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부피가 큰 치환기를 포함하는 폴리이미드의 합성 및 프로필렌/프로판 분리특성

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Propylene/Propane Separation Through Polyimides Containing Bulky Ethyl Substituents

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요 약: 분리막 기반 공정은 기존 공정에 비해 에너지 소비 및 환경 영향을 감소시킬 수 있는 잠재력을 갖고 있다. 분리막 공정의 성능은 분리막의 투과 특성과 직결되기 때문에, 선택도와 투과도가 우수한 새로운 분리막 소재를 개발하기 위해 많은 연구가 진행되어 왔다. 본 연구에서는 기체 투과선택성 향상을 위해 부피가 큰 에틸 치환기를 포함하는 diamine 단량체인 4,4'-methylenebis(2,6-diethylaniline) (MDEA)을 도입한 폴리이미드를 합성한 후 그 특성을 관찰하고 기체 투과 특성을 조사하였다. 이미드링 질소의 오쏘에 위치한 에틸기는 고분자 사슬의 패킹을 방해하고 사슬 강성과 고분자 사슬 간 거리를 증가시켰다. MDEA 기반 폴리이미드 분리막의 기체 투과 특성을 조사한 결과, 프로필렌/프로판 선택도 14.5와 프로필렌 투과도 7.0 barrer의 결과를 얻었다. 부피가 큰 치환기로 인해 기체 확산 길이가 증가하여 기체 투과 선택성이 높아졌음을 확인하였다. 혼합 기체 투과 결과 또한 MDEA 기반 폴리이미드 분리막이 실제 혼합 기체 공정에서 높은 선택도를 달성할 수 있다는 것을 보여준다. 이러한 MDEA 기반 폴리이미드는 우수한 투과도 및 선택도로 경제적인 프로필렌 분리의 가능성을 크게 높일 수 있다.

Abstract: Membrane-based separations have the potential to reduce energy consumption and environmental impact associated with conventional processes. However, many researches have been done to develop new membrane materials with greater selectivity and permeability. Here, we report highly selective membranes by introducing bulky ethyl substituents into the polyimide. The ethyl group in the ortho position to the imide nitrogen interferes the chain packing and increases chain stiffness and the distance between the polymer chains. The polyimide membranes were synthesized from various aromatic dianhydrides and 4,4'-methylenebis(2,6-diethylaniline) (MDEA). The synthesized membranes with increased gas diffusion length due to bulky substituents showed improved propylene/propane (C_3H_6/C_3H_8) selectivity. Single gas permeation showed high C_3H_6/C_3H_8 selectivity of 14.5, and C_3H_6 permeability of 7.0 barrer was found in MDEA-polyimide. Mixed-gas permeation results also demonstrate that MDEA-polyimide can achieve high selectivity in mixed-gas environment. Furthermore, this approach could significantly increase the feasibility of economic propylene separation compared to conventional polymer materials.

Keywords: *polyimides, gas separation, propylene/propane*

1. Introduction

Propylene is the essential feedstock mentioned along with ethylene in the petrochemical industry. The propylene production process is mainly separated by cryogenic distillation, an energy-intensive process because there is little difference in relative volatility between propylene and propane. Therefore, a highly selective

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membrane incorporated distillation process was proposed to reduce energy demand[1]. Membrane-based separation has gained significant attention as an alternative technology with many advantages such as environmentally friendly, low energy costs, and compactness [2-4]. The membrane process highly depends on the gas permeability and selectivity of the membrane. Hence, the development of membrane materials with good separation properties, mechanical and thermal stability is essential[5].

