

Olefin Separation Performances and Coordination Behaviors of Facilitated Transport Membranes Based on Poly(styrene-*b*-isoprene-*b*-styrene)/Silver Salt Complexes

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Received August 4, 2008; Revised September 12, 2008; Accepted September 18, 2008

Abstract: Solid-state facilitated, olefin transport membranes were prepared by complexation of poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer and silver salt. Facilitated olefin transport was not observed up to a silver mole fraction of 0.14, representing a threshold concentration, above which transport increased almost linearly with increasing silver salt concentration. This was because firstly the silver ions were selectively coordinated with the C=C bonds of PI blocks up to a silver mole fraction of 0.20, and secondly the coordinative interaction of the silver ions with the aliphatic C=C bond was stronger than that with the aromatic C=C bond, as confirmed by FT-Raman spectroscopy. Small angle X-ray scattering (SAXS) analysis showed that the cylindrical morphology of the neat SIS block copolymer was changed to a disordered structure at low silver concentrations (0.01~0.02). However, at intermediate silver concentrations (0.15~0.20), disordered-ordered structural changes occurred and finally returned to a disordered structure again at higher silver concentrations (>0.33). These results demonstrated that the facilitated olefin transport of SIS/silver salt complex membranes was significantly affected by their coordinative interactions and nano-structural morphology.

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

Introduction

The separation of olefin/paraffin mixtures is very important in the petrochemical industry.¹ At present, this separation is mostly carried out using cryogenic distillation processes that require enormous capital investment and have high operational costs. Therefore, alternative separation technologies such as membrane separation are demanding and have received much attention for both economic and environmental reasons.²⁻⁵

Many researches on olefin/paraffin separation have been carried out by polymer electrolyte membranes containing silver salt. Binary polymer electrolytes containing silver salt based on poly(2-ethyl-2-oxazoline) (POZ), poly(ethylene oxide) (PEO), poly(N-vinyl pyrrolidone) (PVP), poly(vinyl methyl ketone) (PVMEK), poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) etc. have been used for the solid-state facilitated olefin transport membranes.²⁻¹⁴ However, these materials show the membrane stability

problem because heteroatoms such as O or N in a polymeric matrix leads to the reduction of silver ions to silver nanoparticles.¹⁵⁻¹⁹ To solve this problem, our group proposed novel type of polymer-metal complexes utilizing π -electrons of polymeric ligand without heteroatoms and their applications to separation membranes for olefin/paraffin mixtures.²⁰⁻²² It was found that polymers containing unsaturated C=C bonds can also dissolve transition metal salts by forming π -complexes between C=C bond and transition metal ions.

In our previous report,²³ π -complex membranes were developed based on a silver salt dissolved in a poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS) block copolymer, through which facilitated olefin transport was observed in the solid state. In this study, we have prepared π -complex membranes from a poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer and a silver salt. In particular, the effects of copolymer composition on facilitated olefin transport, coordination behaviors and nano-structural changes of membranes were investigated.

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Experimental

Materials. Poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymers (22 and 14 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. SIS solutions were prepared by dissolving 10 wt% SIS 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 ca. 1 μm , as determined by scanning electron microscopy (SEM).

Gas Permeance Measurements. Permeation tests were performed in a stainless steel separation module as described elsewhere.⁶⁻²³ The flow rates of 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 = $1 \times 10^{-6} \text{ cm}^3 \text{ (STP) / (cm}^2 \text{ s cmHg)}$. Mixed gas (50:50 vol% of propylene:propane mixture) separation properties of the membranes were evaluated by gas chromatography (Hewlett Packard) equipped with a TCD and a unibead 2S 60/80 packed column.

Characterization. For characterization of samples, the polymer 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. Raman spectra were collected for SIS/silver salts films at room temperature using 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

Olefin Separation Performances. The mixed gas perme-

ation properties of SIS/silver salt π -complex membranes for olefin/paraffin separation are shown in Figure 1. SIS block copolymer membranes containing silver salt were characterized with propylene/propane gas mixture at room temperature and 40 psig. The pure polymer membranes without a silver salt exhibited permeances of 38 GPU for SIS (22 wt% PS) and 31 GPU for SIS (14 wt% PS), but the selectivity of propylene/propane was as low as unity for both membranes. However, the selectivity of propylene/propane through the membranes started to increase from 0.2 mole fraction of silver salt, mostly due to facilitated propylene transport. The decrease of mixed gas permeance was also observed up to silver mole fraction of 0.25. Among four kinds of membranes, SIS (22 wt% PS)/ AgBF_4 membranes exhibited the highest separation performances, i.e. the selectivity ~ 60 and mixed gas permeance ~ 4.0 GPU. This result represents that the membrane containing higher concentration of PS are more effective in improving facilitated olefin transport. It is also demonstrated that the use of AgBF_4 leads to higher separation performance than AgCF_3SO_3 .

