

Gas Permeability of Fluorinated Hyperbranched Polyimide

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Received 25 April 2007; accepted 28 February 2008

DOI 10.1002/app.28315

Published online 6 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The gas permeability of carbon dioxide, oxygen and nitrogen for hyperbranched polyimide (HBPI) containing trifluoromethyl groups were investigated. The HBPIs were prepared by condensation polymerization of a triamine monomer, 1,3,5-tris(2-trifluoromethyl-4-aminophenoxy) benzene (TFAPOB) and a commercially available dianhydride monomer 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA). With different monomer addition methods and different monomer molar ratios, amine terminated HBPI (AM-HQDPA) and anhydride terminated HBPI (AD-HQDPA) were obtained, subsequently, the trifluoromethylphenyl amine terminated HBPI (CF₃-HQDPA) was achieved by modifying the end

groups of AD-HQDPA with (3,5-ditrifluoromethyl)aniline. The CF₃-HQDPA exhibited a good mechanical and thermal stability as well as AM-HQDPA, and showed better gas permeabilities than that of AM-HQDPA because of increase of free volume contributed by the bulky trifluoromethyl group introduced, but, the selectivity of CF₃-HQDPA was lower than that of AM-HQDPA. This result was consistent with the trade-off relationship. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2341–2346, 2008

Key words: trifluoromethyl; hyperbranched polyimide; gas permeability

INTRODUCTION

Polyimide membranes have been of great interest in gas transport applications because of their high gas permeability, good selectivity, and excellent mechanical and thermal properties.^{1–3} In the past decade, many research interests have been concentrated on the gas-transport properties of linear polyimides. One of important reason is that the introduction of a bulky group into the dianhydride or diamine monomers is profitable to increase the gas permeability as a result of increased free volume in the polymer.^{4–8}

Recently, HBPIs have been considered for gas transport applications because of their unique structure.^{9–11} It is known that there are some additional open and accessible cavities from the periphery of neighboring branches, which are proposed to be a kind of free volume acting as a pathway for gas transport.^{12,13} Fang et al. first reported the synthesis of a hyperbranched polyimide from (A₂+B₃)-type method as a promising gas transport material.¹⁰ subsequently, Suzuki et al. compared the gas permeability of hyperbranched polyimides with that of linear ones with the similar chemical structure.¹⁴

In this work, we designed and synthesized a kind of CF₃ terminated hyperbranched polyimide (CF₃-

HQDPA) using a triamine monomer, 1,3,5-tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB) (A₃), as a “core” molecule, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA) as a B₂ monomer and 3,5-ditrifluoromethylaniline as an endcapping reagent. In addition, the physical and gas transport properties of CF₃-HQDPA were discussed comparing with the nontrifluoromethyl terminated HBPI (AM-HQDPA).

