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Thin-skinned intrinsically defect-free asymmetric mono-esterified hollow fiber precursors for crosslinkable polyimide gas separation membranes

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ABSTRACT

Engineering of spinning solution compositions, conditions and polymer molecular weight is described to create intrinsically defect-free thin-skinned precursors for high performance ester-crosslinked asymmetric hollow fiber membranes. The ultimate goal is to crosslink the precursors to provide robust performance for an aggressive natural gas feed. To provide insights free from CO_2-induced changes in properties in the uncrosslinked samples, studies with less interacting O_2, N_2 and He feeds were also used to assess properties. The combined analyses indicate an absence of substructure resistance within the hollow fibers and an effective selective layer between 0.1-0.14 μm. This thickness represents a valuable reduction over previously achievable values for this so-called propane-diol monoesterified crosslinkable polyimide (PDMC) polymer in defect-free asymmetric form, which were previously in the range of 0.5 μm. Indeed, the significantly reduced skin layer thickness offers the potential to improve the gas separation productivity by 3.6X if this advantage can be carried forward into the ultimate crosslinked fibers. Additional comparisons to the free acid form of the precursor (without esterification) show advantages to the current less hydrophilic precursor in terms of ability to create a thinner precursor selective layer prior to crosslinking than for the free acid form. To date, the free acid analog to PDMC has only been able to be created with a 0.7 μm selective layer vs. the current 0.1-0.14 μm skin reported here. Optimization of the crosslinking process for both precursors is beyond the scope of this work, since it is itself, complex and still underway.

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Introduction

Membrane-based separation can greatly reduce energy consumption for separating gas mixtures, compared to traditional thermally-driven separation processes, such as absorption and cryogenic distillation [1-7]. Among different types of membrane materials, polymers are the dominant