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Separation of Carbon Dioxide from Natural Gas Mixtures through Polymeric Membranes—A Review

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Abstract: Various technologies are now available to design engineers to condition raw natural gas to pipeline quality. Conditioning of natural gas involves the removal of acid gases like CO₂ and H₂S, besides water vapor. Among different separation methods available, membrane technology has emerged to be a viable and valuable option over conventional techniques like amine absorption, in view of its advantages such as economy, process safety and environmentally benign nature. Semi-permeable membranes were first employed in natural gas processing for more than 20 years. However, the technological breakthrough in the application of polymeric membranes to natural gas separation accelerated with the development of asymmetric membranes, which retain their selective characteristics, but after increased permeation rates as compared to their dense counterparts. Efforts to correlate the basic polymer structure with permeability and selectivity have resulted in the synthesis of novel

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polymers. Membranes for natural gas separation are most generally configured in the form of hollow fibers, capillaries or spirally wound elements, considering their intrinsic separation characteristics, process conditions and design parameters. This review addresses the current *scientific* and *technological* breakthrough that governs the field of application of membranes for natural gas separation. The performance of such membranes and the current research activity on CO₂/CH₄ separation are the main focus of this review. Potential membrane materials for further research in this area are also discussed

Keywords: Natural gas, CO₂/CH₄ separation, polymer selection, membrane formation

INTRODUCTION

Gas separation through membranes has emerged as an important unit operation offering specific advantages over conventional separation methods such as cryogenic distillation and adsorption (1, 2). Over the years, membrane-based technology has contributed tremendously to the growth of new research frontiers such as carbon dioxide capture (3), which serves as an efficient tool for natural gas purification. Even though there are a large number of other potential applications for gas separation using polymeric membranes, only few of them have been adopted in practice. The potential application of any polymer membrane for separation depends upon the possible throughput and purity of the product obtained. This means that both permeability coefficient and selectivity of the more rapidly transporting gas molecule should be as large as possible. Progress in gas separation studies using membranes was greatly accelerated and this technique has emerged as a commercially viable method in the 1980s due to the development and refinement of novel synthetic polymers. Since then, progress has been made continuously in improving membrane formation processes, chemical and physical structures and different modular configurations for specific end applications (3–10).

In order to ensure the performance of a membrane, the *scientific* factors must be considered (11). These include: (i) processing of new materials, with both inherent transport properties and adequate mechanical strength under adverse thermal and feed mixture conditions by applying the tools of synthetic chemistry to control the structure-property relationships, (ii) using thermodynamics, mass transfer kinetics and surface science to control the complex morphologies needed for an efficient use of advanced materials in asymmetric and composite membranes, and (iii) to gain an insight into the behavior of membranes with respect to various feed mixtures under practically realistic operating conditions using analytical techniques. Therefore, the control of gas permeability and permselectivity of polymeric membranes has attracted the attention of a large number of scientific groups all over the world, from industrial sectors as well as academic laboratories.

However, to achieve such control and enable the development of novel membranes, a good understanding of the relationship between the properties of polymers and their gas transport behavior is essential. Technological advancements have clearly demonstrated that simple structural modifications, which lead to increased polymer permeability, usually cause a loss in permselectivity and vice versa (12–15). This so-called trade-off relationship has been described in the earlier literature (16, 17). It is thus possible to use polymers that exhibit high selectivity and low permeability and vice versa, in addition to those that combine low selectivity with low permeability. However, the literature indicates that there appears to be not many polymers that show the desired trend in terms of large values of permeability and selectivity.

Expanding the performance envelope, generally defined by the trade-off relationship has been the major goal of current researchers. For instance, dehydration can be accomplished via glycol or molecular sieves, depending upon the product gas specification. Carbon dioxide (CO₂) and/or hydrogen sulfide (H₂S) removal can be accomplished via amines, hot potassium carbonate or membranes. The choice of technology or combination of technologies is dependent upon the needs of the gas processor. Historically, CO₂ has been removed through the use of amine-based solvents (18). Such systems, even though widely used, can pose operational difficulties due to the challenges involved in keeping the solvent clean and operating within the process constraints of the system. Membrane systems have been widely used for CO₂ removal and within certain process conditions, these can be an attractive alternative. One challenge for membrane systems is to economically reach the minimum allowable CO₂ levels specified for pipelines, which is <2 mol% in the United States (19). For this reason, membrane systems are sometimes integrated with further processing.

In recent years, scientific efforts and successes in synthesizing a variety of nanostructured materials have provided a new horizon for the development of advanced materials with enhanced or novel properties. Nanocomposites represent the current trend in developing novel nanostructured materials. They can be defined as a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime (20). In the membrane science literature, many reviews pertaining to gas separation problems have been covered to address the areas pertaining to CO₂ absorption, solubility of gases in membranes, fabrication of carbon membranes, etc. (21–25), but extensive review on the separation of CO₂/CH₄ gas mixtures is rare. Thus, the goal of this review is to provide a concise update in the area of CO₂ removal from natural gas in addition to presenting an overview of the membranes being used in such applications. A considerable amount of background information pertinent to the currently applicable membranes is also covered. An attempt to describe the current strategies in the development of various types of membranes and their suitability for natural gas sweetening is discussed. In addition to new materials being developed, new membrane preparation techniques to produce ultra-thin defect

free membranes are reviewed. Results from various sources are compiled, compared and discussed critically to evaluate their usefulness for easy reference to future researchers working in this fascinating area.

NATURAL GAS SEPARATION—AN OVERVIEW

Theory

It is a well-known fact that permeation of a gas through a dense homogeneous membrane occurs via solution-diffusion mechanism. The permeability coefficient of a gas is a function of its solubility in the membrane and its diffusion through the membrane. Transport across the membrane, therefore involves: (i) diffusion through the boundary layer at the membrane – feed gas interface, (ii) sorption into the upstream face of the membrane, (iii) diffusion through the thickness, (iv) desorption from the downstream face of the membrane and (v) diffusion from the boundary layer facing the permeate side. Each of these steps constitutes a resistance to mass transport. The gas at high pressure (P_H) in contact with the membrane is sorbed by the polymer (26). The amount dissolved is directly proportional to the pressure and the proportionality constant is termed the sorption coefficient (S). The sorbed gas then diffuses through the film by virtue of its chemical potential gradient (i.e., concentration difference) across the membrane and gets desorbed at the downstream side, which is maintained at a lower pressure (P_L). Under steady-state conditions, the transport rate (flux) is obtained by the equation,

$$F = \frac{DS(P_H - P_L)}{h} \quad (1)$$

where h is the effective membrane thickness and D , the diffusion coefficient. The product, DS is called the permeability coefficient (P), which is usually expressed in terms of Barrers ($=10^{-10}$ cc (STP) cm / cm² · s · cmHg). On the other hand, if the feed is a mixture of gases, the sorption of each gas molecule is proportional to its partial pressure, which depends upon the partial pressures of other components also. In such a case, sorption becomes competitive and diffusion process would be a complex coupled phenomenon (27).

The separation of a binary feed mixture, for example, can be described by an overall selectivity coefficient, $\alpha_{1,2}$ given by,

$$\alpha_{12} = \frac{S_1 D_1}{S_2 D_2} = \frac{P_1}{P_2} \quad (2)$$

where the subscripts 1 and 2 represent the faster and slower permeating gases, respectively, and P_1 and P_2 are their permeability coefficients. For a multi-component mixture, a similar expression can be derived between any two components (i and j), but often, for the sake of convenience, selectivities are expressed with respect to the least or slowest permeating component.

Factors Affecting Membrane Performance

A typical laboratory experimental setup frequently used in gas separation is shown in Figure 1. There are several factors affecting the membrane performance, which are to be addressed by the researcher before attempting to work on gas separation problems. These are discussed here:

Feed Composition and Concentration

A change in feed composition will directly affect the sorption phenomena (degree of swelling) at the gas-membrane interface as envisaged by the sorption-diffusion principle. Since the diffusion of gaseous components in the membrane is dependent upon the concentration of the components (or solubility of the components), the permeation characteristics are greatly influenced by the feed composition (28).

Feed and Permeate Pressure

The driving force in gas separation is the partial pressure gradient across the membrane (29). The flow of a component, say i , across the membrane can thus occur only if the partial pressure (product of mole fraction and total pressure)

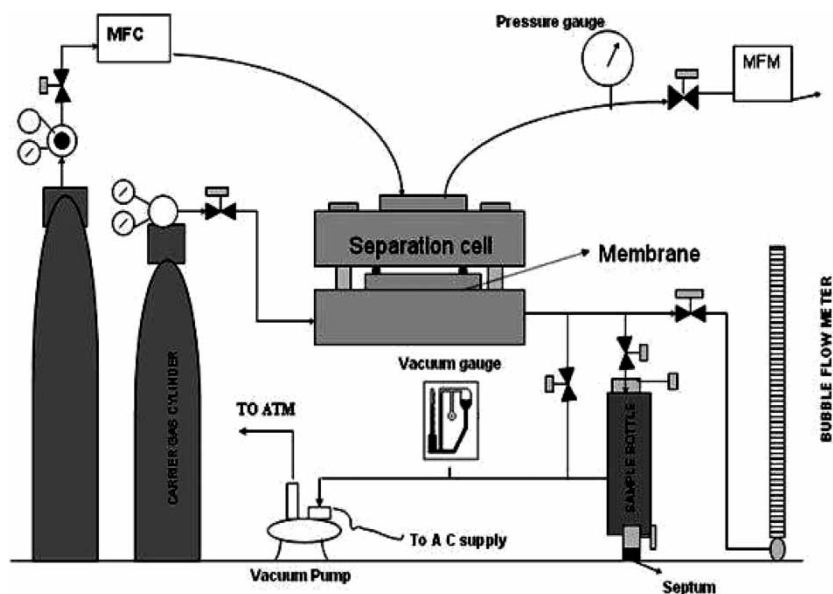


Figure 1. Schematics of gas separation manifold.

of component i at the feed side of the membrane is greater than the partial pressure of the same component at the permeate side.

Temperature

In general, solubility decreases with increasing temperature, while diffusivity coefficients tend to increase with temperature (29, 30). However, an increased diffusivity offsets the solubility decrease. Figure 2 shows that increasing temperature causes the selectivity to decrease while enhancing the rate of permeation. Thus, membranes possessing a high selectivity at room temperature may yield poor separation at elevated temperatures.

Concentration Polarization (CP)

For pervaporation and reverse osmosis liquid feeds, different individual component permeation rates cause an increase of the less permeable component in the boundary layer near the membrane surface. This inhibits the rate of transport of the more permeable species and subsequently the selectivity. However, such effects are rare or nonexistent for gas separations. The difference in behavior reflects the much higher gas phase (vs. liquid phase) external diffusion coefficients found in gases as against liquid feeds.

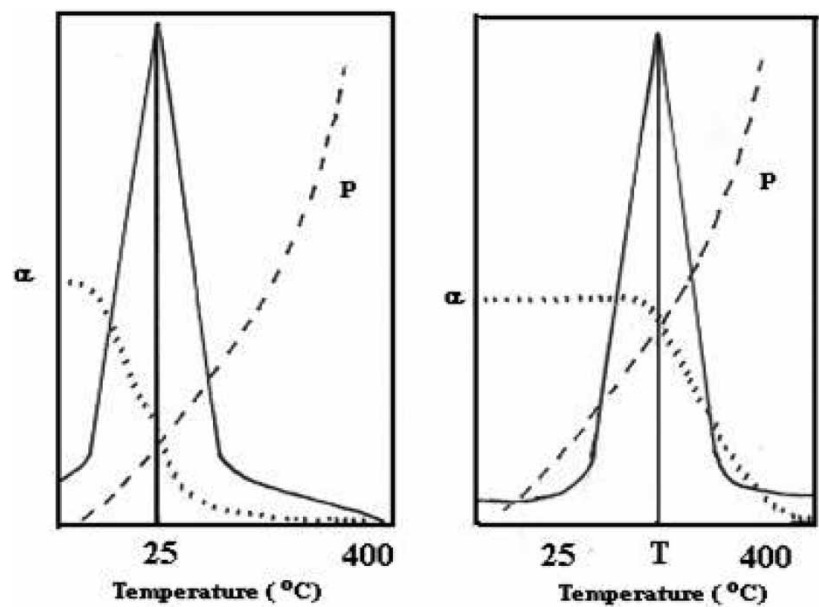


Figure 2. Graphical representation of how peak permselectivity shifts as a function of temperature (selectivity-dots, permeability-dashes, permselectivity-solid line).

ACID GAS PURIFICATION

Acid gas removal generally refers to the removal of CO₂ and H₂S. Even though sulfur dioxide (SO₂) is also an acid gas, its removal is sometimes treated as a separate technology called as flue gas desulfurization. However, the removal of acid gases is important for several reasons such as health, safety, corrosion limitation during transport and distribution, pollution control and catalyst poisoning (31). In industrial processes such as hydrogen manufacture, ammonia production and natural gas purification, the most common impurities are H₂S and SO₂, which are often present in quite large concentrations (5–50%). In general, the cleanup targets for H₂S are particularly stringent, e.g., 4 ppm by volume for pipeline gas at 70 bar and 0.1 ppm for chemical synthesis applications such as ammonia synthesis. The CO₂ specifications may be relatively loose for natural gas (<1%), but for ammonia production, CO₂ must be reduced to 10 ppm. Thus, the cleanup targets play an important role while selecting a gas treatment process (32).

