### **1.1 Introduction**

The synthesis of aromatic polyimide was first reported in 1908 by M. T. Bogert and R. R. Renshaw [1]. However, the class of aromatic polyimide came into focus since 1950, after successful development of the two step polyimide synthesis by DuPont [2]. This class of polymers possesses a number of outstanding properties such as, excellent thermal, mechanical, and electrical properties which lead to their application in several robust fields like aerospace and electronic industries as well as for fibers, adhesives and in matrixes for composite material [3-5]. In addition to the above properties polyimides are endowed with high thermo-oxidative stability, chemical and solvent resistive properties leading to many membrane based applications such as gas separation, pervaporation etc.[6,7]. However, high softening temperature and poor solubility in different organic solvents of these polymers preclude the processing in both melt and solution condition. Several approaches have been taken to circumvent the poor processability of this class of polymer. One successful approach has been executed by General Electrical with an introduction of flexible ether linkage (-O-) [8,9] and isopropylidene  $[-C(CH_3)_2-]$  moiety [10,11] into the polymer backbone resulting the Ultem 1000<sup>®</sup> [12,13]. It exhibited excellent thermal stability and good mechanical properties. Other various approaches investigated to ease the polyimide processing include addition of bulky side groups or bulky units in the polymer backbone [14,15], or noncoplanar [16] or alicyclic monomers [17] in the main chain. In the 1970s, Korshak and coworkers first introduced to the incorporation of bulky cyclic side groups (termed as "cardo groups") in the polymer backbone to make polyimides soluble without compromising the higher glass transitions temperatures  $(T_g)$  and thermomechanical resistance [18]. All these approaches have been made to reduce several types of polymer interchain interactions, chain packing and the charge transfer electronic polarization interactions or charge transfer complex (CTC) formation. Incorporation of hexafluoroisopropylidene [-C(CF<sub>3</sub>)<sub>2</sub>-] or pendent trifluoromethyl (-CF<sub>3</sub>) groups is also of great interest which increases the free volume of the polyimides, thereby improving various properties like solubility, chemical resistivity, and gas permeabilities without forfeiture of thermal stability [19-22]. Moreover, these groups decrease crystallinity, color, water absorption as well as increase optical transparency, environmental stability, and flame resistance [23-25]. Optical transparency of polyimide membranes is an important property because of its demand in many optoelectronic devices

[26]. This chapter will focus on polyimide synthesis, difficulties encountered in processing aromatic polyimides, methods employed so far to overcome the difficulties, a brief review on gas separation membranes followed by objectives and scope of the current thesis. A plan of work is arranged accordingly for improvement of gas transport properties by synthesizing new fluorinated poly(ether imide)s.

### **1.2 Polyimide synthesis**

Polyimides are class of condensation polymers and generally prepared from organic diamines and organic tetracarboxylic acid dianhydrides. There are mainly two synthetic routes for polyimides preparation namely, i) one step and ii) two step polymerization method [3,5,27-29]. Scheme 1.1 shows a generalized synthesis of polyimide from an aromatic dianhydride and an aromatic diamine.



## Scheme 1.1: Synthesis of polyimide

### 1.2.1 One step polymerization

In the one-step polymerization method, completely cyclized polyimides are obtained directly from their corresponding stoichiometric mixture of tetracarboxylic acid dianhydride and diamine in presence of a high boiling tertiary amine (e.g., isoquinoline). Several high boiling solvent used for this direct conversion include m-cresol, p-chlorophenol,  $\alpha$ chloronaphthalene, nitrobenzene, o-dichlorobenzne and, dipolar aprotic amide solvents and their mixtures. During the progress of the polymerization, the byproduct, water, is continually removed by azeotropic distillation. This method of direct polymerization is usually used when working with soluble polyimides and is considered more practical for polymerizing less reactive dianhydrides and diamines. However, this method suffers from some enormous drawbacks, such as the use of very toxic carcinogen solvents and a rather low polymerization concentration (usually less than 10% w/v), which hampers direct processing of the polyimides into the final products (e.g., films and fibers) from their polymerization solutions, and a long reaction time (typically, more than 18 h).

#### 1.2.2 Two step polymerization

In the two-step polymerization method, initially the polyamic acid is formed from an equimolar mixture of dianhydride and diamine in a polar aprotic solvent, such as N,Ndimethylacetamide (DMAc) or N,N-dimethylformamide (DMF) [3,5]. The reaction pathway for the formation of poly(amic acid) involving the intermediates is presented in Scheme 1.2. The reaction mechanism involves the nucleophilic attack of the amino group to the electrophilic carbonyl carbon of the anhydride group. This results in opening of the anhydride ring to form an amic acid group. The formation of the poly(amic acid) is an equilibration reaction where the forward reaction is thought to start with the formation of a charge transfer complex between the dianhydride and the diamine [30]. The susceptibility of the nucleophilic attack increases with increasing the electrophilicity of the dianhydride group. Thus, the reactivity of the dianhydride monomer has been correlated to its electron affinity; higher values indicate greater reactivity of the dianhydride [31]. Strong electron withdrawing groups activate the anhydride toward nucleophilic attack on the anhydride carbonyl. On the other hand, the reactivity of the diamine is related to its basicity. The rate constants for imidization increase as the pKa of the protonated amine increases. Highly basic amines (e.g. aliphatic amines) may form salts during the initial stages of the reaction, upsetting the stoichiometry and preventing the attainment of high molecular weight. Solvent also play an important role in the reaction. Highly polar aprotic solvents used for this type of polymerization form strong hydrogen bonds with the carboxyl group which help to shift the equilibrium to the forward side i.e., to the amic acid side. The reaction rate is generally faster in more basic solvents. Several other minor important side reactions concurrently proceed with the main reaction. This side reaction may become significant under certain conditions particularly when the main reaction is slow because of low monomer concentration and low

monomer reactivity. Any water present in the reaction system causes lower molecular weight development of poly(amic acid) due to the hydrolysis of the dianhydride moiety [32]. During this step, the self-catalyzed cyclization to form polyimides cannot occur due to the strong interaction between the amic acid and the basic solvent or the larger acylation equilibrium constant [3,6].