EXPERIMENTAL

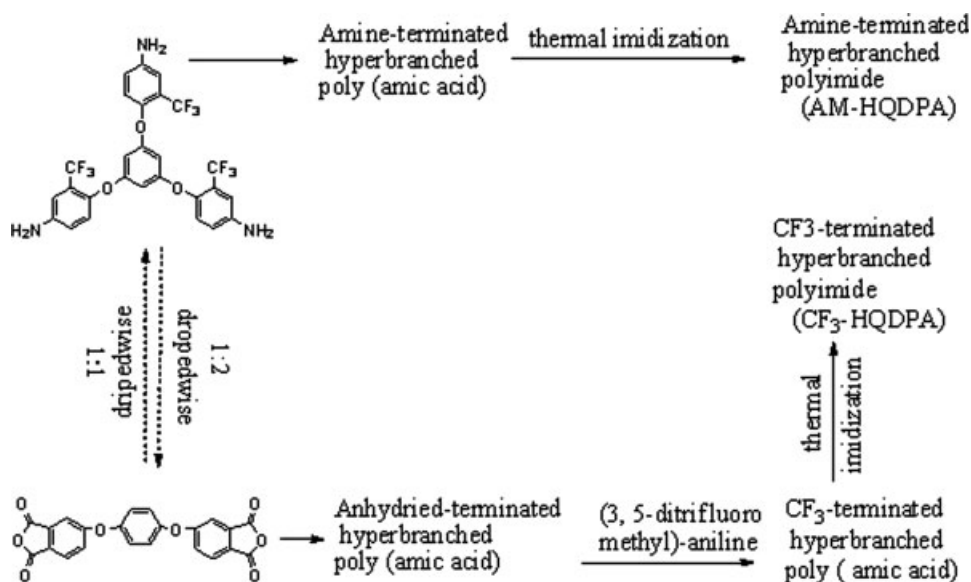
Materials

Phloroglucinol, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA) and 3-trifluoromethyl-4-chloronitrobenzene was purchased from Aldrich Chemical and used without further purification. *N,N*-dimethylacetamide (DMAc) was refluxed in presence of CaH₂ and distilled under vacuum before use. 1,3,5-Tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB) was synthesized by our lab.¹⁵

Synthesis of AM-HQDPA hyperbranched poly(amic acid)

1.5 mmol of TFAPOB was dissolved in 10 mL of DMAc in a 100 mL thoroughly dried three-neck flask under N₂ flow. To this solution, 1.5 mmol of HQDPA in 5 mL of DMAc was added dropwise through a syringe over 3 h. After the addition, the

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Scheme 1 Synthetic route of the HBPIs.

reaction mixture was further stirred for 24 h at room temperature.

Synthesis of AD-HQDPA hyperbranched poly(amic acid)

To a 100 mL thoroughly dried three-neck flask 3 mmol of HQDPA was dissolved in 30 mL of DMAc under N_2 flow. Then 1.5 mmol of TFAPOB in 10 mL of DMAc was added dropwise to the dianhydride solution through a syringe over 3 h. After TFAPOB solution was completely added, the reaction mixture was further stirred at room temperature for 24 h.

Synthesis of CF_3 -HQDPA hyperbranched poly(amic acid)

1.5 mmol of (3,5-dinitrofluoromethyl)aniline was added to the solution of AD-HQDPA hyperbranched poly(amic acid) with stirring and stirred further for 12 h at ambient temperature.

Membrane preparation

The poly(amic acid) solutions were cast on glass dishes and dried at $80^\circ C$ for 2 h. The resulting membranes were peeled off and subsequently thermally imidized at $100^\circ C$ for 1 h, $200^\circ C$ for 1 h and $300^\circ C$ for 1 h in a heating oven under N_2 flow. The films were used for the gas permeation and mechanical test, and the influence of the film thickness had been considered in the calculated equation for the data of the gas permeation and mechanical.

Characterization and measurements

IR spectra (KBr) were recorded on a Nicolet Impact 410 Fourier transform infrared spectrometer. 1H -NMR spectra were taken on a Bruker 510 NMR spectrometer (500 MHz) with tetramethyl silane as a reference. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of $20^\circ C/min$ under nitrogen. Thermal gravimetric analyses (TGA) were determined on a PERKIN ELMER TGA-7 in nitrogen atmosphere at a heating rate of $10^\circ C/min$ and the polymers were

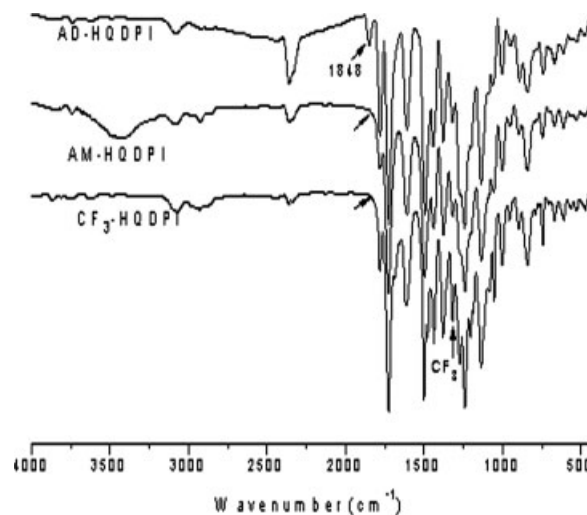


Figure 1 IR spectra of the HBPIs.

