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# Thermally rearranged (TR) poly(benzoxazole-co-amide) membranes for hydrogen separation derived from 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB), 4,4'-oxydianiline (ODA) and isophthaloyl chloride (IPCI)

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## ABSTRACT

Thermally rearranged poly(benzoxazole-co-amide) (TR-PBOA) copolymer membranes were prepared by treating poly(*o*-hydroxyamide-co-amide) (PHAA) precursors by in-situ thermal cyclization reaction for the H<sub>2</sub> separation at high temperature. The physical properties, membrane processability and gas permeation property can be controlled by varying the ratio of diamine compounds. The rigid biphenyl moiety in the copolymer membranes increases gas selectivity whereas the flexible ether moiety improves membrane processability as well as gas permeability. Moreover, thermal rearrangement process affects the gas separation properties of TR copolymer membranes. TR polymer membranes derived from polyhydroxyamides (PHAs) demonstrated high H<sub>2</sub> permeability, but low H<sub>2</sub>/CO<sub>2</sub> selectivity. However, TR-PBOA copolymer membranes improved H<sub>2</sub>/CO<sub>2</sub> selectivity. Both permeability and selectivity of H<sub>2</sub> over CO<sub>2</sub> increased due to the high activation energy for H<sub>2</sub> permeation through the copolymer membranes and can be explained by thermodynamic theory with temperature. The highest performance was 26.8 Barrer of H<sub>2</sub> permeability and 8.0 of H<sub>2</sub>/CO<sub>2</sub> selectivity measured at 210 °C.

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## 1. Introduction

Hydrogen is an important resource for various industrial applications such as a source of ammonia synthesis via the Haber–Bosch process and hydrocracking of fossil fuel [1,2]. Moreover, hydrogen is expected to be an efficient energy carrier as a future clean energy resource with high efficiency and zero pollution emissions [3]. The majority of recent hydrogen production is from industrial processes such as hydrocarbon steam reforming [4], methane plasma reforming [5], and water-splitting iodine-sulfur (IS) process [6,7]. Among those processes, the steam reforming of light hydrocarbons is widely used [8]. More recently, hydrogen production from water gas shift (WGS) reaction in integrated gasification combined cycle (IGCC) for power generation is seriously considered to battle against global warming [9–11]. IGCC process is considered as future a coal-fired power generation process lacking greenhouse gas emissions. This process

would use coal resources where coal deposits are a more abundant fossil fuel resource than oil deposits [10,11]. After WGS reaction, the gas mixture of H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S is generated at high temperature and pressure. H<sub>2</sub> separation as a fuel, as well as CO<sub>2</sub> capture for carbon sequestration, so-called pre-combustion CO<sub>2</sub> capture process, is one of the main issues in IGCC process. High pressure and temperature feed gas after the WGS reaction enables the membrane process as an attractive process because the pressure difference between upstream and downstream functions as a driving force of membrane gas separation [12,13]. However, a drawback that recent commercial polymeric membranes cannot be applied in the pre-combustion process is related with membrane stability at high temperature and pressure. Commercially available gas separation membranes are usually from thermally unstable polymers. Therefore, thermally stable polymers should be applied as membrane materials for pre-combustion process.

As recently reported, thermally rearranged polybenzoxazoles (TR-PBOs) are outstanding gas separation membrane materials with thermal and chemical stability as well as extraordinary permeability for small gas molecules [14–18]. Thermal conversion of hydroxyl-containing polyimide (HPI) precursors into TR-PBOs leads to great improvements of gas permeability while retaining

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high selectivity. However, TR-PBOs rearranged from HPI precursors are not appropriate for the hydrogen separation in the pre-combustion process due to relatively larger cavity sizes than CO<sub>2</sub> molecules in polymers where effective gas separation of H<sub>2</sub>/CO<sub>2</sub> is not possible [19]. For effective separation, we tailored cavity sizes by introduction of TR-PBOs derived from poly(*o*-hydroxyamides) (PHAs) with distinguished thermal conversion based on dehydration reaction [19]. TR-PBOs derived from the PHAs demonstrated smaller cavity sizes, which presented a better selectivity for H<sub>2</sub>/CO<sub>2</sub> separation.

Tuning the microcavities in polymer membranes can be achieved by changing polymer structure. More rigid and aromatic structures in PHAs and their corresponding TR-PBO membranes would improve the gas separation properties with efficient cavity sizes targeting for H<sub>2</sub>/CO<sub>2</sub> separation. However, effective chain packing could reduce polymer solubility and hinder membrane processability. Copolymerization is one way of obtaining better gas separation performances as well as achieving membrane processability. Previous reports have investigated that random copolymerization of highly aromatic PHAs with cycloaliphatic structures enhance solution-processability [20]. Copolymerization of PHA with poly(methoxy amide) units loosens the polymer chain stiffness resulting in lower glass transition temperature [21]. Copolymerization of TR polymers has also been reported for TR poly(benzoxazole-co-imide) membranes to control the membrane performances [22].

