블록 공중합체와 은의 결합에 의한 올레핀 촉진수송용 고분자 전해질 분리막의 개발

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Development of Solid Polymer Electrolyte Membranes for Facilitated Olefin Transport by Block Copolymer/Silver π-complexation

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Introduction

Many researches on olefin/paraffin separation have been carried out by polymer electrolytes containing silver salt.[1-6] Binary polymer/salt electrolytes based on poly(2-ethyl-2-oxazoline) (POZ), poly(ethylene oxide) (PEO) and poly(N-vinyl pyrrolidone) (PVP) etc. have been commonly used for the facilitated olefin transport membranes. However, these materials show the membrane stability problem mainly due to reduction of the silver ion to silver nano-particles.[7]

The polymers containing unsaturated C=C bonds can also dissolve transition metal salts such as silver salts by forming π-complexes between C=C bond and transition metal ions. Especially, the polymeric ligand containing the C=C group may not allow the deterioration of separation performance with time mainly due to the reduction of silver ions to silver nano-particles.[8] Thus, the development of silver polymer complex membranes based upon the polymeric ligand containing C=C group is highly demanding.

Block copolymers may offer an extra degree of freedom in tailoring the coordination behavior to silver ions in silver polymer complex membranes. In this study, the block copolymers were introduced as a polymer matrix to dissolve silver salts.

Experimental

Poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer (22 wt% PS), silver trifluoromethanesulfonate ($AgCF_3SO_3$, 99+%) and silver tetrafluoroborate ($AgBF_4$, 98%) were purchased from Aldrich.

For the morphology analysis, Small angle X-ray scattering (SAXS) measurements were performed at 4C1 SAXS beam line at Pohang Accelerator Laboratory (PAL) in Korea.

The permeation experiments were carried out using the constant pressure/variable volume method. Mixed gas (50:50 vol. % of propylene/propane mixture) separation performance of the membranes was evaluated by gas chromatography (Hewlett Packard G1530A, MA) equipped with a TCD detector.

Results and Discussion

The morphologies in pure SIS and SIS/Ag salt complexes were studied using the SAXS, as shown in Fig. 1. In the SAXS curve of pure SIS, the scattering peaks occur at positions that are multiples of 2 times the position of the primary reflection, indicating that the block copolymer forms a lamellar morphology. Upon incorporation of silver salt, the SAXS profiles for SIS block copolymer are significantly changed. The most significant change in morphology occurs as a result of coordination of the aromatic C=C in PS block with silver salt. After coordination, the ordered state of the pure SIS is severely disrupted. When the silver salt was added to SIS, all peaks of SIS/silver salt complexes shifted to the low q values.

The mixed gas permeation properties of SIS block copolymer containing silver salt were characterized with propylene/propane gas mixture at room temperature and 40 psig. The mixed-gas permeation properties of SIS/silver salt membranes for olefin/paraffin separation are

shown in Fig. 2. The pure SIS membrane exhibited about 38 GPU of mixed-gas permeance and the propylene/propane selectivity of 1. Raising the silver salt concentration decreased the gas permeance up to silver mole fraction of 0.25. On the other hand, the gas permeance for SIS/silver salt membranes were improved above the silver mole fraction of 0.33. Increasing the mole fraction of silver salt above 0.2 led to the increase of the propylene/propane selectivity, from 1.1 to 62 for $AgBF_4$ and to 14 for $AgCF_3SO_3$. However, SIS containing mole fraction of silver salt below 0.14 didn't show the facilitated olefin transport.

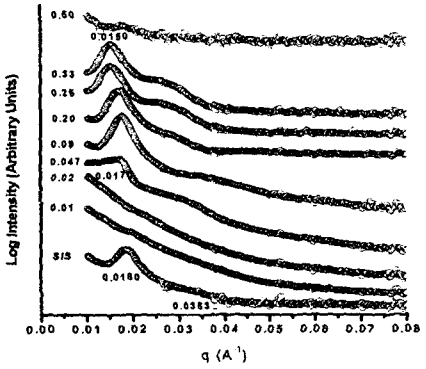

Fig. 1. SAXS spectra for SIS/$AgCF_3SO_3$ complexes with various mole fractions of silver salt.

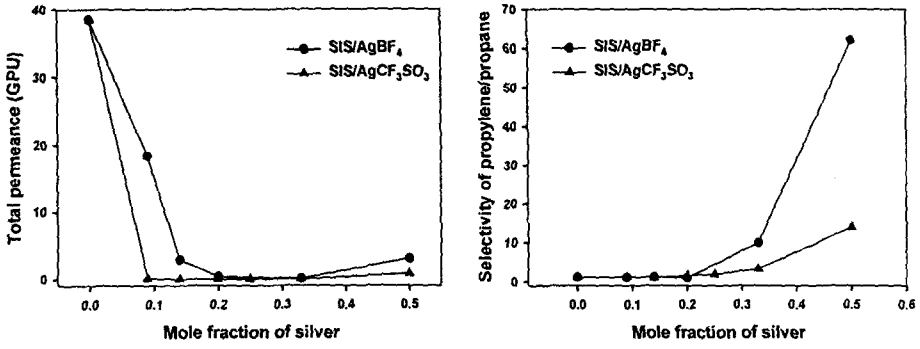

Fig. 2. Separation performance (a) mixed-gas permeance and (b) propylene/propane selectivity for SIS/$AgBF_4$ and SIS/$AgCF_3SO_3$ membranes as a function of silver mole fraction.

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