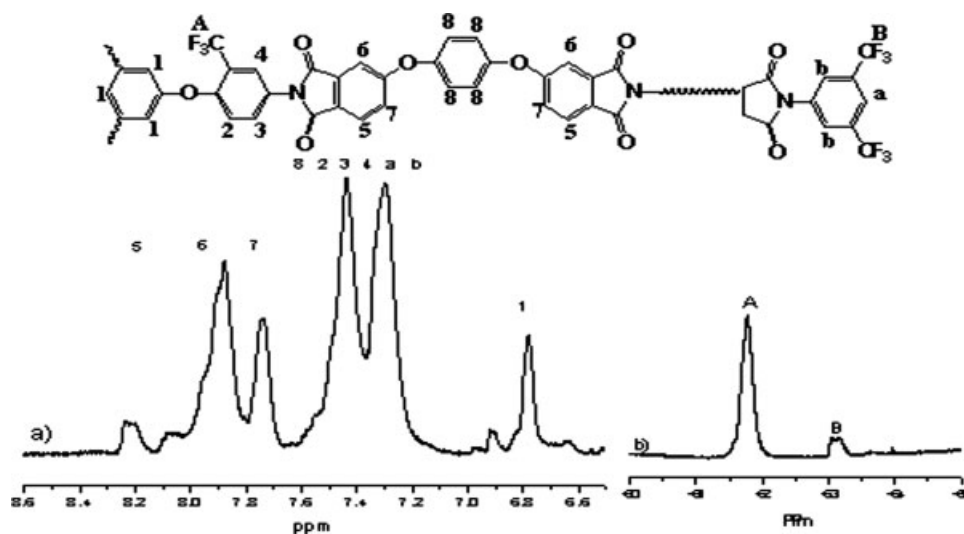


Figure 2 (a) ^1H -NMR and (b) ^{19}F NMR spectrum of the CF_3 -HQDPA ($\text{DMSO-}d_6$).

contained within open aluminum pans. The mechanical tests in tension were carried out using a SHI-MADZU AG-I at crosshead speed of 2 mm/min. For the tensile tests, the samples were machined into dogbone-shape specimens with a gauge length of 18 mm. The clarifications of the film thickness were actualized by the test software. Film density was measured using a top-loading electronic Mettler Toledo balance with a density kit according to the Archimedean principle and by weighing samples in air and ethanol at room temperature. The volume of the sample was calculated from the weight difference of the measurements divided by the density of ethanol. From the weight in air and the calculated volume, film density was determined.

Pure gas permeability coefficients were measured by a constant volume method with an upstream pressure of 1 atm at 20°C . All the gases used here were at least 99.99% in purity. On the high-vacuum downstream side of the membrane a reservoir of 90 cm^3 constant volume was connected with a pressure transducer to monitor the total amount of gas passing through the polymer film.

The gas permeability coefficient can be explained on the basis of the solution-diffusion mechanism, which is represented by the following equation¹⁶:

$$P = D \times S \quad (1)$$

where D (cm^2/s) is the diffusion coefficient and S ($\text{cm}^3\text{ STP}/\text{cm}^3\text{ polym} \cdot \text{cmHg}$) is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method represented by the following equation:¹⁷

$$D = L^2/6\theta \quad (2)$$

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

RESULTS AND DISCUSSION

Polymer synthesis and film formation

The method of synthesis of ($\text{A}_2 + \text{B}_3$)-type HBPI had been reported elsewhere.^{9–11} The synthesis involved two steps as shown in Scheme 1. The hyperbranched polymers were obtained by controlling the addition order and molar ratio of monomers. The addition of a dianhydride to TFAPOB with the monomer molar ratio of 1 : 1 yielded the amine-terminated polymer, while the reverse monomer addition order with the

TABLE I
Physical Properties of the Hyperbranched Polyimide Membranes

Sample	M_n	M_w	M_w/M_n	T_g ($^\circ\text{C}$) ^a	T_5 ($^\circ\text{C}$) ^b	T_{10} ($^\circ\text{C}$) ^c	ρ (g/cm^3)	FFV ^d
AM-HQDPA	26,000	51,000	1.9	222	518	547	1.33	0.170
CF_3 -HQDPA	16,000	41,000	2.5	211	527	562	1.32	0.177

^a From the second heating trace of DSC measurements conducted at a heating rate of $20^\circ\text{C}/\text{min}$.

