.; Kim, C. K.; Won, J.; Kang, Y. S. *Macromolecules* **2001**, *34*, 6052.
9. Sunderrajan, S.; Freeman, B. D.; Hall, C. K.; Pinnau, I. *J. Membr. Sci.* **2001**, *182*, 1.
10. Merkel, T. C.; He, Z.; Morisato, A.; Pinnau, I. *Chem. Commun.* **2003**, 1596.