Scheme 1.2: Reaction pathway in poly(amic acid) synthesis

In the second step, the polyamic acid is cyclodehydrated at elevated temperatures (thermal imidization) or in presence of a cyclizing agent (chemical imidization). The advantages of this method over the one-step polymerization are the use of less toxic solvents and direct processing of the soluble polyamic acids to form the final polyimide products in the form of films or fibers by thermal imidization. However, the stability of polyamic acid on storage and control of thermal imidization are still important issues [33]. A detail description of thermal imidization and chemical imidization is discussed below.

### **1.2.2.1** Thermal imidization of poly(amic acid)

The most common method for the conversion of the poly(amic acid) to the polyimide is the bulk (or melt) imidization [34-36]. Therefore, this thermal imidization method is generally used in industry where poly(amic acid) is heated at ~ 200-300 °C for a given

amount of time to form the imide ring by removing the solvent and the water. At high temperature, irreversible cyclodehydration reaction occurs which leads to a high molecular weight polyimide. In this method, the films of the poly(amic acid)s are often cast from polar aprotic solvents (e.g., N,N-dimethylformamide, N,N-dimethylacetamide etc.) and subsequently dried and imidized. This method is suitable for polyimides in the form of films, coatings and powders in order to allow the diffusion of byproducts and solvent without formation of voids in the final polyimide products. The problem of film cracking as a result of shrinking can be avoided by carefully controlling the curing profile. A typical heating schedule involves a stage below 150 °C, followed by a relative rapid temperature rise to a second stage above the glass transition temperature  $T_g$  of the resulting polyimides. The cast films are dried and heated gradually upto 250 – 350  $^{\circ}\text{C}$  depending on the stability and  $T_g$  of the polyimides. Maximum amount of solvent is slowly driven off in the first stage and the imidization occurs in the second stage, where curing and shrinkage is reliable [37]. The heating cycle allows a conversion of poly(amic acid)s into corresponding imides of about 92-99% and that can be achieved via thermal imidization routes. Further heating at above 300 °C, cannot lead to 100% conversion because of the so called "kinetic interruption" effect [38]. It is noted that hydrolytically unstable residual amic acid units resulting from kinetic interruption are considered as defect sites and therefore complete imidization is more difficult to achieve. At the initial stage of the imidization, a small amount of the poly(amic acid) undergoes a reversible reaction with the anhydride and amine instead of forming the imide ring resulting in a lower molecular weight development [39]. Two possible pathways for the imidization are possible during thermal imidization, as shown in Scheme 1.3 [40].



## Path two

Scheme 1.3: Two possible pathways in thermal imidization

# 1.2.2.2 Chemical imidization of poly(amic acid)

Poly(amic acid)s can also be chemically imidized. This is accomplished by using chemical dehydrating agents in combination with basic catalysts [41]. Various reagents have been employed including acetic anhydride, propionic anhydride, and n-butyric anhydride as

dehydrating agents and pyridine, triethylamine and isoquinoline as basic catalysts. A reaction pathway for chemical imidization is shown in Scheme 1.4.



Scheme 1.4: Reaction pathway in chemical imidization

# **1.3 Difficulties in processing aromatic polyimides**

In spite of an excellent set of thermal, mechanical and chemical resistance properties, aromatic polyimides suffer from severe drawbacks which often limit their wide applicability. Firstly, high melting or softening temperature and lower solubility of the polyimides in common organic solvents arising from their inherent molecular stiffness, high polarity and high intermolecular association forces. Secondly, deep yellow or brown coloration of the polyimides which restricts their applicability in electronic or optoelectronic industries [42,43,44]. This coloration is originating from the strong absorption in the ultra-violet and visible region due to their highly conjugated aromatic structures and formation of intermolecular charge transfer complexes (CTC). Consequently, several strategies have been undertaken to make novel processable aromatic polyimides like, chemical modifications,

mainly by preparing new monomers providing lower molecular order, higher torsional mobility and lower intermolecular bonding. Various approaches adapted for making processable polyimides include introduction of aliphatic or any other flexible segments to reduce chain stiffness, introduction of bulky side pendant substituents to hinder the close molecular packing and crystallization, use of larger monomers containing angular bonds or spiro linkages to disrupt the coplanarity of the polymer backbone, use of meta- substituted instead of para-substituted monomers, and/or asymmetric monomers to lower regularity and molecular ordering, preparation of co-polyimides from two or more different dianhydrides or diamines. However, factors leading to better solubility or lower  $T_g$  or  $T_m$  in a polymer often compromises with the final mechanical properties, thermal resistance or chemical resistance. Therefore, a proper optimization of polymer modification is necessary to achieve the best combination of properties.

# **1.4 Approaches taken to improve the processability**

# 1.4.1 Polyimides with aliphatic and other flexible spacers

Polyimides containing flexible spacers have gained a significant importance as technical materials. Table 1.1 exemplifies few monomers containing flexible spacer used for polyimides preparation. Some segmented, fluorinated polyimides [45] and co-polyimides containing oligoethylene glycol sequences have been presented as processable polyimides with potential application as thermally stable adhesives and thermoplastics [46,47]. Polyimides containing oligosiloxane segments are also included within this class of polyimides [48,49].

