Synthesis and gas transport properties of hyperbranched polybenzoxazole – silica hybrid membranes

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Gas transport properties of hyperbranched polybenzoxazole (PBO) – silica hybrid membranes were investigated. The hyperbranched PBO – silica hybrid membranes were prepared via in-situ silylation method and sol-gel reaction. Thermal decomposition temperature of the hybrid membranes increased with increasing silica content, indicating improved thermal stability brought by the hybridization with silica. The hyperbranched PBO – silica hybrid membranes showed higher gas permeability than corresponding linear-type PBO – silica hybrid membranes with similar chemical structure. It was worth noting that both CO2 permeability and CO2/CH4 selectivity of the hyperbranched PBO – silica hybrid membranes were increased with increasing silica content across the upper bound trade-off line for CO2/CH4 separation. The prominent CO2/CH4 separation ability of the hyperbranched PBO – silica hybrid membranes might be achieved by large amounts of free volume holes, that were fundamentally brought by a characteristic hyperbranched structure and additionally created around polymer/silica interfacial area, equipped with unique distribution and interconnectivity advantageous for a size-selective CO2/CH4 separation.

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1. Introduction

The separation of gases by polymeric membranes has remarkably attracted the attention during several decades [1–4]. Compared to conventional separation processes, membrane-based gas separation provides many advantages such as low capital and operating costs, high energy efficiency, and ease of operation [5–7]. In this regard, a large number of polymeric membranes with high gas permeation and separation abilities have been developed. Especially, a class of rigid-rod aromatic polymers including polyimides (PIs) [8–11] and polybenzoxazoles (PBOs) [12,13] are promising candidates for applications to high-performance gas separation membranes because of their high gas permeation and separation abilities as well as high thermal and mechanical properties. Recently, Lee and his coworkers have reported about gas transport properties of PBOs prepared via thermal rearrangement process of polyimides containing ortho-positioned hydroxyl group, and the thermally rearranged PBOs, named TR-PBOs, have shown extraordinarily high gas permeability and selectivity [7,14–17]. As another way to synthesize PBOs, dehydration reaction of aromatic polyamides containing ortho-positioned hydroxyl group, poly(o-hydroxy amide)s (PHAs), is also available, and gas transport properties of the PBOs prepared from corresponding PHA precursors have been investigated [18–21].

In our previous study, novel hyperbranched PIs and their silica hybrids have been prepared, and their gas transport properties have been investigated [22–24]. It has been found that the hyperbranched PIs and their silica hybrids exhibit outstanding gas transport and separation behaviors, owing to synergic effects of hyperbranched structure and hybridization with silica. However, to our knowledge, there are no experimental reports about gas transport properties of Hyperbranched PBO and its silica hybrid membranes.

In this study, hyperbranched PBO – silica (SiO2) hybrid membranes were prepared via in-situ silylation method [25,26] and sol-gel reaction, and their gas transport properties were investigated. In addition, obtained gas transport properties of the hyperbranched PBO – silica hybrid membranes were compared with those of linear-type PBO – silica hybrid membranes with similar chemical structure.

Generally, for the synthesis of hyperbranched polymers, two different methods are known; the one is the self-polymerization of an AB2-type monomer and the other is the polymerization of an A2-type monomer and a B3-type monomer [27]. For the former method, Hong et al. have reported about the synthesis of a hyperbranched polybenzoxazole and its application for the
chemically amplified materials [28]. On the other hand, for the latter method, Kudo et al. have successfully synthesized hyperbranched polybenzoxazoles through the polymerization of commercially available dihydroxyamine as an $A_2$-monomer and tri-carbonylchloride as a $B_3$-monomer [29]. The polymerization with $A_2$- and $B_3$-type monomers is affected by many factors such as order of monomer addition, molar ratio of monomers, and concentration of reaction system [30].

[Manner 1] When a solution of $A_2$-type monomer is added dropwise to a solution of $B_3$-type monomer in a stoichiometric monomer feed ratio of $A_2:B_3=1:1$ (the molar ratio between functional A and B groups of the corresponding monomers is 2/3), $B$-terminated hyperbranched polymer is obtained.

[Manner 2] When a solution of $B_3$-type monomer is added dropwise to a solution of $A_2$-type monomer in a stoichiometric monomer feed ratio of $A_2:B_3=2:1$ (the molar ratio between functional A and B groups of the corresponding monomers is 4/3), A-terminated hyperbranched polymer is obtained.

