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**Thermal rearranged poly(imide-co-ethylene glycol) membranes for gas separation.**Colin A. Scholes<sup>a\*</sup> and Benny D. Freeman<sup>b</sup><sup>a</sup>Department of Chemical Engineering, The University of Melbourne, VIC, 3010, Australia<sup>b</sup>Center for Energy and Environmental Research, University of Texas at Austin, USA**Abstract**

Thermal rearrangement of  $\alpha$ -functional polyimide membranes into poly(benzoxazole) improves the permselectivity performance compared to the precursor polymer. This is due to the bimodal cavity size distribution generated through the TR process. The cavity volume can be further increased by including segments within the polyimide that undergo degradation at a lower temperature than the TR process. The loss of these segments leaves behind cavity space that can be used to increase gas permeability. This is achieved here for copolymers based on 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) and 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) with poly (ethylene glycol) segments, where the PEG segments undergo thermal degradation below the PI to PBO transition temperature. HAB-6FDA-PEG copolymer membranes, with different weight % PEG, had poor permselectivity for CO<sub>2</sub>-N<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> separation. Undertaking thermal treatment to degrade the PEG segments but retaining the PI polymer resulted in an increased fractional free volume of the resulting membrane and higher gas permeability, but a corresponding loss of CO<sub>2</sub> selectivity. Producing TR-PBO from the copolymers through thermal rearrangement at 450 °C, improved the gas permeability of the resulting membranes by over an order of magnitude, as well as improving the CO<sub>2</sub> selectivity. This was attributed to the degradation of the PEG segments increasing the FFV of the membranes, resulting in over a third of the polymers' morphology being free volume. The resulting TR-PBO membranes formed from copolymers with PEG segment had enhanced permselectivity performance compared to TR-PBO formed from the polyimide homopolymer.

**Keywords:** Thermal rearrangement; polyimide; polyethylene glycol; copolymer; gas separation

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