Considerable studies have been conducted on polymeric membranes with excellent properties mentioned earlier, especially aromatic polyimides. Due to these properties, polyimides have been studied for various industrial applications, including optics, electronics, semiconductors, and gas separations[6-8]. Furthermore, polyimide materials have good processability that can be easily manufactured into flat or hollow fiber membranes for industrial applications. Since the efficiency of the membrane process is directly related to the performance of the membrane, membrane materials with high permeability and selectivity are required. Among the various polyimide studies, polyimide containing fluorine, ketone, and ether in the backbone structure attracted great attention. The fluorine moieties could reduce the intermolecular interaction of aromatic rings and increase solubility[9,10], while ketones and ethers help strengthen the backbone structures[11-15]. Such polyimides, which contain bulky segments, interfere with polymer chain mobility, thus preventing chain packing and strengthening the polymer backbone. Several studies have been conducted on polyimides containing bulky groups to achieve high gas permeability and selectivity. However, most polymeric materials follow the trade-off relation between permeability and selectivity: more permeable material is less selective, and vice versa[4]. An approach to developing polymers by introducing various bulky segments has been proposed as one way to overcome these limitations. Various research has been reported to synthesize polymers with high gas separation performance using bulky monomers and widely applied in the gas separation fields. The synthesis of 6FDA and spirobichroman-based diamines with different substituents (-CF_3, -H, -CH_3) was reported. The 6FDA-FSBC (-CF_3 substituent) with the highest FFV showed 6.6 times higher CO_2 permeability (66 barrer) and slightly lower CO_2/CH_4 selectivity (25) than Matrimid[16]. DOCDA-OPA, which introduced the alicyclic monomer DOCDA, showed moderate permeability of CO_2 (1.71 barrer) and high selectivity of CO_2/CH_4 (74), which are higher than the CO_2 permeability (1.37 barrer) and CO_2/CH_4 selectivity (49) of P84[17,18].

In this study, we demonstrate polyimide containing bulky ethyl substitutes preventing polymer chain packing and observe gas permeability properties of various gases. The polyimides were synthesized from 4,4’-methylenebis(2,6-diethylaniline) (MDEA) as the diamine and three aromatic dianhydrides of 4,4’-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3’,4,4’-benzophenone-tetracarboxylic dianhydride (BTDA), and 4,4’-oxydiphthalic anhydride (OPDA). The four ethyl groups in the phenyl ring of MDEA provides steric hindrance, which disrupts polymer chain packing. The rotation around the central methylene group (-CH_2-) of the ethyl group could affect the inter-chain packing[19-22]. For this reason, MDEA has been used in various studies, including chain extender [23,24] and epoxy resin, due to its structural properties[25]. These structural characteristics of MDEA could enhance the permeation properties of polyimides.

Herein we report the synthesis of MDEA-based polyimides and gas transport properties of common six gases (He, H_2, CO_2, O_2, N_2, and CH_4) and olefin/paraffin gases (C_2H_4, C_2H_6, C_3H_6, and C_3H_8). Moreover, the 6FDA-MDEA polyimide membrane was also characterized under C_3H_6/C_3H_8 mixed gas conditions. The physical properties of MDEA-based polyimides such as density, fractional free volume (FFV), and d-spacing were examined to extend the gas permeation characteristics. The thermal stabilities of glass transition temperatures (T_g) and decomposition temperatures (T_d), and solubility in organic solvents were investigated.

2. Experimental

2.1. Materials

A diamine 4,4'-methylenebis(2,6-diethylaniline) (MDEA, 99%) and three dianhydrides 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%) 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, 98%) and 4,4'-oxydiphthalic anhydride (OPDA, 97%) were purchased from Sigma-Aldrich (USA) and purified by sublimation before use. N-methyl-2- pyrrolidone (NMP, 99.5%) was purchased from Sigma-Aldrich. o-Xylene (97%) and dichloromethane (99.5%) were purchased from Daejung Chemicals & Metals Co, Ltd. (Korea). All reagents were used as received without further purification.

2.2. Synthesis of polyimides

Polyimides were prepared through a conventional two-step imidization method. MDEA (6.2096 g, 20 mmol) was dissolved in NMP (40 mL), and then 6FDA (8.8848 g, 20 mmol) was added under a nitrogen atmosphere. After stirring the mixture at room temperature for 12 h, 40 mL of o-Xylene as an azeotropic agent was added, and the reaction was conducted at 180°C for at least 6 h by reflux in a Dean-Stark trap. The resulting yellow solution was precipitated in water and ethanol (v/v = 3 : 1). The solid was filtered off and washed three times. The obtained polymer was then dried at 120°C for 12 h in a vacuum oven. The polyimide using MDEA and two diamines (BTDA, OPDA) were synthesized in the same procedures.

2.3. Membrane fabrication

The MDEA-polyimide solution was prepared at a concentration of 3~5 wt% in dichloromethane. The prepared solution was filtered with a 0.45-μm filter cartridge and poured into a glass plate with a metal casting ring. The polyimide membranes were formed during two days of slow solvent evaporation at room temperature and atmospheric pressure and dried at 120°C under vacuum for 12 h. The thickness of the membranes was in the range of 40~50 μm.

