Organo-soluble Polybenzoxazoles (PBOs) as Gas Separation Membranes: New Synthesis and Gas Transport Properties

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Membrane materials featuring ultrafast and highly selective transport properties combined with good chemical, mechanical, and thermal stability in the process environment are highly desired for energy-efficient membrane gas separations. Polybenzoxazole (PBO) and PBO-based polymers possess many of the above mentioned attributes and are considered to be excellent candidates for gas separation membranes. A well-known and successful example of PBO-based polymers as gas separation membranes is TR (thermally rearranged) polymers, which possess unprecedented combination of high permeability and selectivity well beyond the upper bound limit. However, cost and difficulty in preparing PBOs and fabrication of PBO-based membranes due to their poor organo-solubility and processability have been reasons why, for many years, PBO has been known only among researchers and scientists.

In this paper, we report a novel new synthetic approach that produces organo-soluble PBOs via a one-pot, silylation-assisted in-situ solution conversion of ortho-functional polyamide precursors. Using this method, a series of organo-soluble PBOs were prepared from a wide pool of monomers, which demonstrated the feasibility and applicability of this new synthetic method. Molecular dynamics studies suggested that silylation played the key role in assisting the cyclolyzation reaction of polyamide precursors by forming a meta-stable intermediate, which significantly lowered the activation energy of ring closure reaction leading to organo-soluble PBOs. All PBOs synthesized using this novel method yielded tough and ductile films via conventional solution casting, which is not possible for the PBOs prepared using conventional single-stage method with phosphoric acid as solvent or two-stage method of solid state conversion of poly(hydroxyamide) precursors. Fundamental membrane properties were comprehensively characterized in terms of thermal and mechanical stabilities, fractional free volume and gas transport properties via pure gas permeation tests with H_2, N_2, Ar, CO_2, and CH_4 in a wide range of feed pressures (2-17 atm, 35 °C). In general, all PBO membranes showed high fractional free volume, which rendered high gas permeabilities in these membranes. Meanwhile, the highly rigid benzoxazole backbone structure enables excellent size sieving properties for these membranes. For example, the PBO membranes prepared from fluorinated monomers (6FC and 6FDA) showed excellent CO_2/CH_4 and H_2/CH_4 separation performances that were beyond the Robeson's upper bounds; the PBO membranes prepared from triptycene-based monomer showed great potential in hydrogen-related separations due to the unique bimodal size distribution of free volume in these membranes. Taking together with their excellent organo-solubility and processability, these newly synthesized PBOs represent a significant leap towards advancing the practical application of PBO-based membranes for gas separations.