Review Article

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Aromatic polyamide nonporous membranes for gas separation application

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Abstract: Polymer membrane-based gas separation is a superior economical and energy-efficient separation technique over other conventional separation methods. Over the years, different classes of polymers are investigated for their membrane-based applications. The need to search for new polymers for membrane-based applications has been a continuous research challenge. Aromatic polyamides (PAs), a type of high-performance materials, are known for their high thermal and mechanical stability and excellent film-forming ability. However, their insolubility and processing difficulty impede their growth in membrane-based applications. In this review, we will focus on the PAs that are investigated for membrane-based gas separations applications. We will also address the polymer design principal and its effects on the polymer solubility and its gas separation properties. Accordingly, some of the aromatic PAs developed in the authors' laboratory that showed significant improvement in the gas separation efficiency and placed them in the 2008 Robeson upper bound are also included in this review. This review will serve as a guide to the future design of PA membranes for gas separations.

Keywords: aromatic polyamide, synthesis, solubility, gas permeability, gas selectivity

1 Introduction

High-performance polymeric materials exhibit several exciting properties, such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties, that make them useful for advanced technologies. Wholly aromatic polyamides (PAs) are a class of high-performance polymers that find applications in different cutting-edge technologies, particularly in aerospace and military applications. Nevertheless, very high glass transition temperatures of PAs, mostly above their thermal decomposition temperatures, and their low solubility in organic solvents resulted in processing difficulties and restricted many of their applications. Consequently, basic and applied research is directed to enhance their processability and solubility and widen the possibility of their industrial applications (1–5).

Separation and purification of gas mixtures are necessary industrial processes in different demanding applications, such as removing carbon dioxide for natural gas “sweetening,” carbon dioxide from greenhouse gas-producing sources, oxygen enrichment from air, (6) etc. Compared to the different traditional separation processes like pressure swing adsorption, cryogenic distillation, etc., gas separation using polymer membranes offers many advantages. The ease of fabrication of polymer membranes, mechanical simplicity, energy efficiency, relatively low cost for small-scale operation, and the overall environment-friendly techniques made them a better choice (6–8). The limited thermal and chemical stability, considerable material cost for high output applications, and the inherent trade-off between gas permeability and selectivity of these polymer membranes are the significant issues that need attention (7–9). The critical paradigm for the successful application of polymer membrane for cost-effective large-scale industrial applications is to develop polymers with high permeability and good selectivity (6,7). Gas molecules permeate through the dense polymer membrane according to the solution diffusion mechanism. According to the model, the permeation of the gas molecules depends on the interaction (solubility) between the

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polymer and the individual gas molecules and on the movement (diffusion) of the gas molecule through the transient opening of the leap channels (linking between the free volume elements in the membranes) of adequate size caused by the segmental mobility of the polymer chains (10).

In short, the permeability and selectivity of the gas molecules through the polymer membrane depends on the interaction between gas molecules and the functional groups (polar groups) present in the polymer chain and also on the polymer chain packing density, which controls the fractional-free volume (FFV) in the dense polymer membrane. However, there is no strict design rule to control these parameters for obtaining an optimal gas separation (11). But, generally, it has been observed that polymers with rigid backbone induce size-based selectivity for small molecules like CO₂ and O₂ (kinetic diameter of the gas molecules, CO₂ (3.3 Å), O₂ (3.46 Å), N₂ (3.64 Å), CH₄ (3.8 Å)), and the incorporation of the bulky groups in the polymer chain, which improve the FFV by limiting the polymer chain packing, helps to enhanced superior permeability and selectivity (12). Different classes of polymers, such as poly(arylene ether)s (13–16), modified cellulose (17), and polyimides (PIs) (18–21), have been investigated for membrane-based gas separation applications. Because of their certain outstanding qualities like excellent thermal, mechanical and dimensional stabilities, and low dielectric constant values, aromatic PIs are known as promising candidate for membrane-based gas separation applications (22). However, the gas separation based on PA membranes has not gotten proper attention.

Aromatic PAs are considered high-performance materials because of their versatile chemistry, superior thermal and mechanical properties, solvent and chemical resistance, high friction resistance, and good film-forming ability, leading to increased importance in advanced technologies (1,21,23). Aromatic PAs were first introduced commercially in the early 1960s, in the form of meta-aramid (Nomex[®]) produced by DuPont and later para-aramid with much higher elastic modulus called Kevlar[®] (Figure 1). Both the polymers are commercial aromatic PAs of great economic relevance. PAs draw attention due to their superior thermal and mechanical properties. PAs are used for several applications, like protective apparel, air filtration, thermal and electrical insulation, as advanced composites in the aerospace and armament industry. However, difficulties in their processability and solubility due to strong interchain hydrogen bonding that result in dense polymer chain packing restricted their use for the industrial membrane-based gas separations (24).

Figure 1: Structures of the aromatic PAs, Nomex, and Kevlar.

This review is intended to address in detail the PA membranes used for gas separation applications. We will focus on their structural modifications, i.e., strategies employed to overcome their processability issue and improve their gas separation properties.

2 PA synthesis

PAs are generally synthesized by condensation polymerization of an aromatic diamine and an aromatic dicarboxylic acid/acid chloride. The synthesis of PAs by different pathways is discussed below.

2.1 Low-temperature polymerization

It is the most common method of preparation of PAs. In this method, diacid chlorides react with diamines at low temperatures (from –10°C to 0°C). This method is generally preferred when acid chloride of the corresponding aromatic diacid monomer is easily obtained (Scheme 1). The solvents used are polar aprotic solvents like *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP). Salts, such as CaCl₂ and LiCl, are often used as solubility promoters because the cations interact with the amide groups, diminishing the interchain hydrogen bonding. During this process, the main difficulty faces the moisture sensitivity of the diacid chlorides, which is required in high purity to obtain the high-molecular-weight polymers (25,26).

Scheme 1: Low-temperature solution polycondensation of diamine and diacid chloride.

2.2 High-temperature polymerization

Yamazaki and Higashi developed this high-temperature polymerization method (27). The condensation reaction occurs directly between diacids and diamines at higher temperatures (from 80°C to 100°C) in the presence of polar aprotic solvents like DMAc, DMF, and NMP. Pyridine and triphenyl phosphite were used as a condensing agent. Also, salts such as CaCl_2 and LiCl are used as solubility promoters. Yamazaki and Higashi proposed that the polymerization proceeds via the formation of an intermediate acyloxy *N*-phosphonium salt of pyridine, as shown in Scheme 2 (27).

Recent efforts have been directed to reduce the polymerization time by applying microwave heating (2 min) instead of the conventional one (4 h) (28). Also, investigations are going on to replace organic solvents like NMP with the “green solvents” like ionic liquids (ILs), which have low vapor pressure, high thermal stability, and high polarity to dissolve the PAs (29).

2.3 Interfacial polycondensation techniques

Interfacial or two-phase polycondensation is one of the promising paths for PA synthesis, and it is a modification of Schotten–Baumann reaction. In this route, monomers are dissolved and reacted in a single solvent path (Scheme 3). Two fast-reacting intermediates dissolved in two immiscible solvents; generally, one of them is water. Usually, the water phase contains an inorganic base for neutralizing acid by-product, and this phase also has the diamine. The other phase includes acid chloride dissolving in organic solvents like hexane, toluene, and dichloromethane. The monomers react at the interface, so the two-phase system was stirred

Scheme 2: Mechanistic overview of the high-temperature polyamide synthesis.

Scheme 3: Interfacial polycondensation of diamine and diacid chloride.

vigorously to obtain a high-molecular-weight product. Low temperature is required to control the side reactions, and the polymers that are unstable at a high temperature can be synthesized (30,31). But the main problem with this technique is the broad molecular weight distribution of polymers, making them unfit for fibers or film fabrication.