Conventional Methods for CO₂, and H₂S Removal

Acid gas purification processes generally fall into one of the categories (32) viz absorption into liquid (31–34), adsorption on a solid, and chemical conversion by oxidation methods (35, 36). The most widely used chemical solvents are alkanolamines such as monoethanol amine (MEA), diethanol amine (DEA), β,β' -hydroxy-amino ethyl ether, etc. The disadvantages of using amine solutions not only include high operating costs, but also severe corrosion problems that makes the usage of special materials for the construction of equipments. In adsorption, impurities are removed from gaseous streams by concentrating on the surface of a solid material. Adsorbents commonly used in this process are based on silica, alumina, carbon, certain silicates, molecular sieves, etc. If adsorption is to be carried out at elevated pressures, pressure swing adsorption is employed (32). However, the process suffers disadvantages that include low recovery rates, stringent pretreatment of the adsorbent and gas thereby, making the mode of operation discontinuous. The process of heterogeneous catalysis using solid catalysts accomplishes chemical conversion by oxidation methods. This entails the transfer of reactants from gas phase to solid surface, activated adsorption onto the surface, chemical reaction on the surface to form an absorbed product and transfer of the product back into the gaseous stream (32). Major drawbacks of this process are large ground space requirements, high labor costs and low-grade sulfur by-products.

Role of Membranes in Acid Gas Treatment

Semipermeable membranes constitute a mature technology that has been applied in natural gas processing for over 20 years (1). Membranes are

currently used for CO₂ removal from natural gas at processing rates from 1 MMSCFD to 250 MMSCFD. New units are in design or construction to handle volumes up to 500 MMSCFD. Excellent reviews on membrane technology are documented in the earlier literature (37–42). A synthetic membrane, which is permselective to acid gases, may as well replace the aforementioned conventional processes. Moderate to high feed pressures (50 bar) and moderate feed temperatures (0–60°C) (43, 44) normally encountered in natural gas streams are favorable for the application of membrane technology.

Advantages and Disadvantages of Amine Absorption and Membrane Processes

Initially, membranes were restricted to either small natural gas streams or those with very high CO₂ content such as in enhanced oil recovery. With the growth in membrane quality, the technology was applied to treat wider variety of natural gas streams. Now that the technology is more mature, the relative strengths and weaknesses of this process versus the more established amine absorption process can be viewed. Table 1 displays at some key areas for comparison (45) of the conventional separation process with the membrane-based separation method.

Membrane Materials

While the early demonstrations of deacidification of natural gas using cellulose membranes was dealt way back in the late 1960s (46), the first technical breakthrough for the removal of CO₂ and H₂S was realized using cellulose acetate (CA) membranes, which were then used mainly for desalination in an asymmetric form (47). The dry cellulose acetate membranes in spiral wound modular configuration exhibited a mixture gas selectivity that is significantly below the selectivity calculated from pure gas measurements reflecting the effect of plasticization caused by CO₂ and heavier hydrocarbons (48, 49). Studies by Mazur and Chan (50) depict the removal of ~95% CO₂ and ~90% H₂S, respectively, using CA membranes. Schell and Houston (51) obtained a selectivity of 20 to 30 for CO₂ over CH₄ and 75 to 110 for H₂S over C₃H₈ using the CA membrane.

During the 1980s, researchers have shown interest in other polymers, like silicones, polysulfones, polycarbonates, polyamides, polyimides, etc., that have good permeability and selectivity for acid gases. Systematic studies on the effect of substituents on gas permeability and diffusivity have been performed by Robeson on a series of rubbery and glassy polymers of the type listed here (52). Of these, silicone polymers were found to be interesting materials for studying gas separation properties due to the presence of flexible siloxane linkages and their potential for accommodating various substituents onto the polymer chain. Up to 1983, silicone rubber was considered to be an excellent candidate for gas separation due to its higher gas permeation properties as compared to other synthetic polymers (53). The high permeability of

Table 1. Comparison of amine and membrane CO₂ removal systems [adapted from (45)]

Factor	Amines	Membranes
Operating issues		
Hydrocarbon losses	Very low	Losses depends on conditions
Meet low CO ₂ specif.	Yes (up to ppm level)	No (<2% is tough)
Energy consumption	Moderate to high	Low (unless compression used)
Operating cost	Moderate	Low to moderate
Maintenance cost	Low to moderate	Low (unless compression is used)
Ease of operation	Relatively moderate	Relatively simple
Environmental impact	Complex	Low
Capital cost issues		
Pretreatment costs	Low	Low to moderate
Recycle compression	Not used	Depends on conditions
On-site installation time	Long	Short for skid-mounted systems
Delivery time	Long for large systems	Modular construction is faster

silicones has been attributed to its large free volume, which may be due to the flexibility of the siloxane linkages in the polymer.

Table 2 shows the permeability, diffusion and solubility coefficients for CO₂ and CH₄ in silicone polymers having various substituents in the side chains and in the backbone. However, the major drawback noted with this category of membranes is that they exhibit poor mechanical properties and selectivities. Further, when they are used in thin film form, they are subjective to pinhole formations. To guarantee integrity, multiple layers are required. To circumvent this setback and to take advantage of their inherently high permeability, two techniques have been developed. The first one is the preparation of block copolymers incorporating hard blocks of a second polymer such as bisphenol-A polycarbonate (54) or polysulfone (55), which have reasonably good permeability. The second technique is to integrally attach rubbers and/or oligomers to a microporous substrate to form a composite membrane (56). The substrate may act as a support or may itself function as the principal permselective barrier (57).

A shift from rubbery to glassy polymers was made with attempts to increase the permeability of the latter. Modifications made to aryl polymers such as polysulfone by introducing methyl groups into the aromatic rings of bisphenol-A and/or sulfone monomer resulted in some improvement in its permeability towards CO₂. Stannett et al. (58) explored the utilization of tetramethyl bisphenol-A polysulfone and found an increase in the gas permeability with no

Table 2. Pure gas permeabilities and ideal selectivities of silicone polymers [Feed pressure = 10 kg/cm² (g)] (3)

S. No.	Membrane type	Pure gas permeability (<i>P</i>) (Barrer) ^a		Selectivity
		CO ₂	CH ₄	<i>P</i> _{CO₂} / <i>P</i> _{CH₄}
1	Natural rubber	134	28.5	4.7
2	Poly(4-methyl-1-pentene)	83	13.2	6.3
3	PDMS (Silicone rubber)	4553	1339	3.4

^a1 Barrer = 10⁻¹⁰ [cc (STP) · cm/cm² · sec · cmHg].

loss in permselectivity. Despite their best efforts, polysulfones, owing to their low free volume, less regularity, lower bulk density and lower glass transition temperature (*T_g*) yielded comparatively lower selectivity. This has led the researchers to investigate straight and short chain structures of polyethersulfones (PES) that make them amenable to pack more tightly in the glassy state than the related polysulfones. The selectivity obtained by PES membranes was slightly higher i.e., *P*_{CO₂}/*P*_{CH₄} for PES is 28 as compared to 26 for polysulfones (57).

Polycarbonates (PC) are another class of polyesters derived from carbonic acid and bisphenol-A. The non-planarity of bisphenol-A in PC results in a large average inter-chain displacement with the result that gas permeabilities are reasonably high. In combination with flexible soft polymers like silicone rubber (58), polyethylene glycol (58), copolymerized PC's exhibit gas permeabilities (59) that are high enough (*P*_{CO₂} = 970 Barrer) to make the membrane separation process economically viable. Membranes resulting from poly(vinyl alcohol) (PVA) modified by methyl vinyl sulfone (MVSF) or t-butyl vinyl sulfone (BVSF) have been reported to exhibit very high permeabilities and selectivities (60). Both permeabilities and selectivities increased with an increase in pressure.

Polyamides are the step reaction products of primary or secondary diamines with dibasic acids. The most important structural feature of polyamides is the amide (-CONH) group. The amide link with the main chain has a strong tendency to form hydrogen bond, leading to high *T_g*'s and poor solubility coefficients. However, the copolymers of polyamides with PVA, polyacrylonitrile and plasticized gelatin have shown good permeabilities (61). Polyimides are presently being used as membranes in gas separation processes (62). Upon incorporation of hexafluoro-isopropylidene groups in the main chain, polyimides could exhibit good gas permeabilities (63). However, selection of a proper membrane material depends upon the optimization of physico-chemical and mechanical properties of the polymers. The types of polyimides and their copolymers used currently for CO₂/CH₄ separations will be dealt with later. The structures of some prominently used polyimides for separating CO₂ from natural gas are shown in Figure 3.

It is thus clear that deacidification of natural gas using membranes still faces challenges vis-a-vis conventional methods inspite of their potentially

(a) Copolyimides (6FDA-based)

Name	Chemical Structure
1. 6FDA-2,6-DAT polyimide	
2. 6FDA-ODA/NDA	
3. 6FDA-BAPAF	
4. 6FDA-DAP	
5. 6FDA-DABA	
6. 6FDA-TrMPD	
7. 6FDA-mPD	
8. 6FDA-4mPD	

Figure 3. Structure of membranes used for natural gas separation.

(continued)

(b) Polyimides (non-6FDA based)

Name	Chemical Structure
1. Matrimid 5218 (BTDA-DAPI)	
2. P84	

(c) Others

Name	Chemical Structure
1. Polyethersulfone	
2. Bisphenol A (polycarbonate)	
3. Tetramethyl Bisphenol A polycarbonate	
4. Poly (2,6-dimethyl p-phenylene oxide)	
5. Cellulose Triacetate	

Figure 3. Continued.

(c) Others

Name	Chemical Structure
6. Cellulose Acetate	
7. Polysulfone	
8. Polyetherimide	

Figure 3. Continued.

greater commercial impact. The major impetus for the commercialization of membranes for natural gas separation should be a clear choice of membrane materials that not only render high permeability ratios, but also yield good permeabilities. Equally important is the specific membrane chemistry, which depends upon the type of separation to be achieved. Therefore, membrane material selection is an area of high significance.

MEMBRANE SELECTION

Separation by membranes is due to the differences in transport rates of molecular species through the membrane inter-phase (64). Transport rate is determined by the driving force (pressure and/or concentration gradient) acting on the individual components by their mobility and concentration within the inter-phase. Mobility is primarily determined by the molecular size of penetrant and physical structure of the inter-phase material (crystallinity, hardness, polymer chain flexibility, etc.), while the concentration of penetrant at the interface of the membrane is primarily determined by the chemical compatibility between the penetrant and the membrane (65).

Simplicity, low-energy requirement, ease of process integration, process flexibility, low capital and production costs make the membrane processes for

gas purification highly competitive (66). Further, the fact that the process does not involve any change in phase, makes it all the more attractive unit operation. In deacidifying natural gas, a feed stream constituting CH₄, CO₂ and H₂S must be dealt with. In order to achieve this, three relevant areas such as material selection, membrane synthesis and system configuration must be integrated.

Right from the early 1960s, when research on membrane separations began, a wide range of materials including dense metals, zeolites, polymers, ceramics and biological polymers have been used for fabricating membranes. Even today, polymers are the most widely used materials for membrane manufacturing. A major consideration in this section will be the theory behind the selection of polymer materials, membrane structures and modifications that can be made to such structures as well as the effect of process variables that have enabled the most appropriate membranes in separating the gaseous mixtures.

Polymer Selection for Development of Membranes

Preliminary criteria for selecting polymeric materials for gas separation are based on chemical resistance, sorption capacity and good mechanical strength. However, the key important factors are: (a) intrinsic membrane permselectivity, (b) ability of the polymer to resist swelling induced plasticization (not chemical attack, which is quite rare) and (c) ability to process the polymer into a useful asymmetric morphology. The polymer should have good interaction, preferably with one of the components of the mixture, for an effective separation. Molecular structure, specific nature and arrangement of chemical groups attached to the main chain are also some of the important factors, which affect the membrane properties and hence, their performance (67). Molecular weight distribution (34, 68) (see Table 3) and membrane polarity (69–71) are other parameters of interest for the development of novel membranes. Molecular architecture, cross-linking and interpenetrating network of

Table 3. Effect of low and high molecular weight (MW) on some polymer properties

Polymer property	Effect of high MW components	Effect of low MW components
Strength	Increases	Decreases
Viscosity	Increases	Decreases
Chemical resistance	Improves	Lowers
Required processing temperature	Higher	Lower


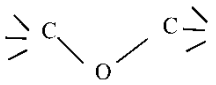
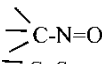

polymers (IPNs) are known to influence the T_g of the polymers (69). Any factor that hinders the free rotation about the bonds generally decreases the flexibility and increases the T_g . However, almost all useful membrane-forming polymers are condensation polymers rather than addition polymers, which do show large polydispersity indices (72). Generally, characteristic polydispersities of 2–2.1 is typical of such condensation polymers.

