

Part I

Novel Membrane Materials and Transport in Them

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Synthesis and Gas Permeability of Hyperbranched and Cross-linked Polyimide Membranes

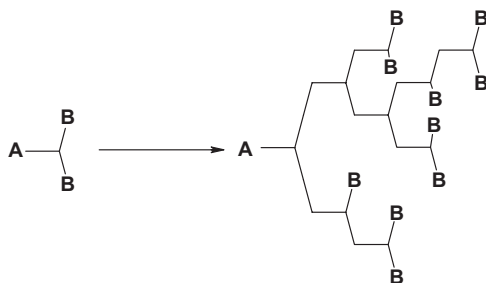
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1.1 Introduction

Recently, the polymer science field has focused on the role of polymers as membrane materials with precise, well-ordered structures through the development of defined synthesis and analysis of polymers. Among these well-ordered polymers are the hyperbranched polymers (e.g. hyperbranched polyimides). Part of the interest in such polymers is due to the expectation that they could have different properties as compared to common linear polymers. Also, cross-linked polyimides have attracted much attention from researchers, as can be judged by a high number of publications.

In general, hyperbranched polymers have many orderly branching units whose structures are different compared to linear and randomly cross-linked polymers [1–3]. According to the Commission on Macromolecular Nomenclature of the International Union of Pure and Applied Chemistry (IUPAC), a crosslink polymer is defined as a polymer having a small region in a macromolecule from which at least four chains emanate [4]. It is formed by reactions involving sites or groups on existing macromolecules or by interactions between existing macromolecules. The word ‘network’ is also defined as a highly ramified macromolecule in which essentially each constitutional unit is connected to each other constitutional unit and to the macroscopic phase boundary by many permanent paths through the macromolecule, the number of such paths increasing



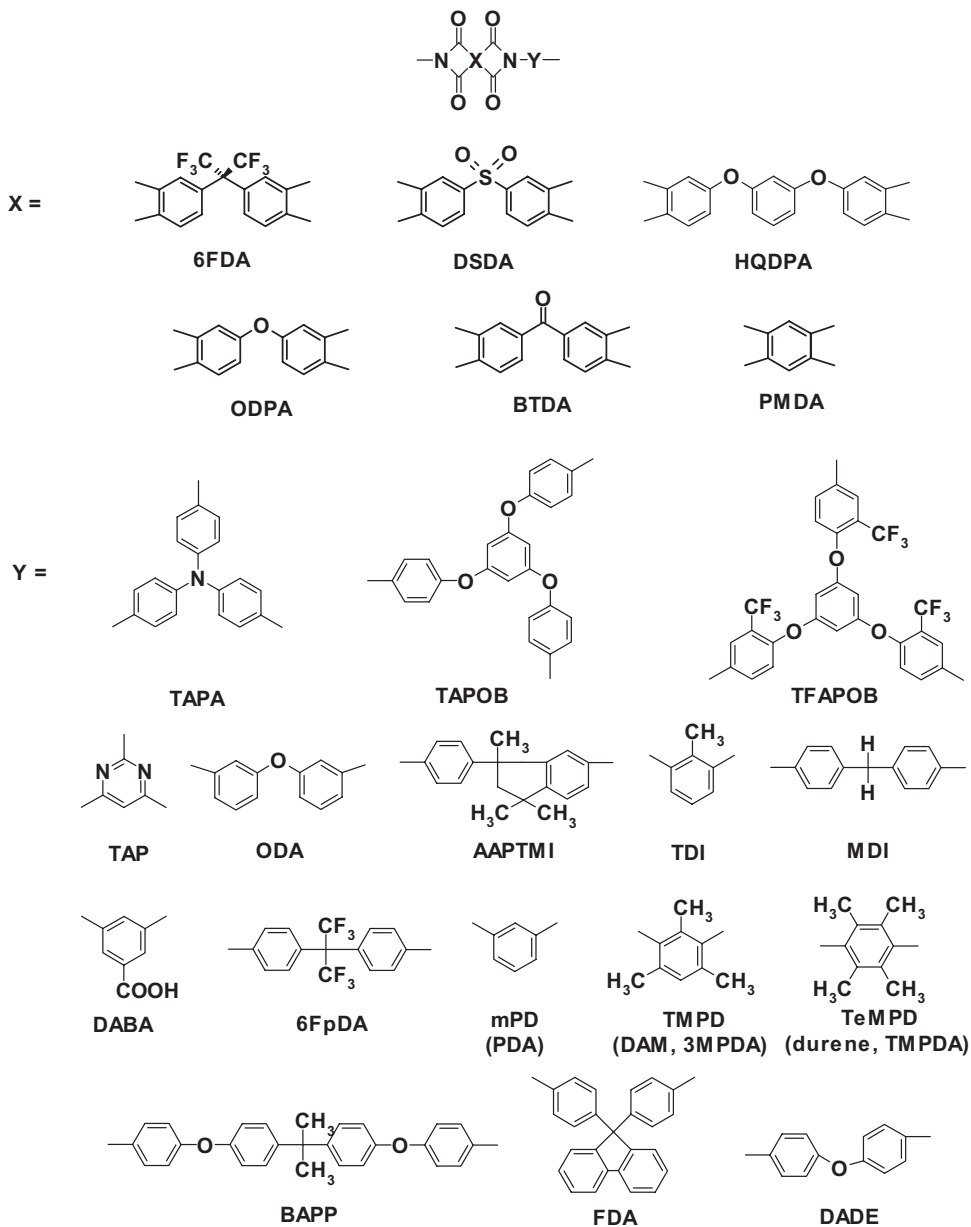
Scheme 1.1

with the average number of intervening bonds; the paths must on the average be co-extensive with the macromolecule [4]. In this chapter, we use the term crosslink polymer to describe a random cross-linked network between polymer segments.

Precisely branched polymers include hyperbranched polymers, dendrimers and dendrons. Dendrimers and dendrons are characterized by perfectly controlled structures in three dimensions such as tree branch architecture, and they have attractive features such as a well-ordered chemical structure, molecular mass, size and configuration of polymers [5]. Although the precise order of shape of hyperbranched polymers is less than that of dendrimers and dendrons, hyperbranched polymers have unique properties such as low viscosity attributed to the lack of entanglement of polymer segments, and the possibility of chemical modification in terminal functional groups such as in dendrimers [1–3].

Synthesis of hyperbranched polymers is typically performed through the self-polycondensation reaction of AB_2 -type monomers (Scheme 1.1) [6,7]. The theoretical study of the random AB_x polycondensation has already been reported by Flory in 1952 [8]. He pointed out that the synthesis of hyperbranched polymers from AB_x monomers should resemble linear polymers in their elusion of infinite network (i.e. gelation) formation, which cannot occur except through the intervention of other interlinking reactions. Since then, there have only been a few experimental data made available on hyperbranched polymers; some have even been overlooked due to the fact that the use of the term hyperbranched polymers began only in the late 1980s. However, in early 1990s, hyperbranched polyphenylene was synthesized from AB_2 -type monomers [9]. This marked the beginning of the reawakened hyperbranched polymer concept. A variety of hyperbranched polymers such as polyphenylene [9], polyimide [10–12], polyamide [13–15], polyester [16], polyetherketone [17] and polycarbonate [18] have been reported in recent years. It is important that hyperbranched polymers with feathers of closed dendrons can be synthesized through the self-polycondensation one-step reaction because dendrimers and dendrons are synthesized by multistep procedures (e.g. protection, coupling and deprotection cycles). Producing dendrimers and dendrons is also costly and requires complicated manufacturing processes for industrial applications.