2.4 Polycondensation of *N*-silylated diamine and diacid chlorides

In most of the synthetic efforts, high-molecular-weight PAs were prepared by the activation of diacids. Still, it is one of those few methods which report the activation of diamine for polymer preparation. In this method, diamine can be activated by the reaction with trimethylsilyl chloride. High-molecular-weight polymers were obtained at low temperatures (from -10°C to -5°C) by the polycondensation of *N*-silylated aromatic diamines and aromatic diacid chlorides (32). This technique involves a subsequent two-step nucleophilic addition–elimination mechanism to react to the acyl-substitution of an acid chloride with an *N*-silylated amine (Scheme 4) (33). *In situ* preparation of polymer was reported by Lozano *et al.*, and it is done by the addition of trimethylchlorosilane and diamine to the diacid chloride (21,34).

2.5 Polycondensation of diisocyanates and dicarboxylic acid

The aromatic PAs are prepared by the reaction (at $\sim 60^\circ\text{C}$) of aromatic diisocyanates and dicarboxylic acid (35,36). This method involves the elimination of CO_2 , and no condensing agent has been used. So various PAs and co-PAs have been synthesized by this method (29,37) (Scheme 5).

Scheme 4: Polycondensation of *N*-silylated diamine and diacid chlorides.

2.6 Polycondensation of aromatic diamines, dihalides, and carbon monoxide

The preparation of PAs is also reported by the reaction (at ~115°C) of aromatic diamines, dihalides, and carbon monoxide in the presence of transition metal catalysts (Pd catalyzed carbonylation coupling of diamines and dihalides; Scheme 6) (21,38). The technique has benefits over the diacid chloride–diamine route due to the ready accessibility of aromatic dibromides and synthesizing of various aramids (38).

3 Structural modifications to improve the processability and gas separation properties

PAs have superior thermal and mechanical properties, making them attractive for different applications, as discussed earlier. However, their processability difficulties hampered their high-end applications. It is difficult to produce thin films out of the PAs or use it for coating because of the PAs' low solubility in almost all solvents except for concentrated sulfuric acid. The strong and highly directional hydrogen bonding between the PAs' amide linkages and their aromatic structure results in a high-level intermolecular packing and cohesive energy which is responsible for their inferior processability (1). Besides, the PAs, owing to their structural properties,

Scheme 6: Transition-metal catalyzed carbonylative coupling of diamines and dihalides.

exhibit extremely high softening and melting temperatures, resulting in their decomposition during or even before melting, ultimately affecting their processability (39). Different strategies have been employed to hinder the chain packing and improve the PAs' flexibility to enhance their solubility without sacrificing their outstanding thermal and mechanical properties to make them suitable for membrane-based gas separations.

Incorporation of flexible spacers like $-\text{O}-$, $-\text{C}(\text{CF}_3)_2-$, $-\text{CH}_2-$, and $>\text{C}=\text{O}$ into the PA backbone improves their solubility (1). Ferreiro et al. reported the synthesis of several polyisophthalamides by the reaction of three aromatic diamine monomers with four new diacid monomers having oxyethylene groups (40). All the synthesized polymers were soluble in organic aprotic solvents even at room temperature, so processable films were obtained by casting from the respective solutions. The introduction of bulky pendant moiety in the polymer matrix is a fruitful way to improve the solubility of PAs without affecting their positive characteristics (1). Sizeable bulky groups hinder close packing between the polymer chains, which inhibit H-bonding; thus, interchain distance increases as well as free volume solubility increases. Yang et al. reported the synthesis of a series of aromatic PAs from different 2-*tert* butylbenzene-substituted diamine and diacid monomers (41). Introducing *tert*-butyl and aryl ether groups in polymer matrix improves their solubility with retention of their thermal properties. Yagci and Mathias synthesized aromatic PAs by the reaction of 2,5-di-*tert*-butylbenzene substituted diamine with several diacids and the polymers were soluble in polar aprotic solvents like DMSO, NMP, and DMAc (42).

Scheme 5: Polycondensation of diacids and diisocyanates.

4 PAs with bulky side substituents and cardo groups

Incorporating the different bulky cardo groups in the backbone of PAs improves its solubility and made it

possible to process membranes from it for membrane-based gas separation applications. Besides, the cardo groups disrupt the polymer chain packing and enhance the polymer chain's rigidity, which resulted in improved gas permeability and selectivity. This section will discuss the effect of the specific cardo groups on the gas permeability of PAs.

Polymers bearing fluorinated groups are of great interest to the material chemists because their presence causes noteworthy improvements in individual polymers' properties compared to their corresponding non-fluorinated analogs. The combination of electronic and steric effects fluorinated groups reduces the interchain interactions and hinders the closer packing of the polymer chains resulting in improved solubility of the polymers (43,44). The C–F bond is a high-energy bond, and the PAs containing fluorine showed excellent thermal properties with enhanced solubility, comparable to those of the conventional aromatic PAs. Incorporation of fluorine as trifluoromethyl ($-\text{CF}_3$) (3F) or hexafluoroisopropylidene ($-\text{C}(\text{CF}_3)_2-$) (6F) groups in the polymer affects several of the polymer properties (43):

- Increases solubility and processability,
- Increases thermal stability,
- Decreases dielectric constant,
- Increases FFV, which resulted in high gas permeability,
- Decreases moisture absorption as well as stability of the polymer membranes.

The greater steric volume of the fluorine relative to hydrogen explained the increase in the polymer's free volume, which may interfere with efficient chain packing. Moreover, the mutual repulsion between fluorine atoms on different chains may increase the free volume by decreasing the close packing. These excellent balances of properties have made fluorinated polymers very attractive for advanced applications, such as in polymeric membranes for gas separation and pervaporation applications, thermally stable coatings and films, and high-performance structural resins (15,18,44–49). A library of fluorinated monomers (3F group) has been reported in the literature as suitable reactants for fluorinated PA preparation (45,50–56). The bulky 6F and *tert*-butyl [$-\text{C}(\text{CH}_3)_3-$] groups were used extensively to improve the PAs' processability and gas permeability.

Freeman *et al.* reported a series of PAs (namely, IP/ SO_2 , TBI/ SO_2 , and PII/ SO_2) with different bulky substituents (57). They have prepared the PAs by the reaction of different isophthaloyl chlorides without or with substitution in the fifth position (*tert*-butyl and phthalimide moiety) and 4,4'-diaminodiphenylsulfone (Figure 2). The

	X	R
IP/6F	H	$-\text{C}(\text{CF}_3)_2-$
TBI/6F	$-\text{C}(\text{CH}_3)_3$	$-\text{C}(\text{CF}_3)_2-$
Ph/6F		$-\text{C}(\text{CF}_3)_2-$
IP/ SO_2	H	$-\text{SO}_2-$
TBI/ SO_2	$-\text{C}(\text{CH}_3)_3$	$-\text{SO}_2-$
PII/ SO_2		$-\text{SO}_2-$
Ph/ SO_2		$-\text{SO}_2-$

Figure 2: Structure of the polyisophthalamides containing different bulky pendant groups (57,59,60).

reported PAs were amorphous due to the disruption of the polymer chain packing caused by the presence of bulky groups. The PA containing *tert*-butyl group was soluble in DMAc, whereas the phthalimide moiety containing polymer was soluble in 1:1 mixture of DMAc and DMSO. The PAs containing the bulky substituents showed higher gas permeability than the unsubstituted analog (Table 1). Generally, in a series, the gas permeability increases with an increase in the substituents' bulkiness. However, the polymers containing the bulkier phthalimide moiety showed lower gas permeability, which has the highest volume of van der Waals ($69.40 \text{ cm}^3/\text{mol}$), than the less bulky *tert*-butyl group ($44.35 \text{ cm}^3/\text{mol}$) (58). The lower gas permeability of the phthalimide moiety containing PAs is attributed to their polarity induced by enhanced chain packing (higher polarity of the phthalimide moiety). The chain–chain enhanced cohesive energy negates the chain disruptive nature of the bulky phthalimide moiety. In a similar vein, Freeman *et al.* also prepared PAs, aromatic polyisophthalamides (PIPAs) (IP/6F, TBI/6F, IP/ SO_2 , TBI/ SO_2 , PII/ SO_2) bearing hexafluoroisopropylidene linkages in the main chain and modified their structure by the incorporation of the *tert*-butyl pendant group at the fifth position of the isophthalic acid moiety (Figure 3) (59). The solubility of the PAs containing these bulky groups improved substantially. The PIPAs were soluble in a 1:1 mixture of DMSO and DMAc. They have studied the gas transport properties of these PIPAs and compared it with a similar series of PIPAs containing sulfonyl ($>\text{SO}_2$) rather than 6F moieties in the main chain to understand the effect of the 6F on the polymers' gas permeability properties. The PIPAs containing 6F moieties are more permeable but comparatively less selective than their sulfonyl analogs.