The thermal stability of these segmented polyimides is dependant on their chemical structure and mainly on the flexible chain. Polyimides containing polyethylene glycol sequences are thermally unstable [46], whereas polysiloxane [50,51], perfluoroalkanes [52], and even alkanes [53,54] provide a reasonable thermal stability. The combination of conventional and new monomers is providing an expansion of the scope to synthesize processable polyimides containing flexible spacers [55,56]. Perfluoroalkylenes are considered as well acceptable groups to be introduced as flexibilizing moieties as they provide a substantial lowering of the  $T_g$  without greatly impairing the thermal, mechanical and chemical properties. Novel soluble and meltable aromatic polyimides containing flexible

linkages have been developed to the growing demand of specific materials for advanced technologies. All of them are soluble in some specific organic media, showing glass transition temperatures in the range 250–380 °C.

Flexibilizing spacer	Monomer	Ref.
Alkane moiety in the diamine monomer	$H_2N \longrightarrow O - CH_2 - C - CH_2 - O - CH_2 - O - R - NH_2$	[57,58]
Oligoethylene glycol sequence in diamine monomer		[47]
Alkyl segment in the diamine monomer	$H_2N$ $O$ $O$ $(CH_2)$ $O$ $O$ $NH_2$	[53]
Perfluoroalkane sequence in dianhydride monomer	H <sub>2</sub> N (CF <sub>2</sub> ) NH <sub>2</sub>	[45]
Perfluoroalkane sequence in diamine monomer	O = O = O = O = O = O = O = O = O = O =	[45,52]
Polysiloxane sequence in dianhydride monomer	O $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$	[51]
Polysiloxane sequence in diamine monomer	$\begin{array}{ccc} CH_3 & CH_3 \\ \downarrow & \downarrow \\ H_2N - (CH_2)_{\overline{3}} & \stackrel{ }{Si} - O - \stackrel{ }{Si} - (CH_2)_{\overline{3}} & NH_2 \\ \downarrow & \downarrow \\ CH_3 & CH_3 \end{array}$	[55,56]

Table 1.1: Monomers for polyimides containing flexibilizing spacers

# 1.4.2 Polyimides containing bridging functional groups

Table 1.2 shows few examples of polyimides containing bridging functional groups in the main chain along with their glass transition temperature values. Aromatic polyimides containing ketone or ether linkages in their repeating units are generally more tractable in nature. Other examples of important bridging linkages are -O-, C=O, -S-, -SO<sub>2</sub>-, -C(CH<sub>3</sub>)<sub>2</sub>-, -CH<sub>2</sub>-, -CHOH-, and -C(CF<sub>3</sub>)<sub>2</sub> [59–64]. Generally, these 'kink' linkages between aromatic rings or between phthalic anhydride units disrupt the planarity and increase the torsional mobility. Furthermore, the inclusion of the additional bonds leads to an increment of the

repeating unit chain length, which, in turn, separates the imide rings leading to a relatively lower density of the imide moiety, which may be responsible for the polymer tractability. The suppression of the coplanar structure is maximal when voluminous groups are introduced in the main chain, for instance sulfonyl or hexafluoroisopropylidene groups, or when the monomers are enlarged by more than one flexible linkage. Hexafluoropropylidene, carbonyl and sulfonyl groups are the most advantageously incorporated concerning processability. This is due to the relatively large volume of these groups, and to the conformational characteristics imparted by them to the polymer chain. The poly(ether imide), marketed under the trade name Ultem<sup>®</sup> is amorphous, soluble polymer that shows T<sub>g</sub> value around 217 °C. They can be processed from the melt by conventional means, and offer a price-performance balance that enables them to compete successfully in the market of engineering thermoplastics.

Bridging group	Polymer	T <sub>g</sub> <sup>o</sup> C	Ref
—0—		370	[61,62]
—C(CH <sub>3</sub> ) <sub>2</sub> —	$\begin{bmatrix} 0 & 0 & 0 \\ N & 0 & 0 \end{bmatrix}_{n}$	297	[63]
—C(CF <sub>3</sub> ) <sub>2</sub> —	$\begin{bmatrix} 0 & & 0 & & 0 \\ \hline N & & 0 & & 0 \\ \hline 0 & & F_{3}C & CF_{3} & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & & 0 \\ \hline 0 & & 0 & 0 \\ $	311	[64]
—SO <sub>2</sub> —	$\begin{bmatrix} 0 & 0 & 0 \\ N & 0 & 0 \end{bmatrix}_{n}$	300	[59]

Table 1.2: Few polyimides prepared from monomers with bridging group

#### 1.4.3 Polyimides with trifluoromethyl groups

Polyimides bearing pendant trifluoromethyl ( $-CF_3$ ) groups are of great interest to the material chemists because the presence of a bulky trifluoromethyl group in the polyimide structure causes noteworthy improvements in their properties in comparison to their corresponding non-fluorinated polyimides. The combination of electronic and steric effects reduces the interchain interactions and, particularly, the steric congestion hinders the formation of charge transfer complexes, which is mainly responsible for the closer molecular packing and intractability of this class of polymers [64]. Furthermore, the C-F bond is a high energy bond, so that polyimides containing fluorine are in general polymers with high  $T_g$  and excellent thermal properties, comparable to those of the conventional aromatic polyimides. Fluorinated polymers show some improved properties, such as:

- increased solubility

– high optical transparency

- low dielectric constant- low moisture absorption
- low optical loss and low refractive index.



Figure 1.1: Diamines and dianhydrides with trifluoromethyl groups

Thus an excellent combination of all these properties has made the fluorinated polyimides very attractive for various applications in advanced technologies, such as in high performance structural resins, thermally stable coatings and films, polymeric membranes for gas separation, polymeric waveguides, and other electronic and optoelectronic applications [65-67]. A library of fluorinated monomers, especially diamine monomers have been reported in literature as suitable reactants for fluorinated polyimide preparation. Some examples have been listed in Figure 1.1.