^b 5% weight loss temperatures measured by TGA at a heating rate of $5^\circ\text{C}/\text{min}$ in nitrogen.

^c 10% weight loss temperature measured by TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen.

^d FFV value based on the fully branched structure.

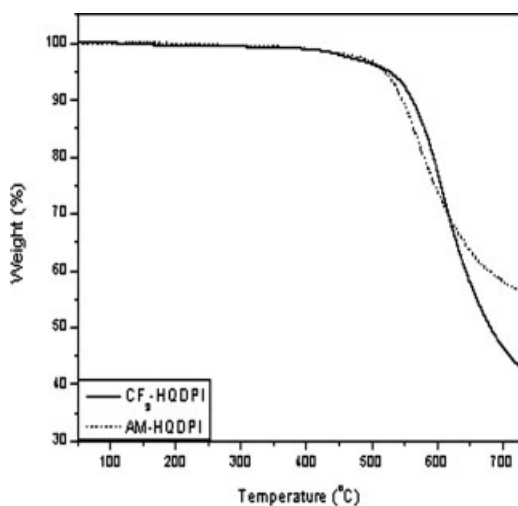


Figure 3 TG curves of the membranes AM-HQDPA and CF₃-HQDPA.

molar ratio (dianhydride over TFAPOB) of 2 : 1 gave the anhydride-terminated polymer. The anhydride-terminated polymer has been endcapped by (3,5-ditrifluoromethyl)aniline to obtain trifluoromethyl-terminated HBPI (CF₃-HQDPA). No gel formed during polymerization process when monomer concentration was controlled low enough (solid content about 10%).¹⁰

IR spectra confirmed that complete imidization was achieved for all the polyimides. Figure 1 showed the IR spectra of AM-HQDPA, AD-HQDPA, and CF₃-HQDPA. The bands around 1784 cm⁻¹ (C=O asymmetrical stretching), 1723 cm⁻¹ (C=O symmetrical stretching), 1376 cm⁻¹ (C–N stretching) were the characteristic absorption bands of polyimides. However, no characteristic band of polyamic acid (around 1680 cm⁻¹) was found. In addition, the bands around 3426 and 1859 cm⁻¹ were attributed to the stretching of N–H of terminal amine groups in AM-HQDPA and the stretching of C=O of the terminal anhydride groups in the AD-HQDPA, respectively. The C–F band at 1326 cm⁻¹ was intensified in the spectrum of CF₃-HQDPA.

In the ¹H-NMR spectrum of CF₃-HQDPA (Fig. 2a), the bands in the range of 7.6–8.4 ppm could be attributed to the resonance absorption of the phenyl hydrogen 5, 6, 7, and of HQDPA residues, and the bands at around 7.20–7.65 ppm could be attributed

to the phenyl hydrogen 2, 3, 4 of the TFAPOB residues, 8 of the HQDPA and a, b of the terminated monomer (3,5-ditrifluoromethyl)aniline. The hydrogen resonance absorption of the 1 can be found at around 6.8 ppm. In the ¹⁹F NMR spectrum (Fig. 2b), the signals at –61.8 and –63.2 ppm were ascribed to the fluorine atoms of the TFAPOB unit and the terminal group, 3,5-ditrifluoromethylphenyl, respectively.

Physical properties of the hyperbranched polyimides

The obtained polyimide films were soluble in a variety of organic solvents such as NMP, DMAc, DMF, and cyclohexanone. Thermal properties of the polyimide membranes were investigated by DSC and TGA. Table I listed the *T_g* of the AM-HQDPA and CF₃-HQDPA. It was seen that the amine-terminated polyimide displayed higher *T_g* than the trifluoromethyl-terminated one, because of the existence of hydrogen bonds between the terminal amine groups in AM-HQDPA.¹⁰ Both the polymers had the temperature of 5 wt % loss over 500°C in N₂. The TG curves (Fig. 3) demonstrated that the polyimide membranes were well imidization and no residual solvent existed because no weight-loss attributed to solvent throughout was observed. Both the polyimides afforded good-quality and creasable films. Tensile properties of the flexible films were summarized in Table II. They showed the tensile strength over 100 MPa, an elongation at break around 6%, and a tensile modulus of 2.5 GPa.

