Journal of Membrane Science 454 (2014) 1–11

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Molecular modeling of poly(benzoxazole-co-imide) membranes: A structure characterization and performance investigation

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ARTICLE INFO

Article history:
Received 10 August 2013
Received in revised form
19 November 2013
Accepted 25 November 2013
Available online 6 December 2013

Keywords:
Molecular dynamics
Monte Carlo
Thermally rearranged
PBO
Free volume

ABSTRACT

The molecular simulation technique was adopted to investigate the structure and transport performance of thermally rearranged poly(benzoxazole-co-imide) membranes. A molecular dynamics (MD) technique was used to construct three models: a poly-benzoxazole (PBO) membrane with high free volume; a polyimide (PI) membrane with dense structure; and their co-polymer, PBO-PI membrane. The MD simulation was performed to characterize the membrane models to understand how the very rigid benzoxazole segments affect the micro-structure, free volume, cavity size, and gas diffusion of the membrane models. A Monte Carlo method was adopted to investigate the gas sorption behaviors in the three types of membranes. The torsional angle and wide-angle X-ray diffraction analyses suggest that the benzoxazole segments stiffened the polymeric chains, leading to the formation of a looser structure. In free-volume and cavity-size studies, the PBO membrane exhibited the highest free volume and largest cavity size, which can be attributed to the presence of the benzoxazole structure constructed by thermal rearrangement. The enlarged free volume in the membranes with benzoxazole segments provided more space for gas sorption and diffusion, which effectively enhanced the gas permeability. In addition, increasing the benzoxazole segments in the membrane structure enhances the gas sorption in accordance with Henry's law, as the PBO membrane provides more inter-polymeric chain space and allows for the larger free volume elements. Fabrication of the poly(benzoxazole-co-imide) membrane with an appropriate PBO/PI composition would help optimize the gas permeability and selectivity in the gas separation process. The results from the simulation agree with the experimental data, indicating that the molecular simulation technique is a useful method in the field of materials design and development for the membrane separation process.

1. Introduction

Thermally rearranged poly-benzoxazole (TR-PBO) membranes show promising performance in the gas separation process [1–5]. The development of PBOs can be traced back to the 1960s, when PBOs received considerable attention and were shown to be naturally very rigid and to possess stable thermal properties [6–8]. Soon after, PBO was adopted for gas separation in membrane technology due to its excellent properties in severe conditions [1–3]. The TR-PBO membrane contained high free volume with a unique shape resembling a series of bottlenecks connecting adjacent cavities, leading to the membrane's excellent permeability and selectivity [4,5]. For further analysis, positron annihilation lifetime spectroscopy (PALS) was used to characterize the TR-PBO membrane. In PALS analysis, a bimodal profile of free volume size was discovered in TR-PBO membranes, allowing for the improvement of gas permeability with good selectivity [9]. With regard to gas transport behaviors, the effective free volume in the TR-PBO membrane was shown to be released after the thermally rearranged reaction, resulting in increasing gas diffusivity and solubility while maintaining comparable selectivity [10–12]. Due to the high free volume of TR-PBO, researchers sought to fabricate a membrane using TR-PBO and highly selective materials to overcome the upper bound of gas separation [13–18]. The TR-poly(benzoxazole-co-imide) ;membranes composed of TR-PBO and polyimide were fabricated

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http://dx.doi.org/10.1016/j.memsci.2013.11.047

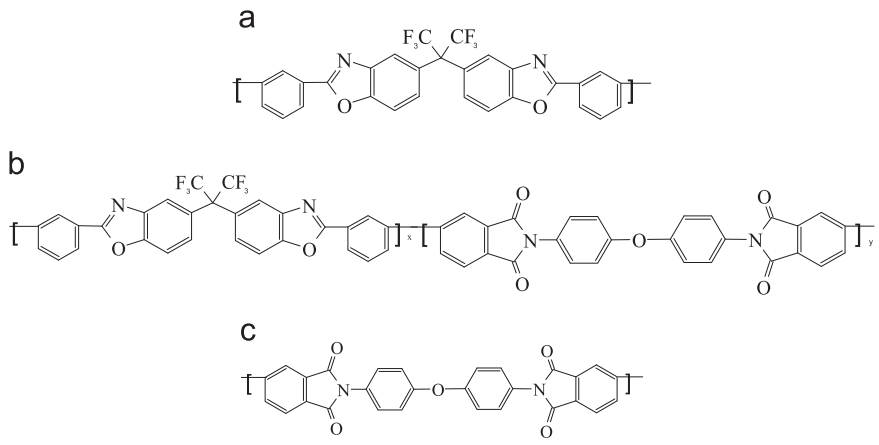

Fig. 1. Monomer structures of the (a) PBO, (b) PBO-PI, and (c) PI membrane models.

