



# Synthesis and gas permeation properties of hyperbranched polyimides membranes from a novel ( $A_2 + B_2B' + B_2$ )-type method

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## ARTICLE INFO

### Article history:

Received 28 May 2013

Received in revised form

30 August 2013

Accepted 2 September 2013

Available online 10 September 2013

### Keywords:

Hyperbranched polyimide

Synthesis

Membrane

Gas separation

## ABSTRACT

A series of hyperbranched polyimides were successfully synthesized by  $A_2 + B_2B' + B_2$  copolymerization from 2,2-bis(3,4-dicarboxylphenyl) hexafluoropropane dianhydride (6FDA), 2,4,6-triaminopyrimidine (TAP) and 4,4'-oxydianiline (ODA). Self-standing polyimides membranes with sufficient mechanical properties were achieved by incorporation of difunctional  $B_2$  comonomer into the hyperbranched polymer structure. The degree of branching was estimated using  $^1\text{H}$  NMR spectroscopy. The morphology structure of the prepared polyimides was evaluated by wide-angle X-ray diffraction patterns, and the d-spacing values first increased gradually to the highest value 5.73 Å with increasing the content of TAP, and then decreased. The densities of these films were tested and the difference in density is probably due to the different inter-macromolecular packing efficiency. Both the 5% weight loss at temperatures and the glass transition temperatures ( $T_g$ ) of the obtained polyimides decreased with decreasing the content of ODA comonomer. Similar tendency was found for tensile strength and elongation at break. Gas transport measurements showed the prepared TAP-ODA-6FDA hyperbranched polyimides exhibited lower permeabilities compared with ODA-6FDA linear polyimides, but higher  $\text{O}_2/\text{N}_2$  and  $\text{CO}_2/\text{N}_2$  selectivities. So they are expected to apply in the field of gas separation.

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## 1. Introduction

In recent years, hyperbranched polymers have attracted much attention in the chemistry, physics, materials, biology, and biomedicine fields for their unique properties which are not shared with linear analogous polymers [1–10]. Among them, hyperbranched polyimides are a new type of polymers based on hyperbranched macromolecules and polyimides. They have the specific three-dimensional molecular structure, highly branched molecular chains and many end-group functional groups on the surface of the molecule. And they possess the combination property of hyperbranched polymers and polyimides, such as high glass transition temperatures and superior solubility. Owing to these unique structural characteristics, excellent physical and chemical properties, hyperbranched polyimides have received increasing interest in many fields [11–22].

Membrane-based gas separations have drawn much attention because they offer many significant advantages over traditional separation processes, and a large number of polymeric materials have been studied for this application. It is well-known that an aromatic polyimide is an important high-performance polymeric material with many excellent properties such as high mechanical

strength, high modulus, low coefficient of thermal expansion and excellent thermal stability [23–26]. Based on these merits, polyimide membranes have been of great interest in gas separation applications [27–30]. However, most of previous experimental studies on gas permeation applications were focused on linear-type polyimides.

It has been reported that there are many open and accessible cavities in rigid hyperbranched polymers according to the results of computer simulation [1,31]. These cavities are formed due to the periphery of neighboring branches. Solvents can be accommodated in these cavities and this is the reason that hyperbranched polymers showed better solubility than corresponding linear ones [1]. And these cavities may function as the pathways for the transport of gas molecules. On the basis of these considerations, we tried to develop a series of hyperbranched polyimides for gas separations.

Hyperbranched polyimides have been successfully synthesized by self-polymerization of  $AB_2$  monomers and  $A_2 + B_3$  monomers [32–40]. However, both the methods of  $AB_2$  monomers and  $A_2 + B_3$  monomers are impractical to prepare hyperbranched polyimides in a large scale. For the former method,  $AB_2$  monomers are hard to prepare because of the too high reactivities of anhydride and amine groups. And for the later method, stringent polymerization conditions such as low monomer concentrations and strictly controlled slow addition rate, are necessary to avoid gel formation.

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Recent years, Ye Liu et al. [38] have realized facile syntheses of hyperbranched polyimides by the polymerization of  $A_2+B_2B'$  monomers. No gelation happened in the polymerization although the monomer conversions surpassed the theoretical gel points. This is due to the different reactivities of amino groups at 2- and 4-/6- positions in 2,4,6-triaminopyrimidine (TAP) [41], which is not in accord with the basic assumption of the equal reactivity of all A groups as well as B groups at any given stage of the reaction in Flory's theory of gelation formation [42,43].

However, it is well known that many hyperbranched polymers exhibit poor mechanical properties which are probably due to the lower molecular weights and a lower number of physical entanglements between the macromolecules. So the pure hyperbranched polyimides are difficult to obtain in the form of self-standing membranes because of cracking. And their gas transport properties were difficult to measure. Until now, hyperbranched polyimides membranes with sufficient mechanical properties were achieved just by crosslinking [44] or by using composite membranes [45], however, these methods adopt two kinds of components and are relatively complicated to prepare self-standing membranes.

In this work, our goal was to prepare hyperbranched polyimides membranes with improved mechanical properties and thus the products are suitable for gas separation applications. As we all know, the linear polyimides exhibit excellent mechanical properties. Based on this consideration, we tried to improve mechanical properties of hyperbranched polyimides by incorporation of difunctional  $B_2$  comonomer into the polymer structure. Higher number of  $B_2$  comonomer could increase distances among branches and thus afford more flexibility in the relatively rigid branched structure and finally the number of chain physical entanglements could increase. We used difunctional 4,4'-oxydianiline(ODA) as such  $B_2$  comonomer. This approach could be described as  $A_2+B_2B'+B_2$  copolymerization. In our previous work, a series of hyperbranched polyimides were prepared based on 2,2-bis(3,4-dicarboxylphenyl) hexafluoropropane dianhydride (6FDA) and TAP, and the molar ratios of TAP:6FDA changed from 1:1 to 1:2. The TAP-6FDA hyperbranched polyimide with the best comprehensive properties has been chosen from these research works and its molar ratio of TAP:6FDA was 1:1.6, while the molar ratio of amine groups:anhydride groups was 3:3.2. On the basis of this consideration, we tried to synthesize a series of TAP-ODA-6FDA hyperbranched polyimides with the molar ratio of amine groups:anhydride groups being 3:3.2. The structure characterization, thermal stabilities and mechanical properties of the prepared membranes were tested, and the gas permeation properties were also investigated.