Rubbery materials have high permeabilities, but poor selectivities due to paucity of polar groups, absence of crystallinity and low degree of cross-linking (73). In the glassy state, chain motion is restricted to bond vibrations only. Density-wise, glassy state lies between the crystalline state corresponding to maximum possible density and the rubbery state. Glassy polymers have higher permselectivity and are thus, suitable in gas separation studies (74). Density of the glassy polymer increases by annealing or plasticization. Annealing could either improve or worsen the separation capability of the membrane depending upon the annealing conditions, but plasticization has an adverse effect on permselectivity. Hence, high permselectivity can only be obtained with polymers of rigid backbone structures having small inter-segmental gaps i.e., high T_g and resistance to plasticization (69). In general, glassy polymer is a combination of amorphous and crystalline phases. The crystallites work as effective cross-links and thus, decrease the area available for permeation (75). But, crystallinity improves the mechanical properties such as stiffness and tensile strength as well as thermal property like T_g . Therefore, an optimum ratio of crystalline to amorphous is important to derive final mechanical properties of the polymeric membranes, which could be related to the performance characteristics such as permeability (69).

Membrane Polarity

Membrane polarity contributes considerably to its separation performance. In order to separate a particular component of an organic feed mixture, the polarity of one of the components must be close to the polarity of the membrane. Generally, the chemical differences between various polymeric materials are due to the differences in polarity and steric effects caused by the attached side groups. Polarity, due to unevenness in electron distribution, is described by group properties, such as charge density, dipole moment, hydrogen-bonding capacity and bulk properties like dielectric constant and surface tension (71). Polarity strongly influences solubility and subsequently the permeability, which is demonstrated aptly by the Hildebrand solubility parameter, δ (76–79). Therefore, it is possible that selectivity for a polar gas in the feed gas stream may be improved with membrane polarity i.e., hydrogen bonding groups present in the polymer matrix. Tables 4 and 5 show some of the important polar groups and hydrogen-bonding groups.


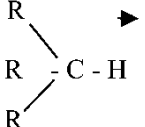

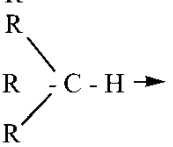
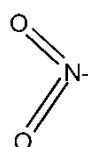
Table 4. Polar groups responsible for intermolecular attraction

Polar group (+ - -)	Dipole moment (Debye units)	Polar group (+ - -)	Dipole moment (Debye units)
H-F	1.9	C=NH	2.5
H-Cl	1.1		3.9
H-O	1.6	- C≡ N	3.8
H-S-	0.9		
H-N	1.6		0.9
C-Cl	1.7		1.9
H-C			
C=O	2.5		3.0
C-F	1.5		

Crystallinity

In the separation of gases, the degree of crystallinity also exerts a great influence on permeability of gas through the membrane, because diffusion generally occurs in the amorphous part of the polymer (80). Highly crystalline polymers do not contribute in enhancing permeabilities and furthermore, crystallites due to lack of flexible groups, act as physical crosslinks, which prevent high-degree of swelling and thereby, show lower permeability compared to amorphous

Table 5. Hydrogen bond donor and acceptor groups

H-Bond donors		H-Bond acceptors	
F-H	Strong	O=C	Strong
O-H	Strong		Strong
	Weak, if R=C or H		Strong
	Strong, if R=F or Cl		Strong

polymers. Indeed, poly(phenylene oxide) (PPO), which can be prepared by melt processing as an amorphous thick film typically tends to crystallize when formed in solvent-nonsolvent induced asymmetric form. While PPO has good separation properties in the amorphous dense film form, the complications with crystallization of casting dopes for this material has prevented its large scale practical applications.

Membrane Structure

It is well established that chemical structures coupled with the subtle physical properties of a membrane influence the permeability and selectivity. The response of polymeric material to permeation is strongly influenced by polarity and steric characteristics of the barrier as well as the permeating component. Size and shape of the bulky groups in the main chain as well as the side chain determine certain fundamental properties like packing density and rigidity, which in turn influence its accessibility. Studies indicate that permeability and selectivity of polymeric membranes cannot be drastically improved by incorporating variations in the basic structure of a particular polymer (81, 82). Such efforts only shift the compromise between permeability coefficient and selectivity, but do not constitute a concrete improvement. Therefore, the dependence of permeability on chemical structure can only be a rough approximation because the chemical structure is only one of the determinants for assessing membrane properties (83). Physical structure is usually as important and therefore, has received a greater attention due to its contribution in practical applications. The physical structure that encompasses the mechanical state of matter (density, mobility and order) has a strong bearing on gas separation properties of the membranes.

For membranes, several physical structures like microporous, dense, asymmetric and composite exist. Generally, membranes used in laboratory scale set-ups for the separation of gaseous mixtures are always homogeneous and symmetric [Figure 4a] because they are easy to cast and will directly give the intrinsic separation properties of the polymer. However, to attain commercial viability, membranes that are successful on a laboratory scale are converted to asymmetric or composite forms. These two morphologies offer the possibility of making a barrier with a thin effective separation layer, which enables high flux, while maintaining the desirable mechanical strength. Asymmetric membranes consist of a thin dense layer on top of a porous support layer of the same material [Figure 4b]. These membranes are prepared by phase inversion technique where a homogeneous polymer solution is cast as a thin film or spun as a hollow fiber and immersed in a non-solvent bath after giving it a brief evaporation time in air. The membrane is formed by the replacement of solvent by non-solvent and precipitation of the polymer.

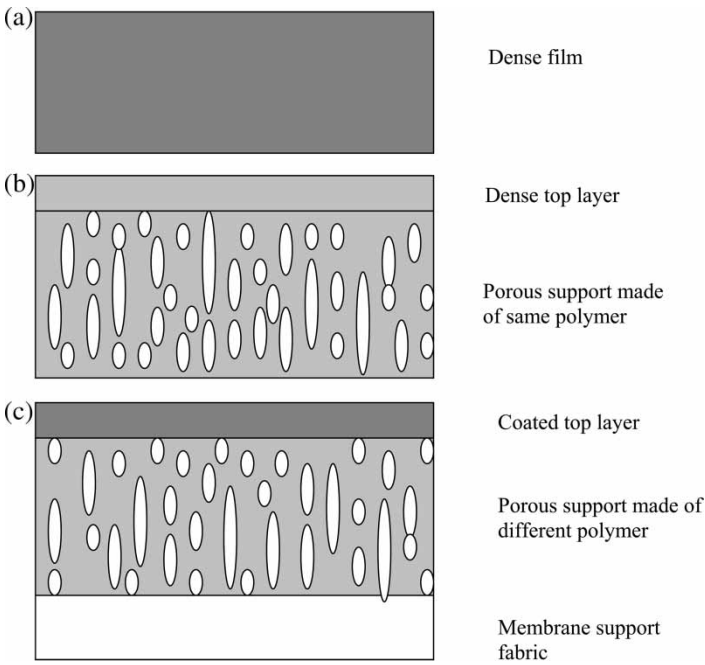


Figure 4. Schematic representation of three different types of membrane morphology (a) Homogeneous symmetric membrane, (b) Asymmetric membrane and (c) Composite membrane.

Composite membranes consist of a porous support layer with a thin dense skin layer coated on top of it [Figure 4c]. The top layer is made of a material different from the support layer. Utilization of composite structures minimizes the membrane cost by reducing the quantity of expensive high performance material used, if any.

Polymer Modification to Improve Separation Characteristics

There are mainly three methods for improving the separation characteristics of membranes. These include cross-linking, grafting and blending.

Cross-linking

The primary reason to cross-link a polymer is to decrease the plasticization of a polymer in order to derive a good selectivity. To develop high performance membranes, there arises a need to adjust membrane swelling while in

contact with the feed mixture. To achieve this, the membrane must be cross-linked and the extent of cross-linking should be thoroughly controlled. Cross-linking can be executed in three ways. One is via chemical reaction by using a compound to connect two polymeric chains, the second by irradiation and third, is a physical cross-linking (84). A good example of chemical cross-linking is modification of polyimide membranes using 3,5-diaminobenzoic acid as the cross-linking agent (85). On the other hand, excessive cross-linking should be avoided as it renders the membrane brittle causing a loss in its dimensional stability, thereby making it unsuitable for high-pressure applications. Especially, in case of a composite membrane, it is rather difficult to ensure controlled cross-linking, because the composite membranes are produced by the usual solution coating-solvent evaporation technique and chemical cross-linking is achieved during the evaporation step.

Polyarylate or polyimide membranes with benzophenone moieties can be cross-linked by exposure to UV radiation. Depending upon the duration of irradiation, a considerable improvement in membrane selectivity can be achieved (86, 87), but permeability is strongly reduced presumably because of densification and reduced mobility of the polymer structure after cross-linking. Commercially attractive processes also demand that reproducible separation and degree of crosslinking can be guaranteed, which are rather difficult to achieve by irradiation methods.

Grafting

Grafting is a polymer modification route in which oligomeric chains are attached as side chain branches in an irregular manner to the main polymer chain. Grafting can be achieved by chemical reaction or by irradiation. If the molecules of a reagent contain a functional group that can react with another group in the polymer, then grafting by chemical reaction can occur. Grafting by irradiation is a versatile technique for the modification of insoluble polymer membranes. Polymers with good chemical resistance can be made into films by melt extrusion/calendering followed by modification through the irradiation-based grafting. A substantial improvement in permeability can be achieved by grafting thin film composite membranes on high flux microporous polyetherimide support (88).

Blending

A mixture of two polymers, which are not covalently bonded is called a polymer blend. In principle, blending is an ideal technique for creating substantial sites in the membrane matrix. The optimum blending ratio can be determined by mixing two polymers at various compositions and measure permeability as well as selectivity. Two types of blends can be distinguished: homogeneous blends, in which two polymers are miscible on a molecular

scale for all compositions and heterogeneous blends, in which two polymers are not completely miscible. In the latter case, domains of one polymer distributed within the matrix of the other polymer can be observed. However, homogeneous blends can be considered as potential membranes for separations because heterogeneous blends do not offer enough mechanical strength to thin membranes. A homogeneous blend not only shows a reduction in CO₂ plasticization, but also contributes to enhanced selectivity for CO₂/CH₄ mixtures (89).

Copolymerization

In copolymerization, two polymers are covalently bonded so as to increase the mechanical stability of the membrane. Besides the grafted copolymers, block and random copolymers can also be synthesized. An important of copolymerization is the degree of crystallinity. Random copolymers might be fully amorphous, while graft copolymers contain a certain degree of crystallinity. A polymer that is significantly plasticized can be copolymerized with another polymer, which undergoes plasticization to a lower extent to obtain not only enhanced selectivity, but also a considerable reduction in plasticization (90).

CURRENT STATUS OF NATURAL GAS DEACIDIFICATION

Published Work

Published literature highlights the developments of various separation technologies that are useful to evaluate their future research possibilities. Figure 5 is an overview of the rapid rate of advancement in research occurring in the field of CO₂ separation from CH₄; the number elucidated does not cover pertinent patents. One can clearly view an increase in the number of publications and patents in the area of gas separation with time. This increment depicts the contribution of various researchers in developing significant membranes to suit the application. Figure 6 shows that CO₂ separation still receives the maximum attention from researchers as compared to separation of other gaseous mixtures. Conventional methods for acid gas removal are compared to various stages in the development of membranes for gaseous separations between 1970 and 1990, while further progress made in gas permeation technique from 1999 till-date has been tabulated. The discussion also includes books and papers published in the well-known international journals. Among several publications, about 70 articles, which have reported very good permeabilities and selectivities for the removal of CO₂ from CH₄ are included in this review.

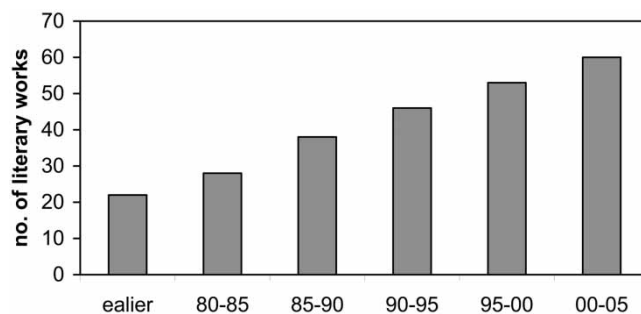


Figure 5. Increasing trend of literary works in CO₂/CH₄ separation from 1970–2004.

Types of Membranes Currently Used in CO₂/CH₄ Separation

Preliminary studies have paved the road to many membrane preparation techniques to obtain reasonable selectivity and permeability. Permeabilities and selectivities for acid gases in different polymeric membranes are listed in Tables 6–9 (89–159). From these data, it can be noted that most of the researchers have found polyimide membranes to be ideal for separating CO₂/CH₄ mixture. The typical trade-off between productivity and selectivity is clearly seen in Figure 7 (160–163). The structure/permeability relationships of polyimides have been investigated extensively since the pioneering work of Hoehn (164) because of the higher selectivities and permeabilities exhibited by these polymers than other glassy polymers.