A systematic demonstration of the effect on introduction of the pendant -CF<sub>3</sub> groups into the polymer backbone has been nicely demonstrated by Matsuura et al. [74]. They synthesized a series of new fluorinated rigid-rod polyimides by the reaction of 2,2'bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) [75], 2,2'-dimethyl-4,4'-diaminobiphenyl with 1,4-bis(trifluoromethyl)-2,3.5.6-(DMDB) and 4,4'-diamino-*p*-terphenyl (DPTP) benzenetetracarboxylic dianhydride (P6FDA), 1-(trifluoromethyl)-2,3,5,6benzenetetracarboxylic dianhydride (P3FDA) and pyromellitic dianhydride (PMDA), and studied the properties of those polyimides (Figure 1.2). They observed that on introduction of the trifluoromethyl side group into the dianhydride units the coefficient of thermal expansion (CTE) increases whereas the dielectric constant, water absorption, refractive index decreases. They also found that polyimides with trifluoromethyl side group in the diamine moiety possess higher decomposition temperatures in comparison to their homologous polymers substituted with methyl group. Moreover, polyimides with trifluoromethyl side groups exhibited lower intrinsic viscosities than those with methyl substituted polyimides.

Summarily, most of the experimental fluorine containing polyimides shows an advantageous balance of permeability and selectivity towards the separation of mixtures of gases and vapours, which makes them very attractive for the fabrication of permselective membranes [76]. The application of fluorinated polyimides in this application field appears a very rapid expansion, where a strong demand for new polymeric materials exists, and where soluble aromatic polyimides are considered as the most appropriate alternative.



Dianhydrides

Figure 1.2: Molecular structures of the diamines and dianhydrides [74]

# 1.4.4 Polyimides with bulky side substituents or cardo group

An attempt to attain soluble aromatic polyimides has also been taken by introducing bulky substituents, aryl or heterocyclic rings. Korshak et al. first introduced with the bulky side groups or cardo groups in 1970s [18]. Later, Rusanov et al. synthesized soluble aromatic polyimides using side phthalimide groups or by introducing pendent imide groups [77,78,79]. Figure 1.3 represents few examples of diamine and dianhydride monomers containing 'cardo' group. The phenyl group containing 'cardo' groups are the most promising among various other group. It does not introduce any relevant weakness regarding thermal stability, and provides a measure of molecular irregularity and separation of chains very beneficial in terms of free volume increase and lowering of the cohesive energy density [80–85]. Fluorene diamines and the so-called "cardo" monomers also mean valuable alternatives for the preparation of processable polyimides [18, 86]. On the other hand, the presence of the bulky side substituents in polyimides or in any other linear polymer causes a lowering of the

chain's torsional mobility and generally an increment of the glass transition temperature [87–88].





# 1.5 Membrane based gas separation

The phenomenon of gas permeation through polymer was first observed by Thomas Graham in 1829 when he found an inflation of a wet pig bladder with CO<sub>2</sub>. In 1866, Graham first postulated the "Solution diffusion process", where he hypothesized that in the permeation process at first the dissolution of the penetrant occurs, and then the dissolved species transmits through the membrane [94,95]. Currently, membrane based gas separation technology is considered as one of the most innovative and rapidly growing fields across

science and engineering. It is an important unit operation technique which can be executed as process intensification strategy to decrease the production costs as well as to reduce equipment size, energy utilization, and waste generation [96]. Membrane processes are classified according to the various types of driving forces by which they achieve the ultimate separation. The membrane materials used for the gas separation are glassy polymers and the basis of ability to separate the gas mixtures is the differences in the penetrant size [97]. A list of commonly known separation processes along with their primary driving force and type of mechanism is shown in Table 1.3. Nowadays, membrane based gas separation has been successfully contending over conventional separation techniques like cryogenic distillation and pressure swing adsorption (PSA) processes [98-100]. Eventually it finds a variety of more economical industrial applications, including hydrogen recovery from reactor purge gas, nitrogen, and oxygen enrichment, and stripping of carbon dioxide from natural gas, etc. [101,102].

101000				
Process	Pore size/ mol wt	Driving Force	Mechanism	
Microfiltration 0.02-10µm		ΔΡ	Sieving	
Illtrafiltration	0.001-0.02µm	٨D	Siguing	
Oluanitation	mol wt 103-106		Sieving	
Nonofiltuation	<2 nm	AD	Solution Diffusion	
Nationitiation	mol wt 102-103	Δ٢		
Reverse	non porolle	$\Delta C$ (chemical	Solution Diffusion	
Osmosis	non porous	potential)	Solution Diffusion	
Electrodialysis	mol wt <200	Electrical potential	Ion Migration	
Dialysis	10-30 Å	Concentration	Sieving plus	
		difference	Diffusion	
Pervaporation	Not mentioned	Partial pressure	Solution Diffusion	
	Not mentioned	difference	Solution Diffusion	
Gas Separation	non porous	$\Delta P$	Solution Diffusion	

 Table 1.3: Various membrane separation processes and their corresponding driving forces

# **1.5.1 Types of membranes**

Various types of membranes used in the gas separation process can be categorized according to their geometry, bulk structure, production method, separation regime, and application [97]. Generally, flat-sheet membranes are used in laboratory experiments because

of their ease of preparation whereas hollow-fiber membranes are commonly used in industries due to their high surface area and compactness. In view of the structure or the distribution of types of pores, membranes can be classified into two groups; asymmetric and symmetric. Symmetric membranes are the membranes where the pore distribution is regular or the diameters of the pores do not vary significantly throughout the sheet. On the other hand, in the asymmetric membranes pore sizes are increased in a regular fashion from one side of the sheet to the other. Membrane composites are good example of asymmetric membranes. They are made by a deposition of a thin polymer film onto a porous base material. The thin films dictate the separation properties while the permeation flux is governed by the porosity of the base material. Membranes are also classified as per their production methods like solution casting, interfacial polymerization, plasma polymerization and nucleation track membrane. Solution casting membranes are fabricated by dissolving the polymer in a solvent and drying the polymer solution into a film, interfacial polymerization method involves contacting two monomers in two immiscible liquids, plasma polymerization condenses gaseous monomers on a substrate layer through a stimulated plasma and nucleation track membranes are the result after compressing the powder into a porous film and then sintering, stretching an extruded polymer into a sheet, irradiating a thin film with nuclear particles and then etching in a bath.