On the one hand, linear aromatic polyimides have been generally used as electronic and aerospace materials because of their excellent mechanical strength, thermal, chemical and electronic/optic properties compared with other common amorphous polymers. Polyimides are also excellent membrane materials for gas separation due to their rigid chemical structures, allowing the production of larger functional free volume. Over the



Scheme 1.2

past decades, numerous polyimides have been synthesized and their gas transport properties have been investigated. Scheme 1.2 shows the chemical structures of acid anhydrides and diamines mentioned in this chapter.

On the other hand, hyperbranched polyimides not only have the features of other hyperbranched polymers (e.g. low viscosity, good solubility) but also possess high thermal

and physical stability, which is attributed to their rigid imide ring. It is commonly known that the kinds of terminal functional groups affect their physical properties, such as glass transition temperature and solubility [19]. Hyperbranched polyimides have weak polymer chain interactions (lack of entanglement) and this affects their density, dielectric constant, refractive index and other properties [19]. It is expected that they could provide an alternative to conventional polymer materials as novel functional and high-value added materials. Furthermore, hyperbranched polyimides could have a well-ordered structure compared with linear polyimides, which have a random distribution of polymer segments. Therefore, hyperbranched polyimides are expected to have favourable gas separation performance since their controlled branched structure could be advantageous in separating small molecules. Since the early 2000s, research on hyperbranched polyimides as gas separation materials has been reported, and these studies are still in progress [20–26].

Plasticization behaviour induced by condensable gases and vapours (e.g. carbon dioxide, hydrocarbons and other organic vapours) in polymer membranes is still a painful problem in polymeric membrane-based gas separation applications [27,28]. Recently, novel hyperbranched polyimides were prepared from telechelic polyimides and an attempt was made to improve its gas separation performance and physical stability by obtaining plasticization-resistant materials [29–33] (see e.g. Chapters 4, 6 and 7 of this book).

This chapter presents a review of numerous publications devoted to the concept and synthesis of hyperbranched and cross-linked polyimides. Also, gas permeation properties of these polymers are considered in detail.

1.2 Molecular Designs for Membranes

There exist different architectures of polymer macromolecules, as is shown in Figure 1.1.

Type I represents common linear polymers such as polysulfone, polycarbonate or polystyrene, for example. In glassy polymers, the movement of segments is frozen, though small-scale mobility of side groups is possible. In general they have good solubility in

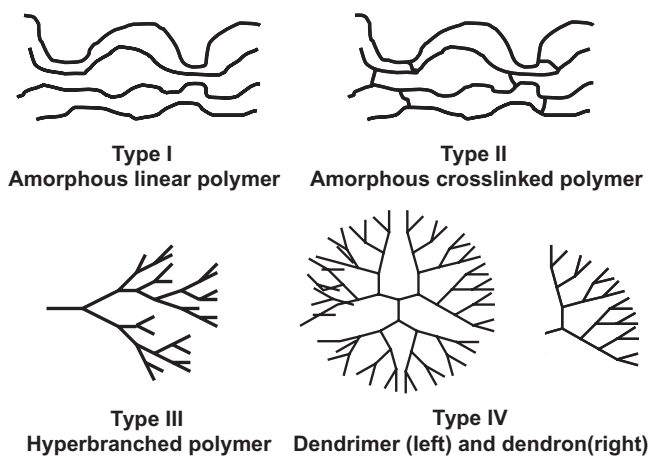


Figure 1.1 Architecture of polymers

various organic solvents; however, their gas permeation properties in the presence of organic vapours are affected by plasticization phenomena.

Type II. In randomly cross-linked polymers the solubility in organic solvents gradually decreases with the increasing degree of crosslink density. Too frequent crosslinks result in the gelation of the polymer and a decline in gas permeability while simultaneously permselectivity can increase.

Type III. Hyperbranched polymers have numerous branch units. They have low viscosity, good solubility and are capable of being chemically modified in terminal functional groups. Hyperbranched polymers have a potential to be good gas separation materials because their molecular-sized spaces between branched polymers can be controlled.

Type IV. Dendrimers and dendrons have perfectly and orderly branched tree-like structures. Their molecular mass increases with the growth of the number of generation. Dendrimers and dendrons, like common organic molecules, are perfectly controlled in terms of chemical structure, molecular mass, configuration and distribution of polymers [5]. Dendrons are well-ordered hyperbranched polymers and dendrimers are assembled from dendrons. It is expected that molecular-sized spaces between branched as well as hyperbranched polymers of dendrimers can be controlled and, therefore, could have high potential as gas separation membranes. An obvious disadvantage of dendrimers as membrane materials is their poor film-forming properties.

One of the key problems for polymeric gas separation membranes is gas and vapour-induced plasticization. The plasticization of polymers produces an enhancement of polymer chain mobility. It is a recognized fact that almost all polymeric membranes undergo swelling and plasticization under high pressure (concentration) of CO₂ and organic vapours, resulting in a significant loss in gas separation performance. One of the effective techniques against plasticization of polymers is the crosslink approach. There is a trade-off relationship between polymer crosslink density and gas permeability.

The mobility of polymer chains is larger for their polymer terminal chain ends as compared to that for the sections of macromolecules inside main chains. Therefore, plasticization may occur more easily around the polymer chain ends than in the polymer main chains. Moreover, if the number of polymer chain ends were minimized in a membrane, plasticization would be prevented. It is the hyperbranch structure that can create such behaviour in the case of rigid polymer chains.

Thus, we can state that the use of hyperbranched polyimides can enhance the resistance to plasticization of polymer membranes.

1.3 Synthesis of Hyperbranched Polyimides

Cross-linked (Type II) and hyperbranched (Type III) polyimides can be prepared for the use as gas separation membranes. There are no dendrimers and dendrons known, which would form free-standing membranes. Therefore, we focus on the synthesis of cross-linked (Type II) and hyperbranched (Type III) polyimides.

1.3.1 Amorphous Cross-linked Polyimides (Type II)

Generally, the aim of the study on crosslink polyimides is an attempt to enhance their gas selectivity and physical stability for gas-induced swelling and plasticization. Several

crosslink techniques such as monoesterification and transesterification reactions of carboxylic acid, imide ring-opening reactions, grafted with epoxy reactions, UV-induced cross-linking and Diels–Alder-type cyclization reactions have been reported.

The monoesterification and transesterification reactions of carboxylic acids were performed using the following steps. The carboxylic acid-containing polyimide was monoesterified under acid catalyst and thermal treatment, and the transesterification reaction was induced through further thermal treatment under vacuum. Many carboxylic acid-containing copolyimides have been synthesized and the crosslink reaction of the varieties of diol agents has been investigated [34–42]. The structure of cross-linked membranes could be strongly affected by structures of the diol agent and polyimide compositions and annealing temperature after membrane formation. In the case of 6FDA-TMPD/DABA (3:2) cross-linked polyimides, 1,3-propanediol can be considered as an efficient crosslink agent [42].

The decarboxylation-induced cross-linking reaction of carboxylic acid is preceded by the reaction of the phenyl radical and the elimination of the carboxylic group by high temperature annealing [43]. This decarboxylation-induced reaction is more sensitive to the reactivity of phenyl radicals rather than the effects of charge transfer complexing, oligomer and dianhydride formation. It was reported that the sites within the diamines section could be the TMPD methyl, biphenyl (between the carboxylic acid group) and at the site of cleaved CF_3 groups in 6FDA.