## 2. Experimental

### 2.1. Materials

Both 2,2-bis(3,4-dicarboxylphenyl) hexafluoropropane dianhydride (6FDA) and 2,4,6-triaminopyrimidine (TAP) were purified by sublimation before use. 4,4'-Oxydianiline (ODA) was recrystallized from tetrahydrofuran and then dried at 373 K under vacuum. *N,N*-dimethylacetamide (DMAc) was distilled after being dried over  $P_2O_5$ . Other solvents and reagents were used as received.

### 2.2. Characterization

Fourier transform infrared (FTIR) spectroscopy was acquired on a TENSOR27 FTIR spectrometer (Bruker).

$^1H$  NMR spectra was recorded by an INOVA-400 spectrometer (Varian), DMSO- $d_6$  as a solvent, and tetramethylsilane (TMS) as an internal standard.

An UV-vis spectrometer analysis was performed on a UV-2550 (Shimadzu) to record the different absorption of the various hyperbranched polyimides in DMSO solution.

The thermogravimetric analyzer (TGA) was performed using a TA instruments Q50 at the heating rate of 10 °C/min from room temperature to 800 °C under nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on a TA instrument 2910 at the heating rate of 10 °C/min from room temperature to 400 °C under nitrogen atmosphere.

Wide angle X-ray diffraction (WAXD) was used to determine the d-spacing in hyperbranched polyimides using a X'Pert MPD PRO X-ray diffractometer. The d-spacing was calculated from the scattering angle ( $2\theta$ ) according to Bragg's equation

$$n\lambda = 2d \sin \theta \quad (1)$$

The tensile properties were performed on a CMT-8502 Tensile apparatus at a crosshead speed of 10 mm/min on strips approximately 40–60  $\mu m$  thick and 1.5 cm wide with a 6 cm gauge length. An average of at least five individual determinations was used.

Density of a polyimide membrane was measured by the suspension method with a mixture of toluene and tetrachloromethane at 25 °C.

Gas permeability coefficient  $P$  [ $cm^3(STP) cm/cm^2 s cmHg$ ] was determined by the vacuum-pressure method using a time-lag apparatus "VAC-V2 gas permeation apparatus" which is produced by Labthink (China). A polyimide film, which was held in the permeation cell sealed with O-rings, was evacuated for 24 h in the gas permeation apparatus. Desired pressure of a gas was introduced on the upstream side, and pressure on the downstream side of the film was initially reduced to high vacuum. The pressure on the upstream side was monitored using a pressure transducer. The permeability coefficient was obtained from the permeation rate that was monitored as the variation of pressure on the downstream side at a steady state using another pressure transducer. The gas permeability coefficient can be explained on the basis of the solution-diffusion mechanism, which is represented by the following equation:

$$P = DS \quad (2)$$

where  $D$  ( $cm^2/s$ ) is the diffusion coefficient and  $S$  [ $cm^3(STP)/cm^3 cmHg$ ] is the solubility coefficient. The ideal selectivity is calculated from the ratio of permeability coefficient

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

where  $P_A$  and  $P_B$  refer to the permeability coefficients of pure gases A and B respectively. The diffusion coefficient  $D$  is calculated by the following equation:

$$D = \frac{L^2}{6\theta} \quad (4)$$

where  $L$  (cm) is the thickness of the membrane and  $\theta$  (s) is the time-lag.

### 2.3. Synthesis

#### 2.3.1. Synthesis of TAP-ODA-6FDA polyamic acids

A series of hyperbranched polyimides were prepared with different molar ratios between TAP and ODA. The amounts for synthesis of hyperbranched polyimides were shown in Table 1. TAP and corresponding amount of ODA in DMAc were added into an oven dried, three-necked flask with stirring and a nitrogen flow at room temperature. Then, corresponding amount of 6FDA in

**Table 1**  
The additions for synthesis of TAP–ODA–6FDA polyimides.

Polymers	TAP (mmol)	ODA (mmol)	6FDA (mmol)
B1	–	20	20
B2	1.875	17	20
B3	3.75	14	20
B4	5.625	11	20
B5	7.5	8	20
B6	9.375	5	20
B7	11.25	2	20
B8	12.5	–	20

DMAc was added to this solution. The reaction mixture was further stirred for 24 h to afford TAP–ODA–6FDA polyamic acids and finally stored in a refrigerator.

### 2.3.2. Membrane formation

The polyamic acids solutions were cast on dry and clean glass plates and dried at 80 °C in an oven with air stream for 1 h. Membranes were subsequently imidized (125 °C/1 h, 200 °C/1 h, 250 °C/0.5 h and 300 °C/10 min). The resulting polyimides membranes were delaminated in boiling water and dried in a vacuum oven at 150 °C for 2 h. Care was taken to ensure that the membranes prepared were completely dense without pores or defects. The membranes were used for gas permeation and mechanical test, and the influence of the membrane thickness has been considered in the calculated equation for the data of gas permeation and mechanical properties.

## 3. Results and discussion

### 3.1. Polymerization and film formation

The method of synthesis of  $(A_2 + B_2B' + B_2)$ -type hyperbranched polyimides is similar to that of  $(A_2 + B_2B')$ -type hyperbranched polyimides, which has been reported elsewhere [38]. A series of TAP–ODA–6FDA hyperbranched polyimides were synthesized with the molar ratio of amine groups which were from TAP and ODA monomers:anhydride groups which were from 6FDA monomer being 3:3.2. The molar ratios of TAP, ODA and 6FDA monomers used in this synthesis were shown in Table 1. The number of linear units and the degree of branching could be easily controlled by changing the molar ratio of TAP:ODA.

The synthesis involved two steps. In the first stage, polyamic acids were synthesized by controlling monomer molar ratio (Fig. 1), and in the second step the precursors were thermal imidized to form polyimide films (Figs. 1 and 2). No gelation occurred during polymerization which was attributed to the different reactivities of the amine groups in TAP, and it would make it easier to prepare hyperbranched polyimides in a large scale. Polyamic acids solutions were cast on dry and clean glass plates and the imidization was carried out by thermal treatment after evaporation of the solvent from cast films, and then the films could be obtained.

