폴리이미드 전구체구조에 따른 탄소막의 분리특성변화

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Structure-Properties Relationship between Polyimide Precursor and Carbon Molecular Sieve Membranes

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1. Introduction

In the carbon molecular sieve (CMS) membranes, the structural characteristics and gas separation properties mainly depend on the types of polymer precursors and pyrolysis conditions. Up to now, the research works on CMS membranes have been widely studied on the kinds of polymer precursors, such as poly(furfuryl alcohol) [1], phenolic resins [2-3] and polyimides [4-5] with various pyrolysis conditions. One of polymer precursors is polyimide that has beeb widely used to prepare CMS membrane on the structural characteristics and gas separation performance with various pyrolysis conditions. Gas separation performance is affected mainly by the pyrolysis temperature and the type of polyimides having bulky groups (-CF_3, CH_3 and -COOH) even though they provided the hindrance to inter-segmental rotation. The steric properties of polymeric membranes having carboxylic acid groups were different from other side groups. The steric properties of polymeric membranes may affect the packing density and gas permeation properties. In this study, some CMS membranes were prepared by pyrolysis of polyimides having side groups such as -CH_3 and

-COOH and studied on the structural characteristics and gas separation properties.

2. Experimental Section

Polyimides were synthesized from benzophenone tetracarboxylic dianhydride (BTDA), 4, 4'-oxydianiline (ODA), 1,3-phenylene diamine (*m*PDA), and 1,3-diaminon benzoic acid (DBA). The imidization was carried out by thermal treatment of PAA solution. The prepared PAA solution was thermally imidized after casting onto glass plate in a vacuum oven using the four-step protocol: 60 ℃ for 1 h, 150 ℃ for 1 h, 200 ℃ for 1 h and 300 ℃ for 30 min, respectively.

3. Results and Discussion

We used thermogravimetric analysis (TGA) to ascertain the thermal decomposition kinetics and stability of polyimides having carboxylic acid groups under an ultra-high-purity argon purge. The mass-loss profiles are

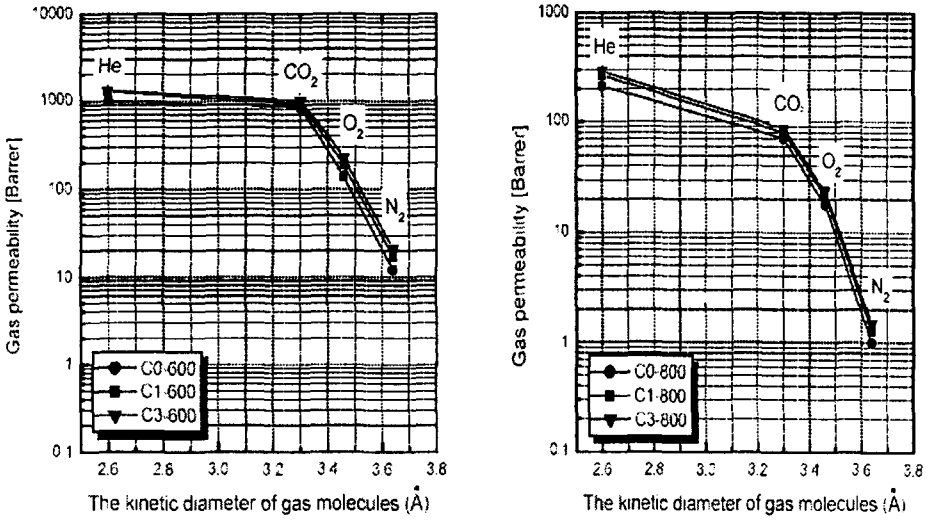

Fig. 1. Gas permeabilities of carbon molecular sieve (CMS) membranes derived from methyl-substituent polyimides. (a) CMS prepared at 600 °C and (b) CMS at 800 °C.

very similar each other but the temperature corresponding to the onset of thermal degradation (T_d) and the residual weight (%) at 800 ℃ are different from all three materials. Between 300 and 500 ℃ about 5% of weight loss occurred and then reaches a local plate.

The gas permeation results of CMS membranes derived from polyimides having different number of methyl groups in repeating unit shown in Fig. 1. While the O_2 permeabilities of CMS membranes pyrolized at 600 ℃ shown in the range of 139-229 Barrer with a O_2/N_2 selectivities of 11-12, CMS membranes pyrolized at 800 ℃ showed the O_2 permeabilities of 18-24 with a O_2/N_2 selectivities of 16-18. The increase of the final pyrolysis temperature may lead to the amorphous carbon membrane having a tighter and more selective pore structure that reduced the gas permeabilities. That is, at the higher final pyrolysis temperature, the average selective ultramicropore size may dwindle. Nevertheless, the gas permeation trends similar to those of the precursors were observed even at the higher final pyrolysis temperature.

4. Conclusions

In this study, the microstructure of the polyimides affected significantly the final gas separation performance of the CMS membranes as well as that of the polyimides. The increase of fractional free volume in the polyimides by methyl substituents led to the increase of permeability coefficients of the polyimides and their CMS membranes, and on the other hand the separation performance was reduced. Although carbonizing conditions such as final pyrolysis temperature, heating rate, pyrolysis atmosphere, and post-treatment are very crucial and important factors determined on the CMS membrane performance, the chemical structure and physical properties of rigid polymer precursors should be significantly considered for the preparation of CMS membranes.

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