2.4. Characterization

The structure of polyimide was confirmed by ^{1}H-NMR spectra (VNMRS 600 MHz NMR spectrometer, Varian, USA) and Fourier transform infrared (FT-IR) spectra (Nicolet 6700, Thermoelectron scientific instruments, USA). The glass transition temperature (T_g) of the membranes was measured using differential scanning calorimetry (DSC) analysis (Q20, TA Instruments, USA). Thermo-gravimetric analysis (TGA, Q50, TA Instruments, USA) was used under a nitrogen atmosphere. X-ray diffraction patterns of membranes were recorded on a spectrometer (Rigaku Miniflex 600, Japan) to confirm the intermolecular distance of polyimide membranes through the d-spacing value obtained from Bragg's equation. The density of polyimide membranes was measured by Sartorius balance (Sartorius LA 120S, Germany) with a density kit in water based on the buoyancy method. The density was then calculated using the equation:

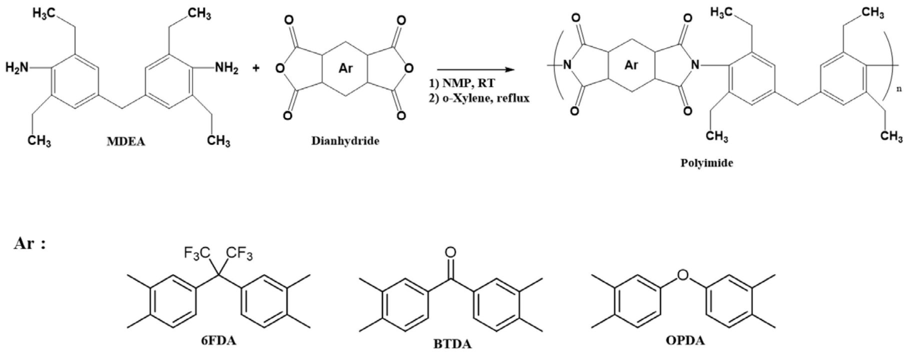
$$\rho_m = \frac{w_{air}}{w_{air} - w_i}\rho_l \tag{1}$$

where w_{air} and w_i are the film weights in air and water, respectively. Fractional free volume (FFV, V_f) was calculated as follows:

$$V_{sp} = \frac{M_0}{\rho} \tag{2}$$

$$V_f = \frac{V_{sp} - 1.3 \times V_w}{V_{sp}} \tag{3}$$

where M is the molar mass of the repeating units, and V_{sp} (cm^3/g) is the specific volume of polymers, which is the inverse value of the measured density, and V_w (cm^3/g) is the van der Waals volume derived from Bondi's group contribution theory[26,27].



Scheme 1. Synthesis of polyimides from MDEA and three dianhydrides.

2.5. Gas permeation measurement

Gas permeation properties were measured using a time-lag method at a feed pressure of 1 atm and a temperature of 35°C with high purity single gases (He, H_2, O_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8). In a steady-state of pressure increment as a function of time, the gas permeability coefficients were calculated by using the following equation:

$$P = \frac{dp}{dt}\left(\frac{VT_0 l}{p_0 T \triangle p A}\right) \tag{4}$$

where P (Barrer) [1 Barrer = 10^{-10} cm^3 (STP) · cm/cm^2 · s · cmHg] is the gas permeability, V (cm^3) is the downstream volume, l (cm) is the membrane thickness, $\triangle p$ (cmHg) is the pressure difference between upstream and downstream, T (K) is the measurement temperature, A (cm2) is the effective membrane area, p_0 and T_0 are the standard pressure and temperature, and dp/dt is the rate of pressure increase at steady state. The ideal selectivity of two components is defined as the ratio of the gas permeability of two species:

$$\alpha = \frac{P_1}{P_2} \tag{5}$$

where P_1 and P_2 represent the permeability of each species, respectively.

The mixed gas permeation properties were measured by the constant-pressure variable-volume method. The feed gas mixture at propylene/propane (50/50) and the gas permeability was measured at 35°C. Helium was used as the sweep gas, and the stage-cut, the ratio of the permeate flow rate to feed flow rate, was controlled below 0.01 to avoid concentration polarization. The flow rate of gas in retentate and permeate was measured by an Agilent ADM flow meter. The permeate composition was determined by using an Agilent 6890A gas chromatography equipped with a flame ionization detector.