Interestingly, the $>\text{SO}_2$ and the 6F groups significantly affected the gas solubility selectivity of the PIPAs (57,59,60). Considering the concentration of the polar

Table 1: Fractional free volume (FFV), glass transition temperature (T_g), and gas permeability (P) (in Barrers) and permselectivity (α) values of the polyisophthalamides containing different bulky pendant groups at 35°C

Polymer	FFV	T_g (°C)	P_{CO_2}	P_{O_2}	α (CO_2/CH_4)	α (O_2/N_2)	Ref.
IP/SO ₂	0.100	323	0.78	0.19	56	6.3	(57)
TBI/SO ₂	0.110	337	8.6	2.0	32	5.4	
PII/SO ₂	0.094	350	2.1	0.44	52	7.3	
IP/6F	0.149	297	9.0	2.4	45	5.7	(59)
TBI/6F	0.153	315	42.5	11.5	23.7	4.6	
Ph/6F	0.152	311	21	5.5	27	4.6	(60)
Ph/SO ₂	0.107	328	3.2	0.75	29	5.8	

groups in this series of PIPAs, the polymers having 6F moiety showed similar CO₂/CH₄ solubility selectivity to the many other polymers containing polar carbonyl linkages. Whereas the polymers containing >SO₂ variant showed surprisingly substantially lower CO₂/CH₄ solubility. The lower solubility selectivity of the >SO₂ containing PIPAs was attributed to its efficient polymer chain packing responsible for the strong amide–amide linkage interaction. Thereby inhibiting the interaction between the polar carbonyl group of the amide linkage and the CO₂ molecule, which is responsible for the observed lower gas solubility selectivity. Also, among all the polymers in this series, PIPAs containing pendant *tert*-butyl group showed higher gas permeability with a substantial decrease in permselectivity than their structural analogs (Table 1). The fact was attributed to the disruption of the polymer chain packing due to the presence of the bulky *tert*-butyl group, which resulted in higher FFVs (0.110 for TBI/SO₂ and 0.153 for TBI/6F) in the polymers than the analogous PIPAs having no bulky pendant groups (0.100 for IP/SO₂ and 0.149 for IP/6F). Interestingly the solubility for all the gases like O₂, N₂, CO₂ and CH₄ and solubility selectivity of the O₂/N₂ gas pair were higher for the PAs containing the bulky *tert*-butyl group (e.g., S_{CO₂} = 2.35, S_{CH₄} = 12.24, S_{O₂} = 1.38, and S_{O₂}/S_{N₂} = 2.3 for TBI/6F; and

S_{CO₂} = 9.37, S_{CH₄} = 2.5, S_{O₂} = 0.6, and S_{O₂}/S_{N₂} = 1.1 for TBI/SO₂) compared to its unsubstituted analogue (e.g., S_{CO₂} = 5.26, S_{CH₄} = 1.17, S_{O₂} = 0.29, and S_{O₂}/S_{N₂} = 0.91 for IP/6F; and S_{CO₂} = 7.48, S_{CH₄} = 1.23, S_{O₂} = 0.56, and S_{O₂}/S_{N₂} = 1.0 for IP/SO₂), where S is in cm³ (STP)/(cm³ polymer atm). The enhancement of solubility was attributed to the increase in polymer FFV due to incorporating the *tert*-butyl group. However, in the case of solubility selectivity of CO₂/CH₄, the effect of *tert*-butyl group is not consistent. Whereas for the PAs having both TBI and 6F moiety (TBI/6F), an increase in CO₂/CH₄ gas solubility selectivity was observed (S_{CO₂}/S_{CH₄} = 5.2) compared to their unsubstituted analogs (S_{CO₂}/S_{CH₄} = 4.5 for IP/6F). But for the >SO₂ containing polymers, the incorporation of the *tert*-butyl group (Figure 2) resulted in a decrease in CO₂/CH₄ gas selectivity (S_{CO₂}/S_{CH₄} = 3.7 for TBI/SO₂) compared to its unsubstituted analog (S_{CO₂}/S_{CH₄} = 6.1 for IP/SO₂). This contrasting effect of the *tert*-butyl group on the CO₂/CH₄ gas selectivity of PAs was not well understood.

In continuation, Freeman et al. studied the gas transport properties of the PAs (namely, IP/6F, Ph/6F, IP/SO₂, and Ph/SO₂) synthesized from isophthaloyl chloride derivatives bearing a pendant phenyl substituents at the fifth position and its unsubstituted analogs (60). They have incorporated the 6F group in the PA structures and also prepared their structural analogs containing the >SO₂ moiety in place of 6F (Figure 2). In general, the substituted polymers were more permeable but less selective than their unsubstituted analog. Also, high permeability was observed for the fluorinated PAs than the non-fluorinated ones. The effect of the phenyl substitution on the gas permeability of the PAs was more prominent in the >SO₂ containing polymers. For instance, in the case of CO₂ almost four times increase in gas permeability was observed compared to the nonsubstituted one. Whereas for the phenyl substituted 6F containing PAs, only 2.5 times increase was observed for the CO₂ gas. The fact was attributed to the higher significant increase in FFV due to the pendant phenyl substitution for the >SO₂ containing polymers (change in FFV = 0.007) than the

Figure 3: Structure of the PAs having different alky side substituents (24).

–CF₃ one (change in FFV = 0.003). It was pointed out that the transport properties of a polymer having low FFV can be influenced more than the high FFV polymers by the introduction of the same bulky pendant group, as it can hinder the polymer chain packing effectively in case of the former. Also, it can be found that the glass transition temperature (T_g) values of all these PIs have a significant role in their permselectivity values. The polymers with higher T_g values than the analogs' polymer structure resulted in higher permselectivity, notably for the less condensable gases.

In another approach, Abajo *et al.* modified the PAs' structure by the systematic incorporation of different alkyl side substituents, such as methyl, isopropyl, or *tert*-butyl in the polymer backbone to investigate their effect on the polymer properties (Figure 3) (24). All the PAs having the side substituents showed improved solubility, and membranes were fabricated by solution casting method using DMAc as a solvent. The PAs showed good CO₂ and O₂ permeability that depends on the side substituents and the linking groups connecting the *p*-phenylene unit. The connecting groups control the torsional mobility of the polymer chains, i.e., with the change in the connecting group from methylene (PA 4) to isopropylidene linkage (PA 3), the rotational freedom of the polymer chain decreased due to an increase in chain rigidity. However, instead of a decrease in gas permeability as expected to the restricted polymer chain mobility, PA 3 showed the highest gas permeability in the series. The higher FFV (FFV = 1.68) of the connecting isopropylidene group in PA 3 nullified restricted chain mobility of the PA 3 and resulted in high gas permeability. This series of PAs showed relatively high gas permeability ($P_{\text{CO}_2} = 43$ and $P_{\text{O}_2} = 9.38$ Barrer) with moderate permselectivity (Table 2) due to packing disruptive *tert*-butyl groups in addition to the side substituents.

Ding and Bikson also investigated the effects of other bulky groups on gas transport properties. They have synthesized a series of PAs reacting 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1*H*-indene-5-carboxylic acid with different aromatic diamines (Figure 4) (61).

