CHAPTER 5 CONCLUSIONS

The principle goal of this research was the synthesis and characterization of high molecular weight, soluble polyimide gas separation membranes. A method was also developed for lightly crosslinking phenol/epoxy systems.

The monomers, diaminophenylindane (DAPI), triaminophenylindane (TAPI) and dihydroxyphenylindane (DHPI), were synthesized and characterized by a number of analytical techniques.

The ester-acid high temperature solution imidization route was utilized to form high molecular weight polyimides of DAPI in combination with a number of commercially available dianhydrides. The isomeric, asymmetric, bulky and rigid nature of DAPI imparted a number of desirable properties to these polymers, including high solubility in common organic solvents, very high glass transition temperatures and good thermal oxidative stability. In addition, the DAPI/6FDA polyimide displayed a low refractive index value due to the fluorine content furnished by 6FDA and the partial aliphatic character of DAPI. The estimated dielectric constant of this polyimide system, which was quite low, make this polymer attractive for use in the microelectronics field. Despite the aliphatic character of DAPI, the long-term stability of the DAPI/6FDA polyimide was comparable to that of a PMDA/ODA based Kapton under nitrogen at 400°C. Further studies on photoinduced crosslinking in copolyimides for microelectronics packaging are planned, following up on research initiated by Eric Moyer in our laboratory.

The rigid, bulky and isomeric structure of DAPI in the polyimide repeat unit imparted excellent film forming characteristics. Cast membranes were produced which displayed a range of O_2 permeability and O_2/N_2 selectivity characteristics. High O_2 permeabilities were observed for polyimides in which DAPI contributed a large portion of its character to the overall polymer repeat unit, i.e. in combination with low molar mass dianhydrides. The more flexible dianhydrides afforded a greater degree of molecular freedom resulting in a more tightly packed polymer conformation, which decreased the rate of gas penetration through thin films and increased the O_2/N_2 selectivity values. The

DAPI/BTDA system showed the best combination of O_2 permeability and O_2/N_2 selectivity values, which were not significantly effected by moderate changes in the isomeric ratio of DAPI.

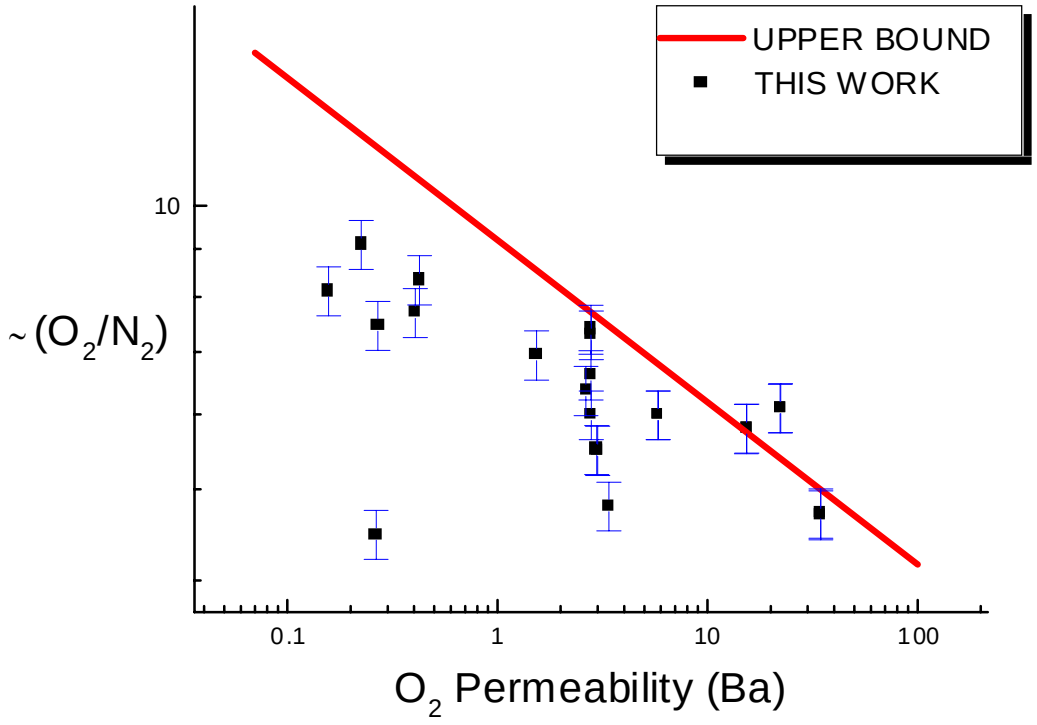
Polyimides derived from 6FDA gave high T_g, soluble systems with good thermal stability. Permselectivity values obtained from thin films of 6FDA based polyimides in combination with FDA and DDBT were excellent. These two polymers displayed a combination of O_2 permeability and O_2/N_2 selectivity values either on or above the so-called "upper bound".

Several novel polyimides containing hydroxyl moieties were synthesized and characterized by molecular weight and thermal techniques. Due to the inherent chemical structure of the monomers coupled with a high degree of hydrogen bonding and possible side-reactions involving crosslinking, many of these were insoluble. Incorporation of hydroxyl moieties in the repeat unit was shown to enhance chain stiffness via intermolecular hydrogen bonding.

High O_2/N_2 selectivity for all of the HAB containing polymers was discovered, but was also combined with quite low O_2 permeabilities, which suggests a tightly packed structure, possibly facilitated by hydrogen bonding. Direct comparison of a polymer repeat unit with and without a hydroxyl group did not reveal a significant change in permselectivity behavior.

The O_2 permeablity and O_2/N_2 selectivity values of the polyimides synthesized and characterized in this thesis are compiled in relation to the "upper bound" in Figure 5.1.

Several thermosetting systems were also designed and synthesized to lightly crosslink thin films at temperatures below the "dry" T_g of the polymer. Both the phenol terminated oligomers and the higher molecular weight phenol containing repeat unit, reacted within 2 hours at 150°C with a tetrafunctional epoxy. The crosslinking reaction occurred ~100°C below the T_g of the "dry" polymer and was thought to be facilitated by residual solvent (NMP) and epoxy content.



*error bars for $\alpha(O_2/N_2)$ values in blue (±6%); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale (±3%)

Figure 5.1 Research Summary: Permselectivity Behavior of Polyimides Synthesized and Characterized in this Research