Aromatic polyimides are formed in a two-step polycondensation reaction of a dianhydride with a diamine (165, 166). In the first step, a tetracarboxylic acid dianhydride is added to a diamine solution leading to a polyamic acid. In the second step, actual imidization takes place by extended heating at the elevated temperature (thermal) or by treatment with dehydrating agents

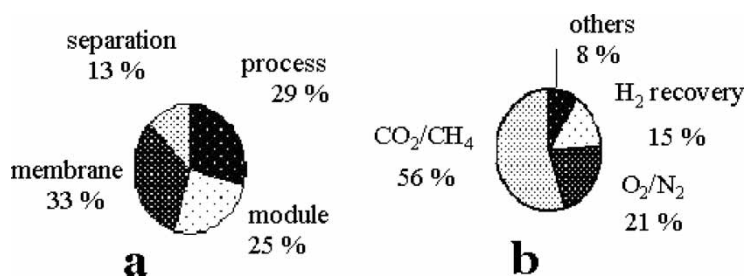


Figure 6. (a) Different fields developed and (b) separations of various mixtures as indicated by patents.

Table 6. Separation of pure CO₂ and CH₄ gases through 6FDA-based membranes

Sl. No.	Membrane	Operating conditions		Permeability (Barriers) ^a /Permeance (GPU) ^b		Selectivity $\alpha = \text{CO}_2/\text{CH}_4$	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
1	6FDA – TAD PO	30	1	27.4	0.52	52.2	(89)
	6 FDA – TABP			63.6	1.37	46.2	
2	6FDA-DAM	35	20	121	4.48	27	(90)
	DABA (2:1 membrane)						
	CHDM cross-linked			22	0.73	30	
	6FDA-DAM						
	DABA (2:1 membrane)						
	BG cross-linked			46	1.35	34	
	6FDA-DAM						
	DABA (2:1 membrane)						
3	6FDA-mPD	35	3.7	11.03	0.19	58	(91)
	6FDA-mPDBA (9:1)			6.53	0.10	65.3	
	X-6FDA- mPD/ DABA (9:1)			9.50	0.15	63.3	
	X-6FDA-DABA			10.40	0.12	87.0	
4	6FDA-durene	35	10	455.8	28.4	16.05	(92)
5	6FDA-TAPA	35	1	65	1.59	41	(93)
	(amine terminated)						
	6FDA-TAPA (anhydride terminated)			6.7	0.11	61	
	DSDA-TAPA (amine terminated)			4.0	—	—	
	DSDA-TAPA (anhydride terminated)			1.0	—	—	
6	6FDA-DATPA	30	10	23	0.68	34	(94)
7	6FDA-PFDAB	25	5	17.77	0.44	40.4	(95)
	6FDA-m-PDA			9.73	0.21	46.3	
	ODPA-PFDAB			11.03	0.36	30.6	
	ODPA-m-PDA			0.301	0.0064	47	

(continued)

Table 6. Continued

Sl. No.	Membrane	Operating conditions		Permeability (Barriers) ^a /Permeance (GPU) ^b		Selectivity $\alpha = \text{CO}_2/\text{CH}_4$	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
8	BTDA-PFDAB	35	3.5	10.10	0.29	34.8	(96)
	BTDA-m-PDA			0.428	0.0086	49.8	
	6FDA-6PDA-ceramic composite before irradiation			47.27	3.65	12.94	
	6FDA-6FPDA-ceramic composite after irradiation			71.52	1.75	40.9	
9	6FDA-1,5-NDA	35	10	22.6	0.46	49	(97)
10	6FDA-HAB	RT	55	6×10^2	10	60	(98)
11	6FDA-durene/mPDA cross-linked with DMEA (6 hrs)	RT	1	49.1	1.63	30.1	(99)
12	6FDA-NDA	2	7	22.6	0.47	48.1	(100)
	6FDA-NDA/durene (75:25)			70.0	1.65	42.4	
	6FDA-NDA/durene (50:50)			96.4	3.93	24.5	
	6FDA-NDA/durene (25:75)			274	12.9	21.2	
	6FDA-NDA/durene			423	28	15.1	
13	6FDA-DDS	30	5	35	0.37	94.6	(101)
14	6FDA-TAB	30	10	54	0.9	60	(102)
	6FDA-TAB/DAM(75:25)			73.7	1.67	44	
	6FDA-TAB/DAM(50:50)			155	7.38	21	
	6FDA-DAM			370	17.6	21	
15	6FDA-terphenyl	31	2	21.48	0.747	28.76	(103)
	6FDA-biphenyl			12.97	0.358	36.23	
	6FDA-phenyl			11.89	0.353	33.68	
16	6FDA-zero generation amino terminated PAMAM dendrimer (100 mm)	30	10	0.5	0.4	25	(104)

(continued)

Table 6. Continued

Sl. No.	Membrane	Operating conditions		Permeability (Barriers) ^a /Permeance (GPU) ^b		Selectivity $\alpha = \text{CO}_2/\text{CH}_4$	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
	6FDA-first generation amino terminated PAMAM dendrimer (100 mm)			0.7	0.6	20	
	6FDA-second generation amino terminated PAMAM dendrimer (100 mm)			0.9	0.8	18	
17	6FDA-BAPAF	30	21	24.6	1.10	22.78	(105)
	6FDA-DAP			38.57	0.49	78.82	
	6FDA-DABA			26.30	0.56	46.96	
18	6FDA-3BDAF	25	2	42.45	0.88	48	(106)
19	6FDA-IPDA	31	0.6	14.8	0.38	43	(107)
20	6FDA-DAFO	30	3.5	26.5	0.44	60	(108)
21	6FDA-APPS	35	2	36.7	0.94	39	(109)
22	6FDA-Durene/1,3-phenylene diamine(mPDA) copolyimide dense film coated with silicone rubber	19.5	14	53.3	1.24	42.9	(110)
23	6FDA-DAT (3900 Å°)	20	7	300	4.60	65	(111)

Permeability units for rows 1–16 are in Barrers, and rows 17–23 in Gas Permeability Unit (GPU).

^a1 Barrer = 10^{−10} cc(STP) · cm/cm² · sec · cmHg.

^b1 GPU = 10^{−10} cc(STP)/cm² · sec · cmHg.

(chemical). The acronyms identifying the polyimides refer to the dianhydride (first part) and the diamine (second part).

6FDA-Based Membranes

To achieve good permeabilities and selectivities, one can vary the chemical structure chain stiffness or packing density. However, improving permeability

Table 7. Separation of pure CO₂ and CH₄ gases through Matrimid and other polyimides

Sl. No.	Membrane	Operating conditions		Permeability		α CO ₂ /CH ₄	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
1	(Non-solvent-treated)	30	2.5				(112)
	CM-MAT-800			611	10.0	61	
	CM-MAT-MeOH-800			423	4.8	88	
	CM-MAT-EtOH-800			191	1.1	169	
	CM-MAT-PpOH-800			565	6.7	84	
	CM-MAT-BuOH-800			547	7.0	78	
	CM-P84-800			499	5.6	89	
	CM-P84-MeOH-800			402	3.7	109	
	CM-P84-EtOH-800			278	2.0	139	
	CM-P84-PpOH-800			428	3.9	110	
2	Matrimid – CMSM	25	1	12	0.36	33	(113)
	Kapton – CMSM			92	5.75	16	
3	Fluorinated Matrimid 1	31	10	0.018	0.20×10^{-4}	94	(114)
	Fluorinated Matrimid 2			0.069	0.05×10^{-4}	130	
4	Hyperbranched PI(HBPI)	30	2	7.4	0.098	75	(115)
	HBPI-SiO ₂ (10)			10	0.13	75	
	HBPI-SiO ₂ (20)			12	0.080	150	
	HBPI-SiO ₂ (30)			19	0.080	237.5	
5	CM-P84-550	27	17	1808	36.1	50	(116)
	CM-P84-650			738	33.5	22	
6	PI/10PS	35	10	2.33	0.049	47.5	(117)
	PI/20PS			2.90	0.34	8.53	
	PI/10PSVP			3.58	0.10	35.8	
	PI/10PSVP			5.65	0.14	40.3	
7	PI	35	1	8.34	6.86	1.22	(118)
	PI/TAP			0.194	0.00231	84.3	
	PI/4A			9.36	4.19	2.23	
	PI/13X			33.4	4.87	6.8	
8	Cross-linked PI/PES dual layer membrane	35	18	28.3	0.28	101	(119)

Permeability units for rows 1–7 are in Barrers and for row 8 in GPU.

Table 8. Separation of pure CO₂ and CH₄ gases through other polymer membranes

Sl. No.	Membrane	Operating conditions		Permeability		α CO ₂ /CH ₄	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
1	CMS-800-2	25	2	43.5	0.21	207	(120)
2	HQDPA-3MPDA	30	10	18.2	0.56	32.6	(121)
	HQDPA-2MMDA			1.67	0.02	79.1	
	HQDPA-BDA			0.69	0.008	85.7	
3	C	30	2	190	4.6	41.3	(122)
	C-CaO			130	3.5	37.1	
	C-MgO			14	1.2	11.7	
	C-FeO			110	4.0	27.5	
	C-SiO			58	2.0	29.0	
	C-AgN			180	1.4	128.6	
	C-CuN			814	0.66	1233	
	C-FeN			310	2.1	147.6	
4	Homogeneous IPO	30	0.15	95	5.8	16.4	(123)
	Composite PPO			82	2.3	38	
5	Polyphosphazene 1	35	2	9.3	0.62	15	(124)
	Polyphosphazene 2			115.9	7.13	16.2	
	Polyphosphazene 3			226.7	19.2	11.8	
6	PPO	30	1	90	5.4	16.7	(125)
	PPO Br			93.6	5.4	17.3	
	SPPO Br 1			84	3.15	26.7	
	SPPO Br 2			62.5	2.8	22.3	
	SPPO Br3			147.2	8.5	17.3	
7	ABS-AC1-M02	30	37	5.04	0.23	21.9	(126)
	ABS-AC1-M05			6.1	0.28	21.8	
	ABS-AC1-M07			9.7	0.36	26.9	
	ABS-AC1-M10			13.4	0.46	29.1	
	ABS			3.43	0.17	20.2	
	ABS-AC1-M20			8.43	0.38	22.1	
	ABS-AC1-M25			11.44	0.45	25.4	
	ABS-AC1-M33			14.43	0.47	30.7	
	ABS-AC1-M40			22.64	0.59	38.4	
8	Hyflon AD 80	21	2	2×10^2	18.2	11	(127)
	AD 1600			6×10^2	96.8	6.2	
	AD 2400			2×10^3	285.7	7	
9	PPOP (50%)	25	4.9	4.73	—	—	(128)
	PPOP(20%)			9.26	—	—	
10	PTBP	30	2.1	17	1.7	10	(129)
	PDTBP			27	5	5.4	
11	TER-BPA	35	1	30.3	1.9	16.13	(130)

(continued)

Table 8. Continued

Sl. No.	Membrane	Operating conditions		Permeability		α CO ₂ /CH ₄	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
12	TER-6FBPA	35	5	37.3	2.2	16.72	(130)
	TER-FLUORENE			41.2	2.8	14.71	
	BPA + 50 mol% 1,1 bi-2-naphthol diol			5.71	0.22	26.1	
	BPA + 70 mol% 1,1 bi-2-naphthol diol			4.62	0.15	30.2	
13	PVTMS	30	1	190	22	8.6	(131)
	PVTMS, doped by 0.1 M HCl)			27.7	2.6	10.7	
	PVTMS – PAN (0.04 mol/l)			60.6	3.6	17.1	
14	Acrylate Urethane PDMS	26	2	175	13.5	12.9	(132)
	Vinyl Urethane PDMS			1071	245	4.4	
	Hydrolyzed PVP			0.067	4.9×10^{-4}	135.9	
16	6 FPT – 6FBTA	35	1	25.29	1.58	16.01	(134)
	6 FPT – BPA			18.53	1.41	13.11	
	6 FPPy – 6FBPA			29.46	1.92	15.32	
	6FPPy - BPA			21.44	1.78	12.04	
17	FBP/6FPT	35	1	25.75	1.59	16.18	(135)
	FBP/6FPP			35.65	1.80	19.82	
18	Poly (ethylene oxide – co – epichlorhydrin)	25	7	105	6.17	17	(136)
19	PFS – H	30	3	0.73	0.032	23	(137)
	PFS – t – butanol			4.12	0.17	24	
	PF6f – H			2.50	0.15	17	
	PF6f – t – But			11.0	0.53	21	
20	Poly(arylene ether)s	35	1	30.3	1.9	16.13	(138)
21	P3AcET	30	1.8	1.42	0.08	18	(139)
	P3HET			336	8	42	
22	Polylactic acid	20	2	1.2	0.075	16	(140)
23	PEI/PEG/NMP (23/0/77) dope	RT	17	7.44×10^{-4}	0.12×10^{-4}	62	(141)
24	PEK – C	30	1	2.73	0.082	33.2	(142)

