

AgBF₄/Al(NO₃)₃ 혼합염이 포함된 PEO/PDMS-*g*-POEM 블렌드 기반의 올레핀 분리막

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Olefin Separation Membranes Based on PEO/PDMS-*g*-POEM Blends Containing AgBF₄/Al(NO₃)₃ Mixed Salts

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요 약: 촉진수송은 기존의 고분자 막에서는 힘든, 투과도와 선택도를 동시에 향상시킬 수 있는 기술 중 한 가지이다. 촉진수송 분리막을 이용한 올레핀/파라핀 분리는 기존의 증류공정을 대체할 수 있는 기술로써 많은 관심을 받아왔다. 본 연구에서는 테트라플루오로붕산은/질산알루미늄의 혼합염이 포함된 고분자 블렌드 기반의 촉진수송 올레핀 분리막을 제조하였다. 자유라디칼중합법을 이용하여 폴리다이메틸실록세인-*g*-폴리옥시에틸렌 메타크릴레이트 가지형 공중합체를 합성하였다. 또한, 폴리다이메틸실록세인-*g*-폴리옥시에틸렌 메타크릴레이트 매질에 폴리에틸렌옥사이드를 다양한 비율로 혼합하였다. 폴리에틸렌옥사이드를 폴리다이메틸실록세인-*g*-폴리옥시에틸렌 메타크릴레이트 가지형 공중합체 질량 대비 70%를 혼합하였을 때, 혼합기체 선택도 및 투과도는 5.6 및 10.05 GPU에 도달하였다. 이와 같은 복합막의 올레핀 분리 성능이 향상된 이유는, 분리막에 첨가된 은이온이 올레핀 기체분자의 선택적인 촉진 수송을 하였고, 또한 고투과성의 고분자 블렌드가 사용되었기 때문이다. 또한 은이온의 은나노입자로의 환원을 억제시키는 질산알루미늄의 첨가로 인해 복합막의 장시간 안정도를 향상시킬 수 있었다.

Abstract: Facilitated transport is one of the possible solutions to simultaneously improve permeability and selectivity, which is challenging in conventional polymer-based membranes. Olefin/paraffin separation using facilitated transport membrane has received much attention as an alternative solution to the conventional distillation process. Herein, we report olefin separation composite membranes based on the polymer blends containing AgBF₄/Al(NO₃)₃ mixed salts. Free radical polymerization process was used to synthesize an amphiphilic graft copolymer of poly(dimethyl siloxane)-*graft*- poly(ethylene glycol) methyl ether methacrylate (PDMS-*g*-POEM). In addition, poly(ethylene oxide) (PEO) was introduced to the PDMS-*g*-POEM graft copolymer to form polymer blends with various ratios. The propylene/propane mixed-gas selectivity and permeance reached up to 5.6 and 10.05 GPU, respectively, when the PEO loading was 70 wt% in polymer blend. The improvement of olefin separation performance was attributed to the olefin facilitating silver ions as well as the highly permeable blend matrix. The stabilization of silver ions in the composite membrane was achieved through the introduction of Al(NO₃)₃ which suppressed the reduction of silver ions to silver particles.

Keywords: *facilitated transport, olefin, graft copolymer, silver ion, mixed salt*

1. Introduction

Olefin gases, i.e. aliphatic unsaturated hydrocarbons, are recovered from paraffin gases and commonly used

as intermediate reactants in industrial chemical synthesis such as polymerization[1]. However, due to the similar volatilities of olefin and paraffin, the separation of these mixture *via* distillation process in the pet-

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rochemical industry is highly energy intensive[2]. Thus, the separation of olefin/paraffin mixture using energy-saving membrane technology has received much attention as an alternative solution to the conventional distillation process.

