폴리이미드의 열분해 조건에 따른 탄소분자체 막의
기체투과거동

김연국, 박호범, 이영무

한양대학교 공과대학 응용화학공학부

Pyrolysis Conditons of Polyimide on Carbon molecular sieve membranes and their gas separation properties

Youn Kook Kim, Ho Bum Park, Young Moo Lee

School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

1. Introduction

Carbon molecular sieve membranes (CMSMs) are very promising materials in the field of gas separation, both in terms of separation properties (permeability and selectivity) and stability (thermal and chemical). CMSMs produced by pyrolysis of different polymeric materials (polyimide-based, PVDC, phenolic resin, polyfurfuryl alcohol, etc.) are characterized by a very narrow microporosity (~3-6Å) which allows discrimination between gas molecules of different size. As reported in the literature, polymers like polyimides are excellent precursors to obtain carbon molecular sieve films [1].

Mainly, two types of carbon membranes have been reported in the literature depending on the separation mechanism. One is a carbon molecular sieve membranes [2]. The other is a surface-selective diffusion carbon membrane [3]. The gas separation performance of

either CMSMs or surface-selective diffusion membranes largely depends on the polymeric precursor, membrane formation method, pyrolysis variable, and posttreatment method [4]. In recent years, pyrolysis of aromatic polymer films such as polyimide films at high temperature has been attracting much attention because high quality graphitized films maintaining their original film shapes can be obtained [5].

This study examines how inert purge pyrolysis and pyrolysis temperature of a metal-containing sulfonated polyimde precursor affect carbon molecualr sieve membrane performance. Additionally, purge gas flow rate and residual oxygen concentration in the purge gas were examined.

2. Experimental

2.1. Materials

Materials used in the synthesis of Na-substituted sulfonated polyimide (Na-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-containing BDSA is a powder and is soluble in dimethylsulfoxide (DMSO), the solvent used for polyimide synthes

2.2. Preparation of M-SPI precursors and carbon membranes

Pyrolytic carbon membranes are readily made by the pyrolysis of suitable polymeric precursors. Pyrolytic carbon membranes produced in this work were prepared by pyrolysis of a Na-SPI precursor. Before starting a pyrolysis trial, the freestanding films of precursors were

completely rinsed with deionized water and stored under a vacuum oven until any residual water and dusts were removed. After these pretreatments, the precursor film was then placed in the middle of a quartz tube. The precursor film was pyrolyzed under a inert purge gas (N_2, He, Ar) flow ($150cm^3(STP)$/min) in a quartz tube furnace supported on an alumina holder plate. The pyrolysis protocol used in this work is determined by the result from thermogravimetric analysis coupled with mass spectroscopy (TGA-MA).

2.3. Characterization

FT-IR spectra of the synthesized polymer were obtained using a Nicolet Model Magna IR550. The substituted alkali metal ions ($Na^{'}$) in sulfonic acid groups were investigated using a Perkin-Elmer PHI 5500 X-ray photoelectron spectrometer. The spectra were collected using monochromatized Al K source (1486.6eV) operated at 14kV and 300W with a takeoff angle of 45. The pressure inside the spectrometer sample chamber was held below 5×10^{8} Torr during the analysis. Thermogravimetric analysis (TGA) was done using a Perkin-Elmer System 7 to study the thermal stability of the polymer. The heating rate was $10°C$/min under argon atmosphere. Wide angle X-ray diffraction (WAXD) patterns of the polymer were obtained using a Rigaku Denki Model RAD-C with a scanning rate of $5°$/min for Na-SPI with various mole ratio of metal-substitution in BDSA. The data were collected in a fixed time mode with a step size of $0.05°$ (2) and run from $2=2°-80°$. Differential scanning calorimeter (DSC) measurement of the annealed film was conducted on a Perkin-Elmer DCS-7, on 6-7mg of sample under a nitrogen purge, at a heating rate of $10°C$/min.

