

## Synthesis and Properties of Novel Hyperbranched Polyimides End-Capped with Metallophthalocyanines

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**ABSTRACT:** A fluorinated hyperbranched polyimide (HBPI) is synthesized by using a triamine monomer, 1,3,5-tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB) ( $B_3$ ), as a “core” molecule, 4,4'-oxydiphthalic anhydride (ODPA) as a  $A_2$  monomer, and 4-aminophthalonitrile as an end-capping reagent. After that, a series of novel fluorinated hyperbranched polyimides end-capped with metallophthalocyanines were prepared by the reactions of dicyanophenyl end-capped hyperbranched polyimide with excessive amounts of 1,2-dicyanobenzene and the corresponding metal salt in quinoline. The resulting polyimides containing metallophthalocyanine unites shows optical absorption in the visible region. The absorption bands of the polymers in chloroform solution are in the range of 665–701 nm. These polyimides show glass transition temperatures between 216 and 225°C, and the 5 wt % weight loss temperature of the polymers varied from 440 to 543°C under nitrogen. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polyimides; dendrimers; hyperbranched polymers and macrocycles; thermal properties; adsorption

Received 25 June 2012; accepted 5 September 2012; published online

DOI: 10.1002/app.38567

### INTRODUCTION

Metallophthalocyanines (MPcs) are a class of macrocyclic compounds. Since their accidental discovery over 70 years ago and subsequent structural elucidation, the phthalocyanines have been one of the most studied classes of organic functional materials.<sup>1</sup> Because of their highly conjugated  $\pi$ -electron system, they are very versatile. They were first developed as industrial pigments, and have been diversely applied in various fields including chemical sensors, solar cells, catalysis, liquid crystals, and photodynamic therapy (PDT),<sup>2–7</sup> due to their stability, diverse coordination properties and optical properties.<sup>8</sup> There are literally thousands of publications and patents related to phthalocyanine and its analog.<sup>9–12</sup> However, it is difficult for most phthalocyanine compounds to dissolve and to melt, which results in the restriction in their applications. In order to enlarge their application, introducing a phthalocyanine compound into a polymer is an effective method to prepare a phthalocyanine polymer that possesses better solubility and processibility.<sup>13</sup>

Polyimide (PI), an important high-performance plastic, has many excellent properties, such as excellent thermal stability, good mechanical properties, low coefficient of thermal expansion, and high radiation resistance. In recent years, hyperbranched PIs have received considerable attention due to their

low viscosity, good solubility, and other attractive properties.<sup>14–18</sup> Recently, our group have explored several PAEKs which contained metallophthalocyanine, here, we prepared a hyperbranched polyimide end-capped with metallophthalocyanine.<sup>12,13,19</sup> In this article, a fluorinated hyperbranched polyimide (HBPI) were synthesized by a triamine monomer, 1, 3, 5-tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB), and a aromatic dianhydride, 4, 4'-oxydiphthalic anhydride (ODPA). Base on this polyimide, a dicyanophenyl end-capped hyperbranched polyimide and a series of novel fluorinated hyperbranched polyimides end-capped with metallophthalocyanines were prepared. Because of the hyperbranched structure, these hyperbranched polyimides containing metallophthalocyanines have good solubility. Characterizations of these polymers were also investigated by means of <sup>1</sup>H-NMR, FTIR, TGA, DSC, and UV-visible absorption spectroscopy.

### EXPERIMENTAL

#### Materials

4, 4'-oxydiphthalic anhydride (ODPA) was purchased from Tokyo Chemical Industry, and used without further purification. 1, 3, 5-tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB) was synthesized according to the literature.<sup>20,21</sup> *N, N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å

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molecular sieves. All other chemicals including phthalonitrile (Aldrich), Zinc powder, quinoline, toluene, chloroform, methanol, acetone, were obtained from commercial sources and used as received.