Compared to other separation techniques, gas separation membranes have some advantages such as their small size of facility and ease of operation[3-7]. The great part of operating cost for membrane based gas separation comes from the creation of pressure difference across the membrane to get the separation driving force. The mechanism of gas separation can be classified into size exclusive molecular sieving, diffusion-solution from the pressure difference and the affinity of membrane surface with gas molecule and facilitated transport using carriers[7-9]. Among these mechanisms, the separation of olefin/paraffin can be done *via* facilitated transport. Many investigations have been performed to find out a proper metal ion that could act as the effective carrier and accelerate the transport of olefin through the membrane. Among diverse metal ions, silver ions that are typically generated from silver salt such as AgBF₄ turned out to interact reversibly and specifically with olefin molecules[10] and could act as the olefin carriers in the membranes, resulting in facilitated olefin transport. On the other hand, paraffin which is a saturated hydrocarbon cannot form the complexes with silver ions, which is an essential factor in facilitated transport for high performance olefin/paraffin separation membranes[1,11-13].

Various polymers such as poly(ethylene oxide) (PEO)[14-16], poly(2-ethyl-2-oxazoline) (POZ)[17,18] and poly(vinyl pyrrolidone) (PVP)[19-22] have been widely used as polymer matrix to dissolve the silver salts such as AgBF₄, AgClO₄ and, AgCF₃SO₃ for facilitated olefin transport membranes due to their polar functional groups in the chains. Meanwhile, a rubbery polymer poly(dimethyl siloxane) (PDMS) is one of representative highly permeable membrane material; its propane (C₃H₈) permeability reaches 4100 Barrer (1 Barrer = $1 \times 10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm/cm}^2 \cdot \text{s} \cdot \text{cmHg}$)[23-28].

However, due to the relatively low selectivity and poor interaction of PDMS with silver salt, PEO segment consisting of poly(ethylene glycol) methyl ether methacrylate (POEM) was grafted into PDMS and was used as the matrix material of facilitated transport membrane in this study.

Here, we prepared facilitated olefin transport membranes based on the polymer blends containing AgBF₄/Al(NO₃)₃. An amphiphilic graft copolymer of poly(dimethyl siloxane)-*graft*- poly(ethylene glycol) methyl ether methacrylate (PDMS-g-POEM) was synthesized via free radical polymerization and mixed with PEO to form polymer blends. AgBF₄ and Al(NO₃)₃ were used as the olefin carrier and silver ion stabilizer, respectively. Recently, it was reported that the introduction of Al(NO₃)₃ in polymer/AgBF₄ complex membrane can prevent the reduction of silver ion and thus improve the long-term stability of membrane[29-31]. The structure and morphology of materials were characterized using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and transmission electron microscope (TEM). The propylene/propane mixed-gas selectivity and permeance were investigated in detail.

2. Experiment

2.1. Materials

Monomethacryloxypropyl terminated poly(dimethyl siloxane) (PDMS-mMA, 150-200 cSt, Mw 10,000 g/mol) was purchased from Gelest corporation. Poly(ethylene glycol) methyl ether methacrylate (POEM, Mn 500 g/mol), 2,2'-azobis(2-methylpropionitrile) (AIBN), ethyl acetate (EtOAc), poly(ethylene oxide) (PEO) (Mv 600,000), silver trifluoromethane sulfonate(AgBF₄, Mw 194.67 g/mol) and aluminum nitrate nonahydrate (Al(NO₃)₃ · 9H₂O, Mw~ 375.13 g/mol) were purchased from Aldrich. Hexane (99.9%) and ethanol (EtOH, 99.9%) were purchased from J. T. Baker. All solvents and chemicals were reagent grade and used as received without further purification.

