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Preparation and gas separation performance of flexible pyrolytic membranes by low-temperature pyrolysis of sulfonated polyimides

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Abstract

Dense flat membranes of sulfonated polyimides (SPIs) were prepared from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and aromatic diamines of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane disulfonic acid, benzidine-2,2′-disulfonic acid, 4,4′-diaminodiphenylether-3,3′-disulfonic acid and 9,9′-bis(4-aminophenyl)fluorene. The SPI membranes were pyrolyzed at a relatively low-temperature of 450 °C for 1.5 h at a nitrogen flow. During the pyrolysis, the $-SO_3H$ groups decomposed without substantial cleavage of the polyimide backbone. The pyrolytic membranes had the interesting intermixed properties of toughness and good flexibility as in polymer membranes and high gas permeability with reasonably high selectivity as in carbon molecular sieve membranes. The gas permeability for the pyrolytic membranes seems to be controlled by the sulfonic acid group content in the precursor polyimides, the relaxation of the polymer chains during the pyrolysis and the gas permeation level of the precursor membranes. Decomposition of $-SO_3H$ groups induced microvoids, which are considered to remain to some extent as larger-size free volume holes in the polymer matrix, resulting in the higher diffusivity to gas with larger diameter. The pyrolytic membranes showed the higher permeability of C_3H_6 and/or the higher selectivity of C_3H_6/C_3H_8 than the 6FDA-polyimide membranes which have defined the upper bound line.

Keywords: Sulfonated polyimides; Template effect; Pyrolytic membrane; Gas permeation; Propylene/propane separation

1. Introduction

Separation of olefin and paraffin gases is one of the most important processes in petrochemical industries and currently performed by low-temperature distillation with large energy consumption [1]. Membrane-based technologies have advantages of both low capital cost and high-energy efficiency compared to conventional separation methods in principle. Facilitated transport membranes containing silver ions as a complex agent have very high olefin/paraffin separation selectivity and high olefin fluxes [2–4]. However, some problems, especially poor chemical stability due to the carrier poisoning, currently limit the practical applications of the facilitated transport membranes. The olefin/paraffin separation through polymeric membranes without carriers has also been studied [5–13]. There have been reported some polyimides having relatively high separation factors of propylene over propane. Most of the polyimides were prepared from 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) [7–13]. However, their permeability to propylene is not high enough for practical uses.

Carbon molecular sieve (CMS) membranes prepared by pyrolysis of polymeric membranes have been reported to display high olefin/paraffin separation performance [14–17]. Hayashi et al. reported the excellent performance of C_2H_4/C_2H_6 and C_3H_6/C_3H_8 separation for carbonized membranes prepared by pyrolyzing composite membranes of polyimide from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and oxydianiline (ODA) coated on porous alumina tubes at temperature of 600–900 °C in a nitrogen stream. The permeance to propylene $R_{C_3H_6}$ was 9 GPU

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(1 GPU = 10^{-6} cm^3 (STP)/(cm^2 s cmHg)) and separation factor of propylene over propane $\alpha(C_3H_6/C_3H_8)$ was 33 at 100 °C for the membrane pyrolyzed at 700 °C [14]. Okamoto et al. prepared carbonized asymmetric hollow fiber membranes by pyrolyzing the precursor asymmetric hollow fiber of BPDA-based polyimide at temperature of 500–700 °C under a nitrogen stream. The membranes showed fairly high C_3H_6/C_3H_8 separation performance such as $R_{C_3H_6}$ of 32 GPU and $\alpha(C_3H_6/C_3H_8)$ of 15 in a mixed gas at 100 °C and 1 atm [17].

Although CMS membranes display better gas separation selectivity and better thermal stability than polymeric membranes, the poor operation property as the result of their inherent brittleness restricts their practical application. Composite CMS membranes composed of a carbonized layer on an inorganic support have an advantage of excellent mechanical strength but have a disadvantage of rather complicated preparation procedure. The self-standing CMS membranes derived from capillary or asymmetric hollow fiber membranes have advantages of simple preparation procedure and large effective membrane area per volume, but in general have poor mechanical strength, especially poor resistance against shock [18,19].