3. Results and Discussion

3.1. Synthesis of MDEA-based polyimides

The polyimides containing MDEA were synthesized by the reaction of MDEA with 6FDA, BTDA, and OPDA, respectively (Scheme 1). The molecular weight of more than M_w = 4.4 × 10^4 g/mol with a polydispersity of 1.9~2.5 were obtained by GPC (Table 1). The intrinsic viscosities of polymers, related to the molecular weight, were measured with a concentration of 0.05 g/dL in NMP at 25°C. The intrinsic viscosities of polyimides were in the range between 0.89 and 0.95 dL/g. The molecular weight and intrinsic viscosity results show the synthesized polyimides are suitable for mechanically robust dense membrane formation. The synthesis of MDEA-based polyimides was verified using ATR-FTIR (Fig. 1), ^{1}H NMR (Fig. 2). The MDEA-based polyimides showed typical absorption bands of polyimide (Fig. 1) around 1780, 1701 (C=O stretching), and

Table 1. Molecular Weights of the MDEA-based Polyimides

Polymer	Intrinsic viscosity (dL/g)	M_n (10^4)	M_w (10^4)	PDI (M_w/M_n)
6FDA-MDEA	0.96	2.3	4.5	1.98
BTDA-MDEA	0.90	1.8	4.4	2.50
OPDA-MDEA	0.98	2.1	4.6	2.24

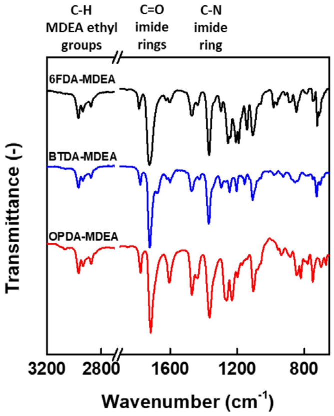


Fig. 1. ATR-FTIR spectra of the MDEA-based polyimide membranes.

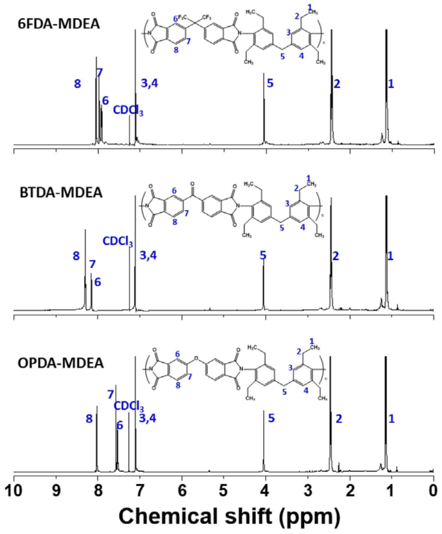


Fig. 2. ^{1}H NMR spectra of the MDEA-based polyimides ($CHCl_3$-d_6, 600 MHz).

1380 cm^{-1} (C-N stretching). Ethyl substituents of MDEA were shown around 2970, 2940 cm^{-1} (C-H stretching). ^{1}H-NMR spectra (Fig. 2) of MDEA-polyimide showed aromatic hydrogens in MDEA 7.15 ppm and ortho ethyl substituents at 2.48 ppm.

Table 2. Thermal Properties of MDEA-based Polyimides

Polymer	T_g (°C)	$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)
6FDA-MDEA	268	509	530
BTDA-MDEA	285	505	523
OPDA-MDEA	267	517	532

$T_{d,5\%}$: Temperature at which 5% weight loss was recorded by TGA.
$T_{d,10\%}$: Temperature at which 10% weight loss was recorded by TGA.