The objective hyperbranched PHA precursor for this study was synthesized on the basis of the Manner 2.

2. Experimental

2.1. Materials

1,3,5-benzenetricarbonyl trichloride (BTC) was obtained from Sigma-Aldrich Japan (Tokyo, Japan). 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAHP), 4,4′-oxybis(benzoic acid chloride) (OBC), and tetraethoxysilane (TEOS) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). N,O-bis(trimethylsilyl)acetamide (BSA) as an amide-type silylation agent was obtained from Sigma-Aldrich Japan (Tokyo, Japan). 3-(trithoxyxyl)propylsuccin anhydride (TEOSPSA) as a coupling agent and $N,N$-dimethylethacamide (DMAc) as a solvent were supplied by AYmax Co. (Tokyo, Japan) and Nacalai Tesque, Inc. (Kyoto, Japan), respectively. These regents and solvent were used as received. Chemical structures of monomers are shown in Fig. 1.

2.2. Polymerization

2.2.1. 6FAHP-BTC hyperbranched poly(o-hydroxy amide) and N,N-thoxysilyl)propylsuccinic anhydride (TEOSPSA) as a coupling agent was obtained from Sigma-Aldrich Japan (Tokyo, Japan). 3-(trithoxyxyl)propylsuccin anhydride (TEOSPSA) as a coupling agent and $N,N$-dimethylethacamide (DMAc) as a solvent were supplied by AYmax Co. (Tokyo, Japan) and Nacalai Tesque, Inc. (Kyoto, Japan), respectively. These regents and solvent were used as received. Chemical structures of monomers are shown in Fig. 1.

2.2.2. 6FAHP-OBC poly(o-hydroxy amide)

5 mmol of 6FAHP was dissolved in 10 ml of DMAc in a 50 ml three-neck flask under $N_2$ flow. 20 mmol of BSA was added to this solution with stirring at room temperature, and the solution was kept stirring for 1 h. After that, the solution was cooled with an ice-ethanol bath at 0–5 °C, and 4.85 mmol of OBC was added with stirring. The mixture was kept stirring at 0–5 °C for 1 h, and then, at room temperature for 3 h under $N_2$ flow. The resulting polymer solution was poured into distilled water. The precipitated polymer was collected and washed thoroughly with distilled water, followed by vacuum drying at 90 °C for 4 h. Finally, polymer solid of 6FAHP-OBC poly(o-hydroxy amide), PHA(6FAHP-OBC), was obtained.

2.3. Membrane formation

0.5 g of PHA(6FAHP-BTC) or PHA(6FAHP-OBC) were dissolved in 5 ml of DMAc, and 0.050 g of TEOSPSA were added with stirring. To this solutions, appropriate amounts of TEOS and distilled water (TEOS:distilled water = 1:6 as a molar ratio) and catalytic amount of diluted hydrochloric acid were added, and the reaction mixture was stirred overnight. Preparation condition of corresponding reaction mixtures is summarized in Table 1. After that, the mixtures were cast on PET sheets and dried at 85 °C for 1 h in a heating oven to form thin membranes. The prepared membranes were peeled off and fixed between two window-opened metal frames and subsequently cyclized and hybridized at 100 °C for 1 h, 200 °C for 1 h, and 400 °C for 1 h in a heating oven under $N_2$ flow. Finally, hyperbranched PBO, PBO(6FAHP-BTC), or linear-type PBO, PBO (6FAHP-OBC), — silica hybrid membranes were obtained.

2.4. Measurements

Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were recorded by a FT/IR-4100 (JASCO Corp.) equipped with an ATR PRO ONE (ZnSe prism) (JASCO Corp.) at a wavenumber range of 700–4000 cm $^{-1}$ and a resolution of 1 cm $^{-1}$. UV/VIS optical transmittances were investigated by a JASCO V-530 UV/VIS spectrometer at a wavelength of 200–800 nm. Scanning electron microscopy (SEM) images were acquired using a Hitachi S-3400N variable pressure scanning electron microscope at an accelerating voltage of 10 kV. Samples for the SEM analyses were coated using a Hitachi E-1010 ion sputter coater with a platinum target. Thermogravimetric — differential thermal analysis (TG-DTA)
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