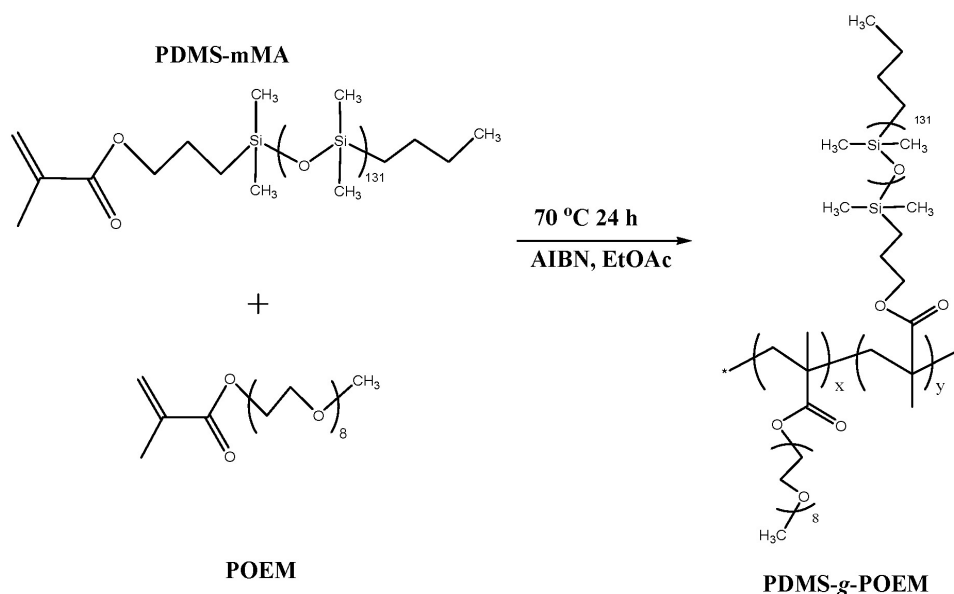


Fig. 1. Synthesis of PDMS-g-POEM amphiphilic graft copolymer via free radical polymerization.

2.2. Synthesis of PDMS-g-POEM graft copolymer

The amphiphilic PDMS-g-POEM graft copolymer was synthesized via free-radical polymerization using PDMS-mMA and POEM as macromonomers in a batch reactor, as shown in Fig. 1. First, 6 mL of PDMS-mMA and 14 mL of POEM were dissolved in 50 mL of ethyl acetate, and then 6 mg of AIBN was added. After sealing tightly, the mixture was stirred and purged with nitrogen for 1 h to remove oxygen in the solution, which deactivates radical polymerization. The reaction was conducted at 70°C in an oil bath and left under constant stirring for 24 h. After the flask cooled down to room temperature, the polymer was precipitated in cold hexane three times and then dried in a vacuum oven at room temperature for 2 days.

2.3. Preparation of facilitated transport membranes

First, the PDMS-g-POEM graft copolymer was dissolved in 50 wt% mixed solvent (EtOH : H₂O = 5 : 5), and then PEO was added into the PDMS-g-POEM solution. The weight ratio of PDMS-g-POEM and PEO varied from 3 : 7, 5 : 5 to 7 : 3 while the total amount of polymer was maintained as 0.1 g. The mixed solution was stirred vigorously at 60°C for overnight. After a homogeneously mixed solution was obtained,

0.443 g of AgBF₄ was added into the solution. Then, 0.0341 g of Al(NO₃)₃·9H₂O was added into the solution in sequence. The solution was then covered with aluminum foil to block out the light and further stirred for 30 min. The solution was coated on the microporous polysulfone support (average pore size = 0.5 μm, Toray Chemical Inc.) using a RK Control coater (Model 101, Control RK Print-Coat Instruments Ltd., UK). After coating, the membranes were dried in a vacuum oven overnight to completely remove the solvent.

2.4. Characterization

FT-IR measurements were performed using an FTIR (Excalibur Series, DIGLAB Co.) between the frequency range of 4000 and 400 cm⁻¹ by using an attenuated total reflectance (ATR) facility. XRD patterns were measured using a Rigaku RINT2000 wide-angle goniometer with a Cu cathode operating at 40 kV and 300 mA. The structure of graft copolymer was confirmed by means of TEM (JEM1010, Japan, JEOL). The gas separation measurement was performed using a constant pressure/variable volume apparatus provided by Airrane Co. Ltd. (Korea). The area of membrane was approximately 10.2 cm². The flow rates of mixed-gas were controlled using a mass flow controller

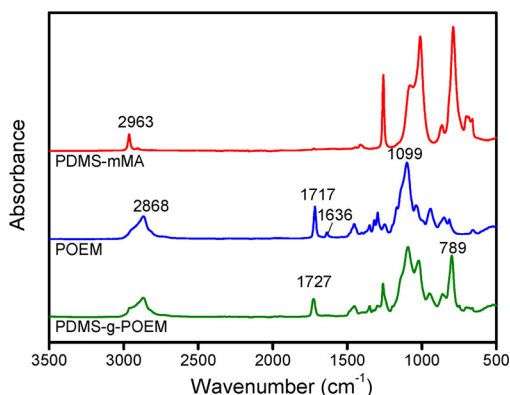


Fig. 2. FT-IR spectra of monomers and PDMS-g-POEM graft copolymer.