### 3.2. Polymer characterization

Chemical structure of TAP–ODA–6FDA hyperbranched polyimides prepared by imidization of corresponding polyamic acids was presented in Fig. 2. TAP is the branched unit and there are three kinds of units which are terminal (T), linear (L), and dendritic (D) units. These units could be confirmed by  $^1\text{H}$  NMR.

The structural perfection of hyperbranched polymers has been generally characterized by degree of branching (DB), which was

defined by Frechet as the following equation [46]:

$$DB = (D + T)/(D + T + L) \quad (5)$$

where  $D$ ,  $T$  and  $L$  represent the contents of dendritic, terminal and linear units respectively. Experimentally,  $DB$  is usually estimated using  $^1\text{H}$  NMR or  $^{13}\text{C}$  NMR spectroscopy by comparing the integrals of peaks assignable to respective units. So  $D$ ,  $T$  and  $L$  are related to the peak intensity  $I_D$ ,  $I_T$  and  $I_L$ . Thus  $DB$  could be defined as the following equation.

$$DB = \frac{I_D + I_T}{I_D + I_T + I_L} \quad (6)$$

Fig. 3 shows  $^1\text{H}$  NMR spectra of the obtained polyimides. The peaks in the range of 8.18–7.64 ppm are assigned to the hydrogens of 6FDA, and the peaks in around 7.70 ppm and 7.20 ppm are assigned to the hydrogens of ODA, while the peaks in the range of 7.80–5.44 ppm are corresponding with the hydrogens in the pyrimidine ring and the free amines in TAP units, which contain the information on degree of branching. The  $^1\text{H}$  shift of TAP units in this range was shown in Table 2.  $H_5$  is the hydrogen in the pyrimidine ring of TAP units. In this research work, there were two kinds of linear units, which were TAP linear units and ODA linear units. So  $I_L$  is the sum of  $I_{L-ODA}$  and  $I_{L-TAP}$ .  $I_T$  is the sum of the peak intensities at 5.44 and 5.79 ppm, while  $I_{L-TAP}$  is the sum of the peak intensities at 6.68 and 6.87 ppm, and  $I_D$  is the peak intensities at 7.80 ppm. The hydrogens of ODA at around 7.20 ppm and 7.70 ppm were overlapped with those of 6FDA and  $\text{NH}_2$  of 4,6-diimide, so  $I_{L-ODA}$  can be obtained by Eq. (7) using the molar ratio of TAP:ODA.

$$\frac{\text{Mol(ODA)}}{\text{Mol(TAP)}} = \frac{(I_{L-ODA})/2}{(I_D/3) + (I_{L-TAP}/2) + I_T} \quad (7)$$

The calculated  $DB$  values of all the obtained polyimides were shown in Table 3. It can be seen that the  $DB$  values increased from 0% to 69% with increasing the content of TAP monomer.

The structures of the prepared polyimides were characterized by FTIR analyses. As shown in Fig. 4, the absorption peaks at about  $1790\text{ cm}^{-1}$  (CaO asymmetrical stretching),  $1730\text{ cm}^{-1}$  (CaO symmetrical stretching),  $1380\text{ cm}^{-1}$  (C3N stretching) and  $720\text{ cm}^{-1}$  (deformation of imide) are the characteristic absorption bands of the aromatic imide group. No characteristic peak of polyamic acids around  $1660\text{ cm}^{-1}$  was detected, which reflected the full imidization of polyamic acids. It can be seen that the absorption band at about  $3360\text{ cm}^{-1}$  generated by N3H stretching of the terminal amino groups increased with increasing the content of TAP comonomer. The aromatic amine absorption of ODA at about  $1500\text{ cm}^{-1}$  decreased with decreasing the content of ODA and disappeared for B8 polymer which no ODA was incorporated in.

All of the prepared TAP–ODA–6FDA polyimides membranes were brown–yellow in color and were completely transparent. The morphology structure of the prepared hyperbranched polyimides was evaluated using wide-angle X-ray diffraction patterns. The curves of all products were broad and without obvious peak features which reflected completely amorphous structure. From the scattering angles ( $2\theta$ ) in the central of the broad peaks, d-spacing values were calculated according to Eq. (1). It is well known that the d-spacing is often referred to the average intersegmental distances in linear polymers. In the case of hyperbranched polymers, d-spacing might contain the information of the average distances between intersegment or neighboring branches. The mean d-spacing and  $2\theta$  values were listed in Table 3. The results suggested that the d-spacing values first increased gradually to the highest value  $5.73\text{ \AA}$  with increasing the content of TAP, and then decreased. However, the d-spacing values of B2, B3 and B4 which were branched polyimides were higher than that of B1 which was linear polyimides. For the hyperbranched polyimides