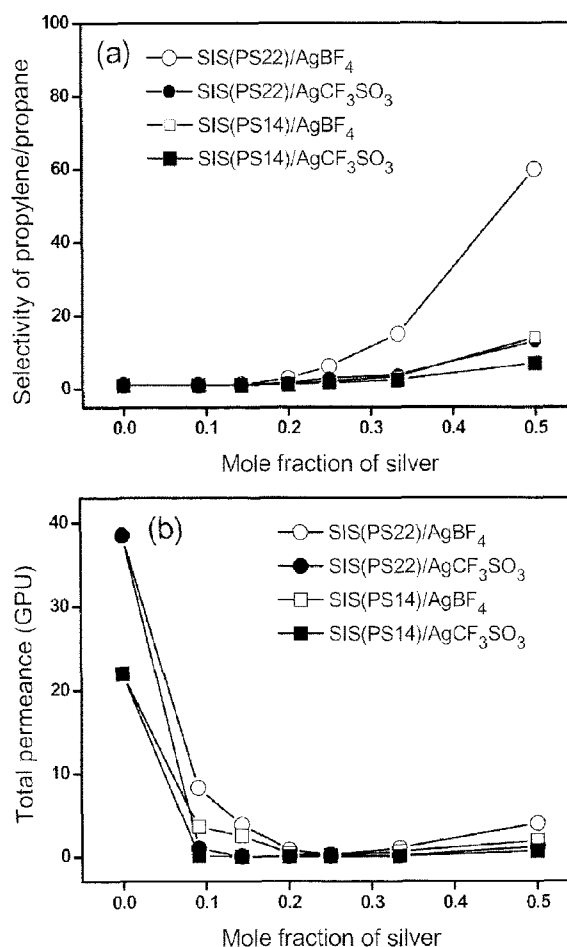


Figure 1. Separation performance in (a) mixed gas selectivity of propylene/propane and (b) total gas permeance through SIS/ AgBF_4 , SIS/ AgCF_3SO_3 (22 wt% PS) and SIS (14 wt% PS)/ AgCF_3SO_3 membranes with various mole fractions of silver salt.

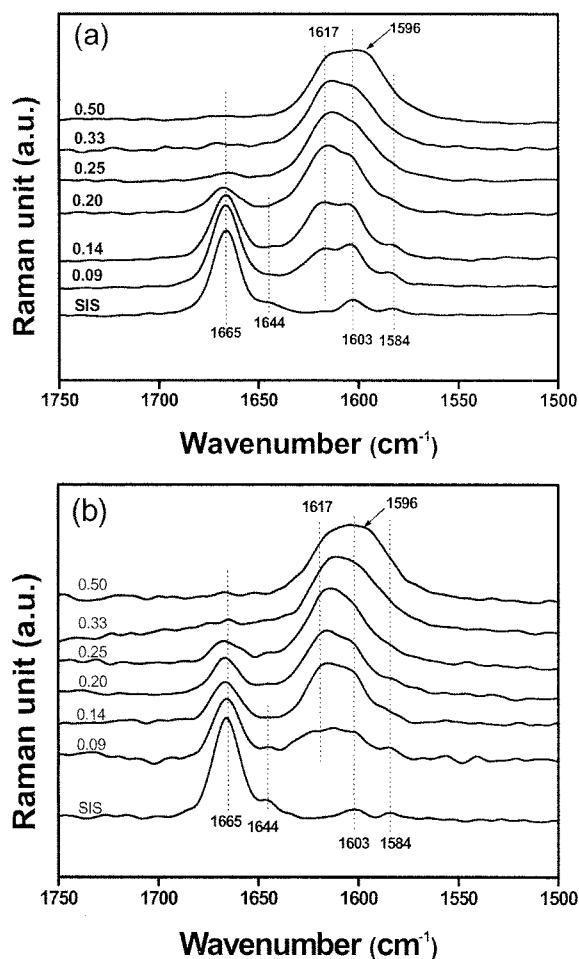


Figure 2. FT-Raman spectra for π -complexation between C=C bonds and silver ions in (a) SIS (22 wt% PS)/AgCF₃SO₃ and (b) SIS (14 wt% PS)/AgCF₃SO₃ complexes membranes.

