

일반강연 A-7

메탈이온이 치환된 술폰화 폴리이미드 탄소분자체 막의 기체투과 거동

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Carbon Molecular Sieve Membranes Derived from Metal-Containing Sulfonated Polyimide and Their Gas Separation Properties

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1. Introduction

The molecular sieve carbon membrane in the application of gas separation have attracted more attention in recent years and is now rapidly developing. This is due to their excellent characteristics for gas separation as compared with conventional polymeric membranes [1]. Koresh and Soffer [2] first formed a carbon molecular sieve membranes (CMSM). Since then, carbonized membranes have been prepared from polyfurfuryl alcohol resin [3], poly(vinylidene chloride) resin [4], phenol formaldehyde resin [5] and polyimides [6]. Carbonization of polyimides has been most intensively investigated [7, 8]. Hayashi et al. [9] coated a polyimide film made from 3,3',4,4'-biphenylcarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) on the outer surface of a porous alumina support tube and obtained a CMSM by carbonization at 600-900°C in an inert atmosphere.

In our previous work, we prepared and characterized metal-substituted 4,4-diamino 2,2-biphenyl disulfonic acid (BDSA) and thus metal-containing sulfonated polyimide membranes. The purpose of this study was to prepare carbon molecular sieve membrane and to investigate the role of the substituted alkali metal ion in sulfonic acid group on the gas permeation properties.

2. Experimental

2.1. Materials

Materials used in the synthesis of metal-substituted sulfonated polyimide (M-SPI) included benzophenone tetracarboxylic dianhydride (BTDA), 4,4-diamino 2,2-biphenyl disulfonic acid (BDSA) and *meta*-phenylenediamine (*m*PDA). BTDA and *m*PDA were purchased from the Aldrich Chemical Co. Before polymerization, all the monomers were purified by the sublimation under reduced pressure. BDSA was purchased from TCI Co. (Tokyo, Japan). BDSA required an extensive purification. BDSA was titrated with an aqueous lithium hydroxide, sodium hydroxide or potassium hydroxide solution. The metal-substituted BDSA is a powder and is soluble in dimethylsulfoxide (DMSO), the solvent used for polyimide synthesis.

2.2. Preparation of metal-containing sulfonated polyimides

Metal-containing sulfonated polyimide (M-SPI) was prepared by casting the M-SPAA solution on the glass plate and then thermally imidized in the vacuum oven by a four-step imidization protocol: 50°C/3hr, 100°C/1hr, and 200°C/1hr and 250°C/30min, respectively. The thickness of the M-SPI film was approximately 40 μ m.

2.3. Carbonization of M-SPI

The pyrolysis protocol used in this work is determined by the result from thermogravimetric analysis coupled with mass spectroscopy

(TGA-MS). The initial rate of heating used was 10°C/min from room temperature to 400°C/min. The heating rate was slowed to 3°C/min until the temperature reached 590°C. The precursors were kept at 590°C for 90min. The furnace was allowed to cool slowly to room temperature. (see Fig. 1)

3. Results and Discussion

The new diamine metal-substitution in BDSA was successfully prepared in this study. The metal-substitution in sulfonated polyimide was prepared by thermal imidization and confirmed the progress of imidization by FT-IR. The substitution of the proton in sulfonic acid groups with a metal cation, therefore, increased thermal stability of the polymeric precursors. For M-SPI, the introduction of metal-substitution in sulfonic acid groups increased both the intermolecular interaction through polar ionic sites and the hindrance of the chain rotation, leading to the increase in T_g values. The glass transition temperature was observed in the range of 280–300°C. The TGA spectrum of the M-SPI, which showed approximately 5% weight loss in a 250–350°C temperature interval due to the removal of sulfonic acid groups. The substitution of the proton in sulfonic acid groups with a metal cation, therefore, increased thermal stability of the sulfonic acid groups existed in polymer backbone. The WAXD spectra of M-SPI showed no crystalline behavior, indicating an amorphous structure of the polymer.

In Table 1, the O_2 permeability slightly increased in the order of Li-SPI<Na-SPI<K-SPI. It might be explained that the d -spacing between polymer interchains increased by the presence of metal ions with different ion radii. Metal-containing sulfonic acid groups on the phenylene also inhibited the close packing of the polymer chains

Table 1. Gas permeation properties and d -spacing of M-SPI

*unit = Barrer (1 Barrer = $1 \times 10^{-10} \times \text{cm}^3(\text{STP})\text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$)

Polymer codes	P(O_2)	P(N_2)	α (O_2/N_2)	d -spacing (Å)
Li-SPI 1091	0.78	0.14	5.6	5.1
Na-SPI 1091	0.90	0.25	3.6	5.2
K-SPI 1091	1.36	0.28	4.9	5.4

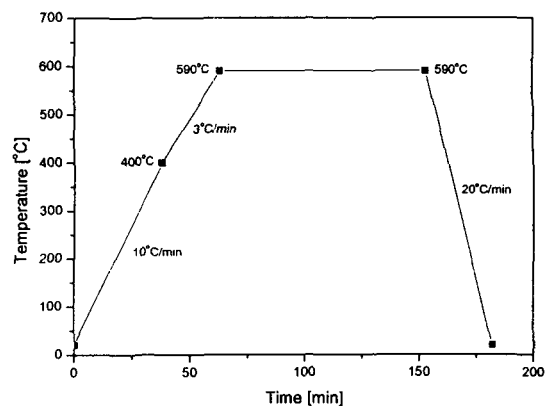


Fig. 1 Temperature protocols for pyrolysis of precursors.

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