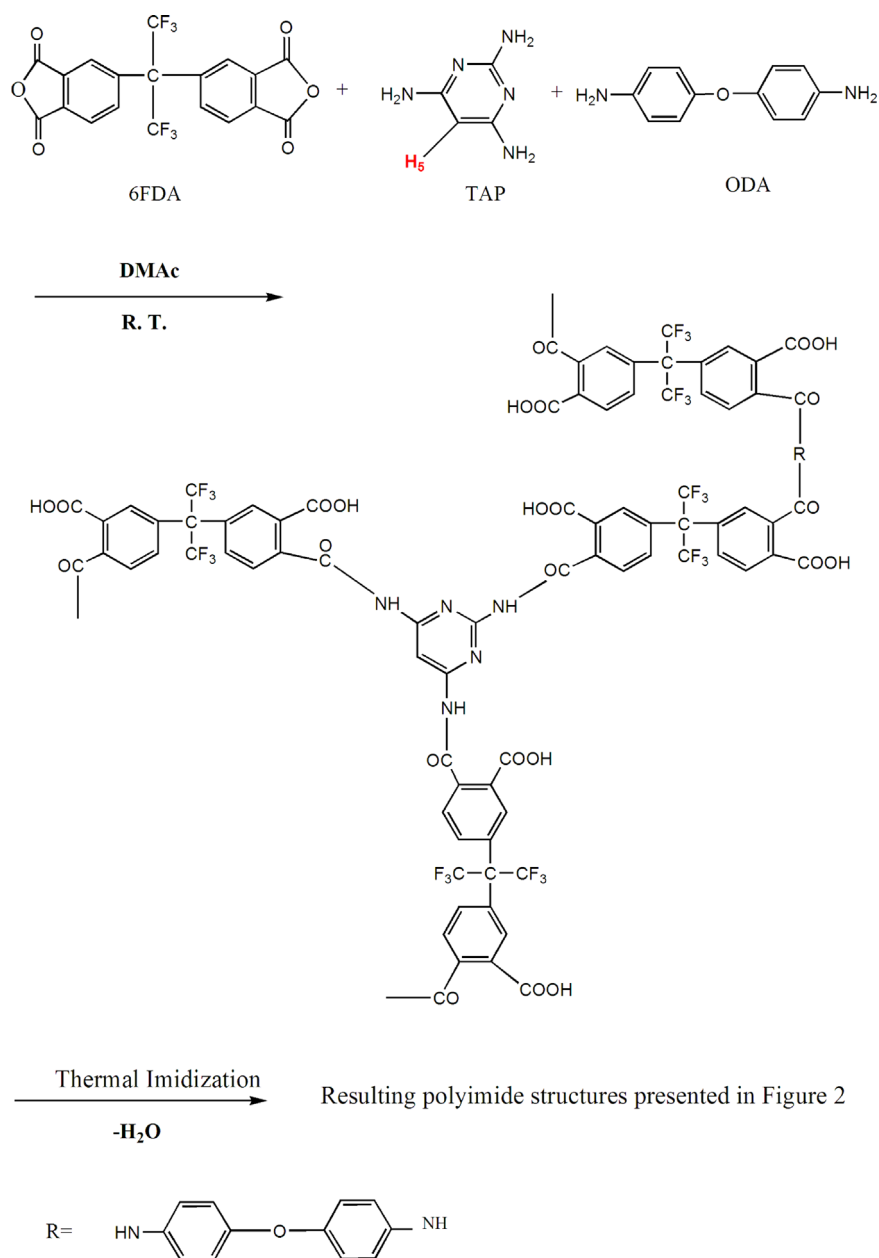


Fig. 1. Schematic diagram for synthesis of hyperbranched polyamic acids.

B3–B8, the d-spacing values decreased with increasing the content of TAP, which reflected that the average distances between inter-segment or neighboring branches decreased.

The densities of the prepared polyimides were shown in Table 3. The variation tendency of densities was found similar with that of d-spacing values. The difference in densities of these polyimides films is probably due to the different inter-macromolecular packing efficiency, which plays an important role in dominating gas permeation properties.

The UV–visible absorption spectra of the obtained polyimides was shown in Fig. 5. All the TAP–ODA–6FDA polyimides showed cut-off wavelengths (absorption edge) at about 400 nm, and the cut-off wavelengths increased approximately with increasing the content of TAP comonomer, which suggested that the polymer chain packaging and aggregates became more compact. It is in good agreement with the analysis of d-spacing values and densities.

The solubility of the products was investigated in various organic solvents and the results were summarized in Table 4. The qualitative solubility was determined with as 10 mg and 20 mg of polymer in 1 ml of solvent respectively. It could be seen that 20 mg of products B1–B7 were partially solubility in 1 ml of DMSO, DMAc, DMF, NMP and THF. It also could be observed that the solubility became better with increasing the content of TAP, which can be attributed to the structural modification. By incorporation of branched unit into the polymer backbone, the polymers' regularity was broken up, thereby the solubility was enhanced.

TGAs were used to study the thermal stabilities of the prepared hyperbranched polyimides. Fig. 6 showed the TGA curves of all obtained polyimides. The 5% weight loss at temperatures in nitrogen was shown in Table 3. The results showed that the 5% weight loss at temperatures increased with increasing the content of ODA comonomer. The B1 linear polymer showed the highest 5%

