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Thermally rearranged polybenzoxazole copolymers incorporating Tröger's base for high flux gas separation membranes

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ABSTRACT

A new class of thermally rearranged (TR) polymers was prepared *via* copolymerization of TR-able *o*-hydroxyl polyimide and non-TR-able polyimide incorporating highly rigid Tröger's Base (TB) units. The effect of TB content, type of TR-able diamine, and TR protocols on polymer properties and gas transport behaviors were thoroughly studied. TB moieties in the copolymers efficiently enhanced polymer rigidity and induced high T_g and TR temperature as confirmed by thermogravimetric analysis and dynamic mechanical analysis. Additionally, as the TB molar ratio increased, the interchain distances of precursor polyimides increased from 0.545 to 0.585 nm. The most important finding in this work was the synergistic effect between TR conversion and TB segments, which provide the optimum contents of TB in the copolymers. As a result, 6F6FTB-0.3-450 presented a maximum *d*-spacing value of 0.609 nm and excellent gas separation performance of 1567 Barrer for H_2 and 1944 Barrer for CO_2 along with a selectivity of 18.6 for H_2/CH_4 and 23.07 for CO_2/CH_4, surpassing the corresponding 2008 upper bounds. In addition, 6F6FTB-0.3 exhibited good plasticization resistance under CO_2/CH_4 mixed gas up to CO_2 fugacity of ~15 bar.

1. Introduction

Hydrogen and methane have received significant attention in energy-related industries due to their high energy density per mass and less CO_2 emission from combustion compared to traditional fossil fuels from petroleum and coal, which cause global warming [1–5]. These clean fuels are expected to play more important roles in home, automobiles and aerospace [6,7]. Membrane technologies have distinctive advantages for gas purifications such as small foot print and size-tunable implementations. These features allow the membrane systems to be applied to special environments such as offshore gas-processing platforms or on-board inert gas generation systems. Also, membrane systems do not require heat energy for phase transitions or physicochemical reactions in contrast with adsorption or distillation processes [8,9]. Polymer membranes have been explored for gas purification due to their advantages of low energy consumption, simple operation and ease of scale-up [10–14]. Commercial polymers such as polysulfone (PSF), cellulose acetate (CA) or polyimide (PI) have been industrially applied in membrane-based H_2 and CH_4 separations [15,16]. Nevertheless, gas separation performance of polymer membranes suffers from a tradeoff relationship between gas permeability and selectivity, and therefore still needs to be improved for practical applications [17].

Thermally rearranged (TR) polymers, first reported by Lee and his colleagues, have been regarded as promising materials in membrane gas separation applications due to their outstanding gas transport properties [18]. TR polymers were obtained from post-fabrication methods on ready-made *ortho*-hydroxyl polyimide (HPI) membranes where structural transformation to rigid, infusible, and insoluble polybenzoxazole (PBO) occurred by a thermally induced solid-state reaction. During TR process, polymer rigidity was significantly improved, and polymer chains were rearranged, forming a microporous matrix with bimodal cavity size distributions in which the smaller cavities around 0.3–0.4 nm showed molecular sieving characteristics, while the larger cavities around 0.7–0.9 nm produced fast gas permeation [18]. Great progress has been made in TR polymers in membrane gas separations based on the optimization of chemical structures, synthetic routes and TR protocols during the last decade [19–23]. Besides the superior gas transport, TR polymers also show good plasticization resistance against

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