3.2. Thermal properties of MDEA-polyimides

The thermal properties of the synthesized polyimides were measured by DSC and TGA (Table 2). The T_g values of the polyimides were observed in the range from 267 to 285°C, in the order of BTDA-MDEA > 6FDA-MDEA > OPDA-MDEA, which can be explained by their chemical structures. The T_g phenomenon suggested that the ketone-bridge is more rigid than the -$C(CF_3)_2$- units and the ether linkage. In addition, these MDEA-based polyimides have slightly lower T_g values compared to other polyimides without ethyl substituents. It is because the bulky alkyl group has two effects on the T_g of the polymer. The first is the introduction of bulky alkyl group in the polymer backbone, reducing intermolecular interaction and chain packing, increasing the free volume of the polymer, and reducing T_g. Second, when the bulky alkyl group is attached to the imide ring, it limits the polymer chain rotation, increasing chain stiffness and T_g. Thus, when large alkyl groups, especially ethyl groups, are introduced, the free volume of polymer increases and T_g decreases[12]. The decomposition temperatures were 505~515°C, and the T_g and T_d values were high enough to withstand the high operating temperatures for practical gas separation applications.

Table 3. Physical Properties of MDEA-based Polyimides

Polymer	ρ (g/cm^3)	FFV	d-spacing
6FDA-MDEA	1.259 ± 0.02	0.164	6.31
BTDA-MDEA	1.157 ± 0.02	0.161	6.29
OPDA-MDEA	1.161 ± 0.01	0.157	6.24

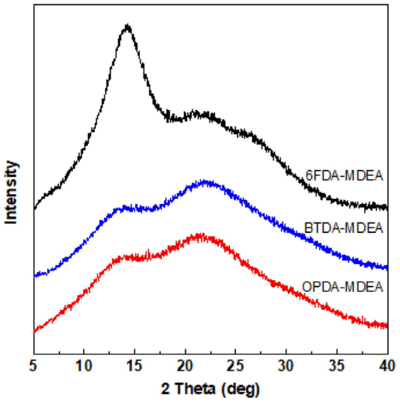


Fig. 3. X-ray diffraction patterns of MDEA-based polyimides.

3.3. Physical properties

The diffusivity in polymer membranes highly depends on the free volume of the polymer. The d-spacing value represents the intermolecular or intermolecular distance of the polymer chain, and the fractional free volume (FFV) indicates the degree of polymer chain packing. As d-spacing and FFV values increase, gas diffusion increases, and gas permeability increases. Thus, as d-spacing and FFV values increase, gas diffusivity increases, and consequently, gas permeability increases. The density of dense membranes was measured to calculate fractional free volume (FFV) values (Table 3). The FFV values were 0.164 for 6FDA-MDEA and 0.161, 0.157 for BTDA-MDEA and OPDA-MDEA, respectively. The polyimide with 6FDA has a higher FFV value due to the bulky -C(CF$_3$)$_2$- units compared with the polyimide derived from BTDA and OPDA, as expected[28]. The XRD data indicate the polymer interchain packing in membranes (Fig. 3). The peak positions and the calculated d-spacing values of the peaks are listed in Table 3. The MDEA-based polyimides showed two broad diffraction peaks located at 2θ = 14.0°, 21.8°. It implies that the structure of the MDEA-based polyimide membranes was mainly amorphous morphology but combined with some ordered chain packing and π-π stacking of aromatic rings. The calculated d-spacing values and FFV values varied in the order of 6FDA-MDEA > BTDA-MDEA > OPDA-MDEA, which are highly dependent on the structures of aromatic dianhydrides.

3.4. Solubility of MDEA-based polyimides in organic solvents

The solubility of the MDEA-based polyimides was measured in various organic solvents (Table 4). The synthesized polyimides reported here are highly soluble in solvents such as chloroform, dichloromethane, and DMAc. The good solubility properties are because MDEA includes methylene bridge and bulky ethyl groups, which inhibited the efficient packing of polymer chains. Due to their excellent solubility properties, the MDEA-based polyimides are good candidates for fabrication into asymmetric or composite membranes.

3.5. Gas transport properties

The single gas permeabilities of three MDEA-based polyimide membranes were measured for common six gases (He, H_2, CO_2, O_2, N_2, and CH_4) and olefin/paraffin gases (C_2H_4, C_2H_6, C_3H_6, C_3H_8) by the time-lag method. The results of single gas permeability and selectivity can be explained based on the solution-diffusion mechanism[29]. Thus, small gases (He and H_2) or condensable gas (CO_2) permeates faster than larger non-condensable gases (O_2, N_2, CH_4). Permeability results for He, H_2, CO_2, O_2, N_2, and CH_4 in MDEA-based polyimides decreased in the order of 6FDA-MDEA > OPDA-MDEA > BTDA-MDEA, which is appropriately consistent with T_g, FFV, and d-spacing values in Tables 2 and 3. Among the MDEA-based polyimides, 6FDA-MDEA showed the highest permeability for H_2 (139 barrer) and CO_2 (116 barrer) and slightly low selectivity of H_2/CH_4 (19) and CO_2/N_2 (19). This implies that the high permeability of the 6FDA-MDEA is mainly due to the high FFV values consistent with the polymer in-