Coordination Behaviors between Silver Ions and C=C Bonds. The FT-Raman spectra for π -complexation between C=C bonds and silver ions in SIS/AgCF₃SO₃ complexes are shown in Figure 2. The free C=C stretching band of pure SIS appeared at 1665, 1644, 1603 and 1584 cm⁻¹. The bands of 1665 and 1644 cm⁻¹ are attributable to free aliphatic C=C stretching in PI blocks. The other two bands result from the free aromatic C=C stretching in PS blocks. Upon the incorporation of silver salt, the intensity of free aliphatic C=C stretching bands at 1665 and 1644 cm⁻¹ was gradually decreased and a new stretching band at 1617 cm⁻¹ grew up with increasing salt concentrations. This new band is attributable to the formation of π -complexation between aliphatic C=C bonds in PI blocks and silver ions. The band shift to a lower wavenumber is due to the weakening of the aliphatic C=C bonds by silver ion complexation. The aromatic C=C stretching bands of PS blocks at 1603 and 1584 cm⁻¹ were not significantly changed up to 0.33 of silver mole fraction but slightly shifted to a lower wavenumber at 1596 cm⁻¹. These results suggest that silver ions preferentially coordi-

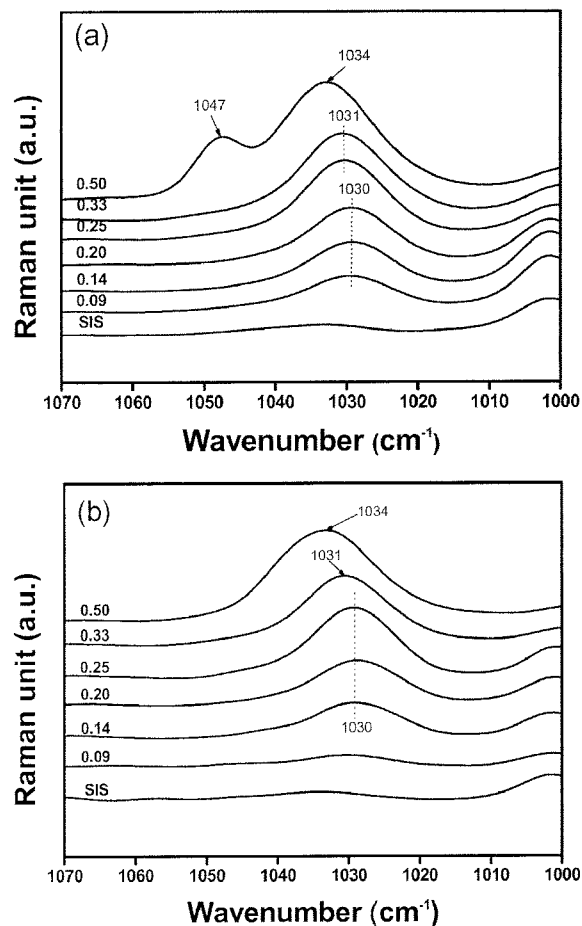


Figure 3. FT-Raman spectra of SO₃⁻ stretching of (a) SIS (22 wt% PS)/AgCF₃SO₃ and (b) SIS (14 wt% PS)/AgCF₃SO₃ complexes of various mole fractions of silver salt.

nate to aliphatic C=C bonds of PI blocks. There was also no significant difference in the coordination behavior between PS 22 wt% and PS 14 wt%.

Interaction of Silver Cation with Anion. The dissolution behavior of silver salts in SIS block copolymer matrix via π -complexation was investigated by monitoring the variation of one SO₃⁻ anion vibrational mode with silver salt mole fraction for the SIS/AgCF₃SO₃ complex. Figure 3 shows the FT-Raman spectra of the ν_1 symmetric stretching vibration of the SO₃⁻ anion for SIS/AgCF₃SO₃ complexes with silver salt mole fractions in the range 0.09 to 0.50. Only a single band at 1030 cm⁻¹ was observed up to 0.2 of silver mole fraction, attributable to the stretching band of free SO₃⁻ anion.^{24,25} At higher silver concentrations, i.e. 0.25 and 0.33 of silver mole fraction, the main band slightly shifted to higher wavenumber at 1031 cm⁻¹, which seems to be still due to free SO₃⁻ anions. When silver concentration was further increased to 0.5, the main band shifted to a higher wavenumber at 1034 cm⁻¹ and a new band appeared at 1047 cm⁻¹. These two bands are attributable to ion pairs and higher order ionic aggregates, respectively.^{24,25} To