Most of the gas separation membranes discussed so far are made from amorphous (noncrystalline) polymers which may be either in the glassy or in the rubbery state. Rubbery polymers (e.g., polyurethanes) possess high permeability and are being applied in  $O_2/N_2$ separation. Silicon polymers, particularly polydimethylsiloxanes (PDMS), are widely studied due to their large free volume, high permeability, and low selectivity. In both academia and industry, the amorphous or the glassy polymeric membranes from various classes of polymers (like polysulfones, polycarbonates, poly(arylene ether)s, poly(aryl ketone)s, polyimides etc.) have been studied [103-106]. However, polyimides are the most investigated toward gas separation application due to their high gas selectivity and good mechanical properties [107-111]. (1994) presented Stern а thorough review on the structure/permeability/selectivity relationship on selected rubbery and glassy polymers [7].

As mentioned earlier, among the various classes of polymers studied it has been observed that polyimides are the most investigated candidate as the basic materials for gas separation application. High gas selectivity for different gas pairs (e.g.,  $CO_2/CH_4$ ,  $H_2/CH_4$ ,  $H_2/CO$ ,  $O_2/N_2$  etc.) along with excellent thermal stability, chemical resistance, film forming ability, mechanical strength and versatile chemistry made polyimides promising materials for gas separation applications [107,112]. Moreover, fluorinated polymers have already been proved as the most attractive materials in terms of higher permeability as well as selectivity [19-22,33]. Introduction of cardo groups into the main chain is another approach to improve the gas separation performances of the polymers. An extensive research has been done on inclusion of various cardo groups like indane [113,114], heterocyclic moieties [115], phenolphthalein or phthalimidine moiety [116-122], cyclo-aliphatic moiety [123,124] etc.

### **1.5.2 Fundamental of gas permeation**

Generally, three transport mechanisms are commonly described in the literature for the membrane based gas permeation [125,126]. These three mechanisms are-

- i) Knudsen diffusion,
- ii) Molecular sieving, and
- iii) Solution-diffusion,
- and these are illustrated in Figure 1.4.

Knudsen diffusion and separation is based on a large difference between the mean free paths of the molecules and the membrane pore radius. The separation factor from Knudsen diffusion is the inverse square root ratio of two molecular weights, assuming the gas mixture consisting of only the two types of molecules. The process is limited to the systems with large values for the molecular weight ratio, such as is found in H<sub>2</sub> separation. Knudsen diffusion membranes are not commercially attractive due to their low selectivities.



Figure 1.4: Gas transport mechanisms for membrane based gas permeation [125]

The molecular sieving mechanism explains the ideal condition for the separation of vapour compounds of different molecular sizes through a porous membrane. In this mechanism the diffusion occur under sufficient driving force and smaller molecules passes through with higher diffusion rates. Therefore, a large difference between the upstream partial pressure of the "faster" gas and the downstream partial pressure has to be maintained. The main limitation in this mechanism is arising from the fact that condensable gases cause fouling, and alter the structure of the membrane. Therefore, this process is only feasible in case of commercial robust systems, where the membranes used for gas separation are based on ultramicroporous carbon or hollow fibre glass.

Solution-diffusion separation mechanism is based on both solubility and mobility factors and it is the most commonly used model describing gas transport in non-porous membranes. This mechanism is applicable for our gas transport study investigated in this present thesis. A meticulous review on polymeric membranes for solution-diffusion based permeation separations has been made by Koros et al. [127]. The review covers membrane based separation not only for gas separations, but also for pervaporation, reverse osmosis, and liquid separation. The solution-diffusion model is described in details in the next section.

## 1.5.3 Solution-diffusion model for gas permeation through polymeric membrane

This model of gas permeation can be viewed as a three step process:

1. adsorption and dissolution of the gas molecules at the polymer membrane interface,

2. diffusion of the gas molecules inside and through the bulk polymer, and

3. desorption of gas molecules into the external phase.

Permeation is related to the overall mass transport process, whereas the diffusion is related to only the movement of gas molecules inside the polymer membrane. This model of mass transport assumes that the pressure within the membrane is uniform and the chemical potential gradient across the membrane is expressed only as a concentration gradient. According to Koros and Fleming [126], solution-diffusion is achieved via random jumps of the penetrant gas species inside the polymer matrix driven by a concentration difference between membrane upstream and downstream. It can be further considered that the jumps of the gas molecules occur through one intersegmental channel to other or more specifically, from one void space to another by transient gap opening and the transient gap opening is driven by the chemical potential gradient and can be related to the accessible free volume with respect to different gas molecules according to free volume theory [100,128,129]. Thus, the diffusion rate is directly controlled by the size of the voids and width of the channels, created by the thermally activated motion of certain intersegments [118,129]. Therefore, a variation of the chemical nature of the polymer allows control of the relative extent of solution and diffusion of different gases through the polymer matrix.