Gas transport properties of the hyperbranched polyimide membranes

Gas permeability, diffusion, and solubility coefficients of the HBPI membranes were summarized in Tables III and IV, respectively. From Table III, it was seen that CF₃-HQDPA had higher permeability than AM-HQDPA. Generally, the diffusion mechanism in glassy polyimide membranes will rest on the nature of their free volume. Therefore, the increase of the free volume leads to improve gas permeability of the polymer.^{18,19} The incorporation of the bulky trifluoromethyl group onto the terminal group of HBPI should be pretty effective in preventing the interseg-

TABLE II
Tensile Properties of the AM-HQDPA and CF₃-HQDPA Films

Polymer ^a	Film thickness (μm)	Strength at break (MPa)	Elongation at break (%)	Tensile modulus (GPa)
AM-HQDPA	43	127	6.9	2.57
CF ₃ -HQDPA	34	113	5.2	2.56

^a The polyimide films were heated at 300°C for 1 h prior to tensile test.

TABLE III
Permeability Coefficients and Ideal Selectivities of HBPI
Membranes at 1 atm and 20°C

Polymer sample	δ	$P \times 10^{10}$ (cm ³ STPcm/cm ² s · cm Hg)					
		H ₂	CO ₂	N ₂	O ₂	α (O ₂ /N ₂)	α (CO ₂ /N ₂)
AM-HQDPA	0.321	7.18	1.55	0.45	0.058	7.7	26
CF ₃ -HQDPA	0.341	10.1	2.72	0.75	0.114	6.5	23

mental packing and increasing the fractional free volume (FFV) value. FFV can be calculated using the following relationship.²⁰

$$V_f = (V_{sp} - 1.3V_w) \quad (3)$$

$$FFV = V_f/V_{sp} \quad (4)$$

where V_f is the free volume, V_{sp} is the specific volume which can be calculated from the experimental density, ρ (g/cm³), V_w is the van der Waals volume, calculated by using the group contribution method of Bondi.²¹ Obtained ρ and FFV values of the HBPIs were listed in Table I. CF₃-HQDPA had larger FFV than AM-HQDPA. It was apparent that the trifluoromethyl group was effective in not only increasing FFV, but also disrupting tighter packing of the hyperbranched macromolecule. On the basis of this point, the trifluoromethyl group was effective in improving gas permeability.

To provide some perspective on the performance of these hyperbranched polyimides, a permeability/selectivity map was present in Figure 4 for the O₂/N₂ pair. The solid lines represent the upper bound lines of Robeson.²² All the experimental ideal gas selectivities for the hyperbranched polyimides were

lower than the upper bound values. A trade-off relationship is usually observed between P and α for common gases in polymers. That is, higher permeability is gained at the cost of selectivity and vice versa.²³ It was seen that CF₃-HQDPA had lower gas selectivity than AM-HQDPA. This result was consistent with the trade-off relationship. The distance (δ) from the permeability point (p_i , versus α_{ij} , where ideal permselectivity $\alpha_{ij} = P_i/P_j$) to the upper bound line was calculated by the method developed by Guiver et al.²⁴ and listed in Table III. The distance (δ) of CF₃-HQDPA and AM-HQDPA were almost equal.

The ideal selectivity for the combination of gases A and B ($\alpha(A/B)$) is defined by the following equation:^{25,26}

$$\alpha(A/B) = \frac{p(A)}{p(B)} = \frac{D(A)}{D(B)} \times \frac{S(A)}{S(B)} = \alpha^D(A/B) \times \alpha^S(A/B) \quad (5)$$