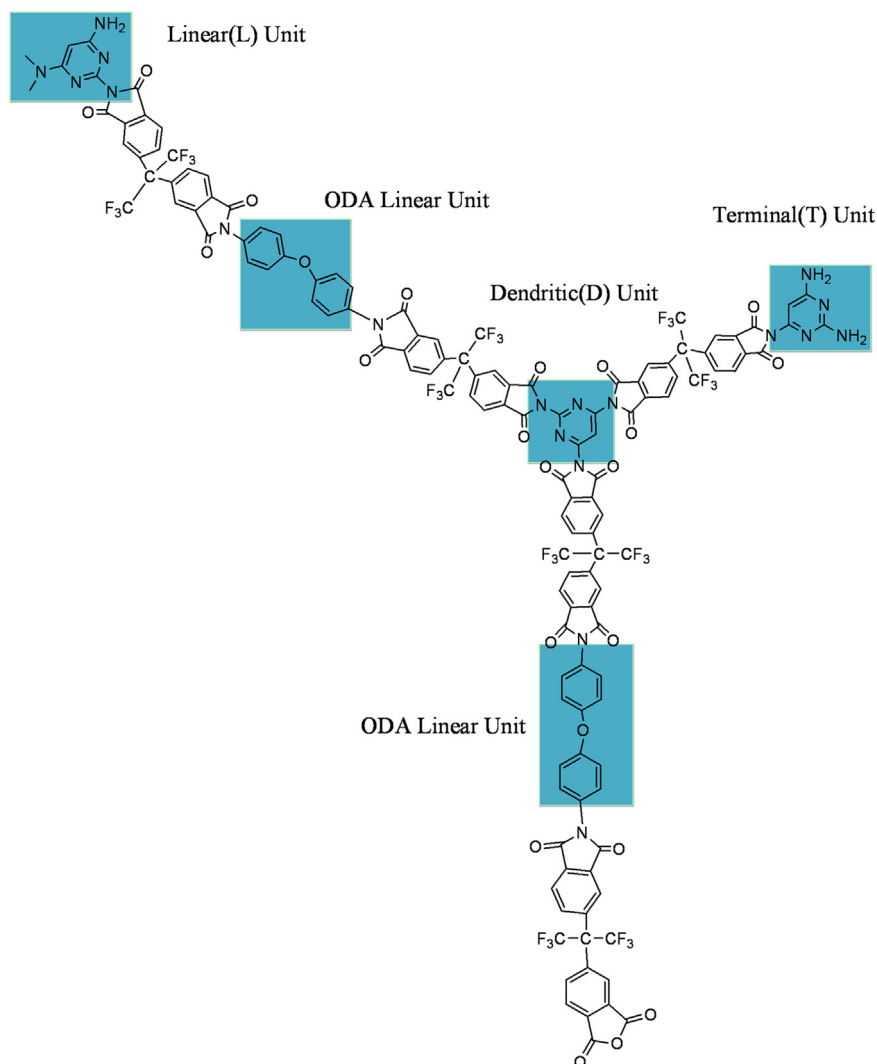


Fig. 2. Chemical structure of the prepared TAP-ODA-6FDA hyperbranched polyimide.

weight-loss temperature 559 °C while the B8 hyperbranched polymer showed the lowest 5% weight-loss temperature 432 °C. It might be given rise to the poor thermal stability of pyrimidine ring than benzene ring. Another reason why the thermal stability increases with increasing the content of ODA is ascribed to the linear ODA-6FDA segment.

The glass transition temperatures ( $T_g$ ) of the hyperbranched polyimides determined by DSC were also shown in Table 3. It can be seen that the  $T_g$  decreased with increasing the content of TAP. It has been reported by Hodgkin that the co-polyimides incorporating TAP were found to have lowered molecular weights [41]. Thus with increasing the content of TAP, the molecular weights would decrease. The lower molecular weights would cause higher segment mobility of the macromolecules and hence lower values of  $T_g$ .

### 3.3. Mechanical properties

Hyperbranched polyimides films with no or low content of ODA units in their molecular structure (such as B7, B8 prepared in this research work) displayed poor mechanical properties because of high brittleness. It might be given rise to a low number of physical enlargements of unmodified hyperbranched polyimides. So the measurement of their properties such as mechanical properties and gas transport properties was very difficult and may be

unrealizable because of cracking in the membrane cell. With the content of ODA monomer increasing, acceptable mechanical properties of films such as B1–B6 were obtained. The mechanical properties of the prepared polyimides films were summarized in Table 5. B7 and B8 were too brittle to get the mechanical properties, and for B1–B6, the tensile strength and elongation at break increased with increasing the content of ODA.

### 3.4. Gas permeation properties

It has been reported by Jean et al. that the gas permeability and/or diffusivity of polymers strongly depend on the fractional free volume in the interior of globular hyperbranched macromolecules [47]. Furthermore, Shimazu et al. have also reported that the molecular sieving ability of polyimides becomes strong with decreasing local chain mobility [48]. And incompact inter-macromolecular packing of the polymer chains has positive effect on the gas permeation properties.

Gas permeability, diffusion, and solubility coefficients and ideal selectivities of the TAP-ODA-6FDA polyimides membranes were summarized in Tables 6–8. As shown in Table 6 and Table 8, the permeability and solubility coefficients decreased with increasing TAP content for all gases except for CO<sub>2</sub>. And most of the prepared TAP-ODA-6FDA hyperbranched polyimides had lower permeability coefficients than ODA-6FDA linear polyimide. The diffusion



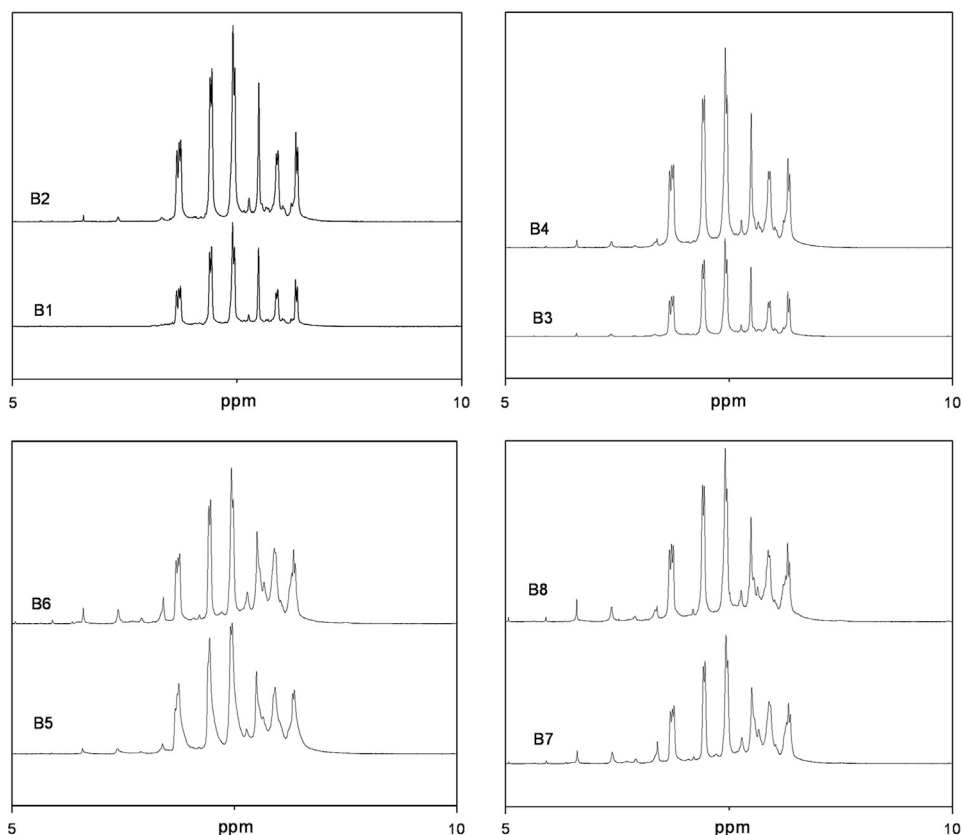


Fig. 3.  $^1\text{H}$  NMR spectrum of the obtained polyimides in  $\text{DMSO-d}_6$ .