Figure 1.5 represents a schematic diagram describing the transport of gas molecules across a membrane.  $P_1$  and  $P_2$  are the gas pressure in the upstream side and the downstream side, respectively.  $N_J$  is the normalized flux calculated by dividing the gas flow rate with the membrane surface area. In the upstream side, the gas molecules first come in contact with the membrane interface. Under the driving force (e.g., chemical potential, concentration gradient, etc.), the permeate gas forms a concentration profile across the membrane with respect to membrane thickness, 'l'. Selective permeation of gas molecules occurs only when one of the components interacts more strongly with the membrane material or, in other words, diffuses faster through the membrane. The diffusion step is the slowest step among the three steps in the solution-diffusion mechanism. Hence, it is the rate



Figure 1.5: Transport of gas molecules across a membrane

determining step in permeation process. In general, the relationship between the linear flux, J and the driving force is:

where 'K' is some phenomenological coefficient, 'X' is the potential, and 'x' is the space coordinate measured normal to the section. In case of gas diffusion in the membrane, Equation 1.1 can be written as:

where 'D' is the diffusion coefficient, and 'X' in Equation 1.1 now defines concentration and is denoted as 'C'. Equation 1.2 is commonly known as Fick's first law.

If the solubility of the penetrant gas in a polymer is sufficiently low then the concentration of the penetrant is proportional to the vapour pressure of penetrant in the polymer. This relationship is expressed as Henry's law, Equation 1.3. 'S' is the solubility coefficient and 'p' is the vapour pressure of the penetrant.

At steady state, the permeation of a pure gas 'A' through a membrane of thickness 'l' is characterized by a permeability coefficient ' $P_A$ '. ' $P_A$ ' is generally defined as:

where, ' $N_J$ ' is the normalized flux, ' $P_1$ ' and ' $P_2$ ' are the upstream and downstream pressures, respectively, and ' $\Delta P$ ' is  $P_1$ - $P_2$ . For binary gas mixture,  $P_1$  and  $P_2$  refer to the partial pressures of penetrant 'A' at the upstream side and downstream side of the membrane, respectively. The permeability coefficient of dense film materials is commonly expressed in units of Barrer.

$$1Barrer = 1 \times 10^{-10} \frac{\text{cm}^3 (\text{STP}) \text{cm}}{\text{cm}^2 \text{ s cm Hg}}$$

If Henry's law applies, then at a given temperature 'S' and 'D' is constant. The permeability coefficient, 'P', can also be defined as:

The diffusion coefficient, 'D', is a kinetic term governed by the amount of energy necessary for a particular penetrant to execute a diffusive jump through the polymer and the intrinsic degree of segmental packing in the polymer matrix. The solubility coefficient, 'S', is a thermodynamic term, it depends on the factors such as condensability of the penetrant, interactions between the polymer and penetrant, and the amount of penetrant-scale non-equilibrium excess volume in glassy polymers.

For a binary gas mixture permeating through a polymer membrane, the ideal permselectivity of the polymer membrane toward a gas 'A' relative to another gas 'B' is commonly expressed in terms of the ideal selectivity or ideal permselectivity,  $\alpha_{P(A/B)}$ . When the downstream pressure is negligible relative to the upstream pressure,  $\alpha_{P(A/B)}$  can be written as the ratio of permeabilities:

Expanding the permeability into diffusivity and solubility terms, the ideal selectivity can be expressed by Equation 1.7.

where,  $D_A/D_B$  is the ratio of the concentration-averaged diffusion coefficients of penetrants '*A*' and '*B*', and is referred as the membrane's "diffusivity selectivity".  $S_A/S_B$  is the ratio of solubility coefficients of penetrants '*A*' and '*B*', and is called the "solubility selectivity" [130]. In typical gas separation applications, the downstream pressure is not negligible; however,  $\alpha_{P(A/B)}$  generally provides a convenient measure for assessing the relative ability of various polymers to separate gas mixtures. High permeability and high selectivity are the main criteria in evaluating a membrane.

### 1.6 Parameters affecting gas permeation in membrane

#### **1.6.1 Temperature**

Permeation (P), diffusion (D) and the solubility coefficient (S) of different gases in a polymer is temperature dependent, and this dependency of D, S, and P with the temperature can be expressed by the Arrhenius relationships:

$$P = P_0 \exp\left(-\frac{E_P}{RT}\right) \dots \qquad \dots \qquad \dots \qquad 1.8$$

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \dots \qquad \dots \qquad \dots \qquad 1.9$$

$$S = S_0 \exp\left(-\frac{\Delta H_s}{RT}\right) \dots \qquad \dots \qquad \dots \qquad \dots \qquad 1.10$$

where  $E_P$  and  $E_D$  are the activation energy of the permeation and diffusion processes, repectivlely.  $\Delta H_s$  is the heat of sorption,  $E_P$  can now be expressed simply as:

A comprehensive data for  $E_P$ ,  $E_D$ , and  $\Delta H_S$  values for many polymers and gas pairs are described in the Polymer Handbook by S. Pauly. [128].

Typically, with an increase in temperature the gas diffusion coefficients increase appreciably when the polymer does not undergo thermally induced morphological rearrangements such as crystallization over the temperature range of interest [130]. Since both diffusivity and solubility coefficients are temperature dependent, the selectivity described by Equation 1.6 is also sensitive to changes in temperature.

The increased segmental motion at higher temperatures undermines the ability of polymer to discriminate between penetrants of different physical dimensions, thereby resulting in a diffusivity selectivity loss. The temperature changes also affect the solubility selectivity, which is governed primarily by the chemical nature of the penetrant and polymer-penetrant interactions. For most gases, as temperature increases, the solubilities increase. The solubility selectivity, therefore, will vary depending on the extent of the temperature effect on each component in the gas mixture [104].

## 1.6.2 Pressure

Change in the pressure of penetrant gases contacting with the polymer membrane may cause large permeability variations. Four typical patterns of response are observed in permeability versus pressure relationships [131], as seen in Figure 1.6.

I. Linear, with slope close to 0. This is an ideal case which satisfies the assumption that diffusion and solution are independent of gas pressure. This transport behavior is found in case of low sorbing  $H_2$ , He or  $N_2$  permeation through polyethylene membrane.