The imide ring-opening reaction occurred between the polyimide and primary diamine agents. Many chemical cross-linking reactions between 6FDA-based polyimides and primary diamines have been investigated [44–52]. They were carried out by immersing the polyimide membranes into the methanol solution of amine compounds. The structure of the cross-linked membranes could depend on the structures of the primary amine agents and the reaction conditions such as the reaction time and temperature. Furthermore, the gas permeation properties in 6FDA-TMPD modified by amine compounds were described [44]. The cross-linking in 6FDA-TeMPD with dendrimers such as polyamidamine (PAMAM) and polypropyleneimide (DAB-AM) has also been reported [53–56]. There was no doubt that they took place, as the measurements of gel fraction and FTIR data showed; in addition, the degree of crosslink density increased in the order of generations $G1 > G2 > G3$ at the same reaction. The dielectric constant increased with the reaction time owing to the decrease in the polymer chain's mobility and free volume.

The etherification reaction of polyimides is similar to the process of the imide ring-opening reaction. It was demonstrated for the reaction of polyimides with primary diamine and epoxy agents [57,58] (for example, for 6FDA-TeMPD polyimides and tetraglycidyl-diaminodiphenylmethane (TGDDM), diethyltoluenediamine (DETDA) [57], TMPDA, 1,3-phenylenediamine (PDA) and 4,4'-(9-fluorenylidene)dianiline (FDA) [58]). The density of polymers and crosslink concentration increased with the increase in epoxy content.

It is known that the crosslink reaction proceeds with participation of photo reactive benzophenone and alkyl chains under UV irradiation [59,60]. Many benzophenone-containing BTDA-based polyimides have been synthesized and their cross-linking investigated [61–69]. The same effects as discussed earlier were observed due to increases in the UV irradiation time.

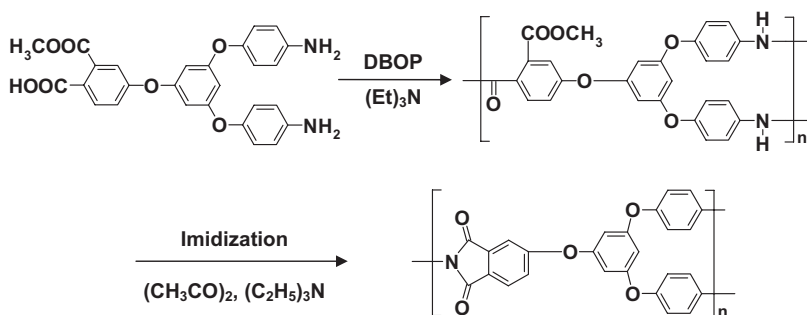
Acetylene-terminated or internal acetylene imide oligomers were investigated for aerospace and electronic applications, in particular because of their good thermal and environmental stability [70–74]. In respect of membrane application the aim of these studies was an enhancement of the physical stability under high pressure CO₂, that is, resistance to plasticization. Recently, a co-polyimide was synthesized from 6FDA, TeMPD and 4,4'-diaminodiphenylacetylene (*p*-intA) having internal acetylene structure [75]. After thermal treatment at 400 °C of such a membrane (an internal acetylene membrane), the cycloaddition of a Diels–Alder-type reaction occurred, according to the results of DSC and FT-Raman spectroscopy. The cross-linked membrane was insoluble; however, no densification of the membrane was observed.

1.3.2 Hyperbranched Polyimides (Type III)

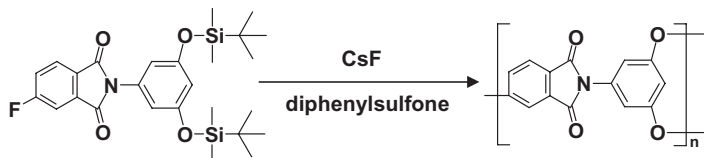
Hyperbranched polyimides can result due to the self-polycondensation reactions of AB₂-, A₂- and B₃-types. The preparation of hyperbranched polyimides involves chemical imidization of polyamic acid ester synthesized from AB₂-monomers, which are carboxylic dianhydrides containing an ether bond and a diamine [6,19,76]. Polyamic acid in combination with a condensation agent is used because it is difficult to separate the synthesized polymer from AB₂-type monomers.

For example, it is possible to prepare hyperbranched polyimides from 3,5-dimethoxyphenol and 4-nitrophthalonitrile in the presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (DBOP) as a condensation agent at room temperature. Hyperbranched polyimide was obtained through thermal or chemical imidization of the precursor (polyamic acid) (Scheme 1.3) [19]. The obtained hyperbranched polyimide had a relatively great molecular mass (M_w) of about 190 000 g mol⁻¹ but low intrinsic viscosity of 0.30 dL g⁻¹. Therefore, it had a compact configuration and the lack of entanglement of polymer chains. The polymer obtained via chemical imidization was soluble in aprotic polar solvents such as tetrahydrofuran (THF), while the polymer from thermal imidization was insoluble in any solvents.

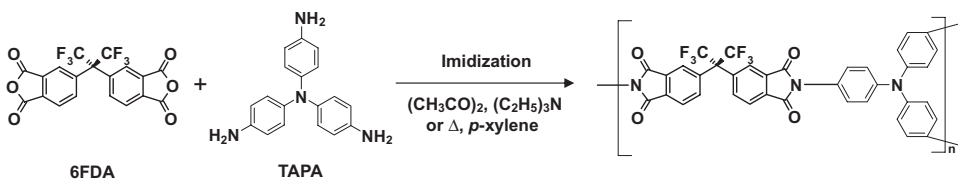
Other examples of self-polycondensation of an AB₂-type monomer containing an imide-ring via etherification reactions can be found in the literature [7,10,77]. The self-polycondensation can be performed through nucleophilic etherification of silylated phenol and aryl fluoride in diphenylsulfone at 240 °C under the presence of caesium fluoride



Scheme 1.3



Scheme 1.4



Scheme 1.5

(Scheme 1.4) [7]. This reaction involved a nucleophilic substitution of the halogen group interacting with the electron-attracting imide-ring. It gave an increase in number average molecular mass (M_n) value from 52000 to 85000 g mol^{-1} . The hyperbranched polyetherimide was soluble in common organic solvents and showed high thermal stability.

The hyperbranched polyimides can be synthesized via using the preparation of polyamic acids from A_2 - and B_3 -type monomers as well. The advantage of this reaction is that it can produce the hyperbranched polyimides from commercially available aromatic dianhydride [11,20] and triamine monomers or trianhydride and diamine monomers [12,78]. Almost all reported hyperbranched polyimides for gas separation applications have been synthesized using this reaction [20–26]. However, the obtained polymers had poor mechanical properties due to high branching and the absence of chain entanglements [8]. Therefore, isolated soluble hyperbranched polyimides should be treated by poor solvents before gelation. By controlling the molar ratio, the addition sequence of each component, the monomer concentration and the imidization method it is possible to obtain polymers with different terminal functional groups (as amine-terminated and anhydride-terminated polymers). For example, the hyperbranched polyimide was prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) as the anhydride and (4-aminophenyl)amine (TAPA) as the triamine (Scheme 1.5) [11]. The synthesized hyperbranched polyimide was soluble in organic solvents, had a M_w value of 37000 for amine-terminated and 150000 g mol^{-1} for anhydride-terminated product. The intrinsic viscosity was 0.76 dL g^{-1} for amine-terminated and was 1.92 dL g^{-1} for anhydride terminated polymers, respectively, higher than for the polymers synthesized via AB_2 -type monomer.