Okamoto and coworkers reported highly permeable CMS membranes prepared by pyrolyzing a thermosetting phenolic resin with a pendant sulfonic acid group at 500 °C [20,21]. Thermogravimetry–mass spectroscopy (TG–MS) showed that the decomposition of sulfonic acid groups occurred but no vigorous decomposition of the skeleton of polymer matrix occurred below 450 °C under a N_2 stream. This indicates that sulfonic acid groups bonded to phenolic resin have “template-like effect” in preparation of CMS membranes. However, the phenolic resin had poor film-forming ability and could be used only in form of composite membranes. Kim et al. prepared CMS membranes by pyrolyzing membranes of sulfonated polyimides (SPIs) from benzidine-2,2′-disulfonic acid (BDSA) with or without metal cations [22]. They pyrolyzed the SPI membranes at 590 °C, where final decomposition of the precursors occurred. The resulting CMS membranes displayed rather poor gas permeation properties.

In a previous paper [23], we briefly reported dense and flexible pyrolytic flat membranes by pyrolyzing sulfonated polyimides at a low temperature of 450 °C, where most of the sulfonic groups decomposed but the polyimide backbone did not substantially decompose. In this paper, the preparation, characterization and gas permeation and separation properties of the flexible pyrolytic flat membranes are reported in detail.

2. Experimental

2.1. Materials

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BAHF), oxydianiline (ODA), BDSA and 9,9′-bis(4-aminophenyl)fluorene (BAPF) were purchased from Tokyo Kasei Co. NTDA and BAPF were purified by vacuum sublimation before use. 2,2-Bis[4-(4-aminopheoxy)phenyl]hexafluoropropane disulfonic acid (BAHFDS) and 4,4′-diaminodiphenylether-3,3′-disulfonic acid (ODADS) were prepared by direct sulfonation of BAHF and ODA, respectively, as previously reported [24]. *m*-Cresol was used as received.

2.2. Preparation of sulfonated polyimides

The chemical structures of homo and copolyimides used as precursors in this study are shown in Fig. 1. NTDA-BAHFDS/BAPF(4/1) copolyimide was prepared by a one-step method as follows [24]. To a 100 ml of completely dried four-necked flask with stirrer was added 1.63 g (2.4 mmol) BAHFDS, 0.7 ml (5 mmol) triethylamine, 0.21 g (0.6 mmol) BAPF and 11 ml *m*-cresol under N_2 flow. After BAHFDS was completely dissolved, 0.80 g (3 mmol) NTDA and 0.54 g (4.5 mmol) benzoic acid were added into this flask. The mixture was heated at 80 °C for 4 h and 185 °C for 20 h in order to carry out condensation polymerization and thermal immidization. After cooling to room temperature, additional 40 ml of *m*-cresol was added to dilute the highly viscous solution, and the resulting dark-brown polyimide solution was poured into acetone. The fiber-like precipitate

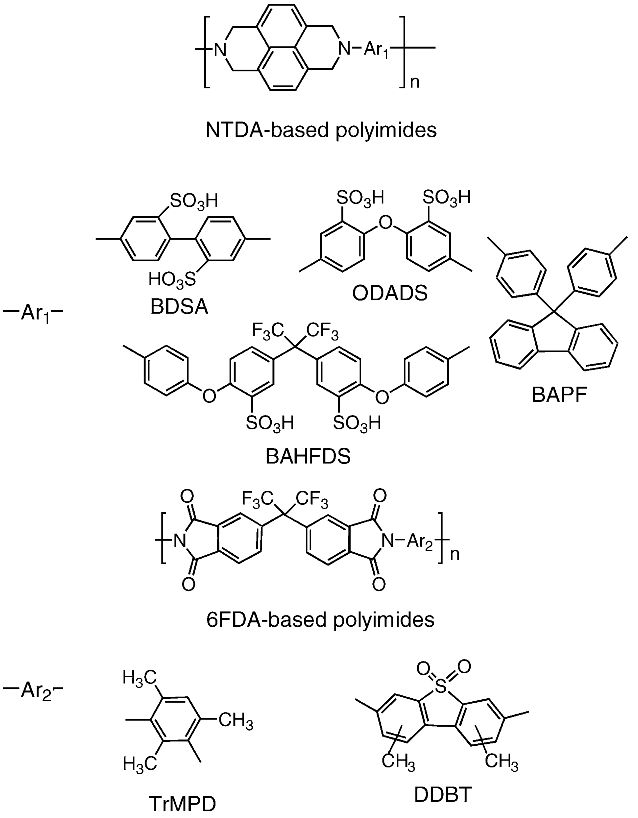

Fig. 1. Chemical structures of NTDA-based and 6FDA-based polyimides.