



Fine ultra-micropore control using the intrinsic viscosity of precursors for high performance carbon molecular sieve membranes



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ARTICLE INFO

Article history:

Received 3 November 2016

Received in revised form 30 December 2016

Accepted 30 December 2016

Available online 31 December 2016

Keywords:

Carbon molecular sieve membrane

Gas separation

Intrinsic viscosity of precursor

Ultramicropores

ABSTRACT

Here we report the permeability and separation performance of self-standing carbon molecular sieve (CMS) membranes formed by pyrolysis of polyimide (PI) precursors derived from poly(amic acid) (PAA) with varying intrinsic viscosity. CMS resulted in ultra-microporous membranes showing a classical molecular sieving structure as gas permeation was high for smaller molecular gas (H₂), which then decreased sequentially as the molecular sizes increased in the order of CO₂, O₂ and N₂. An important relationship was found when the intrinsic viscosity of the PAA precursor decreased from 1.66 to 0.65 dl g⁻¹, the ideal gas selectivity jumped to higher values such as from 101.8 to 163.1 for H₂/N₂, from 21.5 to 34.6 for CO₂/N₂ and from 6.7 to 10.7 for O₂/N₂ while the permeability decreased such as from 1816 to 1487 Barrer for H₂, from 383.4 to 314.8 Barrer for CO₂, from 119.0 to 97.7 Barrer for O₂, from 17.8 to 9.1 Barrer for N₂. The low intrinsic viscosity conferred a superior pore size control of the CMS structure, with an average ultramicropore size around 3 Å. The O₂/N₂ and H₂/N₂ ideal selectivity versus permeability results were all above the Robeson's upper bound line, thus demonstrating the effect of low intrinsic viscosity precursors in the synthesis of high performance CMS membranes.

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1. Introduction

Carbon membranes have attracted a great deal of attention from the research community and industry due to an easy membrane fabrication process, good pore size control and excellent chemical stability. Carbon membranes are generally synthesised from pyrolysis of polymer precursors. These are often known as carbon molecular sieve (CMS) membranes. Therefore, the characteristics of polymer precursor and carbonisation process affect the structure and performance of CMS membranes. There is an array of polymers that have been employed for the preparation of CMS membranes including phenolic resin [1–7], polyimide (PI) [8–17], polyfurfuryl alcohol [18,19], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [20] and poly(phthalazinone ether sulfone ketone) (PPESK) [21]. In addition, carbon templates such as triblock copolymers [22] and surfactant hexyltriethylammonium bromide (C6) [23] have been embedded and carbonised in silica films as molecular sieve structures for desalination and gas separation. Alumina nano wires and silver nanoparticles have been used to improve the performance of CMS membranes [24–26].

Many of the studies reported in the literature have investigated carbon membranes based on the effect of different chemical structures such as sulfonated phenolic resin [27] and poly(furfuryl alcohol) (PFA) [28], or polyimides synthesised with a varying number of carboxylic acid groups [29]. Other studies focused on the effect of cross linking agents on the precursor structure including sulfonated poly(phthalazinone ether sulfone ketone) (SPPEK) [30] and Matrimid® 5218 [31]. During pyrolysis, the polymer precursor undergoes a complex process including thermal decomposition, thermal deformation, condensation and aromatisation. Even for a thermosetting polymer, partial fusion occurs during pyrolysis. The lower molecular weight polymer possesses greater chain mobility and fractional free volume than the higher molecular weight polymer. Viscosity is one of the most widely used methods for the characterization of the molecular weight of polymers, as this method provides the easiest and most rapid means of obtaining molecular weight-related data that require minimal instrumentation [32]. These characteristics are expected to affect structural rearrangement, pore formation of the CMS membranes during carbonisation, and determine the separation performance.

In this work, we investigate the synthesis of CMS membranes by carbonisation of polyimide (PI) precursor from poly(amic acid) (PAA). An important aspect of this study is understanding the effect

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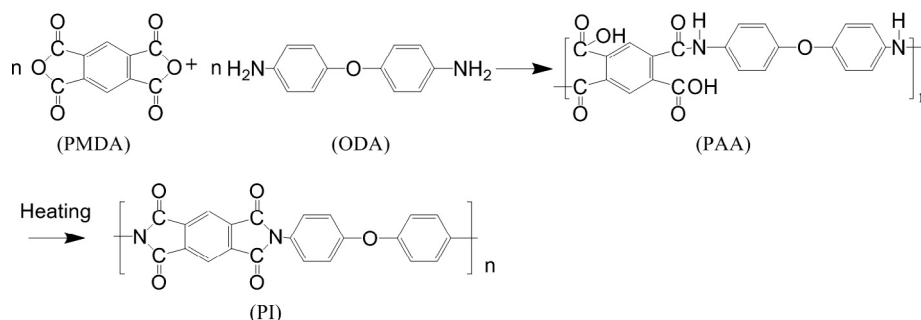


Fig. 1. Schematic illustration of synthesis of PAA and PI.

played by varying the intrinsic viscosity (and likewise the molecular weight) of the resultant polymer precursor. PAA was synthesised from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) with phthalic anhydride (PA) end-capping to control the intrinsic viscosity. The as prepared PI and as-carbonised CMS materials were fully characterised to determine their structural properties. CMS membranes prepared with varying intrinsic viscosity precursors were tested for gas (H_2 , CO_2 , O_2 and N_2) permeability and their ideal gas selectivity was calculated.