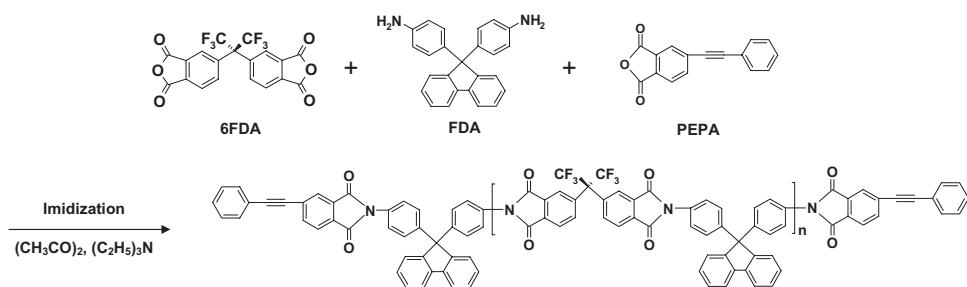
Hyperbranched polymers basically have poor membrane-forming ability due to the lack of chain entanglement. Studies on the enhancement of membrane-forming ability for hyperbranched polymers suggested to use the crosslink approach at terminal functional groups and cross-linkable components [1,18]. Preparation of the crosslink polymers was

reported [20] using reagents such as ethylene glycol diglycidyl ether (EGDE) and terephthalaldehyde (TPA), or anhydride-terminated and 4,4-diaminodiphenyl ether (ODA) and diphenylsulfone (DDS) have also been reported.

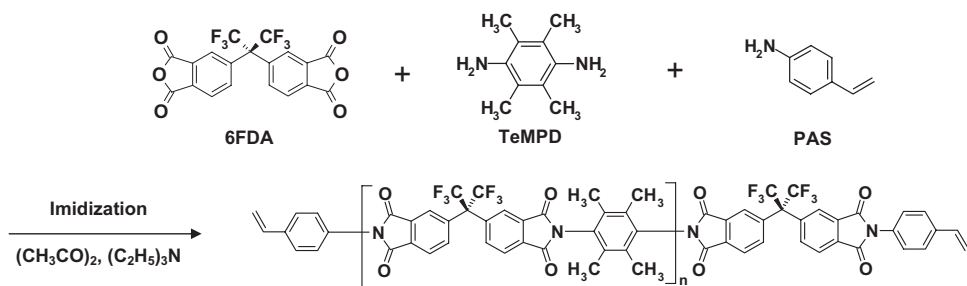
Recently, hyperbranched polyimides were obtained by selective orderly reaction only at polymer ends using telechelic polyimides with terminal reactive groups of acetylene, vinyl and acryl [29–33].

Thus, acetylene-terminated telechelic polyimide was synthesized from 6FDA as the anhydride and 4,4'-(9-fluorenylidene) dianiline (FDA) as an amine, also using 4-(2-phenylethynyl)phthalic anhydride (PEPA) as an acetylene-terminated monomer at room temperature (Scheme 1.6) [29,30]. The obtained telechelic polyimide had $M_w = 12000 \text{ g mol}^{-1}$ and a glass transition temperature of 420°C . The reaction using acetylene moiety is cyclotrimerization of three acetylene groups in three PEPA groups in the presence of tantalum(V) chloride catalyst with subsequent thermal treatment at 250°C . The obtained membrane was brittle, however, making it difficult to measure the gas permeation properties. A free-standing membrane was formed from acetylene-terminated telechelic polyimide using a flexible diamine structure, 3,4-diaminodiphenyl ether (DADE) [31].

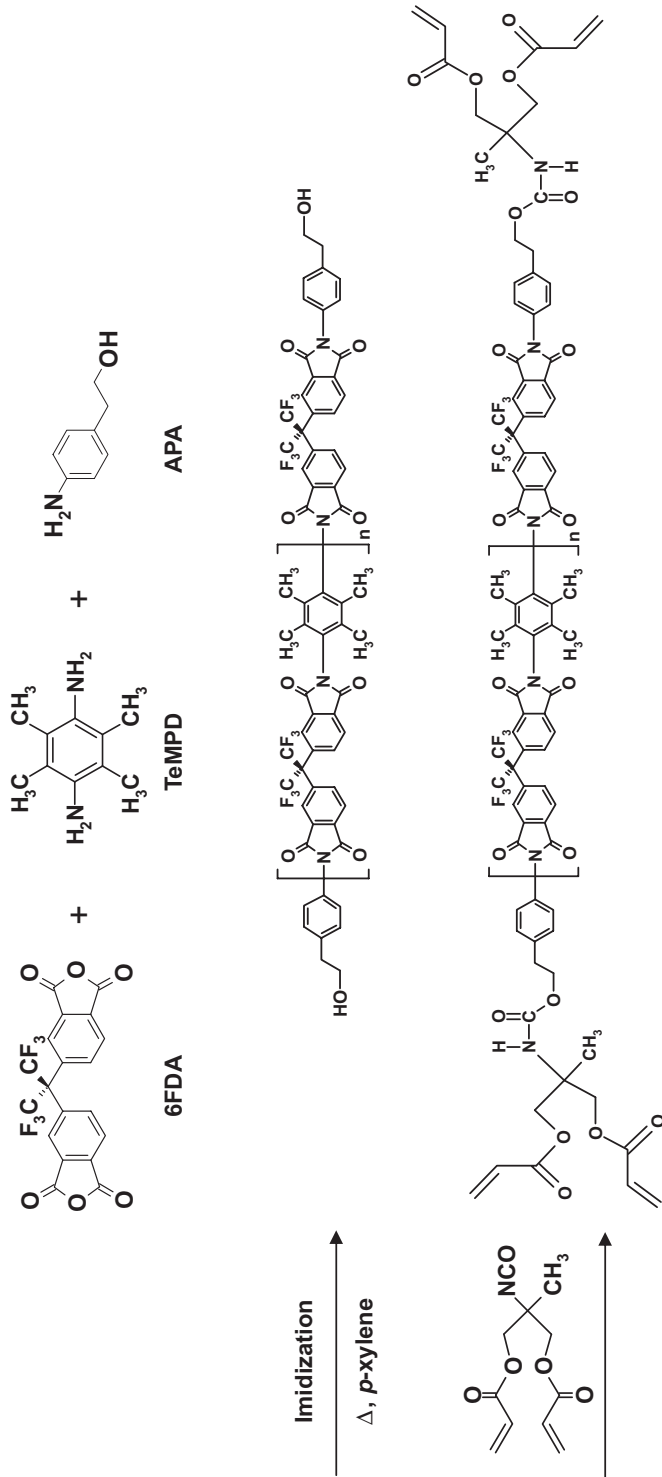
Vinyl- and acryl-terminated telechelic polyimides were also synthesized. The polymers were prepared from 6FDA, 2,3,5,6-tetramethyl-1,4-phenylene diamine (TeMPD), and *p*-aminostyrene (PAS) as a vinyl-terminated monomer, or 1,1-bis(acryloyloxymethyl) ethyl isocyanate (BEI) as an acryl-terminated monomer (Schemes 1.7 and 1.8) [32,33]. Both polymers were soluble in common organic solvents and had low M_n and viscosity.



Scheme 1.6



Scheme 1.7



Scheme 1.8

The reaction in vinyl or acryl-terminated polyimides was preceded by UV irradiation under the presence of a photo initiator. Formation of free-standing membranes was significantly enhanced by UV irradiation.

1.4 Gas Permeation Properties

In this section, we shall consider gas permeation properties of films based on cross-linked and hyperbranched polyimides. We shall focus on CO₂ capture from the flue gases of power plants (CO₂/N₂), CO₂ separation from natural gas (CO₂/CH₄), hydrogen purification (H₂/N₂) and oxygen and/or nitrogen enrichment of air (O₂/N₂) [28]. We shall consider permeability coefficients P_i and ideal separation factors for gas pairs A and B ($\alpha(A/B)$) defined as the ratio $P(A)/P(B)$. The trade-off relationship has been recognized between gas permeability and selectivity in polymeric membranes: highly permeable polymers have low selectivity and vice versa. The general trade-off relationship between gas permeability and selectivity has been summarized by Robeson [79,80], who suggested an idea of the upper bound. Traditionally, an interest of researchers was directed to materials whose data points are located at the Robeson diagrams close to or above the upper bound lines.

