Journal of Membrane Science 475 (2015) 384–394

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Free-standing, polysilsesquioxane-based inorganic/organic hybrid membranes for gas separations

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ARTICLE INFO

Article history:
Received 8 August 2014
Received in revised form
8 October 2014
Accepted 11 October 2014
Available online 31 October 2014

Keywords:
Ladder-like polysilsesquioxane
Free-standing composite membranes
Crosslinking
Gas separations

ABSTRACT

Polysilsesquioxanes (PSSQs) are composite materials consisting of inorganic framework and organic functional groups. Their inherent dual characteristics offer various applications including microelectronics, optics and biosciences. For the first time, free standing ladder-like PSSQ films were successfully prepared for gas separations, allowing practical applications in the membrane area. In order to fabricate a free-standing PSSQ film, a novel ladder-like poly(phenyl-co-glycidoxypropyl) silsesquioxanes with phenyl:glycidoxypropyl copolymer ratio of 6:4 (LPG64) were synthesized by a base-catalyzed sol–gel reaction. Moreover, the LPG64 films were thermally crosslinked with octa(aminophenyl)-T8-silsesquioxane (OAPS) with different concentrations of OAPS. Single gas (i.e. He, H_2, CO_2, O_2, N_2, and CH_4) transport measurements were performed for the LPG64 as well as LPG64/OAPS composite membranes. The LPG64 membrane exhibited a relatively high CO_2 permeability of 47.88 Barrer compared to other gases with CO_2/N_2 permselectivity of 30.5. The annealing effect on the transport results of the LPG64 membrane was negligible due to its rigid inorganic framework. Combination of our transport analysis and XRD characterization demonstrated that the addition of OAPS led to more dense chain packing, reducing permeability for all the gases tested in this work with increase in permselectivities. Especially, the LPG64/OAPS (80/20 wt/wt) membrane improved He/N_2 and H_2/N_2 permselectivities by 98% and 80%, respectively, compared to those for neat LPG64 membranes.

1. Introduction

Polysilsesquioxanes (PSSQs), a general formula of $(RSiO_{1.5})_n$, are hybrid materials consisting of an inorganic framework and organic functional groups [1]. The intrinsic dual characteristics of PSSQs provide various potential advantages; they have high thermal stability as well as good compatibility with organic materials due to the presence of rigid inorganic structures and the organic functional groups [2–4]. In addition, they have low dielectric constants as well as good optical transparency so that their application can be extended to the area of the optics, microelectronics, and biosciences [5–8]. Physical properties of PSSQs can be adjusted by modifying their microstructures, which are affected mainly by organic substituents [9]. Conventionally, they are synthesized by using alkyltrialkoxysilane or alkyltrihalosilane through hydrolysis–condensation reactions. Depending on the type of organic substituents attached to the silicon atoms, various intramolecular or intermolecular interactions exist, determining their microstructures.

PSSQs can be classified into two main structures including cage-like and ladder-like structures. Rigid cage-like structure, *so-called* polyhedral oligomeric silsesquioxane (POSS), consists of a spherical three-dimensional Si–O cage and organic functional groups with an overall diameter of 1–50 nm [10]. At each cage vertex, organic functional groups are attached to silicon atoms, and thereby, have bulky properties with merits of PSSQs [10]. Kim et al. [9] demonstrated that the increase in the size of the alkyl substituents led to closed cage-type structures due to their steric and hydrophobic effects. More recently, a number of POSS have been used as inorganic fillers in a polymer matrix for mixed matrix membranes (MMMs) and incorporated into inorganic/organic

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http://dx.doi.org/10.1016/j.memsci.2014.10.024
0376-7388/

hybrid copolymers as a crosslinking agent or a reinforcing agent [11–15]. Rios-Dominguez et al. [16] demonstrated that incorporation of POSS into polystyrene slightly improved both O_2 and N_2 permeabilities with a small loss in O_2/N_2 selectivity. Iyer et al. [17] incorporated different concentrations of octa(aminophenyl)-T8-silsesquioxane (OAPS) into 6FDA-MDA polymer matrix for MMMs. They observed permeabilities for all the gases studied in their work decreased except for CO_2 with increase in permselectivities for most gas pairs including He/CH_4, CO_2/CH_4 and O_2/N_2 as the OAPS concentration increased.

Ladder-like PSSQs with unique double-stranded molecular structure are more superior in terms of thermal and mechanical stabilities to the PSSQs with other structures [18]. Moreover, unlike fixed-sized POSS, a high molecular weight of ladder-like PSSQs can be obtained by increasing their chain length through polymerization reactions, allowing the feasibility of a free-standing film formation [19–22]. They have been actively investigated for several decades since Brown et al. claimed that they synthesized the first ladder-like PSSQs in the early 1960s [23]. Unfortunately, their PSSQs were proven to be partial cage-like structured by Frye et al. [24]. Since then, a series of ladder-like PSSQs with different organic functional groups were developed [25–28]. For instance, Cao et al. synthesized the ladder-like copolymethyl-hydrosilsesquioxane (Me-H-T) and ladder-like copolymethyl-epoxysilsesquioxane (CPMES) [29]. CPMES showed much higher thermal stability than Me-H-T due to the self-crosslinking by the epoxide group. However, the majority of studies with polysilsesquioxanes have been conducted in the thin film state through the spin coating technique on top of silicon substrates [30,31] and no free-standing, ladder-like PSSQ film formation was reported so far. Free-standing membranes provide an excellent opportunity to investigate the unique properties of the film by eliminating additional effects due to the presence of a mechanical support. Also, free-standing film formation is a critical component in studying the inherent transport properties of a given material.