(continued)

Table 8. Continued

Sl. No.	Membrane	Operating conditions		Permeability		α CO ₂ /CH ₄	Ref.
		Temp (°C)	Pressure (bar)	CO ₂	CH ₄		
25	PEEK – C	30	7	2.17	0.056	38.5	(143)
	PEK – A			4.46	0.155	28.6	
	PEK – H			2.36	0.07	34.2	
	SPPO – Na			4.66 × 10 ^{−4}	0.07 × 10 ^{−4}	67	
	SPPO – K			6.20 × 10 ^{−4}	0.11 × 10 ^{−4}	56.3	
	SPPO – Ca			5.73 × 10 ^{−4}	0.06 × 10 ^{−4}	95.5	
	SPPO – Ba			5.06 × 10 ^{−4}	0.09 × 10 ^{−4}	56.2	
26	PVDC – PVC	25	0.07	6.84	0.52	92	(144)
27	BBL	30	1	0.12	1.7 × 10 ^{−3}	71	(145)
28	BPDA/ODA	35	2.5	0.23	0.02	11.5	(146)
29	BPDA/ODA	30	1	0.45	0.04	11.3	(147)
	SPPO			2.3	0.059	39	
	SPPO – Li ⁺			2.6	0.125	21	
	SPPO – Mg ²⁺			1.54	0.023	67	
	SPPO – Al ³⁺			3.84	0.126	30.5	

Permeability units for rows 1–27 are in Barrers and for rows 28–29 in GPU.

and selectivity by altering the chemical structure has only limited success, as shown by Robeson (52). Permeability data were taken from over 300 references, which included various glassy as well as rubbery polymers. The plots (as seen in Figure 8) of log($\alpha_{i,j}$) versus log(P_i) for different gas pairs, i and j yield an upper bound. This upper bound is an imaginary linear line on the log-log plot above which virtually no data exist. Further, structure-property optimization of polymers will shift the upperbound relationship slightly higher, but the inverse permeability-selectivity trade-off is expected to remain the same. It is beyond the scope of this review to discuss the many types of structural modifications of polyimides and their effect on gas separation properties.

Chain stiffness influences intra-segmental (rotational) mobility, whereas packing density influences inter-segmental spacing. A “trade-off” should be found to inhibit chain mobility, to achieve higher selectivities by molecular sieve mechanism and to achieve higher permeabilities due to an increase in

Table 9. Separation of CO₂/CH₄ gas mixtures through polymer membranes

Sl. No.	Membrane	Gas mixture (% CO ₂ in CH ₄)	Operating conditions		Permeability CO ₂	α CO ₂ /CH ₄	Ref.
			Temp (°C)	Pressure			
1	1 min EDA cross-linked 6FDA-Durene	50	35	10	250	38	(148)
2	Hyflon AD	20	35	8.2 14.3 21.0 35.0 53.2	257 266 286 274 281	10.6 10.3 10.2 9.3 8.7	(149)
3	Matrimid/PES dual layer hollow fiber	40	22	70 175 260	11 10 11	68 42 39	(150)
4	6FDA-DAM: DABA (2:1) annealed at 130°C 220°C 295°C	50	35	10	140 139 115	37 35 31	(90)
5	CM-P84-800	50	35	20	492	97	(116)
6	Matrimid Untreated p-xylene-diamine cross-linked	40	35	10	7.26 3.34	31.6 37.5	(151)
7	Matrimid mixed matrix film (19 vol.% CMS)	10	35	34.5	7	45	(152)
8	Lustran 246 (ABS copolymer)	50	20 30 40 50	20	3.1 3.6 3.9 5.1	—	(153)
9	Ultem mixed matrix containing 35 vol.% CMS	10	35	6 33.5	4.9 4.1	62 59	(120)
10	6FDA-2,6-DAT hollow fiber	—	35	14	59	40	(111)
11	PVSA/PS	50	26	0.5	0.4×10^{-4}	24	(154)
12	SPPO-H ⁺ -PES SPPO-Li ⁺ -PES SPPO-Cs ⁺ -PES	20	35	6.9	0.426 0.585 0.546	37 21.6 32.2	(155)

(continued)

Table 9. Continued

Sl. No.	Membrane	Gas mixture (% CO ₂ in CH ₄)	Operating conditions		Permeability CO ₂	α CO ₂ /CH ₄	Ref.
			Temp (°C)	Pressure			
13	Polyamide-poly- ether copolymer on PVDF support	4	23	27	31	17	(156)
				41	30	16	
				66	29	15	
14	Polymide carbo- nized @ 400 (1°C/min) 500 (5°C/min) 500 (1°C/min)	50	23	1	0.043	104	(157)
					1.43	12	
					3.05	6	
15	1% p-xylenedia- mine cross-linked (3 min) 6FDA-2,6 DAT hollow fiber	40	35	2	12	47	(158)
16	Poly(vinyl pyrro- lidone) by hydrolysis	50	26	0.02	1.69×10^{-4}	48.1	(159)
				0.07	4.59×10^{-5}	39.3	

Permeability units for rows 1–10 are in Barrers and for rows 11–16 in GPU.

free volume. The bulky $-C(CF_3)_2$ groups in dianhydride structure of 6FDA-based polyimides meet both the conditions. Thus, 6FDA-based polyimides are more permselective than other polyimides with comparable permeabilities (89–111). It has also been established that the presence of $-C(CF_3)_2-$ groups in dianhydride as well as diamine moieties exhibit both high selectivity and permeability. This is attributed to increased chain stiffness, resulting due to the bulky groups, which inhibit intra-segmental mobility, thereby resulting in enhanced selectivity. Furthermore, these groups inhibit chain packing due to their size, which serve as “molecular spacers,” thereby increasing the permeability.

Permeabilities of 6FDA membranes and their copolyimides can be enhanced by crosslinking with suitable agents. A simple mechanism of crosslinking elucidated by Bickel and Koros is represented in Figure 9 (91). By crosslinking the copolyimide “additional space” between the polymer chains is introduced, which is an indication of enhanced molecular free volume. As seen from the figure, chains of the non-cross-linked copolyimides being very close to each other result in a three dimensional rigid structure formed due to hydrogen bonding. Actually, there are two hydrogen bondings on every carboxylic acid group and this is the reason for the

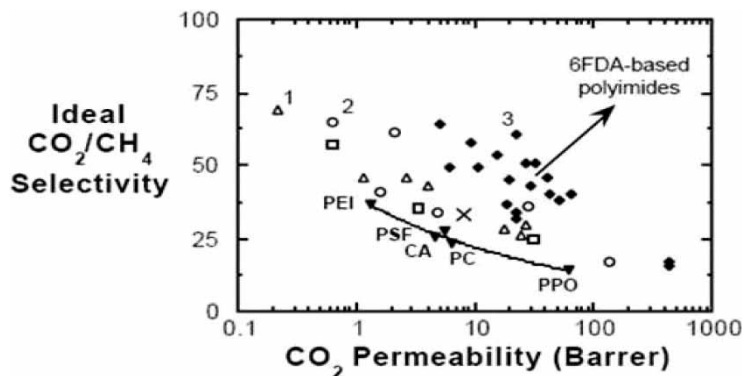


Figure 7. CO₂ permeabilities and ideal CO₂/CH₄ selectivities at 35°C and 10 atm in various polymers (13, 15, 52–55). Polyimides PMDA-based (open triangles), BPDA-based (circles), BTDA-based (open squares) and 6FDA-based (closed diamonds) polyimides with 1. PDMA-ODA, 2. BPDA-ODA, 3. 6FDA-ODA. [The cross refers to BTDA-DAPI (Matrimid 5218)]. Adapted from (159).

“tightening” of molecular free volume giving a strong reduction permeability. The structure of cross-linked copolyimide shows the existence of additional space between polymer chains, resulting due to insertion of cross-linking unit per carboxylic acid group giving enhanced permabilities. Bickel and

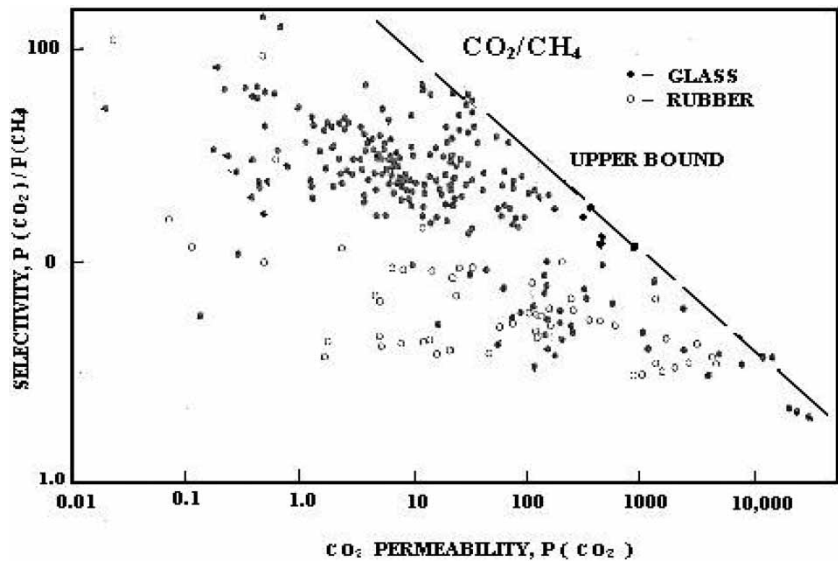


Figure 8. CO₂/CH₄ selectivity as a function of CO₂ permeability for all well-known membrane materials as of 1991. This plot by Robeson (52) illustrates the strong trade-off between permeability and selectivity.

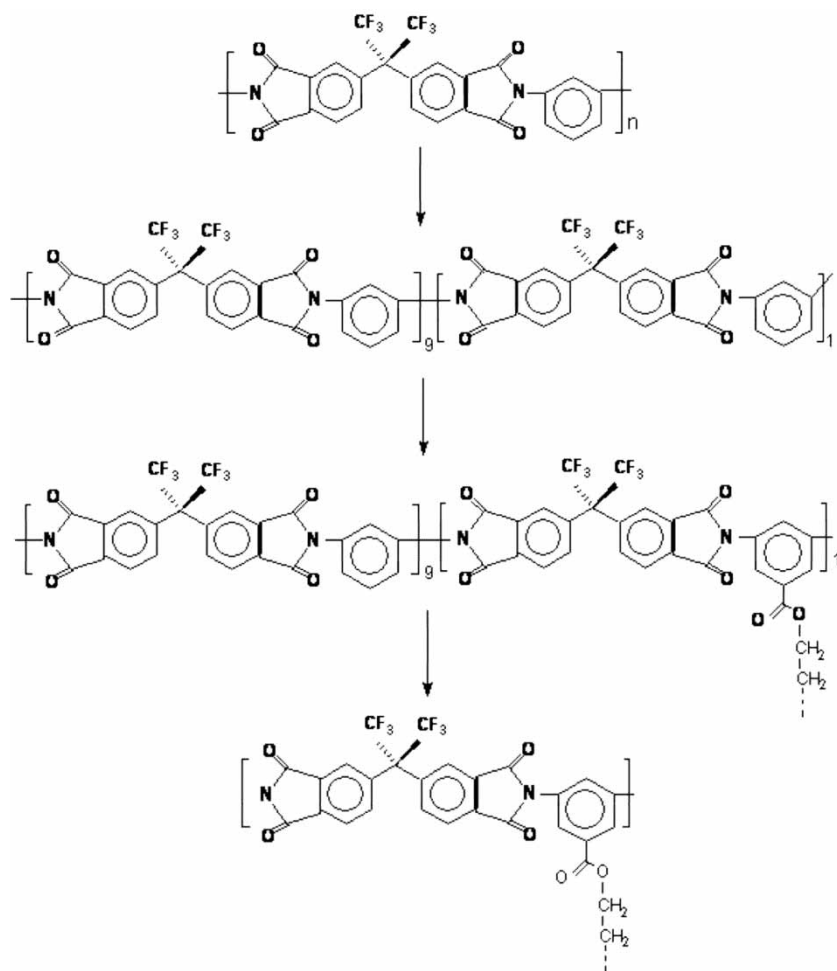


Figure 9. Synthesis of cross-linked and non-cross-linked 6FDA-based polyimides and copolyimides; (a) 6FDA-mPD, (b) 6FDA-mPD/DABA (9:1), (c) 6FDA-mPD/DABA (9:1) cross-linked and (d) 6FDA-DABA (cross-linked). Reprinted from (91) with permission from Elsevier.

Koros (91) observed 45% enhancement in CO_2 permeability of chemicals cross-linked copolyimide when compared to that of the non-cross-linked one. The relationship between the overall CO_2/CH_4 selectivity and the permeability to CO_2 for the crosslinked and the uncrosslinked 6FDA copolyimides is shown in Figure 10. The separation properties of uncrosslinked copolyimides lie close to other “upper bond” polyimides, whereas cross-linked copolyimides show enhanced performance with higher selectivities and permeabilities.