1.4.1 Amorphous Cross-linked Polyimides (Type II)

The gas permeability and selectivity of cross-linked membranes prepared by monoesterification and transesterification reactions between the carboxylic acid in polyimides and diol agents are summarized in Table 1.1 [34–38, 41, 42]. These gas permeation properties are strongly affected by the structures of the diol agent, polyimide composition and the annealing temperature after membrane formation. For example, the range of variation of $P(\text{CO}_2)$ is 10–145 Barrer while the selectivity $\alpha(\text{CO}_2/\text{CH}_4)$ is in the range 29–87 at 35 °C. The 6FDA-TMPD/DABA (3:2) cross-linked polyimides with 1,3-propanediol have better gas separation performance among the other cross-linked polyimides using monoesterification and transesterification reactions: $P(\text{CO}_2)$ of cross-linked 6FDA-TMPD/DABA (3:2) is 77 Barrer and $\alpha(\text{CO}_2/\text{CH}_4)$ is 40 at 35 °C and 4.4 atm [42].

The decarboxylation-induced cross-linked 6FDA-TMPD:DABA (2:1) polyimide reveals enhanced resistance to plasticization by high pressure of CO₂ [43]. This can be a result of high annealing temperature which leads to decarboxylation of the pendant acid groups. In this process phenyl radicals are formed that are capable of attacking other portions of the polyimide macromolecules. The CO₂ permeability of the cross-linked membrane prepared by rapid quenching from above the glass transition temperature is 260 Barrer at 35 °C and 6.8 atm.

The gas permeability and selectivity of cross-linked membranes prepared by the imide ring-opening reaction between the imide ring in polyimides and primary diamine agents are summarized in Table 1.2 [45–56]. As the reaction time increases, the gas permeability gradually decreases, whereas the selectivity increases. However, excess cross-linking leads to a reduction of both permeability and selectivity. The observed transport parameters could be strongly affected by the structures of diamine agent. For example, the $P(\text{CO}_2)$ is in the range 1.9–568 Barrer and the selectivity, $\alpha(\text{CO}_2/\text{CH}_4)$ is in the range

Table 1.1 Gas permeability coefficients and selectivity (at 35 °C) of cross-linked polyimides (Type II) using monoesterification and transesterification reaction of free carboxylic acid

Polyimide	Cross-linkable	Feed pressure (atm)	$P(O_2)$	$P(CO_2)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	Reference
6FDA-DABA	linear (Type I)	2	1.01	3.4	8.0	26.9	63.0	[34]
	Thermal cross-linked	3.74	2.69	10.40	6.7	26.0	87.0	[34]
6FDA-mPD	linear (Type I)	3.74	2.60	11.03	6.5	27.6	58.0	[34]
6FDA-mPD/ DABA (9:1)	linear (Type I)	3.74	1.71	6.53	6.9	26.1	65.3	[34]
6FDA-6FpDA/ DABA (1:2)	Ethylene Glycol linear (Type I)	3.74	1.81	9.50	6.8	35.2	63.3	[34]
6FDA-6FpDA/ DABA (2:1)	linear (Type I)	10	—	29	—	—	45	[35]
	Ion compound (Al(AcAc) ₃)	10	—	19	—	—	—	[36]
6FDA-TMPD/ DABA (2:1)	linear (Type I)	10	—	29	—	—	45	[37]
	Ion compound (Al(AcAc) ₃)	10	—	25	—	—	46	[36,37]
6FDA-TMPD/ DABA (2:1)	Ethylene glycol	10	6.0	35	—	—	42	[37]
	Butylene glycol (140 °C)	2	—	42.8	6.2	44.2	47	[38]
6FDA-TMPD/ DABA (2:1)	Thermal cross-linked (130 °C)	10	—	133	—	—	29	[41]
	Thermal cross-linked (220 °C)	10	—	115	—	—	27	[35,41]
6FDA-TMPD/ DABA (2:1)	Thermal cross-linked (295 °C)	10	—	110	—	—	30	[41]
	Ethylene Glycol (140 °C)	10	—	90	—	—	30	[35]
6FDA-TMPD/ DABA (2:1)	1,4-cyclohexanedimethanol (140 °C)	10	—	21	—	—	30	[35]
	1,4-cyclohexanedimethanol (220 °C)	10	—	22	—	—	30	[41]
6FDA-TMPD/ DABA (2:1)	1,4-cyclohexanedimethanol (295 °C)	10	—	79	—	—	29	[41]
	Butylene glycol (140 °C)	10	—	44	—	—	34	[35,41]
6FDA-TMPD/ DABA (2:1)	Butylene glycol (140 °C)	2	13.7	51	4.8	17.9	37	[38]
	Butylene glycol (220 °C)	10	—	46	—	—	34	[35,41]
6FDA-TMPD/ DABA (3:2)	Butylene glycol (295 °C)	10	—	138	—	—	30	[35,41]
	1,3-propanediol (220 °C)	4.4	—	57.5	—	—	37.1	[42]
6FDA-TMPD/ DABA (3:2)	1,3-propanediol (295 °C)	4.4	—	77.3	—	—	39.9	[42]

1 Barrer = 10^{-10} cm³ (STP) cm cm⁻³ s⁻¹ cmHg⁻¹.

Table 1.2 Gas permeability coefficients and selectivity (at 35 °C) of cross-linked polyimides (Type II) using imide ring-opening reaction by primary amine agents

Polyimide	Cross-linkable	Feed pressure (atm)	$P(O_2)$	$P(CO_2)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	Reference
Matrimid 5218	linear (Type I)	10	1.7	6.5	6.6	25.2	34	[45]
	<i>p</i> -xylenediamine (1 day)	10	1.9	7.4	6.5	25.3	36	[45]
	<i>p</i> -xylenediamine (7 day)	10	1.5	5.1	7.0	23.8	33	[45]
	<i>p</i> -xylenediamine (14 day)	10	1.4	4.7	7.0	23.5	34	[45]
	<i>p</i> -xylenediamine (32 day)	10	0.9	1.9	6.9	14.6	28	[45]
	linear (Type I)	2	–	5.39	–	–	36	[46]
	Poly(ethylene oxide) 2000 (1:0.2)	2	–	7.51	–	–	22	[46]
	Poly(ethylene oxide) 2000 (1:0.5)	2	–	59.16	–	–	18	[46]
	Poly(ethylene oxide) 2000 (1:1)	2	–	115.18	–	–	17	[46]
	Poly(ethylene oxide) 600 (1:1)	2	–	1.47	–	–	23	[47]
6FDA-TeMPD	linear (Type I)	10	125	456	3.7	13.5	–	[48]
	<i>p</i> -xylenediamine (5 min)	10	45.2	136	4.1	12.3	–	[48]
	<i>p</i> -xylenediamine (10 min)	10	28.9	91.8	4.4	14.0	–	[48]
	<i>p</i> -xylenediamine (15 min)	10	26.5	70.0	4.4	11.6	–	[48]
	<i>p</i> -xylenediamine (30 min)	10	13.7	30.3	4.8	10.6	–	[48]
	<i>p</i> -xylenediamine (60 min)	10	2.34	2.14	5.9	5.4	–	[48]
	linear (Type I)	10	186	612	3.36	11.0	13.6	[49]
6FDA-TeMPD	1,3-cyclohexanebis(methylamine) CHMA (30 min)	10	20.2	55.2	4.67	12.7	19.3	[49]
	CHMA (100 °C)	10	14.6	37.2	4.85	12.4	19.9	[49]
	CHMA (150 °C)	10	17.1	54.5	4.57	14.6	22.7	[49]
	CHMA (200 °C)	10	17.4	59.8	4.70	16.2	26.2	[49]