All the PAs in this series containing the bulky rigid phenylindane moiety showed high gas permeability ($P_{\text{CO}_2} = 35.3$ and $P_{\text{O}_2} = 7.35$ Barrer) with high gas separation efficiency ($P_{\text{CO}_2}/P_{\text{CH}_4} = 39$ and $P_{\text{O}_2}/P_{\text{N}_2} = 5.4$; Table 3). Interestingly, the PAs prepared from a nonlinear structure, such as 1,3-phenylene (PA 6), exhibited lower gas permeability and gas selectivity for most gas pairs than their linear analog 1,4-phenylene (PA 10). Also, the PAs containing the packing disrupting trifluoromethyl group (PA 8 and PA 9) exhibit higher gas permeability with

Table 2: FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the PAs having different alkyl side substituents, measured at 30°C and 3 atm pressure (24)

Polymer	FFV	T_g (°C)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)
PA 1	0.142	254	13	3.11	27.7	6.6
PA 2	0.151	275	21	4.50	23.3	5.6
PA 3	0.168	295	43	9.38	19.2	5.5
PA 4	0.166	260	27	6.47	22.3	5.5
PA 5	0.187	268	36	7.88	25.7	5.2

moderate selectivity than other PAs in this series, which is in line with the observed results discussed earlier.

Generally, the PAs' properties were impacted by the number of bulky groups present in it. Hu *et al.* systematically varied the number of bulky *tert*-butyl groups in the PAs and investigated their O₂–N₂ separation properties (62). They have prepared the PAs from 4,4'-hexafluoroisopropylidene-dibenzoic acid with various aromatic diamines containing a varied number of *tert*-butyl groups (Figure 5).

They reported that polymer packing density plays a vital role in controlling their gas transport properties. Both gas diffusivity and permeability increased and were proportional to the number of bulky groups in the PAs. The specific volume of the polymers strongly influences the gas transport properties of the PAs. The specific volume and the hole affinity constant (C_H') (related to the free volume) of oxygen of the membranes increases with the increase in the size of the diamine section in the polymer backbone (Table 4). The PA with 2,5 di-*tert*-butyl benzene (PA 16) showed the highest O₂ permeability ($P_{\text{O}_2} = 3.81$ Barrer) without effecting much O₂/N₂ selectivity ($P_{\text{O}_2}/P_{\text{N}_2} = 4.63$) and the highest selectivity observed for PA 14 with the highest T_g value in the series.

Aguilar-Vega *et al.* have prepared several PAs by reacting to a cardo diamine monomer, namely, 4,4'-(9-fluorenylidene) diamine with several substituted and unsubstituted aromatic dicarboxylic acids and studied their gas transport properties (Figure 6) (63).

The PAs derived from the isophthalic acid showed the lowest gas permeability ($P_{\text{CO}_2} = 5.3$ and $P_{\text{O}_2} = 1.2$ Barrer). In contrast, the analogs' PA bearing the *tert*-butyl group in the fifth position showed the highest gas permeability ($P_{\text{CO}_2} = 37.7$ and $P_{\text{O}_2} = 8.0$ Barrer) as well as high gas diffusion coefficient in this series (Table 5). The high packing density of the former (FFV = 0.134) was due to the meta linked isophthalic acid and was responsible for its low permeation, also reported by other researchers (61). The presence of chain packing

Figure 4: Structure of the polyamides having indene moiety (61).

disrupting *tert*-butyl group later resulted in high FFV (0.149) in the PA (P19) and was responsible for this observed high gas permeability (Table 5).

Kazama et al. also investigated the gas transport properties of the bis(phenyl)fluorene containing PA obtained from Nippon Steel Corp. of the same structure of PA 17 and compared its properties with other types of polymers like PI, polysulfone, and polycarbonate having similar FFV (64). The incorporation of the cardo fluorene moiety increased the polymer rigidity and FFV. The PA showed moderate CO₂ permeability (7.6 Barrer) with high permselectivity of CO₂ over N₂ ($P_{\text{CO}_2}/P_{\text{N}_2} = 37$). They observed that the magnitude of gas permeability was mainly due to the combination of gas diffusivity and solubility (effect of the bulky cardo fluorene moiety). In contrast, the magnitude of the permselectivity of CO₂

over N₂ was attributed to the solubility selectivity. However, the reported diffusion coefficient of the gases through the PA was lower compared to the other polymers like PI, polysulfone, polycarbonate, etc., having similar FFV. The intermolecular hydrogen bonding present in the PA hinders the polymer chain motion, leading to the lower apparent diffusion coefficient values compared to the other types of polymers.

The effect of the -CF₃ and *tert*-butyl groups on the PAs gas transport properties was investigated in detail by Carrera-Figueiras and Aguilar-Vega (65). They prepared a series of PAs from 4,4'-(hexafluoroisopropylidene) dianiline (HFA) and 5-*tert*-butylisophthalic acid (TERT) and its unsubstituted analog (ISO; Figure 7). Also, to understand the effect of both these bulky groups they synthesized co-PAs taking a mixture of ISO/TERT. The PA from HFA/TERT showed 2–6 times more permeability than their unsubstituted analog HFA/ISO (Table 6). The presence

Table 3: FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the PAs having indene moiety measured at 30°C and 1–2 atm upstream pressure (61)

Polymer	FFV	T_g (°C)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)
PA 6	0.188	346	5.2	1.16	58	7.6
PA 7	0.180	302	8.4	1.67	39	6.8
PA 8	0.185	>400	35.3	7.35	39	5.4
PA 9	0.203	>400	31.2	7.23	35	5.5
PA 10	0.187	357	8.9	1.67	49	6.8
PA 11	0.168	323	4.1	0.94	48	8.0
PA 12	0.174	251	9.6	1.91	29	6.1
PA 13	0.168	323	2.2	0.53	55	8.8

Figure 5: Structure of the PAs with varied number of bulky *tert*-butyl group (62).

Table 4: Specific volume, T_g , hole affinity constant (C_H), gas permeability (in Barrers), and permselectivity values of the PAs with varied number of bulky *tert*-butyl groups at 1 atm upstream pressure and 35°C (62)

Polymer	Specific volume (cm ³ /g)	T_g (°C)	C_H	P_{O_2} (Barrer)	α (O ₂ /N ₂)
PA 14	0.534	262	0.136	1.03	5.02
PA 15	0.565	215	0.182	2.74	4.92
PA 16	0.606	220	0.317	3.81	4.63

of the extra bulky lateral substituent *tert*-butyl group, in the former, increased its FFV (0.156 for HFA/TERT and 0.143 for HFA/ISO), which resulted in the observed high gas permeability as discussed earlier for other series of PAs. For the co-PIs, the gas permeability increases with the increase in TERT content in the copolymers but gas selectivity reduces. In a similar context, they have prepared another series of PAs containing the benzophenone (DBF) unit in place of HFA (Figure 7) (66). The gas permeability values of these PAs showed a similar trend to the PAs containing the HFA unit (Table 6). In these polymers, the DBF/ISO behaved as a gas barrier, whereas DBF/TERT showed higher permeability compared to DBF/ISO. For instance, in the case of O₂ permeation, the later was about 17 times more permeable than the former due to bulky *tert*-butyl in it. Another exciting correlation found that the PAs derived from HFA showed much higher gas permeability than analogs' PAs obtained from DBF. Therefore, it is evident that the 6F group plays a vital role in enhancing gas permeability by manipulating the FFV of the polymers.