3. Results and Discussion

Figure 1 is the FT-IR spectrum of Na-containing sulfonated poly(amic acid) (Na-SPAA) and Na-containing sulfonated polyimide (Na-SPI). Absorption band at $3500cm^{-1}$ characteristic of -OH and

1800cm^{-1} characteristic of C=O stretching in imide groups are observed respectively. Absorption band at 1380cm^{-1} characteristic of C–N stretching is not observed at Na–SPAA and C–N imide group is observed at Na–SPI that is indicated the progress of imidization. Absorption band at 1569cm^{-1} characteristic of –NH is observed at Na–SPAA but that is not observed at M–SPI. Also the sulfonic acid group (–SO$_3$Na) was confirmed by a characteristic peak at 1032cm^{-1} assigned to the O=S=O symmetric stretching vibration. The observation of these bands clearly indicates the existence of imide groups and confirms the successful synthesis of polyimide. By FT–IR spectra, the thermal imidization of Na–SPI proceed and the imidization of Na–SPI was progressed at 250°C completely.

In Table 1, the gas permeability and selectivity of Na-containing sulfonated polyimide precursor and carbon membranes that was pyrolyzed at 600°C (Na–SPI 600) were described. The Na–SPI 600 shows that the permeability in the order of N$_2$ (0.364nm)<O$_2$ (0.346nm)<He (0.26nm). It might be explained that the different of kinetic diameter of penetrants. Specifically, helium having the smallest kinetic diameter has the highest permeability, and is followed by progressively larger penetrants such as O$_2$ and N$_2$. From the results, The He, O$_2$ and N$_2$ permeabilities of Na–SPI 600 showed 742, 156 and 26 Barrer and the He/N$_2$ and O$_2$/N$_2$ selectivities are 36 and 8. The permeability and selectivity were much higher than Na–SPI precursor.

References

[1]. H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata, S. Yoshitomi, Carbon 30 (1992) 7

[2]. J. E. Koresh, Sofer, Sep. Sci. Tech. 18 (1983) 723.

[3]. M. B. Rao, S. Sircar, J. Membr. Sci 110 (1996) 109.

[4]. W. Zhou, M. Yoshino, H. Kita, K. Okamoto, Ind. Eng. Chem. Res. 40 (2001) 4801.

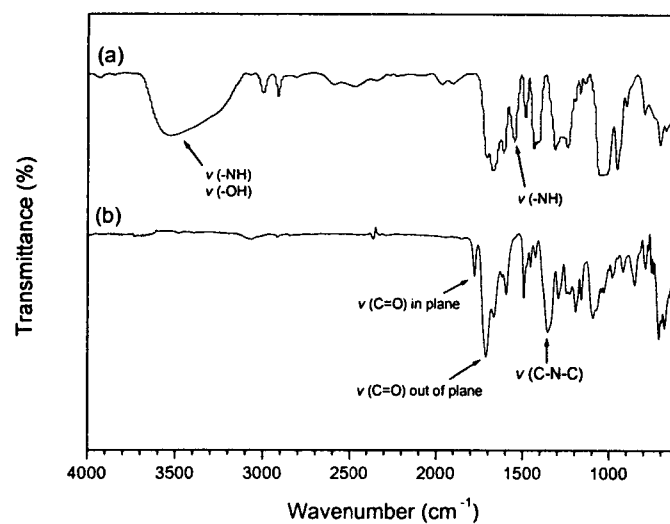[5]. T. Takeichi, Y. Eguchi, Y. Kaburagi, Y. Hishiyama, M. Inagaki, Carbon 37 (1999) 569.

Fig. 1. FT-IR spectra of Na-SPAA and Na-SPI

Table 1. Gas permeation properties of Na-SPI 600

Samples	P(He)	P(O2)	P(N2)	α(He/N2)	α(O2/N2)
Na-SPI precursor	16.49	1.24	0.23	71.70	5.39
Na-SPI 600	742.02	155.73	25.52	36.16	7.59

*unit = Barrer (1 Barrer = $1\times10^{-10}\times cm^3(STP)cm/cm^2.sec.cmHg$)