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Xiao, Youchang; Chung, Tai-Shung; Guiver, Michael

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Synthesis, Cross-linking and Carbonization of Co-polyimides Containing Internal Acetylene Units for Gas Separation

Y. Xiao (Presenting author), National University of Singapore, National University of Singapore
T. Chung (Corresponding author), National University of Singapore, National University of Singapore, chencts@nus.edu.sg
M. Guiver, National Research Council of Canada, National Research Council of Canada

Membranes must meet the following performance criteria in order to have broad and successful applicability in various gas separation environments: 1) high permeability and high selectivity to minimize capital and operating costs; 2) good chemical resistance to prolong the lifetime of membrane systems; 3) thermal stability and mechanical properties to enable systems to operate at elevated temperatures; and 4) superior plasticization resistance to maintain high separation performance in the presence of highly sorbing penetrants, such as CO2 and hydrocarbon gases. Polyimide modification by cross-linking and carbonization has received much attention since it appears to provide a promising approach toward above criteria. In this study, cross-linkable polyimides containing internal acetylene units have been synthesized by random copolymerization of 6FDA dianhydride, 2,3,5,6-tetramethyl- 1,4-phenylenediamine (durene) and 4,4-diaminodiphenylacetylene (p-intA) diamine as materials for gas separation. Compared with 6FDA-Durene polyimide, 6FDA-Durene/p-intA co-polyimide shows denser polymer chain packing, which is confirmed by Wide-angle X-ray diffraction (WAXD). The thermally treated co-polyimides are insoluble in various solvents and show an increase in Tg, indicating the formation of network structures among the polymer chains. Differential Scanning Calorimetry (DSC) and FT-Raman suggest that cross-linking arises from Diels-Alder cycloaddition between the internally arranged acetylene units along the polymer main chain, resulting in extended conjugated aromatic structures. The thermally cross-linked membranes show enhanced resistance to CO_2 plasticization up to 700 psi. The rigidified membrane structure provides increased gas selectivity without severely compromising gas permeability. Moreover, carbonized membranes produced from un-cross-linked and cross-linked polyimide precursors exhibited greatly increased permeabilities and permselectivities, with excellent overall gas separation performance well above the upper-bound performance limit of conventional polymer membranes. A Diels-Alder cycloaddition reaction produces a much more rigid and planar conjugated aromatic structure in the polymer chains and results in a higher degree of graphitization during carbonization, which is confirmed by XPS and WAXD. Therefore, carbon membranes derived from co-polyimides with more internal acetylene units show much better gas separation performance than those derived from polyimides without internal acetylene units.