(continued overleaf)

Table 1.2 (continued)

Polymide	Cross-linkable	Feed pressure (atm)	$P(\text{O}_2)$	$P(\text{CO}_2)$	$\alpha(\text{O}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{CH}_4)$	Reference
6FDA-TeMPD	linear (Type I)	10	190	640	3.5	11.8	14	[50]
	Ethylenediamine (1 min)	10	120	490	4.0	16.3	23	[50]
	Ethylenediamine (2 min)	10	30	120	4.3	17.2	32	[50]
6FDA-TeMPD	Ethylenediamine (5 min)	10	12	25	6.0	12.5	28	[50]
	linear (Type I)	3.5	186	612	3.4	11.0	13.6	[52]
	ethylenediamine (1 min 10wt%)	3.5	108	435	3.8	15.3	21.1	[52]
	1,3-propanediamine (1 min 10wt%)	3.5	26.4	81.1	4.9	15.2	27.8	[52]
	1,4-butanediamine (1 min 10wt%)	3.5	55.5	218	4.2	16.5	24.7	[52]
6FDA-TeMPD	linear (Type I)	10	148.3	517	3.46	12.1	15.7	[53]
	PAMAM (20 min)	10	137.6	568	3.93	16.2	22.8	[53]
	PAMAM (60 min)	10	115.6	451	4.30	16.8	25.1	[53]
	PAMAM (24h)	10	44.1	157	5.38	19.1	35.6	[53]
	PAMAM (7days)	10	7.33	21.6	6.42	18.9	46.8	[53]
	linear (Type I)	3.5	186	612	3.4	11.0	13.6	[54]
6FDA-TeMPD	G1-DAB-AM (5 min)	3.5	130	435	4.6	15.3	23.0	[54]
	G1-DAB-AM (20 min)	3.5	74	220	5.1	15.2	24.4	[54]
	G1-DAB-AM (30 min)	3.5	70	177	5.7	14.5	24.5	[54]
	G1-DAB-AM (60 min)	3.5	50	98	6.9	13.6	21.7	[54]
	G0-PAMAM (1 day)	10	-	160	-	-	36	[56]
6FDA-TeMPD	G0-PAMAM (1 day, 120°C)	10	-	70	-	-	37	[56]
	G0-PAMAM (1 day, 250°C)	10	-	84	-	-	30	[56]

1 Barrer = $10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.

14–47 at 35 °C. The 6FDA-TeMPD cross-linked by PAMAM dendrimer has higher gas permeability among the other cross-linked polyimides using the imide ring-opening reaction [53]: $P(\text{CO}_2) = 568$ Barrer and $\alpha(\text{CO}_2/\text{CH}_4) = 22.8$ at 35 °C and 10 atm. PAMAM dendrimers have good gas separation performance especially for CO_2/N_2 because their amine groups have excellent affinity to CO_2 [81]. The reactions using dendrimers were studied by several authors [53–56]. The cross-linking modification by PAMAM and amine-terminated diaminobutane (DAB-AM) results in a decrease in permeabilities for most gases. In the case of the polyimide cross-linked with DAB-AM dendrimer, the maximum selectivity increases by about 400, 300 and 265% for the gas pairs of He/N_2 , H_2/N_2 and H_2/CO_2 , respectively [54]. The gas permeability decreases in the order of $G1 > G2 > G3$, which is consistent with the increasing order of the degree of gel contents.

The gas permeability and selectivity of cross-linked membranes obtained by UV irradiation of polyimides are summarized in Table 1.3 [63–69]. The gas permeability decreases with the increase in UV irradiation time and is in the range 0.2–21 Barrer for O_2 and 0.6–99 Barrer for CO_2 at 35 °C. The selectivities are 4.3–13.8 for $\alpha(\text{O}_2/\text{N}_2)$ and 21.2–111.4 for $\alpha(\text{CO}_2/\text{CH}_4)$.

The gas permeation parameters have also been reported for polymers obtained via ether reaction of epoxy and diamines [57,58], for polymer blends with acetylene-terminated oligomer [73,74] and internal acetylene polyimide [72,75]. The gas permeability of cross-linked internal acetylene-containing polymer, 6FDA-TeMPD/*p*-intA (4:1) declines from 612 to 186 Barrer, while the selectivity, $\alpha(\text{CO}_2/\text{CH}_4)$ increases from 14 to 25 at 35 °C and 10 atm [75]. Moreover, this cross-linked 6FDA-TeMPD/*p*-intA (4:1) membrane is still stable under CO_2 pressure of about 47 atm.

1.4.2 Hyperbranched Polyimides (Type III)

Almost all hyperbranched polyimides with reported gas permeation parameters were synthesized from A_2 - and B_3 -type monomers. The corresponding transport data are presented in Table 1.4 [20–26]. All the polymers are in a glassy state. The gas permeabilities of hyperbranched polyimides vary from 0.02 to 11 Barrer for O_2 and from 0.08 to 65 Barrer for CO_2 at 20–35 °C. The selectivities vary from 2.0 to 13 for $\alpha(\text{O}_2/\text{N}_2)$ and from 3.4 to 70.1 for $\alpha(\text{CO}_2/\text{N}_2)$.

6FDA-TAPA hyperbranched polyimides with terephthaldehyde (TPA) form a group of the most permeable polymers among those presented in Table 1.4. For example, the $P(\text{CO}_2)$ of cross-linked 6FDA-TAPA is 65 Barrer and $P(\text{O}_2) = 11$ [20]. The gas transport properties of polymer blend with commercial polyimide, Matrimid 5218 (BTDA-AAPTMI) and P84 (BTDA-TDI/MDI), and hyperbranched polyester, Boltorn (H40) have also been reported [25]. Selectivities of Matrimide-H40 (1 wt%) containing membrane show both high and low values: thus, $\alpha(\text{O}_2/\text{N}_2)$ varies from 6.8 to 2.0. The permeability of the $P(\text{N}_2)$ of P84 with various concentrations of H40 membrane decreases with the increase in the concentrations of H40 in comparison to pure P84, while their selectivity generally are almost constant.

Figure 1.2 presents the effects of UV irradiation time on gas permeability and selectivity for acryl-terminated telechelic polyimide, 6FDA-TeMPD-BEI [33]. It is seen that the gas permeability decreases, while the selectivity increases.