where $\alpha^D(A/B)$ is the diffusivity selectivity and $\alpha^S(A/B)$ is the solubility selectivity. The diffusivity and solubility selectivities of AM-HQDPA and CF₃-HQDPA were listed in Table IV. The solubility coefficients for each gas were roughly 1.2 times larger for CF₃-HQDPA than for AM-HQDPA. This may be also interpreted as because of differences in FFV. Solubility of a gas in glassy polymers is considered to depend not only on interaction between the gas molecules and the polymer chains but also on FFV of the polymers.²⁷ Among the polymers having similar interaction to the gas, S seems to be larger for polymers with larger FFV. Free space has a distribution of the size. Free-space elements large enough to accommodate gas molecules can act as Langmuir sorption sites. Polymers with larger FFV tend to have higher concentration of these free-space elements and as the result tend to have larger S . As shown in the Table IV, the gas selectivity of CF₃-HQDPA was lower than that of AM-HQDPA, this may be attributed to the terminal CF₃ groups which destroyed the polymer chain stiffness.

As shown in the Figure 4, the data for linear polyimide HQDPA-ODA, from 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA) and 4,4'-diaminodiphenyl ether (ODA) tested on the condition of

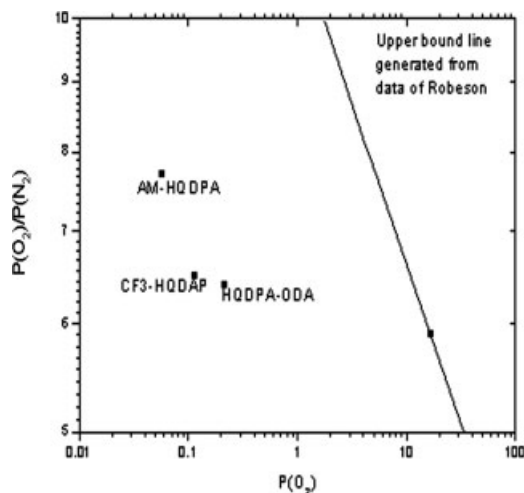


Figure 4 Gas separation properties of the O₂/N₂ pair relative to the upper bound line.

TABLE IV
Solubility and Diffusivity Coefficients and Selectivities of the HBPI Membranes at 1 atm and 20°C^a

Polymer	D _{CO2}	D _{O2}	D _{N2}	α ^D		S _{CO2}	S _{O2}	S _{N2}	α ^S	
				O ₂ /N ₂	CO ₂ /N ₂				O ₂ /N ₂	CO ₂ /N ₂
AM-HQDPA	0.35	1.44	0.3	4.75	1.15	4.45	0.31	0.19	1.61	23
CF ₃ -HQDPA	0.49	1.95	0.43	4.49	1.13	5.54	0.38	0.26	1.46	21

^a S and D are in 10⁻² cm³ (STP) cm⁻³ · cmHg⁻¹ and 10⁻⁸ cm² s⁻¹, respectively.

10 atm 35°C, were shown for comparison.³ The gas separation performance of the CF₃-HQDPA which tested at 1 atm 20°C was similar to that of HQDPA-ODA. The distances (δ) of hyperbranched polyimides were near to that of linear polyimide HQDPA-ODA (0.300), the results suggest that the hyperbranched polyimides may be attractive materials for gas separation.

The above results clearly indicated that although the cavities in interior of the globular hyperbranched macromolecules were mainly responsible for the transport of gas molecules,¹⁴ the intermacromolecular packing also affected on gas permeation properties greatly. As discussed earlier, the introduction of trifluoromethyl group onto the terminal of hyperbranched polymer could lead to relatively loose packing of the globular macromolecules. Thus, the transport of gas molecules through the exterior surfaces became readily, and therefore higher gas permeability coefficients were obtained for the CF₃-HQDPA.

CONCLUSIONS

Two novel amine-terminated and trifluoromethyl-terminated hyperbranched polyimides, AM-HQDPA, and CF₃-HQDPA were prepared by (A₂+B₃)-type method. Both of the HBPIs exhibited good thermal and mechanical properties. Introduction of CF₃ groups at the end of hyperbranched polyimide increased oxygen and nitrogen permeability, while, the selectivity had decrease for the terminal groups. Though in the present studies the difference in properties because of end groups was not very large, it was indicate that end groups influence properties of HBPIs, and by introducing a functional groups at the end of HBPIs should influence solubility as well as thermal and gas transport properties of HBPIs.

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