## Abstract

In recent decades membrane separations technology has been sparked as a substantial research area in material design and development due to its technical advantages such as simple operation, energy saving, the flexibility of raw materials in membrane fabrication and scale up and tailoring. The key parameters for membrane separation performances are permeability coefficients (P), the selectivity ( $\alpha$ ). But, polymeric membranes suffer from an obvious trade-off between the desired permeability and selectivity, as quantified by Robeson upper-bound relationship in 2008. Thus, new membrane materials are required for higher gas throughout by improved permeability and selectivity. In this scenario, aromatic polyamides (PAs) which exhibited high gas selectivity with the moderate permeability for different gas pairs along with a number of outstanding properties such as high thermal stability and high mechanical properties comes as a suitable membrane material. However, PAs exhibited poor processability and limited solubility in organic solvents. The primary goal of the present research was the synthesis of soluble polyamides by incorporation of different bulky pendant groups along the polymer backbone for gas separation applications.

Thus, to accomplish the set of goals, the present research focused on the development of new PA membranes and the systematic investigation of their gas transport properties towards four different gases (CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>). Accordingly, four series of polymers [PA 'A'-'D', PA 'E'-'I', PA 'J'-'M' and PA 'N'-'Q'] were synthesized and characterized. Transparent and flexible membranes were prepared from these polymers by solution casting technique. The membranes were well characterized by different analytical techniques and gas transport properties were investigated. PA 'E' having a bulky pendant phosphaphenanthrene skeleton showed highest gas permeability for CO<sub>2</sub> [164 Barrer] and O<sub>2</sub> [59.7 Barrer] in this investigation. However, PA 'J' having bridged Tröger base (TB) unit exhibited highest permselectivity towards CO<sub>2</sub>/CH<sub>4</sub>  $[P_{CO2}/P_{CH4} = 50.3]$  and PA 'N' having trityl-substituted triphenylamine (TPA) exhibited highest permselectivity towards  $O_2/N_2$  [P<sub>02</sub>/P<sub>N2</sub> = 8.47] gas pair in comparison to other polymers in this present investigation. An explanation for gas transport properties of PAs was explained from the standpoint of the solution-diffusion model. The PA 'N'-'Q' exhibited very promising results in terms of present upper bound limit drawn by Robeson in 2008. Finally, an attempt has been made to understand the structure-property correlationship between polymer molecular structure and their gas transport properties.

*Keywords:* Polyamide membranes, Bulky pendant groups, Gas permeability, Ideal permselectivity, Robeson's upper-bound.