Table 1.3 Gas permeability coefficients (Barrer) and selectivity of UV cross-linked polyimides (Type II)

Polyimide	Temperature (°C)	Feed pressure (atm)	$P(O_2)$	$P(CO_2)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	Reference
BTDA-TMPD (linear (Type II))	35	10	9.84	38.3	5.5	21.4	26.4	[63]
BTDA-TMPD (1 min)	35	10	4.15	17.8	5.5	23.7	33.6	[63]
BTDA-TMPD (10 min)	35	10	0.482	1.48	13.8	42.4	–	[63]
BTDA-TMPD (30 min)	35	10	0.199	0.618	13.2	40.9	111.4	[63]
BTDA/6FDA-TMPD (1:1) (linear (Type I))	35	10	12.3	48.3	4.5	17.7	18.0	[63]
BTDA/6FDA-TMPD (1:1) (30 min)	35	10	1.74	5.58	9.6	30.8	85.2	[63]
BTDA/6FDA-TMPD (1:1) (60 min)	35	10	1.58	4.84	10.5	32.3	–	[63]
BTDA/6FDA-TMPD (1:3) (linear (Type I))	35	10	18.5	83.2	3.6	16.4	23.4	[63]
BTDA/6FDA-TMPD (1:3) (30 min)	35	10	4.57	14.9	5.9	19.3	49.3	[63]
BTDA/6FDA-TMPD (1:3) (60 min)	35	10	3.59	13.3	7.0	25.8	–	[63]
BTDA-BAPP (linear (Type I))	30	1	0.54	2.8	4.9	25.4	–	[64]
BTDA-BAPP (1 min)	30	1	0.45	2.4	7.5	40.0	–	[64]
BTDA-BAPP (5 min)	30	1	0.40	1.9	8.5	40.4	–	[64]
BTDA-BAPP (10 min)	30	1	0.26	1.9	10.4	76.0	–	[64]
ODPA-BAPP (linear (Type I))	30	1	0.49	2.7	7.0	38.6	–	[64]
ODPA-BAPP (1 min)	30	1	0.43	2.2	6.1	31.4	–	[64]
ODPA-BAPP (5 min)	30	1	0.48	2.4	7.4	36.9	–	[64]
ODPA-BAPP (10 min)	30	1	0.37	1.7	7.9	36.2	–	[64]
6FDA-TMPD (linear (Type I))	30	1	130	900	3.6	25.0	28.1	[65]
6FDA-TMPD (30 min)	30	1	14	59	6.1	25.7	42.1	[65]
6FDA-TMPD (BP 0.99 wt% 15 min)	30	1	21	99	5.4	25.4	39.6	[65]
6FDA-TMPD (BP 9.09 wt% 15 min)	30	1	5.2	21	4.3	17.5	21.2	[65]

BTDA-BAPP (linear (Type I))	30	1	0.45	2.3	7.50	38.3	—	[66]
BTDA-BAPP (10 min)	30	1	0.36	1.8	7.83	39.1	—	[66]
BTDA-BAPP (20 min)	30	1	0.36	1.8	8.37	41.9	—	[66]
BTDA-BAPP (30 min)	30	1	0.24	0.97	10.4	42.2	—	[66]
BTDA-BAPP (linear (Type I))	30	1	0.54	2.8	4.90	25.5	—	[66]
BTDA-BAPP (quench 10 min)	30	1	0.47	2.4	7.34	37.5	—	[66]
BTDA-BAPP (quench 30 min)	30	1	0.34	1.5	8.50	37.5	—	[66]
PMDA/BTDA-3MPDA (9:1) linear (Type I)	30	—	22.3	—	4.3	—	—	[69]
PMDA/BTDA-3MPDA (9:1) (2h)	30	—	4.35	—	5.7	—	—	[69]
PMDA/BTDA-3MPDA (9:1) (6h)	30	—	0.67	—	6.7	—	—	[69]
PMDA/BTDA-3MPDA (8:2) linear (Type I)	30	—	21.4	—	4.3	—	—	[69]
PMDA/BTDA-3MPDA (8:2) (2h)	30	—	9.10	—	6.3	—	—	[69]
PMDA/BTDA-3MPDA (8:2) (10h)	30	—	0.21	—	7.2	—	—	[69]
PMDA/BTDA-3MPDA (5:5) linear (Type I)	30	—	12.1	—	4.9	—	—	[69]
PMDA/BTDA-3MPDA (5:5) (2h)	30	—	7.40	—	5.6	—	—	[69]
PMDA/BTDA-3MPDA (5:5) (6h)	30	—	0.40	—	11.0	—	—	[69]
PMDA/BTDA-3MPDA (3:7) linear (Type I)	30	—	9.42	—	4.9	—	—	[69]
PMDA/BTDA-3MPDA (3:7) (2h)	30	—	1.15	—	11.0	—	—	[69]
BTDA-3MPDA linear (Type I)	30	—	5.00	—	5.0	—	—	[69]
BTDA-3MPDA (2h)	30	—	0.84	—	11.0	—	—	[69]

Table 1.4 Gas permeability coefficients (Barrer) and selectivity of hyperbranched polyimides (Type III)

Polymer	Temperature (°C)	Feed pressure (atm)	$P(O_2)$	$P(CO_2)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	Reference
6FDA-TAPA (AM-T) EDGE 1.4	35	1	—	3.7	—	30.8	46	[20]
6FDA-TAPA (AM-T) EDGE 0.34	35	1	1.9	11	5.8	33.3	50	[20]
6FDA-TAPA (AM-T) EDGE 0.15	35	1	—	16	—	—	32	[20]
6FDA-TAPA (AM-T) TPA 0.25	35	1	11	65	5.1	30.1	41	[20]
6FDA-TAPA (AH-T) ODA 0.04	35	1	—	6.7	—	26.8	61	[20]
DSDA-TAPA (AH-T) TPA 0.05	35	1	—	4.0	—	43.5	—	[20]
DSDA-TAPA (AH-T) DDS 0.03	35	1	—	1.0	—	41.7	—	[20]
6FDA-TAPOB	25	1	2.25	12.80	6.2	35.3	—	[21]
6FDA-TAPOB (6FMA)	25	1	1.9	9.0	6.3	30.0	—	[22]
6FDA-TAPOB (p-3FMA)	25	1	1.5	7.2	6.5	31.3	—	[22]
6FDA-TAPOB	25	1	1.2	5.4	7.5	33.8	—	[22]
6FDA-TAPOB (m-3FMA)	25	1	1.3	6.3	6.8	33.2	—	[22]
HQDPA-TFAPOB(amine-terminated)	20	1	0.058	1.55	7.7	3.4	—	[24]
HQDPA-TFAPOB(CF3-terminated)	20	1	0.114	2.72	6.5	3.6	—	[24]
Matrimid 5218 (H40 0.0wt%)	35	3.5	1.02	5.20	6.8	34.7	—	[25]
Matrimid 5218 (H40 1.0wt%)	35	3.5	1.31	5.25	2.0	8.2	—	[25]
Matrimid 5218 (H40 5.0wt%)	35	3.5	0.70	3.29	6.4	29.9	—	[25]
Matrimid 5218 (H40 10.0wt%)	35	3.5	0.61	2.85	6.8	31.7	—	[25]
P84 (H40 0.0wt%)	35	3.5	0.57	1.67	11.4	33.4	—	[25]
P84 (H40 1.0wt%)	35	3.5	0.51	1.20	13	30.0	—	[25]
P84 (H40 5.0wt%)	35	3.5	0.39	1.00	13	33.3	—	[25]
P84 (H40 10.0wt%)	35	3.5	0.37	0.94	12	31.3	—	[25]
ODPATAP/ODA (AM-T) (1/1/0)	30	1.5	0.024	0.096	12	48.0	48	[26]
ODPATAP/ODA (AM-T) (1/0.95/0.05)	30	1.5	0.043	0.156	10.8	39.0	52	[26]
ODPATAP/ODA (AM-T) (1/0.75/0.25)	30	1.5	0.056	0.246	9.3	41.0	62	[26]
ODPATAP/ODA (AM-T) (1/0.5/0.5)	30	1.5	0.101	0.352	7.8	27.1	50	[26]
ODPATAP/ODA (AM-T) (1/0.25/0.75)	30	1.5	0.087	0.450	8.7	45.1	75	[26]
ODPATAP/ODA (AH-T) (2/1/0)	30	1.5	—	0.079	—	—	—	[26]
ODPATAP/ODA (AH-T) (2/0.95/0.05)	30	1.5	0.024	0.140	8.0	46.7	47	[26]
ODPATAP/ODA (AH-T) (2/0.75/0.25)	30	1.5	0.054	0.135	10.8	27.0	36	[26]
ODPATAP/ODA (AH-T) (2/0.5/0.5)	30	1.5	0.065	0.257	9.3	36.7	66	[26]
ODPATAP/ODA (AH-T) (2/0.25/0.75)	30	1.5	0.071	0.285	8.9	35.6	51	[26]