II. Nearly linear, increase of permeability with increasing pressure. This type often describes the permeability of an organic vapor into a rubbery polymer. The plot is for propane permeation through polyethylene membrane.

III. A decreasing trend of permeability with increasing pressure. This is typically observed with highly soluble gases such as  $CO_2$  in glassy polymers. The particular plot is for permeation of  $CO_2$  through polycarbonate membrane.

IV. Concave upwards. This can be perceived as a combination of (II) and (III), and is typical of a plasticizing penetrant such as organic vapor in a glassy polymer. The plot is from the acetone permeation through cellulose acetate membrane.



Figure 1.6: Effect of penetrant pressure on various polymer membranes [131]

# **1.6.3 Plasticization**

The pressure at which the permeance starts to increase (the minimum in the permeance versus pressure plot (IV) in Figure 1.6) is called the plasticization pressure. At such gas pressure, the gas concentration in the polymer material disrupts the chain packing. The polymer matrix gets swollen and the frequency of the segmental mobility of the polymer chain increases resulting in an increase in gas diffusivity and permeability [126]. Therefore, at the time of plasticization the diffusion coefficient of the penetrant or the gas molecules may become a function of time and of history. This non-ideal behavior after polymer plasticization can be explained by free volume theory.

Free volume theory of diffusion suggests that molecules can only diffuse through the free volume present in a molecule matrix [132]. Theoretically, diffusion in a rubbery polymer

is a result of redistribution of free volume within a matrix and migration of the penetrant among these volumes. Studies have been done to suppress the plasticization effect on gas permeability and permselectivity by means of crosslinking, blending, or annealing of the polymer membranes [133-135].

### **1.6.4 Other parameters**

Beside the affect of different operating conditions (e.g., temperature and pressure), several other factors related to gas permeation are like composition of the gas mixture, penetrant condensability, polymer-penetrant interactions, and polymer crystallinity. All these factors affect the gas solubility which in turn, affects the permeability. Furthermore, gas diffusivity is sensitive to properties such as penetrant size, polymer morphology, and polymer segmental dynamics.

In case of a binary or multi-component gas mixtures, the case of  $P = \sum P_i$ , may be referred to as an ideal mixed gas transport system. It is assumed that each single component behaves ideally, but the assumption will not hold when one of the permeants has a much higher permeation flux than the other permeants. The non-ideality of this type of multi-component system must be accounted for to avoid invalid assumptions for permeability and permselectivity calculations. Models and descriptions of multi-component systems can be found in Kamaruddin and Koros [136].

Generally it is accepted that the gas solubility in polymers increases with increasing the gas condensability. Condensability can be measured from the gas critical temperature  $T_c$ , or the normal boiling point  $T_b$ . Diffusion coefficients of penetrants are found to decrease with increasing penetrant size. Diffusion coefficients in polymers are also sensitive to penetrant shape. Linear or oblong penetrant molecules like CO<sub>2</sub> exhibit higher diffusivities than those of spherical molecular shape of equivalent molecular volume such as CH<sub>4</sub>. Specific interactions between gas and polymer molecules (i.e., polarity) also affect gas solubility. Gases such as CO<sub>2</sub>, which has a quadrupole moment, are generally more soluble in polar polymers.

Crystallinity of the polymers is another parameter which tends to reduce both penetrant solubility and diffusivity, thereby reducing permeability, which is generally undesirable. Polymer crosslinking reduces polymer segmental mobility; therefore, diffusion

coefficients of the penetrant gas typically decrease with an increasing degree of crosslinking in the polymer. In lower molecular weight polymers, chains are more mobile and penetrant diffusivity decreases with increasing molecular weight. At higher molecular weights, when the concentration of chain ends is low, diffusivity is relatively independent of molecular weight as is solubility [130].

## **1.7 Applications**

Membrane based gas separation began in a commercial scale only in late 1970's after the synthesis of asymmetric cellulose acetate membranes by Sourirajan. Membrane based gas separation is now successfully competing over highly sophisticated techniques like cryogenics, adsorption and absorption. Three main industries have shown great interest in its commercial application [7,126,130,131]. These applications, referred to earlier in the introduction, are divided into three main categories as mentioned below:

- 1.  $O_2$  or  $N_2$  enrichment of air.
- 2. Acid gas and water vapor separation from natural gas, and
- 3. H<sub>2</sub> separation from variety of gases, such as CO, CH<sub>4</sub>, N<sub>2</sub>.

## 1.7.1 O<sub>2</sub>-N<sub>2</sub> Separation

Nitrogen gas accumulation towards its usage for making an inert atmosphere for foods and fuels is an important industrial application. The first such system based on membrane was developed in 1987 by Monsanto using the Prism Alpha<sup>®</sup> membranes. At present, 95% nitrogen recovery with the target set at 99.99% recovery is possible. Enriched oxygen for home medical applications (respirators) and for improving gas combustion is another potential application. The use of oxygen enriched air in biotechnology is also being explored as an important application of membrane based gas separation. The summary of membrane based gas separation applications can not be completed, as new processes are being developed every day, and many more applications are being explored for gas separations by polymer membranes. With various possibilities present in selecting the type of modules and the number of modules, the custom design of specific gas separation systems has emerged as a whole new research field.

### 1.7.2 CO<sub>2</sub> and H<sub>2</sub>O removal

Membrane based gas separation technology has been successfully applied in oil recovery from production wells. With high  $CO_2$  removal from other light gases (usually methane), the increase in mole fraction of condensable components leads to an increase in the dew point of the mixture. This condition is usually avoided by either heating the gas stream or monitoring  $CO_2$  removal rate. A study by Shell Oil Company on commercial cellulose acetate membranes has shown its importance in comparison to physical and chemical solvent scrubbing and cryogenic treatment. However, details about the economic comparison are not available.