Table 4. Solubility of the MDEA-based Polyimides

Polymer	Acetone	Chloroform	DCM	DMAc	DMF	NMP	THF	Toluene	MeOH
6FDA-MDEA	-	++	++	++	+	+	+	-	-
BTDA-MDEA	-	++	++	++	++	++	++	-	-
OPDA-MDEA	-	++	++	++	++	++	++	-	-

++: soluble, +: partially soluble, -: insoluble at room temperature.

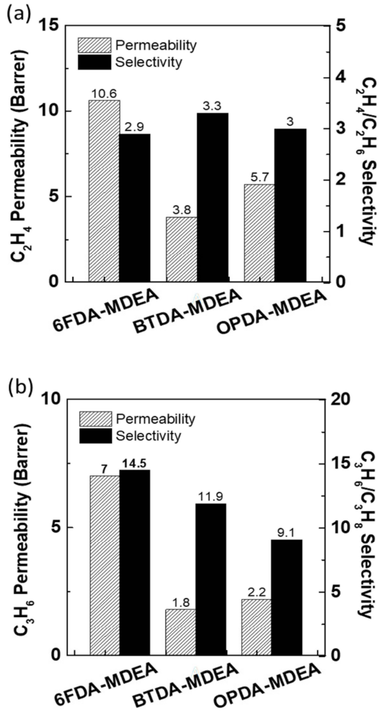


Fig. 4. Olefin/paraffin single gas transport properties of MDEA-based polyimides (measured at 1 atm, 35°C).

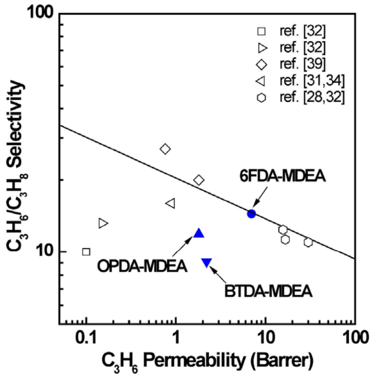


Fig. 5. Gas permeability and selectivity of MDEA-polyimides in comparison with C_3H_6/C_3H_8 upper bound (references: BTDA-DAPI, 6FDA-DMDB[32], 6FDA-6FpDA[31,34], 6FDA-DDBT[39], 6FDA-DAM[28,32]).

terchain distance. BTDA-MDEA has the same FFV value as other MDEA-based polyimides. However, the T_g value is significantly higher, resulting in the lowest gas permeability due to its rigid ketone group.

Meanwhile, the propylene/propane single gas transport results showed both the highest permeability and selectivity of C_3H_6 (7 barrer) and C_3H_6/C_3H_8 (14.5) in 6FDA-MDEA. BTDA-MDEA and OPDA-MDEA showed C_3H_6 permeability about 1.8 and 2.2, respectively, and C_3H_6/C_3H_8 selectivity of 11.9 and 9.1 (Fig. 4). The ethylene/ethane separation performance were obtained the highest C_2H_4/C_2H_6 selectivity (3.3) in BTDA-MDEA and the highest C_2H_4 permeability (10.6 barrer) in 6FDA-MDEA. Due to the bulky -C(CF$_3$)$_2$- unit of 6FDA, the 6FDA-MDEA with the highest FFV value had the highest ethylene and propylene permeability. In addition, the highest C_3H_6/C_3H_8 selectivity of 6FDA-MDEA is attributed to its high diffusivity selectivity, as typical polymeric membranes have solubility selectivity about around[13,31]. The propylene permeability results were close to or beyond the so-called upper bound lines (Fig. 5). BTDA-MDEA shows higher C_3H_6/ C_3H_8 selectivity than conventional polymer material Matrimid (BTDA-DAPI), which is attributed to the increased polymer chain flexibility due to the bulky ethyl substituents of MDEA[32]. 6FDA-MDEA reaches high C_3H_6/C_3H_8 selectivity and moderate permeability compared to 6FDA-DAM, which has C_3H_6 permeability of about 15.7 Barrer and C_3H_6/C_3H_8 selectivity of 12.4 [32,33]. It is considered that MDEA contains four bulky ethyl groups, which leads to higher diffusivity selectivity. The high C_3H_6 permeability and C_3H_6/C_3H_8 selectivity results of MDEA-based polyimide indicate