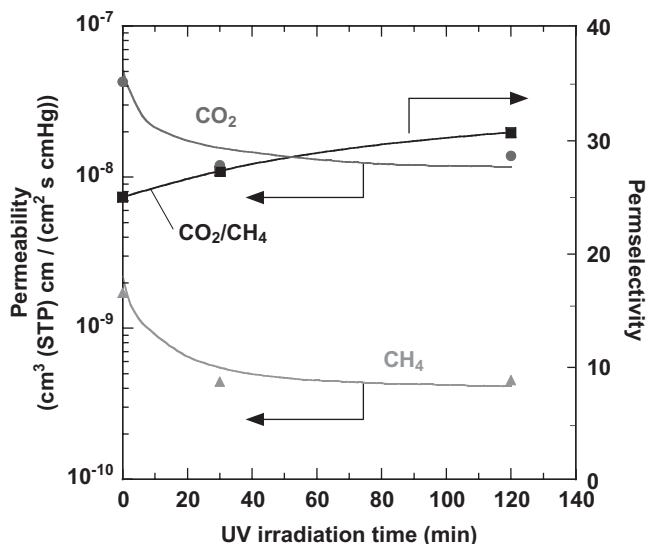


Figure 1.2 Dependence of $P(\text{CO}_2)$ (\bullet), $P(\text{CH}_4)$ (\blacktriangle) and $\alpha(\text{CO}_2/\text{CH}_4)$ (\blacksquare) on irradiation time in UV-cross-linked 6FDA-TeMPD-BEI membranes at 35 °C. Data from Reference [33]

In the same manner the gas permeability in hyperbranched polyimide prepared from vinyl-terminated telechelic polyimide, 6FDA-TeMPD-PAS is reduced by UV irradiation [32]. The gas permeabilities of this polymer after 120 min of irradiation are as follows: 50 Barrer for O_2 and 345 Barrer for CO_2 at 30 °C and 1 atm. The selectivities are 3.5 for $\alpha(\text{O}_2/\text{N}_2)$ and 24 for $\alpha(\text{CO}_2/\text{CH}_4)$.

1.4.3 Selectivity and Permeability

Figures 1.3–1.5 present Robeson diagrams for different gas pairs, in various polyimide membranes. The first examination of these plots shows that the data points for Type II (cross-linked) and Type III (hyperbranched) structures can be found in the whole ‘cloud’ of the data points including those of linear structures (Type I). However, the data points for some hyperbranched and cross-linked polyimides are located near the upper bound for O_2/N_2 pair as shown in Figure 1.3. On the other hand, the majority of the hyperbranched polyimides tend to be located among the common linear polyimides, as well as that of cross-linked polyimides in the diagram for CO_2/N_2 pair relationship as shown in Figure 1.4. Finally, the data points for all three types of the structures are far from upper bound for the pair CO_2/CH_4 , as seen in Figure 1.5. Apparently, more data are required in order to discuss more specifically the relationship between gas permeation properties and the structure of hyperbranched and cross-linked polymers.

1.5 Concluding Remarks

Initially, hyperbranched and cross-linked polymers were the subject of investigation in the field of polymer science (both polymer chemistry and physics). Gradually, since the

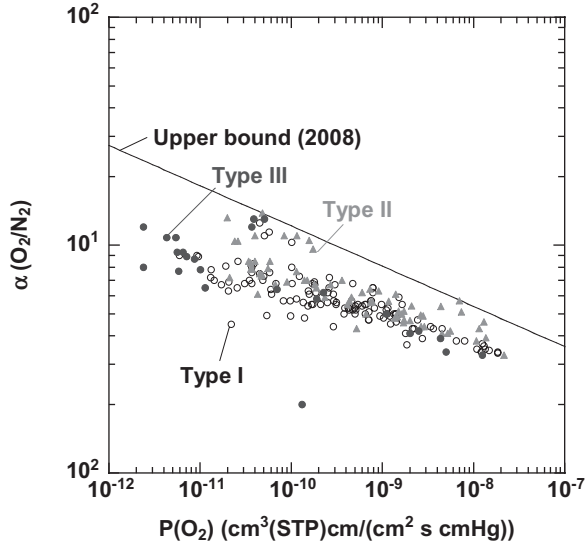


Figure 1.3 Relationship between $\alpha_{(O_2/N_2)}$ and $P(O_2)$ in polyimide membranes. Type I: linear (○), Type II: cross-linked (▲) and Type III: hyperbranched (●)

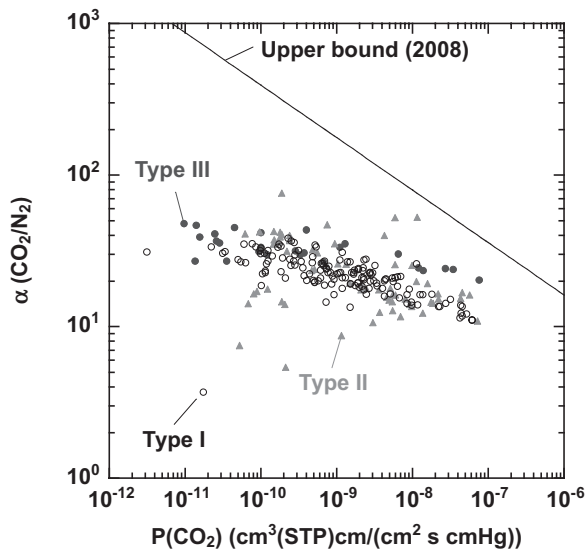


Figure 1.4 Relationship between $\alpha_{(CO_2/N_2)}$ and $P(CO_2)$ in polyimide membranes. Type I: linear (○), Type II: cross-linked (▲) and Type III: hyperbranched (●)

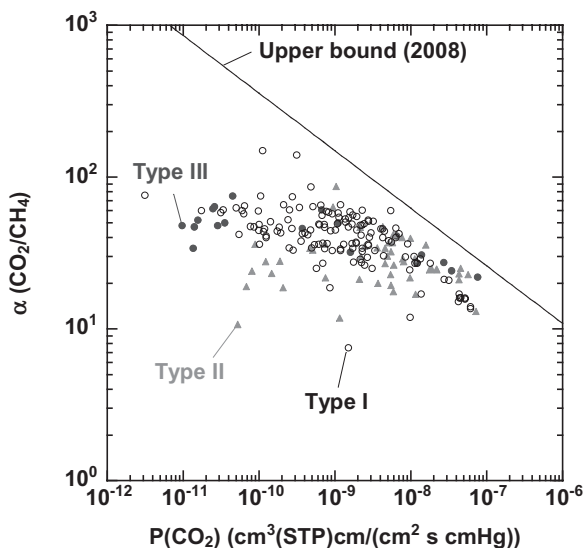


Figure 1.5 Relationship between $\alpha(\text{CO}_2/\text{CH}_4)$ and $P(\text{CO}_2)$ in polyimide membranes. Type I: linear (○), Type II: cross-linked (▲) and Type III: hyperbranched (●)

early 2000s, hyperbranched and cross-linked polyimides attracted interest as materials for gas separation membranes. Bearing in mind the general requirements for ‘good’ gas separation materials (high permeability, selectivity, physical stability, processability and low cost) they did not demonstrate so far (as the classes of polymer architecture) the desired combination of the properties. However, since some promising results have been obtained and experience has been accumulated, further investigations in the synthesis, modifications and membrane properties are important: these should show the real potential impact of these polymers in membrane science and technology.

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