#### 1.7.3 H<sub>2</sub> Separation

The application of membrane process to  $H_2$  separation is feasible due to the high permeation rate of hydrogen with respect to other supercritical gases like nitrogen (in ammonia purge stream), carbon monoxide (CO/H<sub>2</sub> ratio adjustments), and methane (in refineries and petrochemical process). For illustration, a case of initial composition adjustment of synthesis gas for the manufacture of methanol is considered. The output from the synthesis rector containing H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, N<sub>2</sub> and water vapor is preheated to vaporize the water before allowing it flow through a series of membrane separator. These Prism® membrane separated the H<sub>2</sub> and CO<sub>2</sub> from the rest of the gases and these gases are then returned to the feed stream. This then lead to an increase of 2.4% in production in a low pressure methanol plant owned by Monsanto at Texas City. Similar advantages were observed in recovery of hydrogen from ammonia purge gas, as hydrogen was enriched from 61% to 86%.

## 1.8 Scope and objectives of the present investigation

From the foregoing review it is now well established that incorporation of bulky trifluoromethyl (- $CF_3$ ) group as pendant group and inclusion of cardo moiety into the polymer backbone reduce the inter chain packing density and thereby enhance the fractional free volume of the polymer which in turn increase the solubility, processability and gas permeability without compromising their thermal and mechanical properties.

Moreover, introduction of flexible ether linkage in the polyimide backbone also enhances the polymer solubility by disrupting the co-planarity of the polymer chain. Fractional free volume of the polymers can also be manipulated by changing the polarity and the bulkiness of the monomeric building units.

Hence, in this present study it was decided to synthesize new organosoluble and processable poly(ether imide)s incorporating both trifluoromethyl groups and cardo moieties in the polymer backbone. It was also planned to fine tune the gas separation properties of the polymers by varying the cardo groups during the preparation of different monomeric building blocks. Accordingly, the following objectives were set for the present work.

### Research objective #1

Preparation of four fluorinated PEIs of different polarity and intersegments length and their gas transport study as an initial investigation.

# Research objective #2

Synthesis of new series of processable poly(ether imide)s (PEIs) from newly prepared fluorinated diamines based on different cardo groups like phthalimidine, benzoisoindoledione and spiro-biindane using different aromatic dianhydrides.

# Research objective #3

Characterization of the PEIs by GPC, spectroscopic (FTIR, NMR) and thermal techniques (DSC, TGA). Evaluation of the mechanical properties.

### Research objective #4

Investigation of gas transport properties of the PEIs towards four different gases (e.g.,  $CO_2$ ,  $O_2$ ,  $N_2$  and  $CH_4$ ) at three different temperatures.

# Research objective # 5

Establishment of structure property correlationship with respect to polymer glass transition temperatures (T<sub>g</sub>), molecular structures and their FFVs'.

# 1.9 Plan of work

To achieve the aforesaid objectives the following work plans were set:

• The first objective was achieved by preparing four fluorinated PEIs on reaction with 4,4'- (hexafluoro-isopropylidene)diphthalic anhydride (6-FDA) with four different diamine

monomers of different polarity and chain length e.g. 4,4-bis[3'-trifluromethyl-4'(4"aminobenzoxy)bezyl]biphenyl (BAQP), 1,4-bis[3'-trifluromethyl-4'(4"-aminobenzoxy) benzyl]benzene (BATP), 2,6-bis[3'-trifluromethyl-4'(4"-aminobenzoxy)benzyl]pyridine (BAPy) and 2,5-bis[3'-trifluromethyl-4'(4"-aminobenzoxy)bezyl] thiophene (BATh) by following previously reported literature.

- Gas transport property measurement of the PEIs towards four different gases (e.g., CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>) at three different temperatures (at 35, 45 and 55 °C) was investigated. The effect of the glass transition temperature (T<sub>g</sub>), molecular structure and fractional free volume (FFV) towards the gas permeability as well as the ideal permselectivity of the PEI membranes were attempted to establish. The activation energies of all the PEI membranes for the permeation of different gas molecules were calculated from the slopes of the respective Arrhenius plots.
- In order to optimize the thermal, mechanical and other allied properties of the PEIs as well as to fine tune their gas separation performances, three new diamines were synthesized namely, 3-*bis*-[4-{2'-trifluoromethyl 4'-(4"-aminophenyl) phenoxy} phenyl]-2-phenyl-2,3-dihydro-isoindole-1-one (BAPA), 4,9-bis-[4-(4'-amino-3-trifluoromethyl-biphenyl-4-yloxy)-phenyl]-2-phenyl-benzo[f]-isoindole-1,3-dione (BIDA) and 6,6'-bis-[2"-trifluoromethyl 4"-(4"'-aminophenyl)phenoxy]-3,3,3',3'-tetramethyl-1,1'-spirobiindane (SBPDA), and accordingly three new series of PEIs were synthesized and characterized.
- The polymers were well characterized. Structural elucidation of the polymer backbones was done by elemental analyses, FTIR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopic techniques. GPC was used to determine the number average and weight average molecular weight of the polymers. Thermal properties of the polymers were investigated by TGA and DSC; mechanical properties of the polymers were measured using a universal testing machine.
- To achieve the final objective, gas transport study was performed using these newly synthesized PEIs based on BAPA, BIDA and SBPDA. The effect of the T<sub>g</sub>, molecular structure and FFV towards the permeation of different gases as well as the ideal permselectivity of the PEI membranes were investigated. The activation energies for the permeation of different gas molecules through all these PEIs were calculated from the slopes of their respective Arrhenius plots. An attempt has been taken to draw a structure-

property correlation of the chemical structures of the newly prepared polymers with their gas separation performances.

The plan of work and the structure of the thesis is depicted in Figure 1.7.



Figure 1.7: Structure of the thesis

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