Table 5. Single Gas Permeability and Ideal Selectivity of MDEA-based Polyimide Membranes

	Permeability (Barrer)						Ideal selectivity (α)		
Polymer	He	H_2	CO_2	O_2	N_2	CH_4	O_2/N_2	CO_2/N_2	H_2/CH_4
6FDA-MDEA	109	139	116	25	6.1	7.2	4.2	19	19
BTDA-MDEA	45	63	41	9.3	1.8	2.5	5.1	22	25
OPDA-MDEA	45	66	44	9.5	2.1	2.8	4.6	21	24

Measured at 1 atm, 35°C. Ideal selectivity α = P_1/ P_2.

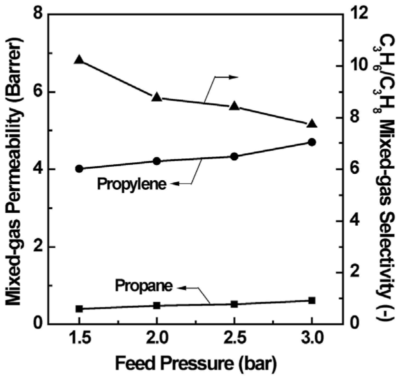


Fig. 6. Mixed C_3H_6/C_3H_8 gas permeation data of 6FDA-MDEA membrane. (feed gas C_3H_6/C_3H_8 (50/50), measured at 35°C.)

the possibility of being utilized as membrane materials for separation of C_3H_6/C_3H_8 mixtures.

The mixed gas separation experiment was conducted on 6FDA-MDEA with the best single gas separation performance among MDEA-based polyimides. The C_3H_6/C_3H_8 (50/50) mixed-gas separation results showed lower C_3H_6/C_3H_8 selectivity than those achieved in the single gas condition (Fig. 6). The ideal C_3H_6/C_3H_8 selectivity of 6FDA-MDEA was 14.5, while under mixed gas condition was 8.7 at 1 bar. The reduction in C_3H_6/C_3H_8 selectivity is due to the competitive sorption of C_3H_6 and C_3H_8, and the plasticization effect. Both C_3H_6 and C_3H_8 are condensable gases, which tend to plasticize polymeric membranes even at low pressures of 3 bar[34]. The swelling in the polymer leads to an increase of the C_3H_6 or C_3H_8 permeability and decreases the selectivity of the membrane. In mixed-gas compositions, the increase in the FFV of the polymer due to the swelling in the matrix may result in loss of the size discrimination ability. Thermal annealing and chemical crosslinking methods to suppress plasticization are proposed[35-38], and the resulting crosslinked membrane could mitigate the polymer matrix swelling. For further development of the synthesized membranes, a method for suppressing plasticization is being studied and will be discussed in our future work.

4. Conclusions

MDEA-based polyimides were synthesized by using chemical azeotropic imidization method using three other anhydrides (6FDA, BTDA, and OPDA) and MDEA, which contains bulky ethyl groups. The rigid dense membranes were fabricated based on molecular weight, intrinsic viscosity, solvent solubility, and thermal stability results of MDEA-based polyimides. The gas permeability of synthesized polyimide membrane for six gases (He, H_2, CO_2, O_2, N_2, and CH_4) and olefin/paraffin gases (C_2H_4, C_2H_6, C_3H_6, C_3H_8) is in the order of 6FDA-MDEA > OPDA-MDEA > BTDA-MDEA, supported by FFV values and d-spacing values. Among the three MDEA-based polyimides, 6FDA-MDEA showed the highest selectivity of C_3H_6/C_3H_8 (14.5) and C_3H_6 permeability (7 barrer). Compared with conventional polymer membranes for propylene separation, the synthesized polyimide membranes exhibited better C_3H_6/C_3H_8 selectivity. This study increases the feasibility of a propylene separation process that is more economical than conventional polyimide materials.

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