Wind et al. (90) studied the performance of cross-linked polyimides (6FDA-DAM:DABA and 6FDA-6FpDA:DABA copolymers) for CO_2/CH_4

separation and observed the performance to this covalently cross-linked polyimide to lie near the pure gas upper bound performance line, despite the measurements being done for high pressure mixed gas separations, which is a representation of practical feed streams. Their results indicated that a simple covalent cross-linking approach is more effective for stabilizing membranes against CO₂ plasticization and render these materials more stable than the commercial membrane materials such as cellulose acetate (167) and Matrimid (168), which have more attractive CO₂/CH₄ separation properties. The performance of their cross-linked polyimide as against the commercial representation is shown in Figure 11 (90).

Matrimid Based Membranes

Matrimid 5218, manufactured by Ciba-Geigy, is a soluble thermoplastic polyimide, which consists of 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and diaminophenylindane (DAPI) (168). In the synthesis of DAPI monomer, two isomeric products are obtained. The final polyimide is therefore, a mixture of 6-amino and 5-amino isomers of DAPI, but Matrimid (113) is not as permeable as 6FDA-polyimides of interest. However, in the same way as 6FDA-polyimides, matrimid-based polymers have a high tendency to plasticize and are therefore, the useful candidates to demonstrate possible effects of suppressing plasticization.

Organic-inorganic hybrid materials consisting of highly selective rigid phases such as carbon molecular sieves dispersed in a continuous polymeric matrix also are another set of potential candidates for challenging membrane applications (112, 113, 116). One approach for generating organic-inorganic hybrids is based on the tethering of organic compounds to the porous surfaces of inorganic substrates. The chemical modification of inorganic substrates to form self-assembled monolayers (SAMs) has been a field of interest for number of applications such as wetting, electrochemistry, bioactive surfaces and catalysis (120, 152). With the "mixed matrix composite" membranes, it is possible to achieve highly improved membrane properties without sacrificing the ease of membrane formation associated with the conventional polymers. Of late, greater attention has been focused on inorganic membranes as they show absolute selectivity for gas separation. However, results and discussions pertaining to separations using purely inorganic membranes is beyond the scope of the present review.

Commercially Available Membranes

Membranes have been successfully commercialized by many companies (169–173). From the list of companies that supply membrane modules for gas separations summarized in Table 10, one can view that industries that have achieved success in commercializing the membrane technology for

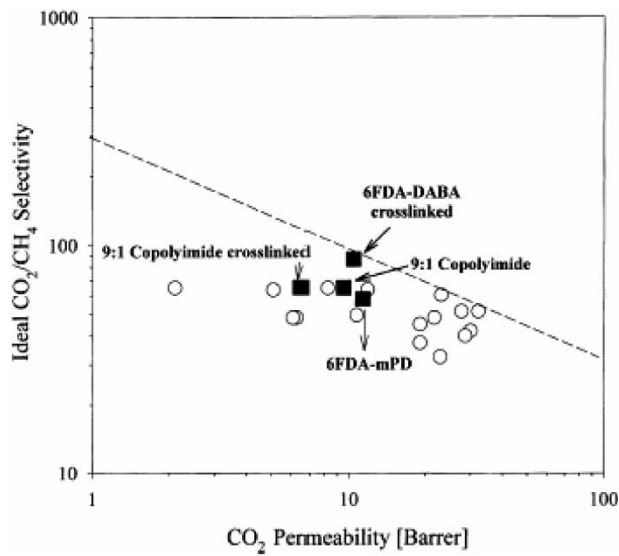


Figure 10. Relationship between the overall CO₂/CH₄ selectivity, and the permeability to CO₂ for the cross-linked and the non-cross-linked 6FDA copolyimide. Reprinted from (91) with permission from Elsevier.

separation of gases are still scarce. Even though commercialization achieved by industries for air separation competes with that of CO₂ separation, commercialization is not significant enough in developing and underdeveloped countries. For the acceleration of this technology, considerable amount of

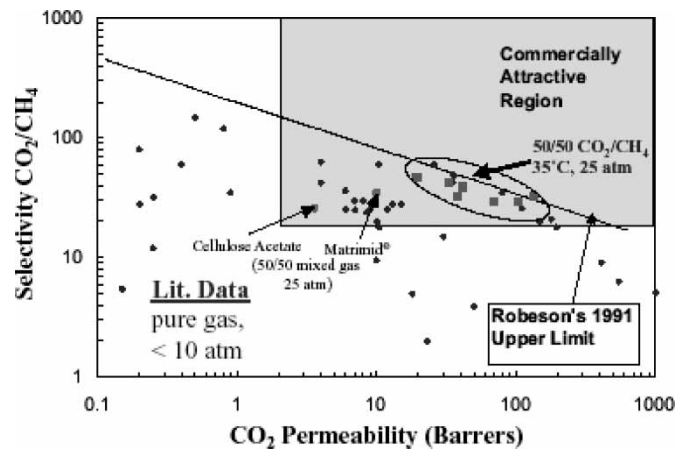


Figure 11. CO₂/CH₄ upper bound plot for DABA-containing polyimides cross-linked with various diols, compared to the commercial gas separation polymers cellulose acetate (167) and Matrimid®. Reprinted from (90) with permission from Elsevier.

developmental activities, both academic and industrial, are essential. Academicians can support the development of demonstration projects that showcase the membrane-based separation technology, validate product reliability and output, to provide data necessary for commercialization. Industry, on the other hand, can engage in standardizing the module configuration and increasing production volumes, which can result in the reduction of production costs.

MEMBRANE FORMATION

Critical Fabrication Factors

Membrane fabrication properties are quite important in the development of a successful commercial gas separation membranes. Literally speaking, any environmental factor that affects the membrane structure will in turn have an influence on permeability, selectivity and physical properties. Literature points towards number of variables that have significant impact on gas separation properties (174, 175). These include polymer type, purity, molecular weight, solvent strength, solvent volatility, concentration of residual solvent, temperature of casting surface, relative kinetics, enriching solvent and its type, etc. Depending on the casting surface, polymeric properties can be varied. It has been noted that the membranes cast on a glass plate

Table 10. Commercial scale gas membrane suppliers

Company	CO ₂	H ₂ S	H ₂	Air NO ₂	N ₂
A/G Technology (AVIR)	X	—	—	X	X
Air products (Separex)	X	—	X	—	—
Asahi Glass (HISEP)	—	—	—	X	X
Cynara (Dow)	X	—	—	—	—
Dow (Generon)	—	—	—	X	X
Dupont	—	—	X	—	—
Grace Membrane Systems	X	—	X	—	—
International Permeation	X	—	—	—	—
Monsanto	X	—	X	X	X
Osaka Gas	—	—	—	X	—
Oxygen Enrichment Co.	—	—	—	X	—
Techmash export	—	—	—	X	—
Toyobo	—	—	—	X	—
Ube Industries	—	—	X	—	—
Union Carbide (Linde)	—	—	X	X	X
UOP / Union Carbide	—	—	X	—	—
Delta Projects Ltd.	X	—	—	—	—
Envirogenics System Co.	X	—	—	—	—
ENSTAR Engineering Inc.	X	X	—	—	—

will result in tougher and rigid films when compared to the ones cast on mercury. Sometimes, during manual casting or machine casting, orientations get introduced in the flow direction of solution, which can influence the subsequent alignment of the macromolecular coils, nodules or nodule aggregates. On the other hand, films cast on liquid surfaces are not subjected to orientation and hence, become isotropic and exhibit lower strengths (176).

Both isotropic and aggregated films experience structural variations occurring on account of solvent-based differences. The presence of water vapor (a non-solvent for polar polymers) in the air above the desolvating films hastens the gelation process, thereby resulting in increased free-volume and micropore size. Various strategies for controlling orientation and compactness/stretching of the free volume of the films include annealing, plasticization and ageing (177–180). Annealing of polymeric films improves the packing density, thereby reducing free volume and hence, the permeability. Reduction in free volume can also be accomplished by solvent exchange and drying, physical ageing and plasticization. The afore-mentioned techniques have profound effects on gas selectivity. Thus, an appropriate control on critical fabrication properties is essential to attain the defect-free membrane modules.

Membrane Module

The heart of any membrane plant is the module, i.e., the technical arrangement of membranes. Some important aspects to be considered for module design include packing density, cost-effective manufacture, easy access for cleaning and cost effective membrane replacement. Based on these considerations, modules can be distinguished into four major classes as discussed next.

Tubular Module

The tubular membrane is in the hose form on the inside of pressure-tight tubes having 12–24 mm internal diameter (Figure 12) (181–183). If the material of

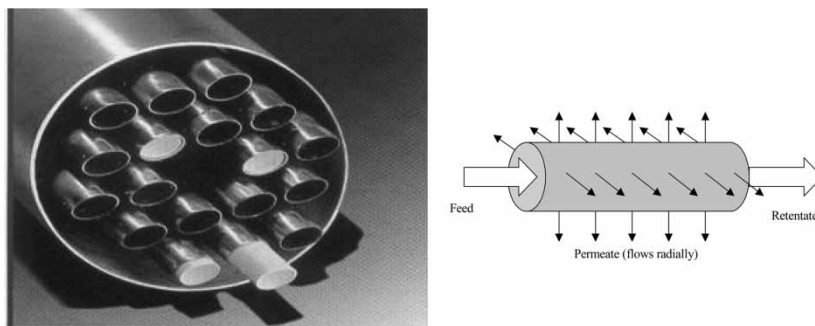


Figure 12. Tubular membrane module. Reproduced with permission from Genesis Membrane Sepratech Pvt. Ltd., Mumbai, India



Figure 13. Capillary membrane module.

the support tube is impermeable, then a thin porous tube is fitted between the support tube and the membrane. In many cases, several tubular membranes are assembled in a common support block to increase the packing density. Even though the manufacturing costs of these modules are high, they offer excellent resistance to fouling with low pressure-drop, but are not suitable for high-pressure operations.

Capillary Module

The capillary module has a tube bundle of fibers arranged parallel to each other with either end attached to a head plate (Figure 13). The active layer is usually on the inside of the capillary, which means that feed flows inside the capillaries and permeate is collected at the outside. This module has a high packing density with a higher mass transport resistance as compared to all other modules, due to predominant laminar flow (184). Capillary module offers moderate pressure-drop, but is not suitable for high-pressure operations.

Hollow Fiber Module

This module consists of a pressure vessel containing a bundle of individual fibers (Figure 14). The active layer is usually coated on the outer surface of the fiber, which is in contact with feed and permeate flows inside the fibers. Open ends of the fibers are potted into a head plate and the feed solution flows radially or parallel to the hollow fibers. Permeate is collected at the open end of the fibers and hence, parallel flow can be co-current or counter-current, depending upon the direction of permeate flow with respect to feed. Literature shows that counter-current flow is always superior to co-current flow in parallel flow conditions (185, 186). The module lends the membrane higher packing density, thus enabling the production of modules at a lower cost per unit product.

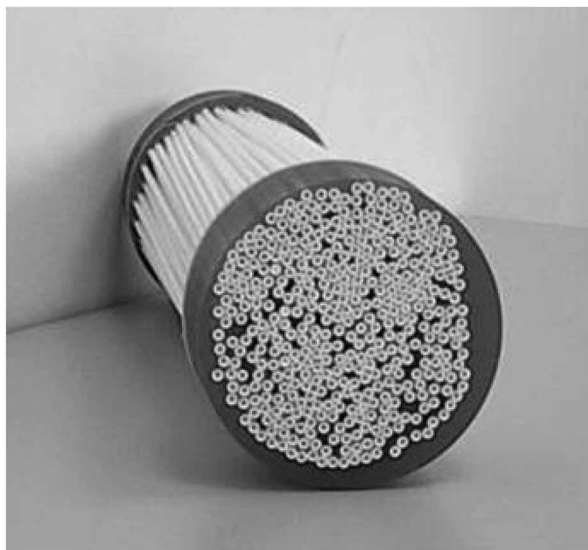


Figure 14. Hollow fiber membrane module.

The fabrication of polymeric membranes commonly involves a phase inversion process, wherein a polymer solution is extruded through an annular die and contacted with a non-solvent (i.e., water) (187). The diffusion of water into polymer solution causes phase separation by yielding polymer-rich phase and solvent-rich phase. The solvent-rich phase contains water, which can then be extracted from the resultant porous hollow fiber membrane. If an air gap exists between the exit of the die and coagulation bath, a thin dense skin layer of the order of 100 nm or even less will exist on the top of a porous and highly permeable polymer support. In order to assure pinhole-free hollow fibers, various coating and repair techniques can be employed as noted by Henis and Tripodi (188). The hollow fibers are then assembled into a cylindrical module with both ends of the fiber bundle encapsulated in a thermosetting polymer (e.g., epoxy). The gas mixture to be separated can then be introduced on the outer area of the fiber bundle and in some cases, the gas mixture is introduced to the bore of the fibers. The construction of these modules and their operation is discussed in detail by Kesting and Fritzche (189). Of late, this module has attracted the attention of many researchers for the effective separation of gaseous mixtures.