2. Experimental

2.1. Materials and synthesis

PMDA (pyromellitic dianhydride) and ODA (4,4'-oxydianiline) were purchased from Sinopharm Chemical Reagent Co. Ltd. PMDA was dried at 160 °C before use and ODA was purified by recrystallisation using ethanol as solvent. PA (phthalic anhydride) (AR) was procured from Xilong Chemical Co., Ltd. *N,N*-dimethylacetamide (DMAC) (AR) was obtained from Beijing Chemical Factory.

The synthesis of PAA and PI were schematically illustrated in Fig. 1.

ODA was dissolved in DMAC in a three-necked flask with a stirrer and was isolated from air by a drying tube. When the solution was completely dissolved, PA (end-capping reagent) was added to the solution to control the intrinsic viscosity. Then the PMDA was added into the solution by three times, each time a third. The solution was stirred for 8 h at room temperature. The resultant poly(amic acid) PAA solution was kept at 0–5 °C.

2.2. Preparation of PI and CMS membranes

The solution was coated on a clean glass plate using an automatic coating machine (Sheen 1132N, UK) with an applicator of width 100 mm and dried at 80 °C for 24 h, then at 150 °C for 1 h to prepare the PAA membranes. The PI membranes were obtained after imidising the PAA membranes with a three-step protocol: 100 °C for 30 min, 200 °C for 30 min and 300 °C for 1 h, always at a heating rate of 2 °C min⁻¹. The CMS membranes were prepared by carbonising the PI membranes in an inert high purity argon atmosphere. The PI membranes were heated at a rate of 2 °C min⁻¹ and held at 100 °C, 200 °C, 300 °C, and 400 °C for 30 min respectively, before heating to 700 °C at a rate of 1 °C min⁻¹ for 60 min. The CMS membranes generally had a thickness of 35–37 μm. The thickness was measured by a micrometer thickness gauge (CH-1-S, Shanghai Liuling Instrument, Shanghai, China).

2.3. Characterisation

A STA449C (Simultaneous Thermogravimetry – Differential Scanning Calorimetry, Netzsch, Germany) was used to test the

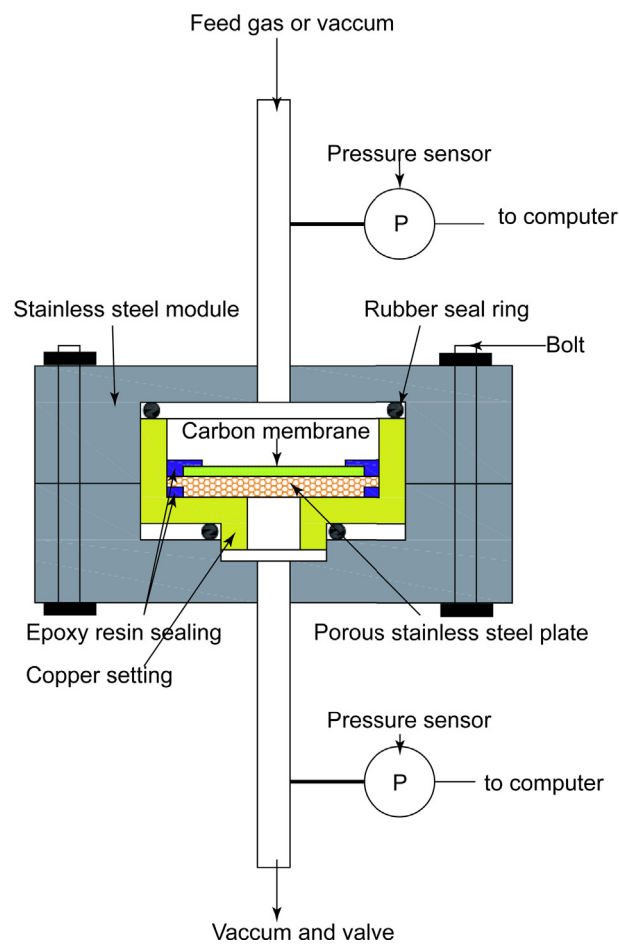


Fig. 2. Schematic diagram of the setting for test of gas permeance of CMS membranes.

Table 1
PAA membrane ID and the viscosity of the PAA precursor.

PAA samples	Intrinsic viscosity	PMDA (mmol)	ODA (mmol)	PA (mmol)
PAA-166	1.66	120.0	120.0	0
PAA-145	1.45	120.0	120.0	1.7
PAA-95	0.95	120.0	120.0	5.1
PAA-65	0.65	120.0	120.0	8.7
PAA-17	0.17	120.0	120.0	63.5

thermal stability, mass loss with temperature, and the glass transition temperature (T_g) of the membranes, under an argon gas flow of 30 ml min⁻¹ and a heating rate of 10 °C min⁻¹. Nitrogen and

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