Table 2

$^1\text{H}$  shift of TAP units in  $\text{DMSO-d}_6$ .

Structure unit		Chemical shift (in ppm)	
		H <sub>5</sub>	NH <sub>2</sub>
T	2-Monoimide	5.44	6.45
	4-,6-Monoimide	5.79	6.67
L	2,4-, 2,6-Diimide	6.68	7.74
	4,6-Dimide	6.87	7.20
D	Triimide	7.80	–

Table 3

Properties of the prepared hyperbranched polyimides.

Polymer	DB (%) <sup>a</sup>	2 $\theta$ (°) <sup>b</sup>	d-Spacing (Å) <sup>b</sup>	Density (g cm <sup>-3</sup> ) <sup>c</sup>	5% Weight loss (°C) <sup>d</sup>	T <sub>g</sub> (°C) <sup>e</sup>
B1	0	15.6	5.67	1.385	559	313
B2	13	15.5	5.73	1.371	557	307
B3	27	15.5	5.73	1.376	508	295
B4	37	15.6	5.67	1.375	488	289
B5	48	15.7	5.63	1.382	455	276
B6	56	15.8	5.60	1.388	447	271
B7	62	16.3	5.44	1.394	434	269
B8	69	16.5	5.38	1.398	432	266

<sup>a</sup> Degree of branching determined by  $^1\text{H}$  NMR analysis.

<sup>b</sup> Determined by WAXD.

<sup>c</sup> Measured by the suspension method.

<sup>d</sup> Measured by TGA in nitrogen.

<sup>e</sup> Measured by DSC.

coefficients shown in Table 7 decreased with increasing the content of TAP for all gases. For  $\text{CO}_2$ , from B1 to B2 the reason of  $P$  increasing may be that hyperbranched polyimides with high content of TAP monomer are higher branched and thus it can be

expected that they will be less packed and with larger cavities. However, from B2 to B6, the  $P$  decreases, which indicates that increasing the content of ODA would increase the fractional free volume of polyimides, and in addition the interactions of gas molecules with the polymers increases, represented by the solubility coefficients.

Gas permeabilities given in Table 6 increased in the order  $P(\text{CO}_2) > P(\text{O}_2) > P(\text{N}_2)$ , and solubility coefficients increased in the same order  $S(\text{CO}_2) > S(\text{O}_2) > S(\text{N}_2)$  shown in Table 8, which trend is consistent with that the kinetic diameters of  $\text{CO}_2$  (3.3 Å) is smaller than those of  $\text{O}_2$  (3.5 Å) and  $\text{N}_2$  (3.6 Å). However, gas diffusivities increased in the order  $D(\text{O}_2) > D(\text{CO}_2) \approx D(\text{N}_2)$  shown in Table 7, which is because the diffusion of  $\text{CO}_2$  could be suppressed by polar interaction with the polymer.

The ideal selectivity for the combination of gases A and B ( $\alpha(A/B)$ ) is defined by the following equation [49]:

$$\alpha(A/B) = \frac{P(A)}{P(B)} = \frac{D(A)S(A)}{D(B)S(B)} = \alpha^D(AB)\alpha^S(AB) \quad (8)$$

where  $\alpha^D(A/B)$  is the diffusivity selectivity and  $\alpha^S(A/B)$  is the solubility selectivity. These selectivities were listed in Tables 6–8 respectively. It can be recognized that the polyimide membranes show that the  $\text{O}_2/\text{N}_2$  selectivity depends on the diffusivity rather than the solubility selectivity, but  $\text{CO}_2/\text{N}_2$  selectivity is the opposite and depends on solubility rather than the diffusivity selectivity. The ideal selectivities of  $\text{O}_2/\text{N}_2$  were in the range 4.1–7.0, and that of  $\text{CO}_2/\text{N}_2$  were in the range 23.8–31.7. It can be seen that the ideal selectivities of the TAP-ODA-6FDA hyperbranched polyimides were higher than that of the ODA-6FDA linear polyimides. The values increased with increasing the content of TAP. The result is consistent with the general understanding that the polymers, which are more permeable, are less selective and vice versa [49,50].

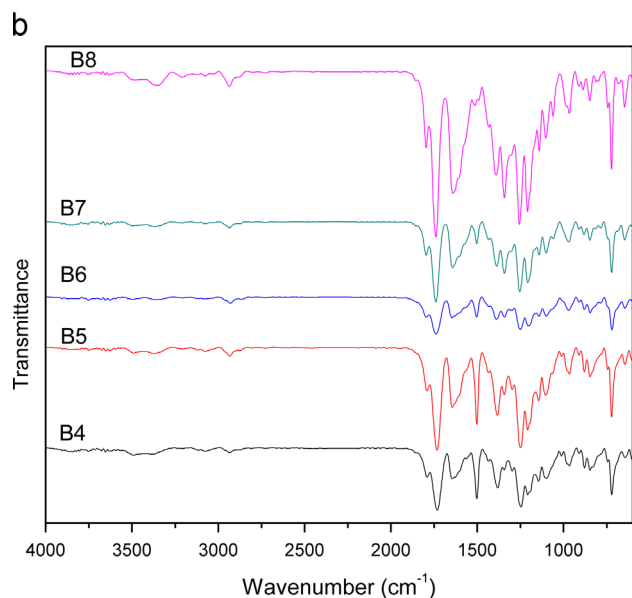
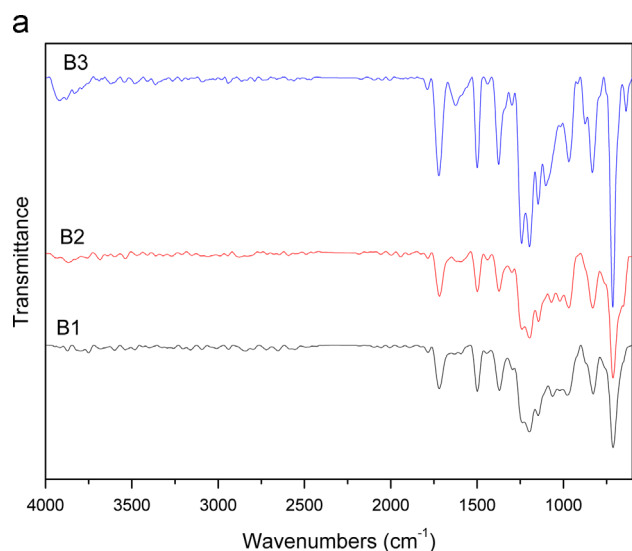


Fig. 4. FTIR spectra of the obtained polyimides: (a) B1–B3 and (b) B4–B8.