Spiral Wound Module

These are characterized by high packing density ($>900 \text{ m}^2 \text{ m}^{-3}$) and a simple design. Essentially, two or more membrane pockets are wound around a centrally located permeate collecting tube with a special mesh used as the

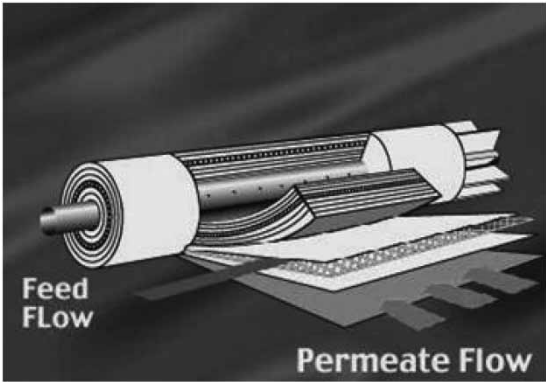


Figure 15. Spiral wound membrane module. Reproduced with permission from Genesis Membrane Sepratech Pvt. Ltd., Mumbai, India

spacer (Figure 15). The membrane pocket consists of two membrane sheets with a highly porous material in between, which are glued together along the three edges. The fourth edge of the pocket is connected to the collecting tube. Several such pockets are spirally wound around the perforated permeate tube with a feed-side spacer placed between the pockets (190). Usually, several such membrane elements are arranged in one pressure vessel. The feed side flow is strictly axial, while the permeate flows through a porous support inside the pocket along the spiral pathway to the collecting tube (191, 192). Table 11 provides a comparison of different membrane modules in terms of diameter, packing density, relative cost and ease of cleaning.

Module Design

The cost of membrane systems is greatly influenced by their design. Membrane modules can be put together in one stage or multistage designs. Each stage consists of a bank of membrane modules arranged in parallel or series. For relatively low flow rate applications, a single-stage membrane

Table 11. Comparison of membrane modules

Type	Tubular	Capillary	Hollow fiber	Spiral wound
Diameter	5–15 mm	0.5–5 mm	< 0.5 mm	50–200 mm
Packing density, m ² /m ³	30 to 200	600 to 1200	500 to 9000	200 to 800
Ease of cleaning	Excellent	Fair	Poor	Fair
Relative cost	High	Low	Low	Low

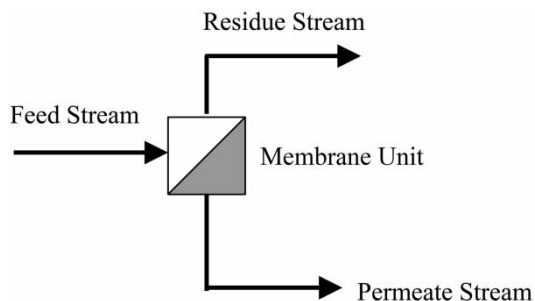


Figure 16. Schematics of single-stage flow.

system provides the most economical result (193). As the size of the process and/or the value of desired compound increases, more complex designs are needed.

Single-Stage Membrane System

A single stage unit is the simplest application of membrane technology for CO₂ removal from natural gas. Figure 16 is a typical schematic representation of a single-stage membrane system having a feed stream, which has been pre-treated and enters the membrane module, preferably at high system pressure and high partial pressure of CO₂. High-pressure residue is delivered for further processing or to the sales gas pipeline. Low-pressure permeate is vented, incinerated or put to use as a fuel gas with low-to-medium heating value. There are no moving parts, so the system works with minimal attention from an operator. As long as the feed stream is free of contaminants, the elements last easily for 5 years or more, making the system extremely reliable and inexpensive to operate (194, 195). Since no membrane acts as a perfect separator, some of the slower gases permeate through the membrane, resulting in hydrocarbon loss. This is the main drawback of single-stage membrane system. In order to recover hydrocarbons that would otherwise be lost in the permeate stream, a two-stage system can be employed (Figure 17).

Two-Stage Membrane System

Permeate from the first stage, which may be moderately rich in hydrocarbons, is compressed, cooled and sent to a second stage of pretreatment to remove the entrained lube oil and provide temperature control. A second stage membrane is then used to remove CO₂ from the stream prior to recycling the residue gas to the first stage membrane. The investment and operating cost of a two-stage system can be substantially higher than a single-stage unit, due to the use of

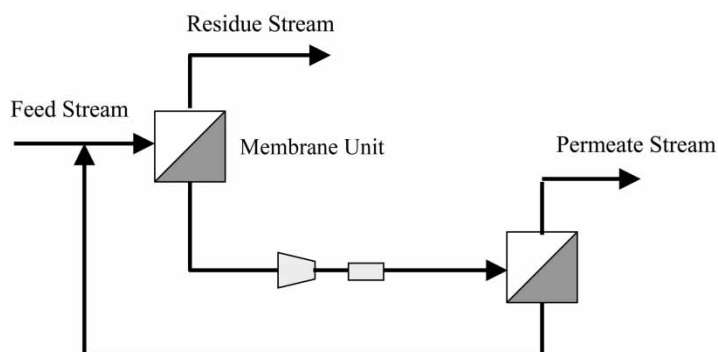


Figure 17. Schematics of two-stage flow.

compression. It should be noted that this compression does not require any spare capacity (196). The first stage in this flow scheme will continue to produce specification CO₂ at full capacity even if the second stage is off line. There would be a temporary increase in hydrocarbon loss until the recycle compressor is put back on the line. This operating penalty is typically small as compared to the cost of spare compression.

Similar improvements can be made to these process flow schemes to improve performance and reduce the capital cost. When deciding whether to use a single-stage or a multistage system, many factors must be considered. An economic analysis is generally advisable to ensure that the cost of installing and operating a recycle compressor does not exceed the savings in hydrocarbon recovery.

Economic Feasibility

The economic comparison between membrane systems and the competing technologies indicates that membranes are most cost-effective in applications where high CO₂ concentration, e.g., 10–70% and/or low flow rates are encountered. Babcock et al. (197) compared single and multistage membrane systems with amine treatment for a wide range of operating conditions. They concluded that membranes are economical compared to the amine process over a wide range of feed flow rates and acid gas concentrations. Purgason et al. (198) compared the performance of a single-stage membrane with DEA and membrane systems and concluded that membrane system costs 24% less than the DEA process. Table 12 compares the amine and membrane CO₂ removal system in terms of cost. It can thus be said that gas purification using membrane separation is more economical (199–202) due to low energy requirements, ease of operation and high recovery rates. Also, membranes are inherently easier to operate than an amine unit because there are fewer unit operations. Readers seeking further in-depth

Table 12. Comparison of amine and membrane CO₂ removal systems in terms of cost [adapted from (198)]

Type	DEA amine	Membrane	Membrane/ DEA hybrid
Relative capital cost	1.0	0.26	0.72
Relative operating cost	1.0	1.51	1.14
Relative net present cost at 15%	1.0	0.76	0.89

information on membrane module design and staging can refer to an interesting review by Tabe-Mohammadi (203).

CURRENT CHALLENGES AND FUTURE OUTLOOK

Considering the discussions and status noted here, it may be stated that even though researchers have attempted to synthesize/use different varieties of membranes for the effective separation of CO₂, some restrictions for its applications still exist (204). Few of the prominent cases and potential routes to overcome these drawbacks are discussed.

Development of Advanced Membrane Material

As discussed earlier, permeability and selectivity of a membrane are the deciding factors in separating gaseous mixtures. Molecular sieve and selective surface flow membranes, also represent the “revolutionary” sorption-diffusion materials, that could ideally open up many new opportunities for higher performance and convenient separations that are not achievable with today’s membrane forming materials (205–210). Ultimately, for each separation, one can consider using pure or modified polymers. However, the penetrant size and shape-discriminating ability will be limited by the flexibility of a polymer itself. Therefore, the development of a potential polymer still remains as the key research area in membrane technology. The aim in the development of new membranes is either to increase the permeability, keeping the selectivity constant or aiming for higher selectivities at constant permeability or both. Few of the prominent approaches are:

- Synthesizing facilitated transport membranes to enhance selectivity.
- Developing mixed matrix materials to improve permeability without loss in selectivity.
- Cross-linking the mixed matrix membranes to attain enhanced permeability and selectivity.

- Blending inorganic materials with mixed matrix materials to achieve high permeability and selectivity.
- Developing new polymer structures for high performance.

Of the probable approaches and likely improvements suggested here, the first two approaches have received considerable attention and are discussed in detail.

Development of Polymeric Fixed Site Carrier Membrane for Selective CO₂ Capture

As an alternative to conventional polymeric membranes, facilitated transport membranes have attracted much attention because of the potential of achieving both high permeabilities and high selectivities. Facilitated transport membranes may selectively permeate CO₂ by means of a reversible reaction of CO₂ with an incorporated complexing agent (carrier) in the membrane. These fixed-site-carrier (FSC) membranes contain compounds that are covalently bonded to polymeric backbone and hence, the carriers have restricted mobility, but are favorable when stability is considered. It is obvious that diffusivity (and thus, permeability) in an FSC membrane is lower than that of a mobile carrier membrane. The mechanism of transport, as suggested by many researchers, is that CO₂ will be transported as carbonate or bicarbonate anions in anion exchange membranes and as anions of various amines in cation exchange membranes.

Notice that grafting of polymers or monomers containing amine groups onto rigid polymers, such as polyimide or cellulose acetate, may render enhanced transport of CO₂ across the membrane cross-section, thereby resulting in enhanced permeabilities without significant reduction in selectivities. The facilitated transport of CO₂ through ethylenediamine (ED) fixed sodium alginate (SA) membrane was investigated by Kim et al. (211). The main reaction of ED with carbon dioxide in the membrane as suggested by Kim et al. is illustrated in Figure 18. The authors noted that increase in the duration of immersion (from 0–24 hrs) of the SA membranes resulted in an increase in the permeability from 129 Barrers to 342.3 Barrers. Furthermore, an increase in EDA concentration (from 0–5 mmol/g) in the membrane brought about an increase in CO₂ selectivity of 7.8 to 24.7 along with a sudden rise in its permeability. Alternately, crosslinking the available polymers (that will yield high permeability and moderately good selectivity) with the competent agents such as for instance, epichlorohydrin can result in the deposition of active amine groups onto the side chain of the polymer, which may aid CO₂ transfer.

Synthesis of Mixed Matrix Membranes for Optimization of Flux and Selectivity

Pure inorganic and carbon membranes (212) offer ways to overcome such separation performance limitations, but as noted here, manufacturing cost and

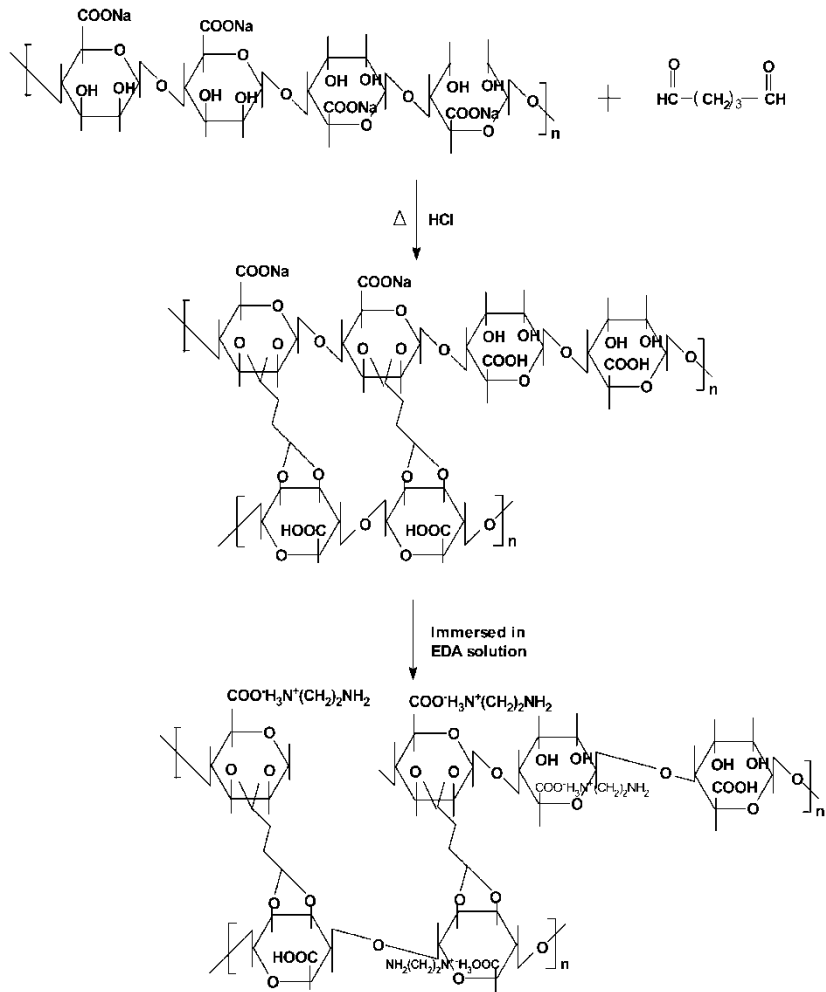


Figure 18. Schematic representation of ethylene diamine-fixed sodium alginate membrane. Reprinted from (211) with permission from Elsevier.

durability are the two major drawbacks, except in small-scale operations. However, an evolutionary approach involving hybrid materials comprising blends of organic and inorganic materials can be formulated to combine the best characteristics of both the components. Incorporation of sub-micron level particles of metal(IV) oxides or phosphates such as zirconium phosphate (ZrP), doping of solution containing M(IV) ions within an appropriate polymer matrix such as polyethyleneimine, can offer advantages such as: (i) decline in the plasticization of membrane material, resulting due to proper mixing of inorganic and organic components at the molecular level, thereby offering

good mechanical stability as compared to pure organic membrane, (ii) similar costs when compared to conventional polymers, (iii) appreciable degree of improvements in permeability, especially at high temperature can be anticipated with increasing proportion of metal particles. However, the influence of metal particles on mechanical characteristics needs further investigation.

