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#### Publisher's version / Version de l'éditeur:

*2008 International Congress on Membranes and Membrane Processes (ICOM 2008) [Proceedings], p. 1, 2008*

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## **Poster Session II – 179**

Tuesday July 15, 6:30 PM-9:30 PM, Lana'i Ballroom

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

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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 CO<sub>2</sub> 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 T<sub>g</sub>, 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<sub>2</sub> 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.