**Table 4**

Solubility of the prepared TAP–ODA–6FDA polyimides.

	Solvents <sup>a</sup>					Solvents <sup>b</sup>				
	DMAc	NMP	DMF	DMSO	THF	DMAc	NMP	DMF	DMSO	THF
B1	+-	+-	+-	+-	--	+-	+-	+-	+-	--
B2	++	+-	+-	+-	+-	+-	+-	+-	+-	+-
B3	++	+-	+-	+-	+-	+-	+-	+-	+-	+-
B4	++	+-	++	++	+-	+-	+-	+-	+-	+-
B5	++	++	++	++	+-	+-	+-	+-	+-	+-
B6	++	++	++	++	+-	+-	+-	+-	+-	+-
B7	++	++	++	++	+-	+-	+-	+-	+-	+-
B8	++	++	++	++	+-	++	++	++	++	+-

++: soluble at room temperature; +-: soluble partially at room temperature; --: insoluble.

<sup>a, b</sup> NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

<sup>a</sup> Qualitative solubility was determined with as 10 mg of polymer in 1 ml of solvent.

<sup>b</sup> Qualitative solubility was determined with as 20 mg of polymer in 1 ml of solvent.

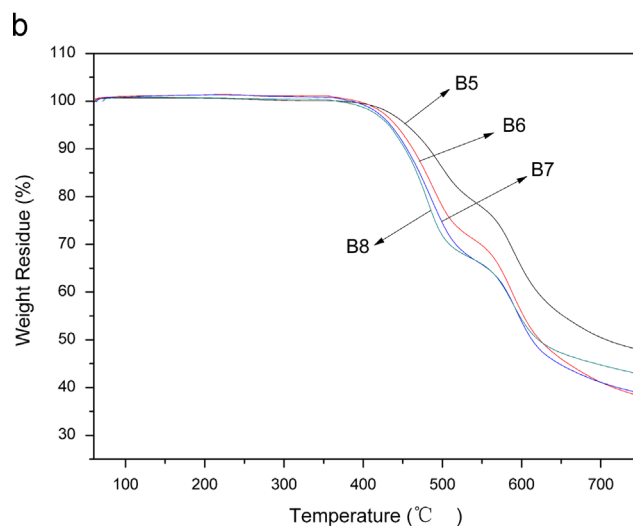
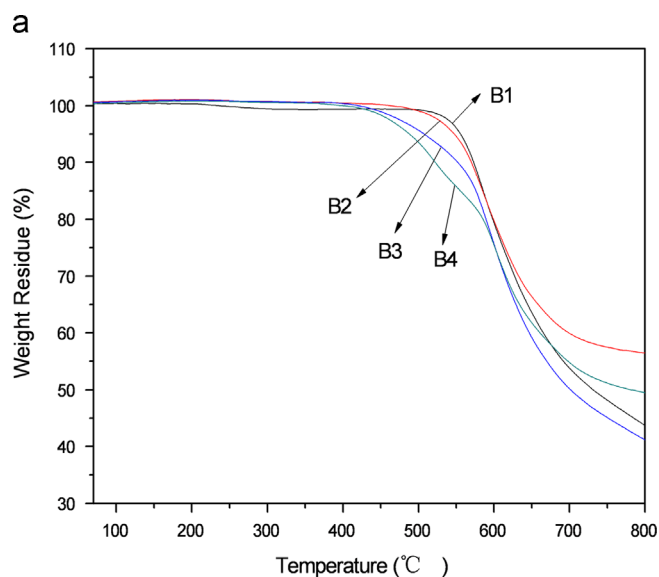


Fig. 6. TGA curves of TAP–ODA–6FDA polyimides in nitrogen: (a) B1–B4 and (b) B5–B8.

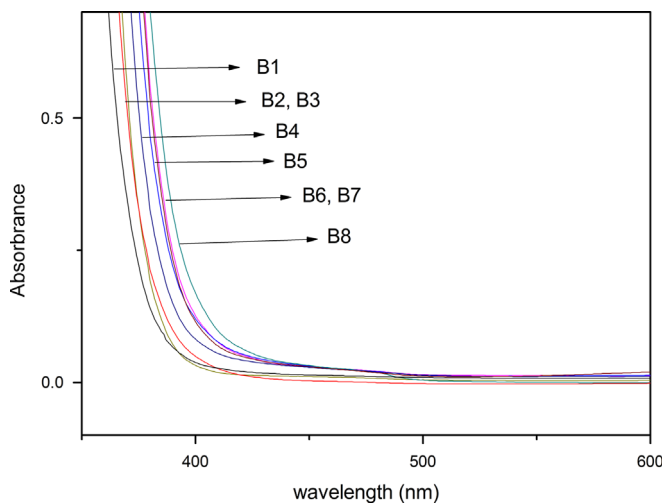


Fig. 5. UV-vis spectra of the prepared TAP–ODA–6FDA polyimides.

**Table 5**  
Mechanical properties of the prepared TAP–ODA–6FDA polyimides membranes.

Polymer	B1	B2	B3	B4	B5	B6	B7	B8
Tensile strength (MPa)	113	98	90	84	77	61	–	–
Elongation at break (%)	14.1	9.7	7.8	5.6	3.5	3.2	–	–

**Table 6**  
Permeability coefficients and O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity of TAP–ODA–6FDA polyimides membranes at 76 cmHg and 25 °C.

