열변환을 통해 아민기를 포함한 폴리이미드로부터 얻어진 고성능 고분자막의 제조 및 특성

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Preparation and Characterization of Thermally Rearranged Polymer Membranes Derived from Amine-containing Polyimide

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1. Introduction

Highly permeable polymer materials have received much attention as gas separation membranes. Recently, glassy polymers like PTMSP or PIM were reported to show good gas permeation characteristics from their regular free volumes in the polymer matrix. In company with these advances, extraordinary polymer materials were developed via thermal rearrangement at elevated temperature.[1] The unusual rearrangement of ortho-functional polyimides produced uniform micropores in the dense polymer films. These thermally rearranged polymers such as polybenzoxazole, polybenzothiazole and polypyrrolone showed both the drastically increased gas permeabilities for small gas molecules and the advanced thermal and mechanical properties.

In this study, we would like to describe the results from the modified polypyrrolone membrane to investigate the structural changes at alkaline solution. The resultant polybenzimidazole(PBI) is known as an excellent high performance material because of its remarkable

thermal, mechanical and chemical stabilities [2-5]. Accordingly, we would focus on polyimide having diamine groups in ortho-position, which was converted to polypyrrolone and its derivatives.

2. Experimental

2.1. Material and monomers

The 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 3,3′-diaminobenzidine (DBZ) were purchased from Tokyo KASEI (Tokyo, Japan) and purified at 220-230℃ for 6FDA and at 85-90℃ for DBZ. 1-methyl-2pyrrolidinone (NMP) as a solvent was obtained from Aldrich and used without further treatment.

2.2 Membrane Preparation

10 mmol of DBZ were dissolved in the round bottom flask filled with NMP for 2 hr at inert atmosphere. Before anhydride solution were added, the DBZ solution was preheated to 60℃. 10mmol of 6FDA were dissolved and added to DBZ solution very slowly to avoid the gelation of tetra-amino monomers. After 6FDA was completely added to the DBZ solution, 6F-poly(amino amic acid) solution was stirred under nitrogen purge gas during 12 hours.

After the resulting solution was obtained, it was cast onto a glass plate and then thermally imidized to 250℃ under vacuum. The obtained films were thermally rearranged in a tubular furnace at 400 to 450℃. Therefore we obtained the polypyrrolone (PPy) membrane, which was converted from polyimide having diamine groups. The membrane was treated in 1M NaOH solution at around 100℃ and then rinsed in distilled water. After dried in a vacuum oven at 120℃ to remove water completely, polybenzimidazole(PBI) membrane was finally obtained.

2.3 Characterization

To confirm the structural rearrangement of the polymers, Atteuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectra and X-ray diffraction patterns were recorded. The thermal conversion was confirmed by using thermogravimetric analysis. N_2 adsorption and desorption isotherms of thermally treated samples were analyzed using a surface area and porosimetry analyzer (ASAP 2020) to evaluate the pore volumes after thermal rearrangement reaction. Gas

permeation properties were measured using single gas permeation experiments of H_2, O_2, N_2, CO_2, and CH_4 by time-lag method at feed pressures of 760 Torr.

3. Result and Discussion

ATR-FTIR was used to study the chemical structure of 6F-PAAA, PPy and treated PPy membranes as shown in Fig.1. First, two peaks at 1786cm^{-1} and 1726cm^{-1} referred to the asymmetrical and symmetrical C=O in 6F-PAAA. In 6F-PPY 450, the peak at 1758cm^{-1}, which could be found in PPY, accounted for C=N. Contrarily, after 1M NaOH treatment, characteristic polybenzimidazole peaks appeared at 3400cm^{-1} and 1438cm^{-1} as shown in Fig.1 and Table.1.

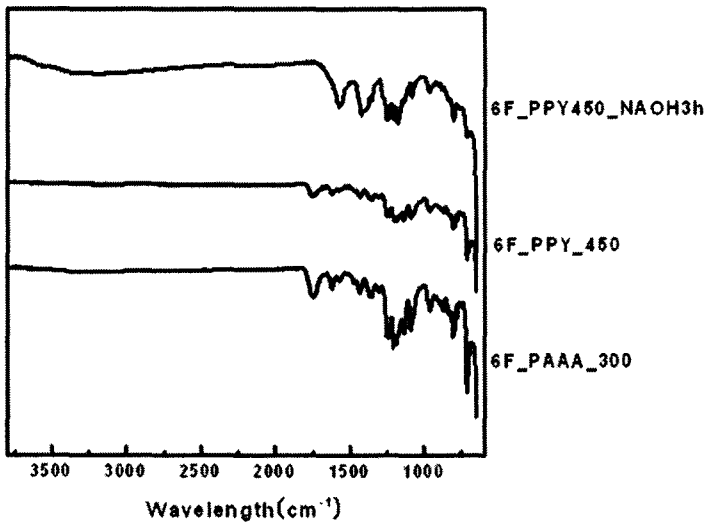

Fig. 1 FT-IR spectra of 6F-PAAA, PPY and 1M NaOH treated PPY film.

In gas permeation measurement, PPy membrane and the alkaline-treated membrane showed visible differences at permselectivities. PPy membrane has higher permeability than PBI, which has very low permeability. O_2 permeability of polypyrrolone is 120 Barrer(1 Barrer= 1 x 10^{-10} cm^3 (STP) cm/ cm^2 s cmHg). After 1M NaOH treatment, it showed very low permeabilities like the typical

polybenzimidazole. However, it showed relatively high H_2 permeability of 70 Barrer with H_2/CH_4 selectivity of 580.

Wave Number(cm^{-1})		
PBI		
Reported[a]	This Work	Assignment
3398	3400	Free non-hydrogen-bonded N-H stretching
1614	1605	C=C/C=N stretching
1527	1543	Ring-vibration characteristic of conjugation between benzene and imidazole rings
1431	1438	Inplane deformation of benzimidazole rings
1408	1411	
1277	1265	Breathing mode of the imidazole ring
1225	1224	Inplane C-H deformation
800	801	Out-of-plane C-H bending of the benzene rings

Table 1. FT-IR Spectra of Polybenzimidazoles

4. Conclusions

In this study, PBI membrane was prepared by treating polypyrrolone derived from amine-containg polyimide at alkaline solution. ATR-FTIR and thermogravimetric analysis were used to investigate the structural transformation of the polypyrrolone membrane. Nitrogen adsorption/desorption isotherm and wide angle X-ray diffraction were investigated to understand pore characteristics, and gas permeation test were carried out using He, H_2, CO_2, O_2, N_2, CH_4, etc. Hydrogen permselectivity of the resultant membrane was increased with the structural changes.

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