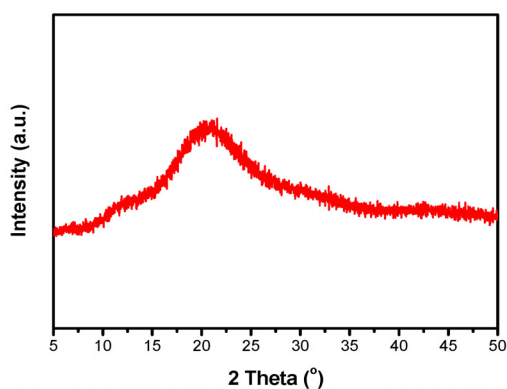


Fig. 3. XRD pattern of PDMS-g-POEM graft copolymer synthesized *via* free radical polymerization.

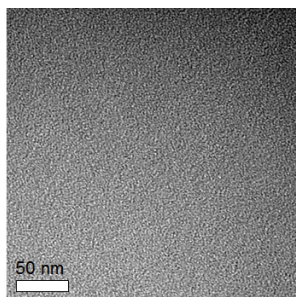


Fig. 4. TEM image of PDMS-g-POEM graft copolymer synthesized *via* free radical polymerization.

(MFC). The gas permeance was measured with a bubble flow meter for various upstream pressures (psig) and atmospheric downstream pressure. Monitoring the difference in the pressure between permeate and retentate and measuring the gas flow rate of component *i* through the permeate, the permeance, (GPU) ($1 \text{ GPU} = 10^{-6} \text{ cm}^3 \text{ (STP)/(s cm}^2 \text{ cmHg)}$), of mixed-gas was calculated. The

mixed-gas (50 : 50 vol% propylene/propane) separation properties were confirmed using gas chromatography (Young Lin 6500 GC system).

3. Results and Discussion

The synthesis of PDMS-g-POEM graft copolymer via free radical polymerization of PDMS-mMA and POEM macromonomers was confirmed by FT-IR spectroscopy, as shown in Fig. 2. The neat POEM macromonomer exhibited strong absorption bands at 2868, 1717 and 1099 cm^{-1} which are assigned to the stretching vibration modes of methyl (CH_2), carbonyl (C=O) and ether (C-O-C) bonds, respectively. A weak band at 1636 cm^{-1} was additionally observed due to the C=C stretching mode of POEM. Compared to the neat POEM, the absorption band at 1636 cm^{-1} was hardly observed for the PDMS-g-POEM graft copolymer, indicating successful polymerization and complete removal of residual monomers. In addition, the absorption band at 1717 cm^{-1} was shifted to a higher wavenumber at 1727 cm^{-1} due to the loss of conjugation in POEM macromonomer[32,33].

XRD analysis has been firmly established as an effective method to characterize the microstructures of polymers[32,33]. The XRD pattern of PDMS-g-POEM graft copolymer is shown in Fig. 3 in which the intensity of X-ray scattering is plotted against diffraction angle (2θ). The PDMS-g-POEM graft copolymer exhibited a broad peak at a diffraction angle of around 21°. According to the Bragg equation, the interchain *d*-spacing was determined to be approximately 4.3 Å. These results represent that the PDMS-g-POEM graft copolymer was a structureless, amorphous and randomly moving coil state. The morphology of PDMS-g-POEM graft copolymer was characterized by TEM image as shown in Fig. 4. The PDMS-g-POEM exhibited microphase-separated structure into the dark PDMS and the bright POEM domains. Two domains could clearly be differentiated from each other due to the greater electron density of Si in PDMS than those of other atoms (i.e. H, C, O) in POEM[34,35].