P <sup>a</sup>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	$\alpha(\text{O}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{N}_2)$	Reference
B1	17.3	3.14	0.725	4.33	23.8	<sup>c</sup>
B2	17.4	2.73	0.653	4.18	26.6	<sup>c</sup>
B3	12.8	2.10	0.500	4.2	25.6	<sup>c</sup>
B4	9.22	1.82	0.34	5.35	27.1	<sup>c</sup>
B5	7.35	1.64	0.243	6.74	30.2	<sup>c</sup>
B6	6.82	1.49	0.215	6.92	31.7	<sup>c</sup>
B7	–	–	–	–	–	–
B8	–	–	–	–	–	–
CF <sub>3</sub> –HQDPA	2.72	0.114	0.75	6.5	23	[14]
6FDA–TAPA–EGDE <sup>b</sup> (amine-terminated)	11	1.9	0.33	5.7	33	[44]

<sup>a</sup> P is in barrer (1 barrer = 10<sup>−10</sup> cm<sup>3</sup>(STP) cm<sup>−1</sup> s<sup>−1</sup> cmHg<sup>−1</sup>).

<sup>b</sup> The content of EGDE is 0.34 mmol g<sup>−1</sup> (polymer).

<sup>c</sup> This study.

**Table 7**  
Diffusion coefficients and O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity of TAP–ODA–6FDA polyimide membranes at 76 cmHg and 25 °C.

D <sup>a</sup>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	$\alpha(\text{O}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{N}_2)$
B1	0.64	2.24	0.63	3.56	1.02
B2	0.56	2.1	0.54	3.89	1.04
B3	0.47	1.89	0.45	4.2	1.05
B4	0.38	1.86	0.37	5.03	1.03
B5	0.32	1.86	0.30	6.2	1.07
B6	0.31	1.79	0.29	6.17	1.07
B7	–	–	–	–	–
B8	–	–	–	–	–

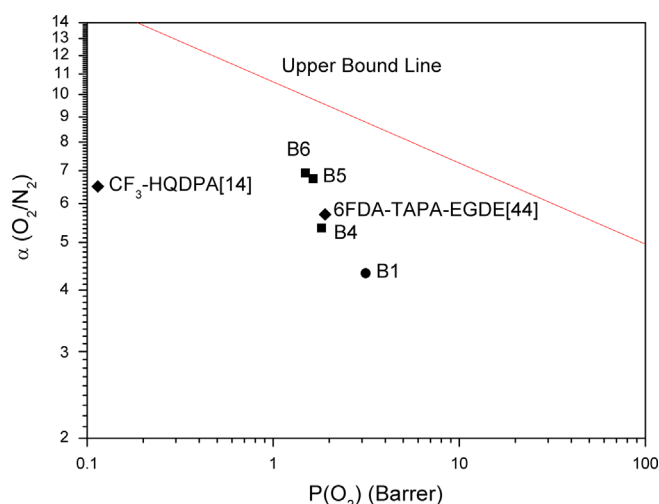
<sup>a</sup> D is in 10<sup>−8</sup> cm<sup>2</sup> s<sup>−1</sup>.

**Table 8**  
Solubility coefficients and O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity of TAP–ODA–6FDA polyimide membranes at 76 cmHg and 25 °C.

S <sup>a</sup>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	$\alpha(\text{O}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{N}_2)$
B1	27	1.4	1.15	1.22	23.5
B2	31	1.3	1.21	1.07	25.6
B3	27	1.11	1.11	1.01	24.3
B4	24	0.98	0.92	1.07	26.1
B5	23	0.88	0.81	1.09	28.4
B6	22	0.83	0.74	1.12	29.7
B7	–	–	–	–	–
B8	–	–	–	–	–

<sup>a</sup> S is in 10<sup>−2</sup> cm<sup>3</sup>(STP) cm<sup>−3</sup> cmHg<sup>−1</sup>.

To compare the performance of these hyperbranched polyimides with that of other similar membrane materials, two particular polymers which are similar with our prepared polymers were chosen from the literatures, and a permeability/selectivity map was present in Fig. 7 for the O<sub>2</sub>/N<sub>2</sub> pair. The solid line represents the upper bound line of Robeson [51]. It can be seen that the polymers B5 and B6 displayed better separation performance than other hyperbranched polyimides membranes such as CF<sub>3</sub>–HQDPA [14] and 6FDA–TAPA–EGDE (amine-terminated) [44].



**Fig. 7.** Plots of ideal O<sub>2</sub>/N<sub>2</sub> selectivity [ $\alpha(\text{O}_2/\text{N}_2)$ ] vs. O<sub>2</sub> permeability coefficient  $P(\text{O}_2)$  for hyperbranched polyimides (■) and other similar hyperbranched polyimides (◆) [14,44] and linear polyimides (●).

The results suggest that the prepared hyperbranched polyimides may be attractive materials for gas separation.

Compared with linear polyimides, the prepared TAP–ODA–6FDA hyperbranched polyimides exhibited lower permeabilities (and the polymers B2 and B3 exhibited slightly lower permeabilities), but higher selectivities. So this material is potential for use in many gas separation applications like O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, etc.

#### 4. Conclusions

A series of self-standing polyimide membranes from a novel polymerization of A<sub>2</sub>+B<sub>2</sub>B'+B<sub>2</sub> monomers were successfully prepared and characterized for physicochemical properties. No gelation occurred during polymerization which was attributed to the different reactivities of the amine groups in TAP, and it would make easier to prepare hyperbranched polyimides in a large scale.



The degree of branching of the prepared hyperbranched polyimides increased with increasing the content of TAP. The morphology structure of the prepared hyperbranched polyimides was evaluated and the d-spacing values first increased with increasing the content of TAP, and then decreased. Both the 5% weight loss at temperatures and the glass transition temperatures ( $T_g$ ) decreased with decreasing the content of ODA comonomer. Hyperbranched polyimides films with no or low content of ODA units such as B7, B8 were too brittle to measure their mechanical and gas separation properties. Gas transport measurements for hyperbranched polyimides B2–B6 showed slightly lower permeability coefficients than linear polyimides B1. However, the ideal selectivities were significantly higher for the hyperbranched polyimides and they increased with increasing the content of TAP. From these results, it can be concluded that the TAP-ODA-6FDA hyperbranched polyimide membranes are expected to apply in the field of gas separation.

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