In continuation to their effort to modify the PAs for gas separation applications, Aguilar-Vega *et al.* synthesized rigid block copolyaramides comprising earlier investigated

Figure 6: PAs having cardo fluorene derivatives (63).**Table 5:** FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the fluorene containing PAs, measured at 35°C and 2 atm pressure (63)

Polymer	FFV	T_g (°C)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)
PA 17	0.141	319	15.3	3.0	27.9	5.8
PA 18	0.134	301	5.3	1.2	41.3	6.1
PA 19	0.149	284	37.7	8.0	24.4	5.7

high gas permeable HFA/TERT block and barrier DBF/ISO block (Figure 8) with a different block length of 9:9, 12:12, and 18:18 repeating units on each block (67). The longer block segments showed high permeability and permselectivity ($P_{CO_2} = 20.9$ and $P_{O_2} = 4.7$ Barrer, $P_{CO_2}/P_{CH_4} = 37.42$ and $P_{O_2}/P_{N_2} = 6.4$) compared to the shorter block segment ($P_{CO_2} = 18.5$ and $P_{O_2} = 4.1$ Barrer, $P_{CO_2}/P_{CH_4} = 28.68$ and $P_{O_2}/P_{N_2} = 5.5$; Table 7). This was ascribed to the inefficient packing of the copolymer molecules with the increase in the block lengths. A similar observation of gas permeation was also reported for the block copolyaramides when they replaced the DBF/ISO block with the barrier HFA/ISO block (Figure 8) and varied the chain length of different blocks as discussed earlier (68). The presence of additional $-CF_3$ groups in the barrier block enhanced their permeability more than the copolymers with DBF/ISO unit while having almost similar selectivity. For instance, $P_{CO_2} = 70.93$ and $P_{O_2} = 15.43$ Barrer, $P_{CO_2}/P_{CH_4} = 33.3$ and $P_{O_2}/P_{N_2} = 5.04$ was observed for the longer block segments in this series of copolymers. Interestingly, this series of co-PAs displayed higher permeability than their parent polymers due to the different building blocks' inefficient packing. It can be concluded from this work that with proper selection of permeable and barrier block, the block copolymer presents an

Figure 7: Structure of the PA having different bulky pendant groups (65,66).

Table 6: FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the PA having different bulky pendant groups at 35°C

Polymer	FFV	T_g (°C)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)	Ref.
HFA/ISO	0.143	294	6.5 ^a	1.68 ^b	50.00	6.00	(65)
HFA/ISO(0.8)/TERT(0.2)	0.146	296	9.13 ^a	2.25	51.58	6.26	
HFA/ISO(0.5)/TERT(0.5)	0.150	300	10.21 ^a	2.86	39.26	5.60	
HFA/ISO(0.2)/TERT(0.8)	0.153	304	17.87 ^a	5.32	31.35	5.52	
HFA/TERT	0.156	306	22.05 ^a	5.88 ^b	30.31	5.06	
DBF/ISO	0.0912	272	0.32 ^b	0.069 ^b	—	—	(66)
DBF/ISO(0.8)/TERT(0.2)	0.0944	276	0.51 ^b	0.100 ^b	—	—	
DBF/ISO(0.5)/TERT(0.5)	0.0965	284	1.16 ^b	0.308 ^b	—	6.16	
DBF/ISO(0.2)/TERT(0.8)	0.0974	294	3.20 ^b	0.76 ^b	—	5.84	
DBF/TERT	0.1004	297	4.96 ^b	1.16 ^b	—	5.04	

^a Measured at 10 atm pressure. ^b Measured at 2 atm pressure.

advantage on gas permeation over their homopolymer analogs due to the block copolymers' inefficient packing properties.

Lozano et al. have synthesized two PAs from a rigid diamine monomer with spiro carbon moiety and bulky adamantane in its backbone structure, namely, spiro-(adamantane-2,9'(2',7'-diamino)-fluorene (SADAF) and isophthaloyl chloride (IPC), and the diacid chloride of 2,2-bis(4-carboxyphenyl)hexafluoropropylene (6FC) (Figure 9) (69). The adamantane group is relatively free of conformational stress because it consists of three rigid cyclohexane rings with chair conformation, restricting close chain packing. The 6F-SADAF polymer showed an ideal O₂ and CO₂ permeability coefficients of 3.4 and 14 Barrer, with permselectivity values of 5.37 and 41 for O₂/N₂ and CO₂/CH₄, respectively. They also prepared the PAs from the diamines. The PI from SADAF and hexafluoro diphthalic anhydride (6FDA) reported having nearly two times more gas permeabilities with somewhat improvement in gas selectivity. However, no report on the gas permeability values of IP-SADF (P20) is found.

González-Díaz et al. have reported prepared aromatic PAs (PA 22) and several co-PAs, which contain a free hydroxyl pendant group in its repeating unit (70). They further modified PA 22 by post-polymerization technique and introduce different bulky pendant groups in it (Scheme 7) (71).

The polymers showed high solubility due to the presence of –CF₃ group and bulky pendant groups in the PA backbone. These modified structures reduce close chain packing, as evident from the FFV values (Table 2). In comparison to their unsubstituted precursor PA 22, the modified polymers possess 13.2–31.4 times higher permeability for CO₂ and 3.4–4.3 times more selectivity value for CO₂/CH₄ (Table 8). This study indicates how nicely the gas permeation properties can be manipulated by simple structural modification of the polymers.

Banerjee et al. is actively working on the development of PA membranes for gas separation applications. His group is designing the diamine monomers to modify the polymer structure to understand the structure–property relation of the polymers for the future development

Figure 8: General structure of the block copolyamids having different gas permeable and barrier blocks (67,68).

Table 7: Gas permeability (in Barrers) and permselectivity values of the copolyaramids having bulky groups at 2 atm upstream pressure and 35°C

Polymer	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	α (CO_2/CH_4)	α (O_2/N_2)	Ref.
DBF/ISO	0.32	0.069	—	—	(66)
HFA/TERT-b-DBF/ISO 18	20.9	4.7	37.42	6.4	(67)
HFA/TERT-b-DBF/ISO 12	16.6	3.3	31.18	7.4	
HFA/TERT-b-DBF/ISO 9	18.5	4.1	28.68	5.5	
HFA/TERT	26.82	5.88	31.18	5.07	(68)
HFA/TERT-b-HFA/ISO 18	70.93	15.43	33.30	5.04	
HFA/TERT-b-HFA/ISO 12	37.94	8.59	34.80	5.33	
HFA/TERT-b-HFA/ISO 9	40.09	8.27	39.69	5.10	
HFA/ISO	7.60	1.68	42.22	6.00	

of the membrane materials. In their work, flexible ether linkages ($-\text{O}-$) and pendant $-\text{CF}_3$ groups were incorporated in the rigid aromatic PAs' backbone to enhance the polymer solubility and gas permeability. In addition to the above strategies, diamine monomers were synthesized with different cardo groups like cyclohexylidene (72), fluorene (73), and spiro (fluorene-9,9'-xanthene) (74), etc. to obtain the intended properties of the PAs 65–67. The synthesized diamines were reacted with the commercially available diacids (Figure 10) to prepare the PAs. Subsequently, the membranes were fabricated thereof and were subjected to gas permeation applications.

The incorporation of the cardo groups in addition to the $-\text{CF}_3$ moiety and the flexible ether linkage helps to improve the solubility of the PAs without sacrificing its thermal ($T_{\text{d}5} > 200^\circ\text{C}$) and mechanical properties. All the polymers were amorphous in nature, as a broad amorphous halo were observed in their corresponding X-ray diffractograms (72–74). The amorphous nature is due to the presence of the above bulky structural moieties, which disrupts the $\pi-\pi$ stacking of amide and phenyl rings of the aromatic PAs and hinders their chain packing.

All the PAs were readily soluble in a common organic solvent like THF, NMP, DMAc, DMF, and pyridine. PA membranes were prepared by casting from their corresponding DMAc solution showed a good set of mechanical properties. The gas transport properties of the PA

Scheme 7: Scheme for the post modification of the PAs (70).

membranes were investigated at 35°C and 3.5 Barrers pressure. The gas permeability and selectivity values are given in Table 9. Among all these PAs, polymers containing bulky cardo bis(phenylphenyl)fluorene moiety showed the highest permeability (P in Barrers) for different gases ($P_{\text{CO}_2} = 67.42$, $P_{\text{O}_2} = 15.00$) and highest permselectivity

Figure 9: PAs derived from SADAF (69).