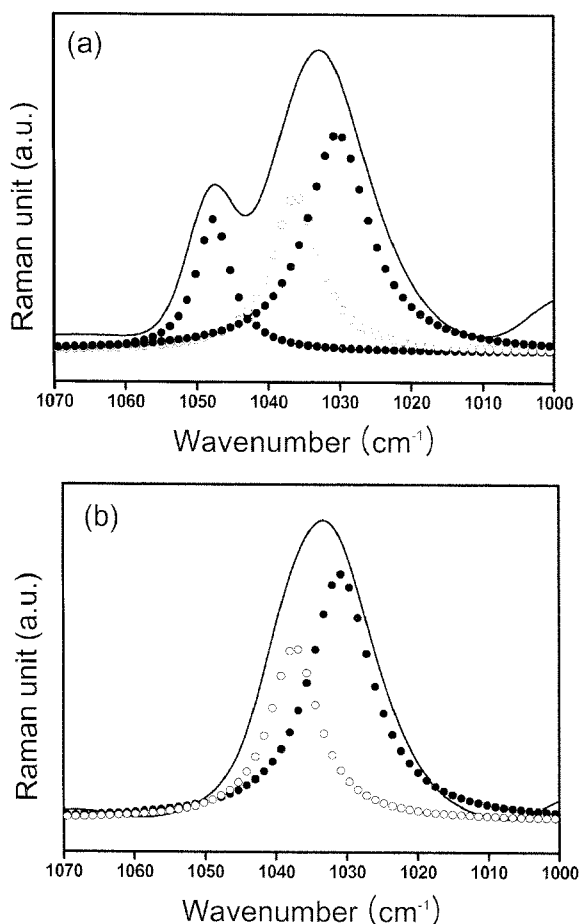


Figure 4. The deconvoluted curves for free ion, ion pair and higher-order ionic aggregates in (a) SIS (22 wt% PS) and (b) SIS (14 wt% PS) complexes with AgCF_3SO_3 from Figure 3.

clearly identify the ionic species in SIS complexes with AgCF_3SO_3 , the stretching band of the SO_3^- anion in Figure 3 was deconvoluted into free ion, ion pair and higher order ionic aggregates, as shown in Figure 4. In the case of SIS (14 wt% PS)/ AgCF_3SO_3 , higher order ionic aggregates were not observed, implying that higher concentration of PI in a block copolymer is effective in dissolving silver salt. This result can be explained by FT-Raman results that silver ions preferentially coordinate to aliphatic C=C bonds of PI blocks.

Structural Changes of SIS/Silver Salt Complexes. The morphologies in pure SIS and SIS/Ag salt complexes were studied using the SAXS, as shown in Figure 5. It is well established that the structure of a block copolymer can be determined from the q values at the intensity maxima, e.g. 1, 2, 3, 4... for lamellar structures, 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$... for cylinder structures, and 1, $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$... for sphere structures.²⁶⁻²⁹ The neat SIS block copolymer (both 22 and 14 wt% PS) showed the hexagonally packed cylinder morphology. Relatively less-developed morphology of SIS block

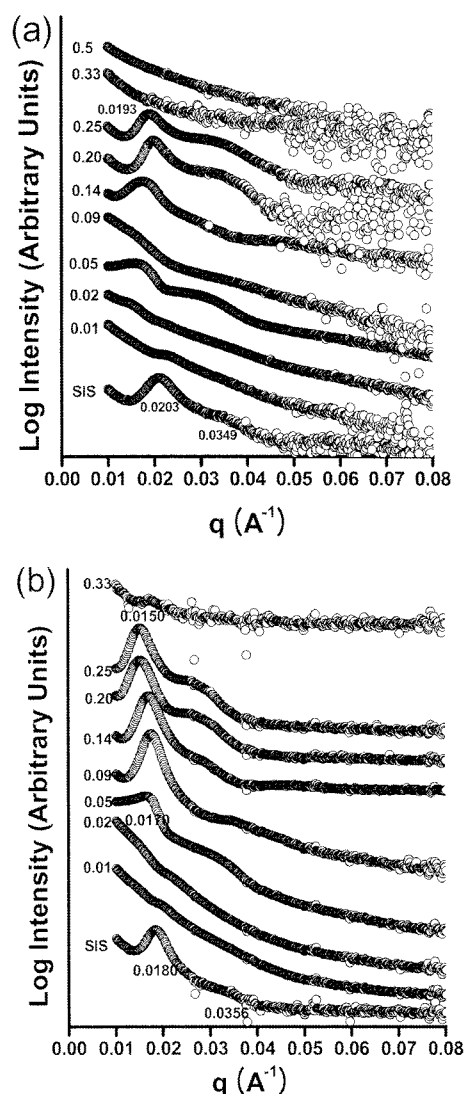


Figure 5. SAXS spectra of (a) SIS (22 wt% PS)/ AgCF_3SO_3 and (b) SIS (14 wt% PS)/ AgCF_3SO_3 complexes with various mole fractions of silver salt.

