일반강연 A-13

금속이온으로 치환된 술폰화폴리이미드의 합성 및 기체분리특성

김연국, 박호범, 이영무
한양대 응용화학공학부

Synthesis and characterization of metal-containing sulfonated polyimide 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

Aromatic polyimides (PI) are well known as high performance polymers, which possess excellent thermal stability, inert behavior against organic solvents, and good mechanical properties. Therefore, they are being used in applications such as automobile and aircraft parts, electronic packaging, films, adhesives, and matrix materials for composites [1-3]. Aromatic polyimides are generally prepared through a two-step procedure by the ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides in aprotic solutions giving soluble polyamic acids [4-8].

Recently, metal-substitution in sulfonated polymer membrane materials have been studied. Chen and Martin reported a significant improvement in permeability ratios of metal-substitution in sulfonated polystyrene membranes compared to unsubstituted ones. This improvement was achieved by a sacrifice in gas permeability [9]. Fu et al. reported that substitution of the proton in sulfonic acid groups of low molecular weight sulfonated polyphenylene oxide (SPPO) by sodium cation resulted in an increase in gas permeability and a decrease in permeability ratio [10].

This study shows the preparation procedure and characterization of metal-substitution in monomer (4,4-diamino 2,2-biphenyl disulfonic acid (BDSA)) and metal-substitution in sulfonated polyimide (M-SPI) membranes (see Fig.1). This M-SPI membrane will be described the synthesis and characterization in terms of crystallinity and thermal stability properties. The structures of the polymers were investigated by FT-IR and their thermal stability was also characterized by differential scanning calorimeter (DSC) and thermogarvimetric analysis (TGA).

2. Experimental

Materials used in the synthesis of M-SPI included 3,3,4,4-Benzophenone tetracarboxylic dianhydride (BTDA), 4,4-diamino 2,2-biphenyl disulfonic acid (BDSA) and meta-phenylenediamine (mPDA). BTDA and mPDA were purchased from the Aldrich Chemical Co. Metal-substitution in sulfonated polyamic acid (PAA) from BTDA, mPDA and metal-substitution in BDSA were prepared as follows: Into a 200mℓ flask equipped with nitrogen inlet and magnetic stirrer, metal-substitution in BDSA (1.00mmol and 2.00mmol) and DMSO were placed. The mixture was stirred until getting clear solution. Equimolar amount of solid BTDA (10.00mmol) and mPDA (8.00mmol and 9.00mmol) were added in one batch to the metal-substitution in BDSA solution. M-SPI was prepared by casting the PAA solution on glass plate and then thermally imidized in the vacuum oven by a four-step imidization protocol: 50 ℃/5hr, 100℃/1hr, 200℃/1hr and 250℃/30min, respectively.

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 sulfonic acid groups. For M-SPI, the introduction of metal-substitution in sulfonic acid groups increasing both the intermolecular interaction through polar ionic sites and the hindrance of the chain rotation, leading to the increase in Tg values. The glass transition temperature was observed in the range of 280-300℃. The TGA spectrum of the M-SPI, which showed approximately 5% weight loss in a 250-350℃ temperature interval due to 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. The density of polymer increased in the order of Li-SPI<Na-SPI<K-SPI. The WAXD spectra of M-SPI show no crystalline behavior, indicating an amorphous structure of the polymer.

4. References

[1]. Mittal KL, editor. Polyimides: synthesis, characterization, application, vols. 1 and 2. New York: Plenum, 1984.

[2]. Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. Glasgow: Blackie, 1990.

[3]. Bessonv MI, Kotton MM, Kudryavtsev VV, Laius LA. Polyimides: thermally stable polymers. New York: Consultants Bureau, 1987.

[4]. Sroog CE, Encycl. Polym. Sci. Tech. 11 (1969) 247.

[5]. Bessonov MI, Koton MM, Kudryavtsev VV, Laius LA, Polyimides: thermally stable polymers. Consultants Bereau, New York. (1987).

[6]. Wilson D, Stenzenberger HD, Hergenrother PM. Polyimides. Blackie, New York (1990).

[7]. Sroog CE. Prog. Polym. Sci. 16 (1991) 561.

[8]. Se Abajo J. Polyimides. In: Kricheldorf HR (Ed) Handbook of polymer synthesis, pt B. Dekker, New York. (1992) 941.

[9]. W. J. Chen, C. R. Martin, Gas transport properties of sulfonated polystyrenes, J. Memb. Sci. 95 (1994) 51.

[10]. H. Fu, L. Jia, J. Xu, Studies on the sulfonation of polyphenylene oxide (PPO) and permeation behaviour of gases and water vapor through sulfonated PPO membranes II. Permeation behaviour of gases and water vapor through sulfonated PPO membranes, J. Appl. Polym. Sci. 51 (1994) 1405.

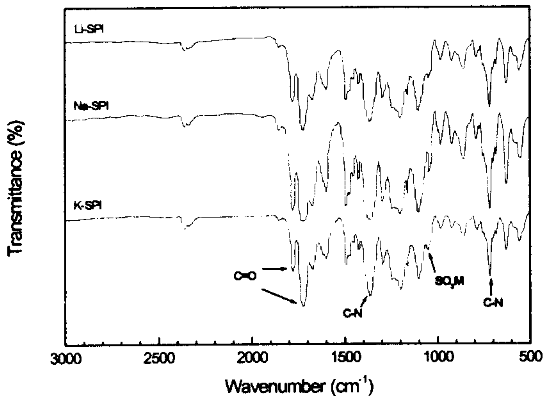

Fig. 1 FT-IR spectra of metal-substitution in sulfonated polyimides

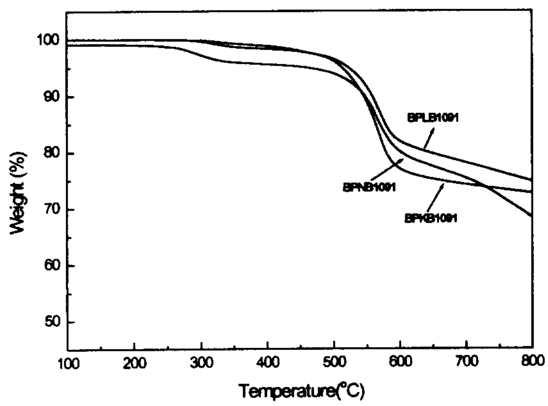

Fig. 2 TGA thermograms of metal-substitution in sulfonated polyimide