Table 8: FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the post modified PAs at 2.02 bar upstream pressure and 35°C

Polymer	FFV	T_g (°C)	P_{CO_2}	P_{O_2}	α (CO_2/CH_4)	α (O_2/N_2)	Ref.
PA 22	0.131	309	2.82	0.66	5.64	1.65	(70)
PA 23	0.155	298	38.9	7.3	24.3	3.84	(71)
PA 24	0.152	302	37.2	7.0	26.6	4.12	
PA 25	0.167	312	88.1	17.5	19.2	3.72	
PA 26	0.156	308	43.1	8.5	20.52	3.86	

selectivity for both CO_2/CH_4 (88.37) and O_2/N_2 (10.84) gas pairs compared to the other PAs containing cardo bis (phenyl)fluorene and cyclohexylidene moiety. The order of gas permeability through the PAs containing these bulky cardo groups followed the increasing order of FFV of the PAs, i.e., bis(phenylphenyl)fluorene > bis(phenyl)fluorene > spiro (fluorene-9,9'-xanthene) > cyclohexylidene. The observation clearly states that in these PAs, the disruption of the polymers' chain packing due to the steric hindrance of the cardo group plays an important role in controlling their gas transport behavior. Significantly, the higher gas permeability in bis(phenylphenyl)fluorene was attributed to the steric hindrance caused by the extra two phenyl groups, responsible for the reduction in H-bonding and an increase in the effective FFV.

Banerjee et al. took another approach and varied the number of aromatic rings, the pendant group, etc., between the diether linkages (Figure 11) (75–78). They have introduced bulky pendant groups like *tert*-butyl and adamantane in the phenyl ring and investigated the effect of the different structural modification on the PAs' properties in detail.

The prepared PAs were amorphous and showed good solubility in different organic solvents, and transparent and flexible membranes were obtained for all PAs from their corresponding DMAc solutions. The incorporation of the *tert*-butyl groups and adamantyl moiety as the pendant group in polymer backbone improves their gas permeation properties (Table 9) without negatively affecting their properties. For instance, the PAs' membranes containing the di-*tert*-butyl groups (PA G-i to G-v-iii and G-v) exhibited high mechanical and thermal stability (tensile strength ~107 MPa and ~431°C in air for 10% weight loss) despite the presence of bulky and thermally labile two extra *tert*-butyl moieties. The properties make these PA membranes interesting to investigate for gas separation applications. The PAs containing di-*tert*-butyl pendant groups exhibited the highest permeability with relatively low gas selectivity ($P_{CO_2} = 173$ Barrer and $P_{O_2} = 44$ Barrer, $P_{CO_2}/P_{CH_4} = 24.03$, $P_{O_2}/P_{N_2} = 7.33$ for PA G-i) for different gases. Interestingly these PAs showed higher permeability (Table 9) for bigger penetrant CH_4 (kinetic diameter ~3.8 Å) over the smaller N_2 (kinetic diameter ~3.64 Å). The fact can be attributed to the higher affinity between the nonpolar CH_4 molecule and the alkyl *tert*-butyl moieties' ("like dissolves like") presence in the PAs (79). The fact was well supported by the observed higher solubility of the CH_4 (for PA G-i, $S_{CH_4} = 0.80 \times 10^{-2}$ and for PA G-v $S_{CH_4} = 0.56 \times 10^{-2} \text{ cm}^3/\text{cm}^3 \text{ cm Hg}$) over the N_2 (for PA G-I, $S_{N_2} = 0.37 \times 10^{-2}$ and for PA G-v $S_{N_2} = 0.28 \times 10^{-2} \text{ cm}^3/\text{cm}^3 \text{ cm Hg}$). In general, the PAs' PA G-i to G-iii and G-v with extra two *tert*-butyl groups showed extremely high permeability with comparable gas selectivity than their analogs' one (Table 10). For instance, a 12-fold increase in P_{CO_2} and 8-fold increase in P_{O_2} was

Figure 10: Different bulky cardo groups incorporated to modify the polyamides structures (72–74).

Table 9: FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the synthesized PAs measured at 3.5 bar pressure and 35°C

Polymer	FFV	T_g (°C)	P_{CO_2}	P_{O_2}	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)	Ref.
PA A-i	0.146	258	30.40	6.30	33.78	6.30	(72) ^a
PA A-ii	0.159	256	27.50	6.20	34.37	6.89	
PA A-iii	0.132	239	9.80	2.80	32.67	5.60	
PA A-iv	0.060	n.d.	7.00	1.90	53.84	7.60	
PA A-v	0.044	n.d.	4.50	1.60	64.29	10.67	
PA B-i	0.161	273	52.00	12.15	60.47	10.21	(73) ^a
PA B-ii	0.192	297	60.23	12.92	47.05	8.85	
PA B-iii	0.179	285	21.53	5.70	43.06	8.14	
PA B-iv	0.153	294	19.76	4.93	61.75	8.36	
PA B-v	0.144	299	15.92	4.18	54.90	8.20	
PA C-i	0.174	274	60.32	13.55	60.32	10.84	(73) ^a
PA C-ii	0.207	274	67.42	15.00	50.69	8.82	
PA C-iii	0.180	272	40.38	9.05	43.42	8.15	
PA C-iv	0.160	273	38.00	7.37	88.37	9.21	
PA C-v	0.145	278	32.00	6.22	80.00	9.01	
PA D-i	0.176	283	48.00	14.00	32.00	7.45	(74) ^a
PA D-ii	0.192	289	45.00	11.70	35.43	7.80	
PA D-iii	0.174	273	14.00	5.10	21.88	8.50	
PA D-iv	0.162	278	19.00	7.70	27.14	8.85	
PA D-v	0.152	288	14.50	3.80	29.00	7.04	
PA E-i	0.133	275	55.41	14.09	24.20	5.92	(75) ^a
PA E-ii	0.139	281	21.36	5.23	36.83	8.05	
PA E-iii	0.150	243	13.01	3.27	32.53	6.17	
PA E-v	0.125	290	5.72	2.14	12.43	4.37	
PA F-i	0.248	278	42.60	10.00	23.67	4.76	(76) ^a
PA F-ii	0.257	267	28.70	8.50	26.09	7.08	
PA F-iii	0.262	252	14.80	3.70	24.67	5.29	
PA F-iv	0.224	n.d.	12.10	3.40	30.25	6.80	
PA F-v	0.207	n.d.	8.40	2.30	28.00	5.75	
PA G-i	0.190	284	173.00	44.00	24.03	7.33	(77) ^a
PA G-ii	0.171	276	157.00	40.00	30.78	7.69	
PA G-iii	0.153	275	80.00	20.10	26.67	7.44	
PA G-v	0.145	286	70.00	17.80	25.93	6.85	
PA H-i	0.20	238	34.0	9.5	37.8	7.3	(78)
PA H-ii	0.19	235	29.2	8.2	41.7	8.2	
PA H-iii	0.12	219	13.0	3.5	32.5	5.8	
PA I-i	0.293	274	164.7	59.7	39.6	5.4	(83)
PA I-iii	0.253	267	81.1	29.7	39.8	5.3	
PA I-iv	0.255	272	87.6	34.8	33.1	5.2	
PA I-v	0.232	273	82.0	27.8	48.7	5.8	
PA I-vi	0.264	264	103.4	45.5	37.7	5.3	

^a FFV values were calculated using the equation $FFV = (V_s - V_o)/V_s$. V_o was computed from the van der Waals' volumes (V_w) of the various groups in the polymer structure provided by Park and Paul (85) using the equation $V_o = 1.3\sum V_w$, and the specific volume of the polymers (V_s) was calculated from the density values of the respective polymers and the molar mass of the repeat units.

observed for the PA G-v compared to its analogs' one, PA E-v. The fact can be attributed to the reduction in the polymer chain packing and enhancement in the polymer FFV due to packing disruptive bulky *tert*-butyl groups. The bulky *tert*-butyl hindered the polymer chains proximity, resulting in lowering H-bondings and related interactions between the polymer chain that enhanced the

membrane FFV and gas permeability (Figure 12). Also, the *tert*-butyl groups increase the polymer chains' rigidity and restrict their segmental movements, which also help maintain higher or moderate gas selectivity. This effect of the *tert*-butyl groups is not limited to only the PAs but also observed for other polymer membranes like polyacrylates (80), PIs (81), etc.

Figure 11: Different structural variations to modify the polyamides (75–78).