In this study, we introduced copolymers of thermally rearranged poly(benzoxazole-co-amide) (TR-PBOA) membranes to investigate the gas separation performances with favorable polymer processability. PBOA copolymers were prepared by thermal

rearrangement of poly(*o*-hydroxyamide-co-amide) (PHAA) with rigid biphenyl moiety as well as a flexible ether chain in the amide moiety. The various ratios of monomers in copolymers are expected to control the gas separation performance.

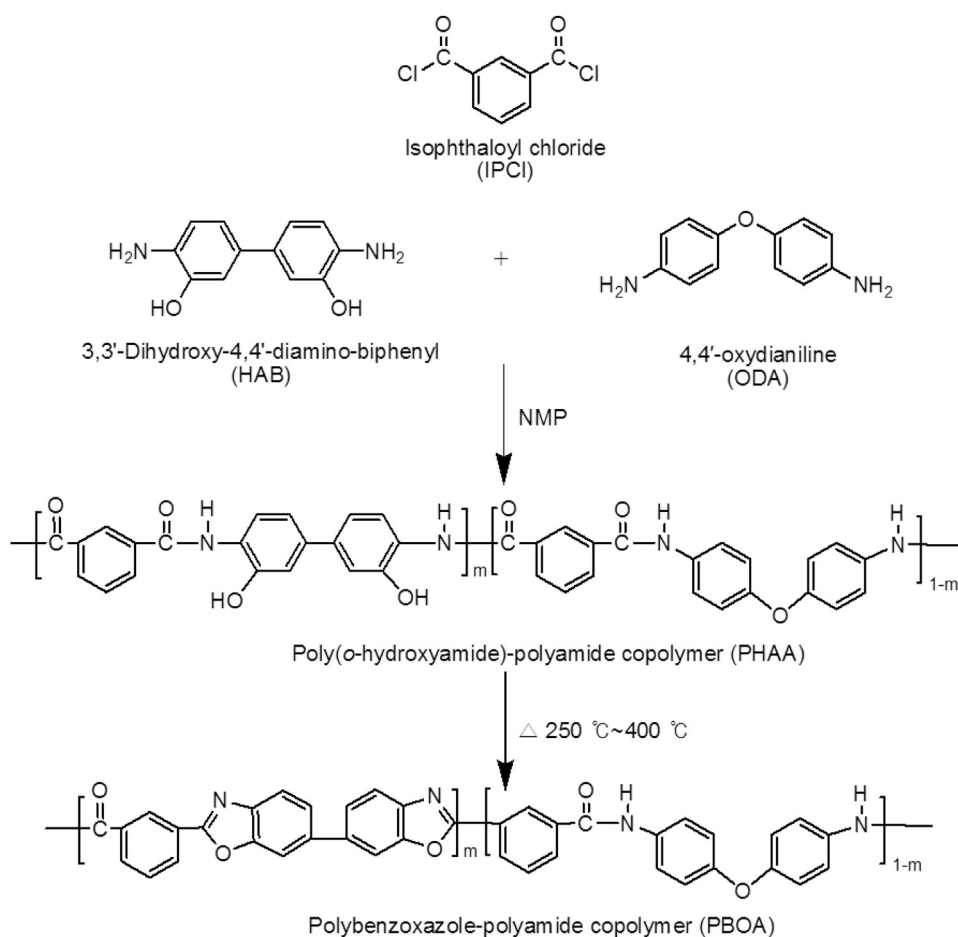
## 2. Experimental

### 2.1. Materials

Isophthaloyl chloride (IPCl) was purchased from Sigma Aldrich Co. (Milwaukee, WI, USA). 3,3'-Dihydroxy-4,4'-diamino-biphenyl (HAB) and 4,4'-oxydianiline (ODA) were purchased from Wakayama Seika Co. Ltd., (Osaka, Japan). Anhydrous *N*-Methyl-2-pyrrolidinone (NMP, > 99.5% purity), as a solvent, was purchased from Sigma Aldrich Co. (Milwaukee, WI, USA). All diamines were dried under vacuum at 40 °C for at least 12 h to remove the absorbed water. They were used immediately, when opened, without further treatment.

### 2.2. Preparation of polymer precursors

Synthesis of five PHAA precursor copolymers in various compositions was conducted by the condensation reaction of an acid chloride and diamines as described in Scheme 1. The synthesis was performed in three-neck and round-bottomed flask under nitrogen atmosphere. 30 mmol of diamines with HAB and ODA were added and stirred in 60 ml of NMP. The molar ratio of HAB and ODA as diamines was varied respectively to 10:0, 8:2, 5:5, 2:8 and 0:10 for copolymerization. When diamines were completely



**Scheme 1.** The preparation of poly(*o*-hydroxyamide-co-amide) copolymer and their thermally rearranged poly(benzoxazole-co-amide) copolymer.

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