Another approach to enhance the selectivity of aromatic polymers would be incorporation of heteropolyacids (HPA), an inorganic filler. The heteropolyacids, viz., phosphotungstic acid, being highly polar in nature, will exhibit affinity towards CO₂ gas molecules, thereby enhancing the selectivity. In a recent study (213), the authors achieved 40% enhancement in selectivity using HPA-incorporated poly(phenylene oxide) (PPO) for separating CO₂/CH₄ mixtures. An alteration of this could be the doping of HPA into sulfonated aryl polymers, wherein the formation of hydrogen bond between sulfonyl groups and HPA could yield higher selectivities without any significant loss in mechanical stability. Despite these positive aspects, the feasibility in constructing practical large-scale membrane modules based on such hybrid materials involves an array of queries related to fundamental science that must be addressed substantially.

Lack of Comprehensive Understanding of Module Construction

The present inability of membranes to broadly displace the conventional technology is not purely identifying the right membrane material, but also the processing hurdles associated with the membrane materials. Indeed, expanding the membrane prototype is relatively a more challenging task than simply identifying additional materials with higher intrinsic transport performance. In fact, despite the existence of superior materials, lack of economical processes to form large modules using these materials has limited their applications in large-scale systems. Transformation of scientifically sound techniques required for processing advanced materials into commercially viable modules appears to be the most challenging task faced by the researchers of this decade. While greater chemical and thermal resistances are still the forefront requisites, the current need is higher intrinsic selectivity and more resistance to plasticization-induced losses in selectivity. Dealing with this challenge will finally enable the application of the already developed high performance materials that have depicted good results in small-scale lab tests (214–220). One way of balancing this problem would be to modify the existing commercially available cellulose acetate or polyimide membranes in modular form, a concept, which involves in-depth research.

An Insight into the Needs of Gas Processor

It is a well-known fact that the performance of both the amine and membrane-based CO₂ removal systems differs according to the natural gas being

processed, the location of the installation and the economic parameters used by the end customer. Hydrocarbon recovery and low sales specification are the important issues in natural gas purification (221). In general, the hydrocarbon losses in a single-stage membrane can run from 2% to 10% of the feed gas or more. In order to recover hydrocarbons that would otherwise be lost in the permeate stream, a two-stage system can be employed. Two-stage membrane units have typical losses ranging from 2 to 5% of the feed gas hydrocarbons, whereas the amine units do lose some feed gas hydrocarbons to a flash gas stream or the acid gas stream due to solubility and entrainment, but typical losses are less than 1% of the feed gas. This makes amine process more attractive.

Another issue that demands attention is the choice of operating pressure. The size of an amine unit is directly related to the moles of CO_2 removed from the feed gas. As CO_2 content rises from low to moderate partial pressures in the feed, the rich solvent loading increases, somewhat offsets the increased demand for solvent. However, as partial pressures increase to high levels, the solvent approaches maximum loading. At this point, the removal of excess CO_2 necessitates increase of circulation rate, which makes this process expensive. In case of membranes, permeation rate increases as the CO_2 partial pressure increases, making the membrane process much more efficient for high CO_2 feed concentrations (2). Thus, for treating gas mixtures with minimum hydrocarbon losses, a combination of both the technologies in series is the most viable option i.e., bulk removal of CO_2 is done using membranes and final clean up by amine solvent system (222). The presence of one unit eliminates the shortcomings of the other and the combined "hybrid" system becomes less expensive to build and operate, which also exhibits flexibility in handling changes in feed gas conditions. Purgason et al. (198) conducted a study on CO_2 removal systems as against the hybrid process and concluded that membrane system costs 24% less than the DEA process and 15% less than the hybrid system. Their economic evaluation is presented in Table 12.

CONCLUDING REMARKS

Among the membranes commercialized for treating natural gas, cellulose acetate derivatives and polyimides were found to be the best materials for CO_2/CH_4 separation, while poly(ether-block-amide) was the bench-mark for $\text{H}_2\text{S}/\text{CH}_4$ mixture. In most polymer membranes, separation factors for $\text{H}_2\text{O}/\text{CH}_4$ and $\text{H}_2\text{S}/\text{CH}_4$ were generally greater than those for CO_2/CH_4 , which means that high selectivity for the latter system is critical for purification of natural gas in totality. The permeability and selectivity of CO_2/CH_4 in natural gas mixtures were found to be lower than the values exhibited during binary mixture permeation due to plasticization by condensable higher hydrocarbons. Membranes were required to be fabricated in asymmetric/TFC form to achieve higher flux and lower surface area.

Within the framework of this review, it can be concluded that the membrane-based gas separation technology competes well with the established separation technologies due to its distinctive advantages. The attractiveness of the membrane systems in natural gas separations is evidenced by an increasing number of patents and publications appearing in scientific journals on this subject. In the near future, it is believed that the hybrid process of *amine* and membrane will find new opportunities, especially in tackling the challenging separation problems encountered in various industries, thereby opening up new avenues for its wide-spread industrialization.

Even though there might be some restrictions to overcome, the development of suitable membranes and the possibility of up-scaling membranes, keeping in mind the structure-property relationships of the materials, the membrane formation techniques and modular configurations that yield not only high permeabilities, but also moderately good selectivities, still deserves considerable attention, especially in separating acid gases from natural gas streams. On the other hand, ignoring this reality will cause the field to remain stagnant with scientifically outmoded materials and limited applications of membrane technology in the area.

ABBREVIATIONS

4A	Zeolite 4A
ABS	Acrylonitrile–butadiene–styrene
AC	Micro-mesoporous activated carbons
BAPAF	2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane
BDAF	2,2-bis(4-(4-aminophenoxy)hexafluoropropane
BBL	Ladder polymer derived from polycondensation reaction of 1,2,4,5-tetraaminobenzene tetrahydrochloride (TABH) with 1,4,5,8-naphthalenetetracarboxylic acid (NTCA)
BDA	1,2,3,4-Butanetetracarboxylic dianhydride
BG	1,4-Butylene glycol
BPA	Bisphenol A
BPDA	3,3',4,4'-Biphenyltetracarboxylic dianhydride
BTDA	3,3',4,4'-Benzophenone tetracarboxylic dianhydride
BuOH	Butanol
C	Cellulose
CHDM	1,4-Cyclohexanedimethanol
CM	Carbon membranes
CMS	Carbon Molecular Sieves were formed by pyrolysis of a polyimide (Matrimid) precursor
DABA	3,5-Diamino benzoic acid
DAFO	2,7-Diaminofluorenon
DAM	Trimethylphenylenediamine

DAP	2,4-Diaminophenol dihydroxychloride
DAT	2,6-Toluene diamine
DATPA	4,4-Diaminotriphenylamine
DBA	3,5-Diaminobenzoic acid
DBr	Degree of bromination
DDS	3,3'-Diaminodiphenylsulfone
DMEA	<i>N,N</i> -Dimethylaminoethyleneamine
DSDA	3,3',4,4'-Diphenylsulfonetetracarboxylic dianhydride
Dsul	Degree of sulfonation
EDA	Ethylenediamine
EtOH	Ethanol
6F	Hexafluoroisopropylidene
6FBPA	2,6-bis(fluoro bisphenol-A)
FBP/6FPPr	Poly(arylene ether)containing diphenylfluorene (FBP) and 2,6-bis(trifluoromethylphenylene)pyridine (6FPPr) groups in the main chain
FBP/6FPT	Poly(arylene ether)containing diphenylfluorene (FBP) and 2,5-bis(3-trifluoromethylphenylene)thiophene (6FPT) groups in the main chain
6FDA	2,2-bis(3,4-Dicarboxyphenyl) hexafluoropropane dianhydride
6FpDA	4,4'-Hexafluoroisopropylidene dianiline
6FDA-6FpDA	Hybrid materials based upon a 6FDA-6FpDA polyimide
6FDA-1,5-NDA	Poly(1,5-naphthalene-2,2'-bis(3,4-phthalic)hexafluoropropane) diimide
6FPPy	2,6-bis(trifluoromethylphenylene)pyridine unit (6FPPy series)
6FPT	2,5-bis(3-trifluoromethylphenylene)thiophene unit (6FPT series)
HAB	4,4'-Diaminobiphenyl-3,3'-diol
HQDPA	1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride
Hyflon AD	Amorphous fluoropolymer prepared from 80 mol% 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) and 20 mol% tetrafluoroethylene (TFE), commercially known as Hyflon AD 80
IPDA	4,4'-(Hexafluoroisopropylidene)diphthalic dianhydride
M	Mixed matrix
MAT	Matrimid
MeOH	Methanol
2MMDA	3,3'-Dimethyl-4,4'-methylene dianiline
3MPDA	2,4,6-Trimethyl phenylenediamine
NDA	Diamine
ODA	4,4'-Diaminodiphenyl ether

ODPA	Oxydiphthalic dianhydride
P3AcET	Poly(3-(2-acetoxyethyl)thiophene)
PAMAM	Polyamidoamine
<i>m</i> PD	<i>m</i> -Phenylene diamine
PDA	<i>m</i> -Phenylene diamine
PDBA	Phenyldiboronic acid
PDMS	Polydimethylsiloxanes
PDTBP	Poly[bis-(3,5-di- <i>tert</i> -butylphenoxy) _{1.2} -(chloro) _{0.8} phosphazene]
PEI/PEG/NMP	Polyethyleneimine/polyethylene glycol/ <i>n</i> -methyl Pyrrolidone
PEK-A	Alkyl-substituted polyaryletherketone
PEK-C	Cardo polyaryletherketone
PEK-H	Hydrogen-bonded polyaryletherketone
PEKK-C	Cardo polyaryletherketoneketone
PES	Polyethersulfone
PFDA	2-(Perfluorohexyl)ethyl-3, 5-diamino benzoate
PFS/PF6F-H	Poly(aryl ether ketone)s with/without 6F in the backbone
P3HET	Poly(3-(2-hydroxyethyl)thiophene)
PI	Polyimide
PMDA	Pyromellitic anhydride
PPO	Poly(2,6-dimethyl-1,4-phenyl oxide)
PPOBr	Brominated PPO (%DBr = 20)
PPOP	Poly[bis-(phenoxy)phosphazene]
PrOH	Propanol
PS	Polystyrene
PSVP	Poly[styrene-co-(4-vinyl-pyridin)]
PTBP	Poly[bis-(4- <i>tert</i> -butylphenoxy)phosphazene]
PVC	Polyvinylchloride
PVDC	Polyvinylidenechloride
PVDF	Polyvinylidene fluoride
PVP	Poly(<i>N</i> -vinylpyrrolidone)
PVSA	Poly(<i>N</i> -Vinyl- <i>y</i> -sodium aminobutyrate)
PVTMS	Polyvinyltrimethylsilane
PVTMS-PANI	Composite films based on the polyvinyltrimethylsilane (PVTMS) with polyaniline (PANI) coating
SiO ₂	Silicon-dioxide
SPPO	Sulfonated poly(phenylene oxide)
SPPOBr1	Sulfonated brominated PPO (% DBr = 20; % Dsul = 10)
SPPOBr2	Sulfonated brominated PPO (% DBr = 37.4; % Dsul = 7.8)

SPPOBr3	Sulfonated brominated PPO (% DBr = 60; % Dsul = 8.7)
SPPO-Li ⁺ / Mg ²⁺ , Al ³⁺	Metal ion incorporated SPPO
TAB	1,2,4,5-Tetraaminobenzene tetrahydrochloride
TADPO	3,3', 4,4'-Tetraaminodiphenyl ether
TAP	2,4,6-Triaminopyrimidine
TAPA	Triamine monomer, tris(4-aminophenyl)amine
TrMPD	2,4,6-Trimethyl-1,3-phenylene-diamine
13X	Zeolite 13X

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