Also, the PAs having adamantyl moiety exhibited a good combination of permeability and selectivity ($P_{CO_2} = 34$ Barrer and $P_{O_2} = 9.5$ Barrer, $P_{CO_2}/P_{CH_4} = 37.8$, $P_{O_2}/P_{N_2} = 7.3$ for PA H-i. In general, the PAs synthesized from the 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) have the best combination of permeability and selectivity (e.g., $P_{CO_2} = 157$ Barrer and $P_{O_2} = 40$ Barrer, $P_{CO_2}/P_{CH_4} = 30.78$, $P_{O_2}/P_{N_2} = 7.69$ for PA G-ii) due to disruption of polymer packing and the restricted torsional motion of phenyl rings around the 6F linkage. Also, for all these series of polymers, the PAs synthesized from naphthalene-2,6-dicarboxylic acid showed relatively lower permeability, which is attributed to the presence of rigid compact naphthalene unit responsible for the lowest FFV and observed gas permeability.

Figure 12: General cartoon representation on the effect of the bulky groups (*tert*-butyl) on the polymer chain packing and FFV. (a) Compact polymer chain packing in case of polymer without bulky groups. (b) Disruptive polymer packing and higher free space for the polymers having the bulky groups.

Table 10: FFV, T_g , and gas permeability (in Barrers) and permselectivity values of the TPA containing PAs measured at 35°C and 3.5 bar pressure

Polymer	FFV ^{EXP}	FFV ^{SIM}	T_g (°C)	P_{CO_2}	P_{O_2}	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)	Ref.
PA J-i	0.143	0.139	303	53.5	13.0	48.64	10.0	(92)
PA J-ii	0.159	0.163	309	61.5	14.2	51.25	10.14	
PA J-iii	0.088	0.088	299	14.5	3.8	48.33	9.50	
PA J-iv	0.095	0.095	328	23.5	5.0	47.00	8.34	
PA J-v	0.061	0.063	330	12.6	3.5	63.00	11.67	
PA K-i	0.160	0.228	263	86.0	20.2	29.65	8.08	(93)
PA K-ii	0.188	0.250	271	119.0	29.0	37.19	9.67	
PA K-iii	0.105	0.194	258	51.0	12.8	24.28	7.53	
PA K-iv	0.122	0.202	281	69.7	17.0	30.30	8.5	
PA K-v	0.089	0.166	284	41.5	10.8	24.41	7.71	
PA L-ii	0.315	0.340	291	141	33.4	44.33	8.47	(94)
PA L-iv	0.243	0.270	273	83	19.8	37.89	6.87	
PA L-v	0.229	0.210	271	78	18.1	43.82	8.22	
PA L-vi	0.266	0.290	283	97	23.6	36.74	7.46	

Introduction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) into the polymer structure is beneficial in many respect. This unit has a typical spatial conformation free of conformational stress and a bulky structure that hinders close packing between polymer chains and effectively used in polymer to improve their solubility and thermal stability. This phosphorus-containing moiety also improves flame retardancy (82). To take the advantages of DOPO unit, Banerjee *et al.* has prepared a diamine monomer containing this unit and finally designed a series of PAs (Figure 13) (83). Introduction of bulky DOPO unit restricts efficient packing of polymer chains, chain-chain interactions decreases, and increases solubility (84) and permeability like many other PAs with bulky groups (77). The PAs showed high thermal stability, and T_g values were in the range of 265–275°C. The polymers showed very high gas permeability ($P_{CO_2} = 164.7$ and $P_{O_2} = 59.7$ Barrer) and maintained a high selectivity. Gas permeability through the polymer membrane depends on the kinetic diameter of the penetrator gas molecules, packing density (FFV), and mobility of the polymer chains. PA with *tert*-butyl group and DOPO unit, i.e., PA I-i possesses the highest FFV and the most increased permeability in the series. The high glass transition temperature of the PAs affects their selectivity value by restricting their intersegmental motion.

5 PAs containing triphenylamine (TPA) moiety

Polymers with TPA core exhibits several unique properties, e.g., electrochromic properties (86) and hole-transporting properties (87). The propeller-shaped TPA structure is also known for packing disruptive group that inhibits the polymer chain packing and draws the attention for developing polymer membranes for gas permeation applications (88–91). Liou *et al.* used different triphenyl amine-containing PIs for membrane-based gas separation applications (88,89). In addition to the above properties, the propeller-shaped structure improves the solubility of the PAs (86). Accordingly, Banerjee *et al.* have designed and prepared different TPA core containing diamines that bear other bulky pendant groups like adamantane (92), tri-*tert*-butyl phenol (93), and trityl (94). They have prepared several PAs using these diamines and investigated the gas permeation properties of the synthesized PAs (Figures 14 and 15).

The PAs with the TPA core showed improved solubility in common organic solvents like NMP, DMAc, DMF, pyridine, and DMSO despite the absence of any fluorinated amines' solubility improving ether linkage as was in the case for the another PAs discussed in the above sections. The improvement was due to the propeller-shaped structure of the TPA, which inhibits the polymer chain packing. Also, the bulky pendant groups improve the steric hindrance between the polymer chains. The membranes from these polymers were subjected to gas permeability studies for different gases like CO_2 , O_2 , N_2 , CH_4 , etc. (Table 10). The PAs containing the tri *tert*-butyl phenyl pendant group showed higher permeability for all the gases ($P_{CO_2} = 119$, $P_{O_2} = 29$ for PA K-ii) compared to analogs' PAs containing adamantane moiety ($P_{CO_2} = 61$, $P_{O_2} = 14$ for PA J-ii). The higher permeability of the former is due to their higher FFV that arises from the three *tert*-butyl substitutions in the pendant phenyl group. In contrast, the adamantane moiety containing PAs showed high gas selectivity (e.g., $P_{CO_2}/P_{CH_4} = 63$, $P_{O_2}/P_{N_2} = 11.67$ for PA J-v). This is attributed to their more compact chain packing, and high rigidity, which is evident from their higher glass transition temperature (330°C for PA J-v) compared to the *tert*-butyl phenyl containing analogs (e.g., $P_{CO_2}/P_{CH_4} = 24.4$, $P_{O_2}/P_{N_2} = 7.7$ for PA H-v, $T_g = 284^\circ C$ PA K-v).

The molecular dynamics' simulations allowed us to analyze and correlate the free volume distribution (FVD) of elements in these PAs with gas permeability and selectivity. The FVD and sizes of the free volume elements (Figure 16) influenced the polymer membranes gas permeability, diffusivity, and permselectivity. The FVD largely controls the permeability of small- and medium-sized gas molecules. The FVDs for PAs were following the bulkiness of the diacid moiety in the PAs (Figure 14). Higher free volume elements bigger than $60 \text{ \AA}^3$ in PA k-i and ii are due to more *tert*-butyl groups and the 6F moiety, respectively. The diffusion coefficients for all the gases were in concurrence with the more significant free volume elements in the PAs (93).

In continuation to our work, Banerjee *et al.* incorporated a bulky trityl group into the TPA core-based diamine and used it to synthesize the PAs (Figure 15) (94). The PAs showed high gas permeability with good permselectivity. As discussed earlier, in the case of this series of PAs, the gas permeability is controlled by their high FFV. The presence of a bulky pendant trityl group is responsible for such high FFVs (0.315 for PA L-ii). The trityl group makes the polymer chain labile, which helps to create micropore in the polymer, responsible for high

Figure 13: Structure of the PAs containing DOPO moiety PA I-(i-vi) (83).

FV elements in this series of PAs. The PA L-ii, containing the 6F group, showed highest gas permeability and selectivity in this series ($P_{\text{CO}_2} = 141$, $P_{\text{O}_2} = 33.4$, $P_{\text{CO}_2}/P_{\text{CH}_4} = 44.33$, $P_{\text{O}_2}/P_{\text{N}_2} = 8.47$), whereas PA L-v having the naphthalene moiety showed the lowest gas permeability ($P_{\text{CO}_2} = 78$, $P_{\text{O}_2} = 18.1$). Another interesting observation was that the series of PA K-vi showed high gas permeability (e.g., $P_{\text{CO}_2} = 97$, $P_{\text{O}_2} = 23.6$) over the PA K-iv (e.g., $P_{\text{CO}_2} = 83$, $P_{\text{O}_2} = 19.8$) despite the presence of the additional phenyl moiety in the former. The high gas permeability values were due to the flexible ether linkage ($-\text{O}-$) between the two phenyl rings in the former. In this series of PAs, the FFV morphology was analyzed using MD simulation to understand the effect of the PA structure on the FV distribution and their gas transport properties. From Figure 17, it can be observed that the well-connected large microcavities (FV elements) of the PA L-ii was responsible for its high permeability and selectivity. The microcavities gradually become smaller

and discontinuous in the following order, from PA L-vi > PA L-iv > PA L-v, i.e., with the decrease in the FFV size of the PA building blocks.