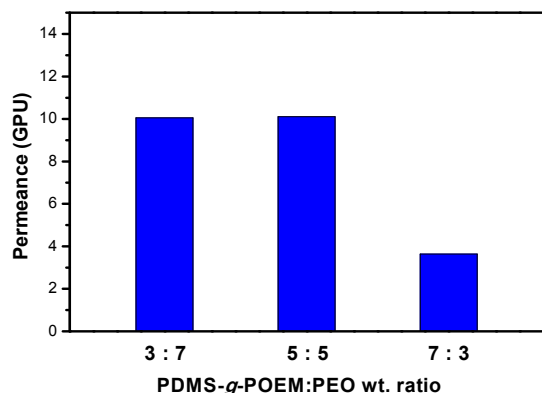


Fig. 5. Mixed-gas permeance through PDMS-*g*-POEM/PEO composite membranes containing AgBF₄/Al(NO₃)₃ with different PDMS-*g*-POEM : PEO ratios.

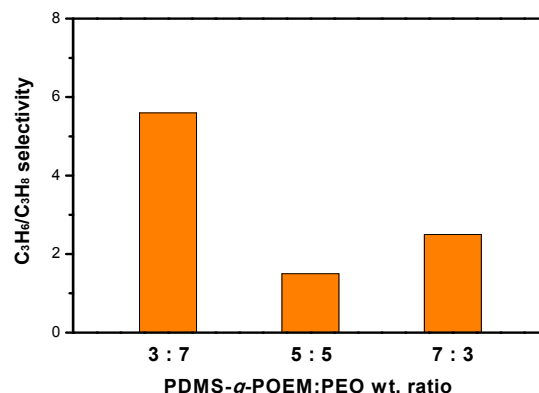


Fig. 6. Mixed-gas selectivity of propylene/propane through PDMS-*g*-POEM/PEO composite membranes containing AgBF₄/Al(NO₃)₃ with different PDMS-*g*-POEM : PEO ratios.

The propylene/propane mixed-gas separation performance of the PDMS-*g*-POEM/PEO blend membranes containing AgBF₄/Al(NO₃)₃ was evaluated as shown in Figs. 5 and 6. The gas separation results show that the selectivity of propylene/propane and the mixed-gas permeance through the membrane tend to increase with the increase in PEO. The blend membrane with 30 wt% PEO loading showed a propylene/propane selectivity of 2.5 and a gas permeance of 3.64 GPU. However, when the PEO loading increased up to 70 wt%, the selectivity of propylene/propane mixed-gas was improved up to 5.6 as well as the gas permeance up to 10.05 GPU. The improvement of membrane performance was attributed to the PEO application which is a highly permeable matrix and also possesses a good affinity with silver salt due to the ether group of PEO[36]. Thus, the successful olefin separation property fundamentally comes from the application of silver ion from AgBF₄ which could act as an olefin carrier and facilitate the selective permeation of olefin such as propylene compared to paraffin such as propane. The obtained performances were not significantly changed up to approximately 100 hours, indicating good long-term stability of membranes. It might be because the introduction of Al(NO₃)₃ stabilized the silver ions and restrained the reduction of the silver ions otherwise might have turned to silver metal nanoparticles and lost their roles as the olefin carrier[29-31].

4. Conclusion

In this study, the olefin/paraffin separation property of composite membranes containing AgBF₄/Al(NO₃)₃ mixed salts was investigated based on the PDMS-*g*-POEM/PEO blend. The PDMS-*g*-POEM graft copolymer was synthesized via free radical polymerization and was used with PEO as the matrix of silver ion applied membranes. The PDMS-*g*-POEM graft copolymer showed structureless, amorphous state and microphase-separated structure into the dark PDMS and the bright POEM domains. The highest propylene/propane selectivity of 5.6 and mixed-gas permeance of 10.05 GPU were obtained when the PDMS-*g*-POEM to PEO ratio was 3 : 7. Such olefin separation property arose from the silver ions which acted as the olefin facilitating carrier as well as the PDMS-*g*-POEM and PEO matrix which contains highly permeable and functional groups segment. Furthermore, the stability of silver ions applied composite membranes was improved due to the presence of Al(NO₃)₃ which suppressed the reduction of silver ions to silver metal nanoparticles.

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