using different compositions [13,14]. Thermal rearrangement process enhances the backbone rigidity and free volume of the co-polymer membranes to improve gas separation performance. These TR-poly (benzoxazole-co-imide) membranes exhibit good permeability, and their gas selectivity is improved with an increase in polyimide content, which is proportionally more concentrated around the Robeson Upper Bound. Pyrrolone segments were added to the TR-PBO membranes to enhance the selectivity, and these modified membranes exhibited a selection factor twice as high as that of the pure TR-PBO membrane [15]. Previous efforts also attempted to control the conditions of thermal treatments to adjust the formation of the thermally rearranged benzoxazole segment in the membrane to fine-tune the relationship between permeation and separation factors [15,16]. TR-poly(benzoxazole-co-amide) membranes have been studied and they showed good hydrogen separation performance [17]. Moreover, cross–linked TR-poly(benzoxazole-co-imide) membranes have been investigated to improve gas separation performances [18].

Recently, theoretical study at the microscopic scale has been regarded as a promising method for developing and designing novel materials [19–32]. In a microstructure analysis, the torsional angle was adapted to investigate the packing efficiency of polymeric membranes [19]. Simulated wide-angle X-ray diffraction has been used to accurately describe the bulk membrane free space [20]. In addition, the molecular dynamics (MD) technique has enhanced several methods for analyzing the cavity or free-volume size distribution, including the concepts of an energetic sizing algorithm [21], geometrics [22], and image analysis [23]. With regard to gas diffusion and sorption behaviors, the MD and Monte Carlo (MC) simulations have been applied and shown to be highly consistent with experimental results. The MC method has been applied to study the effects of material structure, fabrication parameters, and operational conditions on the gas sorption behaviors [24–26]. The MD simulation has been used to investigate the areas of thermal motion mechanisms, mobility, and self-diffusivity of small molecules in the membrane matrix [27–29]. Through the solution–diffusion model, the simulated gas permeability can be estimated based on the solubility and diffusivity, and such estimations have compared favorably with experimental results [19,20,30,31].

The TR-PBO membrane has shown promising performance in applications for gas separation. Combining the highly permeable TR-PBO membrane and highly selective membrane materials is a key criterion in the development of useful membranes in membrane technology. The molecular simulation technique has been shown to be both feasible and valuable in investigations of membrane structure and performance at an atomic scale. Therefore, the aim of the present work was to evaluate the performance of a poly(benzoxazole-co-imide) membrane composed of PBO chains with high permeability and segments and polyimide chains with good selectivity using a molecular simulation technique. Three types of membrane models were constructed in this study: poly-benzoxazole (PBO), poly(benzoxazole-co-imide) (PBO-PI), and polyimide (PI) membranes. The physical properties of these membranes for model construction were based on previous studies [13]. Details of the model construction are illustrated in Section 2.

Table 1
Details of the simulated models constructed in this work.

	Repeat unit (–)	Chain no. (–)	Cell length (Å)	Atom no. (–)	ρ (g/cm^3)
PBO	60	1	36.19	3182	1.13
PBO-PI	60[a]	1	33.19	3058	1.35
PI	60	1	32.05	2940	1.39

[a] The ratio of PBO monomers to PI monomers is 1:1.

2. Theoretical method

In this work, three types of membrane models, PBO, PBO-PI, and PI, were constructed to analyze how the rigid benzoxazole segments affect membrane structure and gas transport behaviors. The MD technique was used to construct the membrane model and to analyze the membrane structure and gas diffusion. The MC method was applied to simulate the gas sorption behaviors in the membrane. All molecular models were constructed using the Materials Studio software from Accelrys Inc. The model construction and physical property estimations are described in detail below.

2.1. Model construction

In this study, repeating units of PBO and PI were constructed and used to build the three membrane models. These structures are shown in Fig. 1. Details of the molecular model information are summarized in Table 1. All the membrane models were constructed through the Amorphous Cell module, in which the density values were initially set as 0.01 g/cm^3. The structural optimization was performed using the energy minimization process with 3000 iterations to obtain a reasonable membrane structure. Later, a lager pressure, 0.3 GPa, as adopted to pack the membrane models to those from previous experimental work [13]. To eliminate the effect of higher pressure on the membrane models, an MD duration at 800 K (above the glass transition