6 PAs containing Tröger's base moiety

In recent days, polymers of intrinsic microporosity (PIMs) have drawn much attention. The PIMs have high free volume and are rapidly expanding a class of solution-processable amorphous polymer. Several types of PIMs with a bulky and kinked structure have been reported, of which Tröger's base (TB) is one of them. TB is a bridge bicyclic diamine 2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine (95). Generally, *N*-containing functional groups in polymer structure increase CO_2

Figure 14: Structure of the PAs synthesized from TPA containing bulky pendant groups (92,93).

Figure 15: Structure of the PAs having TPA containing pendant trityl moiety (94).

affinity, which gives high CO₂ solubility in the polymer matrix. As a result, solubility and selectivity increase. The alkaline *N* atom of a tertiary amine in TB is mainly

responsible for the high affinity between CO₂ and polymer matrix (96). TB-based intrinsic microporosity combined with rigid PAs is expected to be a good performer in gas

Figure 16: Free volume distributions (FVDs) of the PAs (PA I to PA V = PA K-i to PA K-v in Figure 14) (93). Copyright 2015, Reproduced with permission from American Chemical Society.

Figure 17: MD simulations of the FV (void space in gray region) morphologies of the PAs having pendant trityl group (94). Copyright 2017, Reproduced with permission from Elsevier Science Ltd.

separation applications with good permeability and selectivity. In this context, Banerjee et al. has synthesized four aromatic PAs (Figure 18) with TB-derived diamine 2,8-diamino-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo [1,5]-diazocine and four different aromatic acids (97). The polymers were soluble in DMAc, and membranes were fabricated through solution casting. The PAs showed thermal stability (T_{d10}) in the range of 351–461°C, and high glass transition temperature, 283–290°C. The polymers showed high gas permeability (P_{CO_2} up to 109.1 Barrer and P_{O_2} up to 21.6 Barrer) and maintained a good selectivity. The $-\text{CH}_3$ group in TB-moiety reduces close packing between two polymer chains; thus, openness and permeability increase. Gas permeability of the

membranes depends on interchain spacing (d -spacing) and FFV (Table 11). Gas permeability of this series of PAs followed the order PA M-i > PA M-ii > PA M-iii > PA M-iv, depending on their chemical structure.

In the series, PA M-i has the highest gas permeability, the presence of 6F groups in this polymer is responsible for its relatively higher permeability. TB units in the polymer backbone also improve the permeability compared to the analogous 6F group containing polymers (74,78). The presence of flexible ether linkages in the polymer chain makes PA M-ii more permeable than PA M-iii or PA M-iv. The PA M-iii showed higher permeability than PA M-iv because of the unsymmetrical structure of the acid moiety, except CO_2 gas. PA M-iv has the lowest FFV and consequently the lowest permeability; this is due to their high chain packing density. The ideal selectivity, CO_2/CH_4 and O_2/N_2 were in the range of 48.4–53.6 and 6.5–7.5, respectively. High selectivity for CO_2/CH_4 and O_2/N_2 gas pairs was because of the amide bonds that enhance intramolecular rigidity by densifying the polymer chains. Incorporation of TB units into the polymer backbone notably increases the selectivity with moderate permeability.

7 Future outlook

Polymeric membrane-based gas separation is an essential unit operation in many industries to recover valuable gases and facilitate pollution control and reduce capital investment, operating cost, and process safety (5–8). The success of separation of gas mixtures to their individual components from a feed lies in designing new membranes that can address the trade-off relationship between gas permeability and selectivity (3,9). The PAs are an essential class of high-performance polymers and

Figure 18: Structure of the PAs having TB unit (97).

Table 11: FFV, T_g , and gas permeability (in Barrers) and perm-selectivity values of the TB-based PAs measured at 3.5 bar pressure and 35°C

Polymer	FFV ^{EXP}	T_g (°C)	P_{CO_2}	P_{O_2}	α (CO ₂ /CH ₄)	α (O ₂ /N ₂)	Ref.
PA M-i	0.245	283	109.1	21.6	50.3	7.52	(97)
PA M-ii	0.229	284	92.2	18.3	46.8	7.20	
PA M-iii	0.168	285	84.7	16.8	48.4	7.21	
PA M-iv	0.166	290	86.4	14.1	53.7	6.52	

had shown great promise in this direction, though their utilization as gas separation membranes is not fully exploited (3). The improvement in PAs' solubility without affecting their properties is the scope of research in the field. The incorporation of different packing disrupting bulky pendant groups resulted in an increase in the PAs' solubility in selective solvents and allowed of fabrication films by solution casting route (1). It is observed that structural modifications of the PAs by incorporating different bulky groups largely affect their gas permeation behavior. The effect of structural alterations on the PAs (Tables 1–11) gas permeation properties, the selectivity values of O₂/N₂ and CO₂/CH₄ gas pairs have been presented against the O₂ and CO₂ permeability values, respectively (Figures 19 and 20). From the plots, it can be observed that the incorporation of the bulky groups, especially the packing disrupting *tert*-butyl, biphenyl fluorene, and adamantane, showed an exciting combination of gas permeability and selectivity (77,78,92,93). In O₂/N₂ gas pairs, the PAs having those bulky groups exceeded or closed to the Robeson present upper bound.

Figure 19: Robeson plot of permeability/selectivity trade-off for O₂ and N₂ gas pair. Values are taken from Tables 1–11.

Figure 20: Robeson plot of permeability/selectivity trade-off for CO₂ and CH₄ gas pair. Values are taken from Tables 1–11.

Whereas for CO₂/CH₄ gas pair, the PAs having the above-described bulky groups come in close proximity to the upper bound and even touched in case of the bulky trityl and *tert*-butyl containing PAs. The propeller-shaped TPA core and the bulky pendant group in PAs showed a synergistic effect on both gas permeability and permselectivity (94). The observed properties make this structural variation a useful tool for designing the polymers for superior gas permeation properties. TB-based polymers are absorbing and provides both high permeability and selectivity (97). The designing of new TB-based PAs by incorporating bulky trityl and *tert*-butyl moieties may be beneficial in improving their separation performance. The molecular dynamic simulation can be employed beforehand to predict the gas separation behaviors and understand which structural variation is paramount to obtain better separation efficiency. Also, experimental techniques like positron annihilation may enlighten better to understand the gas separation performance of the prepared membranes by calculating their free volume.

8 Summary

In summary, the PA membranes are making steady progress for being used in membrane-based gas separation applications. But still, some issues should be considered for the further development of the PAs as membrane materials for gas separation applications. First of all, there remains the trade-off between gas permeability and selectivity, as expressed in Robeson's upper bound. Development of PAs with proper selection of bulky

pendant groups like *tert*-butyl, combined with a propeller-shaped TPA structure, can be a way forward to achieve higher permeability with higher selectivity. However, mechanical properties tend to decrease when bulky groups are incorporated in the PAs. The bulky groups reduce the H-bonding between the polymer chains and disrupt chain packing, affecting the membrane suitability at high-pressure, high-temperature gas separation applications. Another approach should also be considered, mixing the PAs with the inorganic filler particles for the preparation of the mixed matrix membranes. This approach will allow the opportunity to effectively use the strength, stability, and permeation efficiency of the PAs with the better selective properties of the inorganic fillers. Also, cardo groups with different functionalities in the PAs may help to achieve intended gas separation efficiency. Physical aging and plasticization of the polymer membranes are the significant issues for successful membrane-based separation for commercial applications (98). Hence, the gas-separation studies with aged PA membranes also need to be investigated to qualify these classes or polymers for an industrial separation process.

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