In order to obtain mechanically robust free-standing inorganic–organic hybrid PSSQ-based films, two main critical prerequisites are of the utmost importance. First, the molecular weight of the PSSQ should be high enough to attain chain–chain entanglement at an intra-/ intermolecular level between the siloxane ladder-structure and between the unilateral pendant organic functional groups. Second, the PSSQ must have imperceptibly few uncondensed silanol groups, as these Si–OH groups render significant film shrinkage, causing film cracks. While cage-structured POSS materials satisfy the ladder condition, POSS materials lack the high molecular weight, which is required to fabricate free standing films. In order to satisfy both criteria, while simultaneously imbuing crosslinking functionality, we synthesized a novel ladder-like poly(phenyl-co-glycidoxypropyl) silsesquioxanes with phenyl:glycidoxypropyl copolymer ratio of 6:4 (LPG64) by the base-catalyzed sol–gel reaction. With this new hybrid polymer, nonporous, free-standing films were prepared using a Doctor Blade apparatus. These hybrid films exhibited unique separation properties imparted by their molecular structure as illustrated from single gas permeation test. To our best of knowledge, it was the first time that free standing ladder-like PSSQ films were successfully prepared for gas separations, allowing their practical applications in the membrane area. Moreover, the LPG64 films were thermally crosslinked with OAPS and their physical and transport properties were investigated with different concentrations of OAPS.

2. Experimental

2.1. Chemicals

Phenyltrimethoxysilane (PTMS) and 3-glycidoxypropyltrimethoxysilane(GPTMS) were obtained from Shin Etsu and vacuum distilled over CaH_2 prior to use. Potassium carbonate (99%, Daejung Chemicals & Metals Co. LTD., South Korea) was used as received. Cage-like octa(aminophenyl)-T8-silsesquioxane (OAPS) (M_W; 1153.64 kg/mol) as the crosslinking agent was purchased from the Gelest, Inc. (USA). Tetrahydrofuran (THF) with a purity of∼99.0% (Daejung Chemicals & Metals Co. LTD., South Korea) was used for the solvent. OAPS and THF were also used as received.

2.2. Synthesis of ladder-like poly(phenyl-co-glycidoxypropyl) silsesquioxane with phenyl:glycidoxypropyl copolymer ratio of 6:4 (LPG64)

The synthesis of LPG64 followed a modified literature procedure, where a monomer mixture solution of phenyltrimethoxysilane (PTMS) and epoxy-functionalized glycidoxypropyltrimethoxysilane (GPTMS) were hydrolyzed and condensed in a base-catalyzed sol–gel reaction (See Fig. 1) [20,32,33]. This synthesis method is highly effective to obtain fully condensed, high molecular weight of PSSQs with various organic copolymer compositions [20]. Typically, a transparent mixture of potassium carbonate (0.04 g, 0.29 mmol), deionized water (4.8 g, 0.27 mol), and THF (16 g, 0.22 mol) was prepared in a 100 ml round bottom flask. To this solution, a monomer mixture of PTMS (9.52 g, 0.48 mol) and GPTMS (7.95 g, 0.32 mol) was added dropwise under N_2. The reaction mixture was stirred vigorously for five days. After evaporation of the volatiles, the white resinous portion was dissolved in 100 ml of dichloromethane and extracted with water several times. After collection of the organic portions, drying with anhydrous magnesium sulfate, filtering, and evaporation of

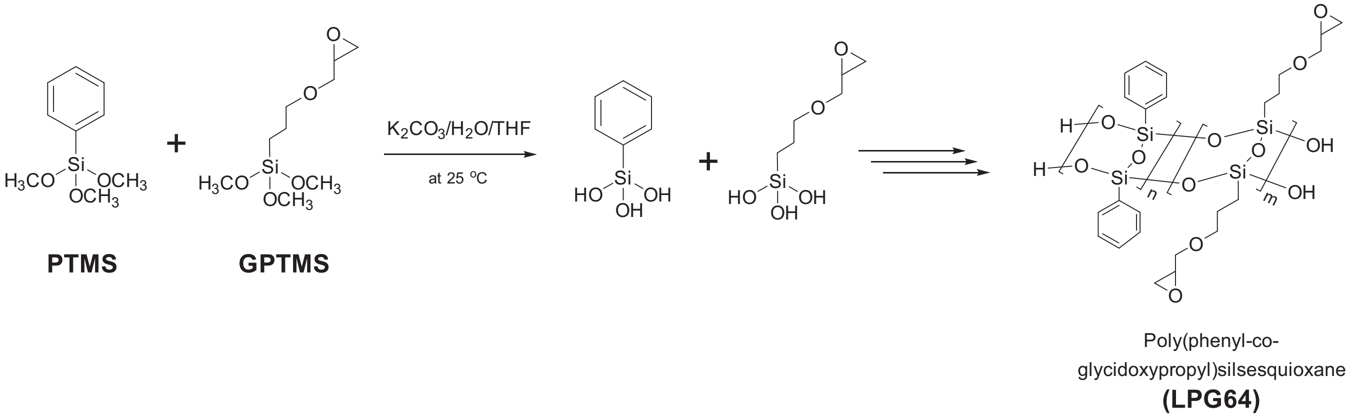

Fig. 1. Synthesis of LPG64 under a mild base-catalyzed system.