copolymer is seemingly due to the fast evaporation THF whereas the hexagonally packed cylinder morphology is commonly obtained from toluene solution and slow evaporation conditions. For low salt concentrations of the range 0.01 to 0.02, the SAXS spectra for both systems showed no second peak, indicating their morphologies look apparently different from the neat SIS. The structural change is presumably due to the preferential dissolution of silver salts in PI domains, which is possible because the coordinative interaction of the silver ion with the aliphatic C=C bond is stronger than that with the aromatic C=C bond. When the salt concentration was increased up to the silver mole fraction of 0.14, the second peak in SAXS profiles is observable again, indicating disorder-order transition. At much higher silver concentrations, i.e. above 0.33, the second peak dis-

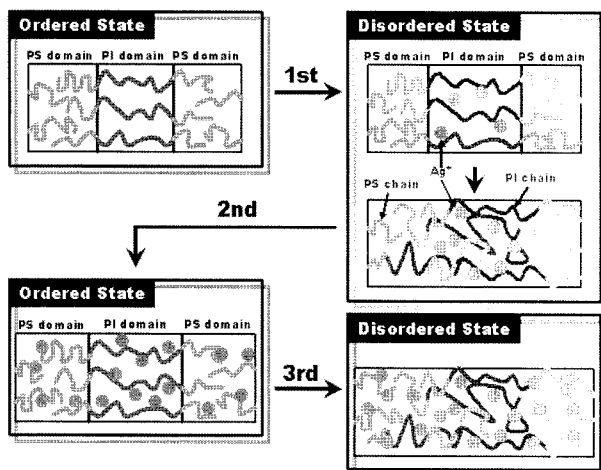


Figure 6. Schematic illustration of the changes in the structures of SIS/silver salt complexes produced by increasing the concentration of the silver salt.

appeared once again, presenting order-disorder transition of SIS/Ag salt complex membranes. It is also observed that the first peak shifted to lower q values from 0.0203 to 0.0193 (22 wt% PS) and 0.015 (14 wt% PS), indicating domain extension of PS.

A schematic illustration of the structural changes of SIS block copolymer complexes with increasing silver salt concentration is presented in Figure 6. In the pure SIS, the block copolymer forms cylinder morphology. Upon the incorporation of silver salt, the ordered state of the pure SIS is severely disrupted at low silver concentrations. The significant change in morphology occurs as a result of coordination of the aromatic C=C in PS block with silver salt. Interestingly, the threshold concentration (a silver mole fraction of 0.14–0.20) 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 from disordered to ordered structure start to occur. At silver concentrations ranging 0.2–0.25, the ordered structures are developed and disordered structures are obtained at much higher silver concentrations above 0.33.

Conclusions

The SIS/silver salts complex membranes exhibit good performance in separation of olefin/paraffin mixtures (mixed gas selectivity ≈ 60) due to facilitated olefin transport. According to the FT-Raman spectra, silver ions preferentially coordinate to the C=C bonds of PS as the form of free ions up to 0.20 of silver mole fraction, and at a higher concentration the silver salts were dispersed as the form of higher-order ionic aggregates, participating in facilitated olefin transport. Upon incorporation of the silver salt, the extension of PS domain was observed appeared in SIS/sil-

ver complexes. Furthermore, it is found that the threshold silver salt concentration of SIS/silver salt membranes for facilitated olefin transport is not different from that of PS/silver salt membrane and at a higher concentrations the silver salts couldn't coordinate with C=C of PS as the form of ions. These morphologies of the complex membranes are significantly changed upon the incorporation of a silver salt into the SIS 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.

Long-term stability of polymer/silver salt complex membranes is also of critical importance for a practical application. A during problem is to maintain the stability of silver ions as an olefin carrier. The disadvantage of silver ions might include that the lack of tolerance to hydrogen or sulfur. Thus our groups are currently investigating the development of an alternative olefin carrier for the use of solid-state olefin transport membranes.²²

Acknowledgement. This work was supported by Energy Technology R&D program (2006-E-ID11-P-13) under the Korea Ministry of Knowledge Economy (MKE). The authors acknowledge the financial support of the Ministry of Education, Science and Technology through the Brain Korea 21 Program at Hanyang University.

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