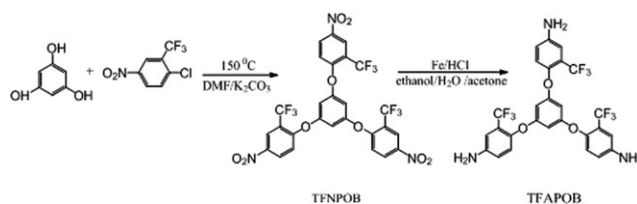
### Characterization

The  $^1\text{H-NMR}$  spectra were recorded on a Bruker 510 instrument with dimethylsulfoxide- $d_6$  (DMSO- $d_6$ ) as the solvent. The FTIR spectra were recorded via the KBr pellet method by using a Nicolet Impact 410 FTIR spectrophotometer. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument with *N,N*-Dimethylformamide (DMF) as an eluent at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a DSC (Model Mettler DSC821 $^{\circ}$ ) instrument at a heating rate of 20 $^{\circ}\text{C}/\text{min}$  under a nitrogen flow of 100 mL/min. A reported  $T_g$  values were recorded during the second scan. The thermo gravimetric analysis was determined by using a Perkin-Elmer Pyris 1 TGA analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ . The UV-visible absorption spectrum was recorded on a UV2501-PC spectrophotometer.

### Monomer Synthesis

**Synthesis of 1,3,5-Tris(2-trifluoromethyl-4-nitrophenoxy)benzene (TFNPOB).** Phloroglucinol (12.6 g, 0.1 mol), 3-trifluoromethyl-4-chloronitrobenzene (22.55 g, 0.3 mol), and  $\text{K}_2\text{CO}_3$  (24.84 g, 0.18 mol) were dissolved in *N,N*-dimethylformamide (DMF) (500 mL) and toluene (90 mL) in a 1000-mL three-necked flask fitted with a nitrogen inlet, a thermometer, a Dean-Stark trap, and a mechanical stirrer, and the apparatus was purged with nitrogen. The reaction mixture was refluxed at 120 $^{\circ}\text{C}$  for 3 h to ensure complete dehydration. After removing toluene, the reaction mixture was heated to 150 $^{\circ}\text{C}$  and refluxed for 8 h under a nitrogen atmosphere. After being poured into water (1 L), the yellow precipitate was collected by filtration and dried under vacuum. The crude product was washed with ethanol to give yellow powder. Yield: 86%. Mp: 162 $^{\circ}\text{C}$  (DSC in  $\text{N}_2$ ). MS:  $m/z = 694$ . IR (KBr): 1 347, 1 236, 1 132  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO- $d_6$ ):  $\delta = 7.43$  (t,  $J = 9.5$ , 3H), 7.87 (dd,  $J = 5.5$ , 3H), 7.97 (d,  $J = 8.5$ , 3H), 8.39 (d,  $J = 8.5$ , 3H) (See Supporting Information).

**Synthesis of 1,3,5-Tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB).** TFNPOB (13.88 g, 0.02 mol), Fe (26.16 g, 0.36 mol), ethanol (30 mL), acetone (30 mL), and deionized water (30 mL) were placed into a 250-mL three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to reflux with stirring, which was followed by the addition of HCl (1 mL, 0.118 mol) and a mixture of 10 mL of deionized water and 10 mL of ethanol. After complete addition, the reaction mixture was further refluxed for 3 h. The hot mixture was then filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected and recrystallized from anhydrous ethanol. Yield: 70%. Mp: 180 $^{\circ}\text{C}$  (DSC). MS:  $m/z = 604$ . IR (KBr): 3509, 3 407, 3 368, 3 222  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO- $d_6$ ):  $\delta = 5.49$  (s, 6H,  $\text{NH}_2$ ), 5.97 (s, 3H), 6.70 (dd,  $J = 7.5$ , 3H), 6.87 (s, 3H), 6.89 (d,  $J = 8.5$ , 3H).



Scheme 1. Synthesis of triamine monomer.

### Polymer Synthesis

**Synthesis of Anhydride-Terminated Hyperbranched Polyimide (AD-HBPI) $^{20}$ .** ODA (0.6205 g, 2 mmol) was dissolved in 15 mL DMAc in a thoroughly dried 50-mL three-necked flask under a nitrogen flow. To the solution TFAPOB (0.6034 g, 1 mmol) in DMAc (5 mL) was added dropwise through a syringe over 1 h under magnetic stirring at 40 $^{\circ}\text{C}$ . The reaction was further conducted for 12 h. A mixture of 3 mL of an acetic anhydride/pyridine (5/4 v/v) was then added, and the reaction mixture was stirred at 60 $^{\circ}\text{C}$  for 10 h. After cooling to room temperature, the mixture was precipitated from methanol (200 mL). The product was collected by filtration, washed thoroughly with methanol and dried under vacuum at 80 $^{\circ}\text{C}$  for 24 h.

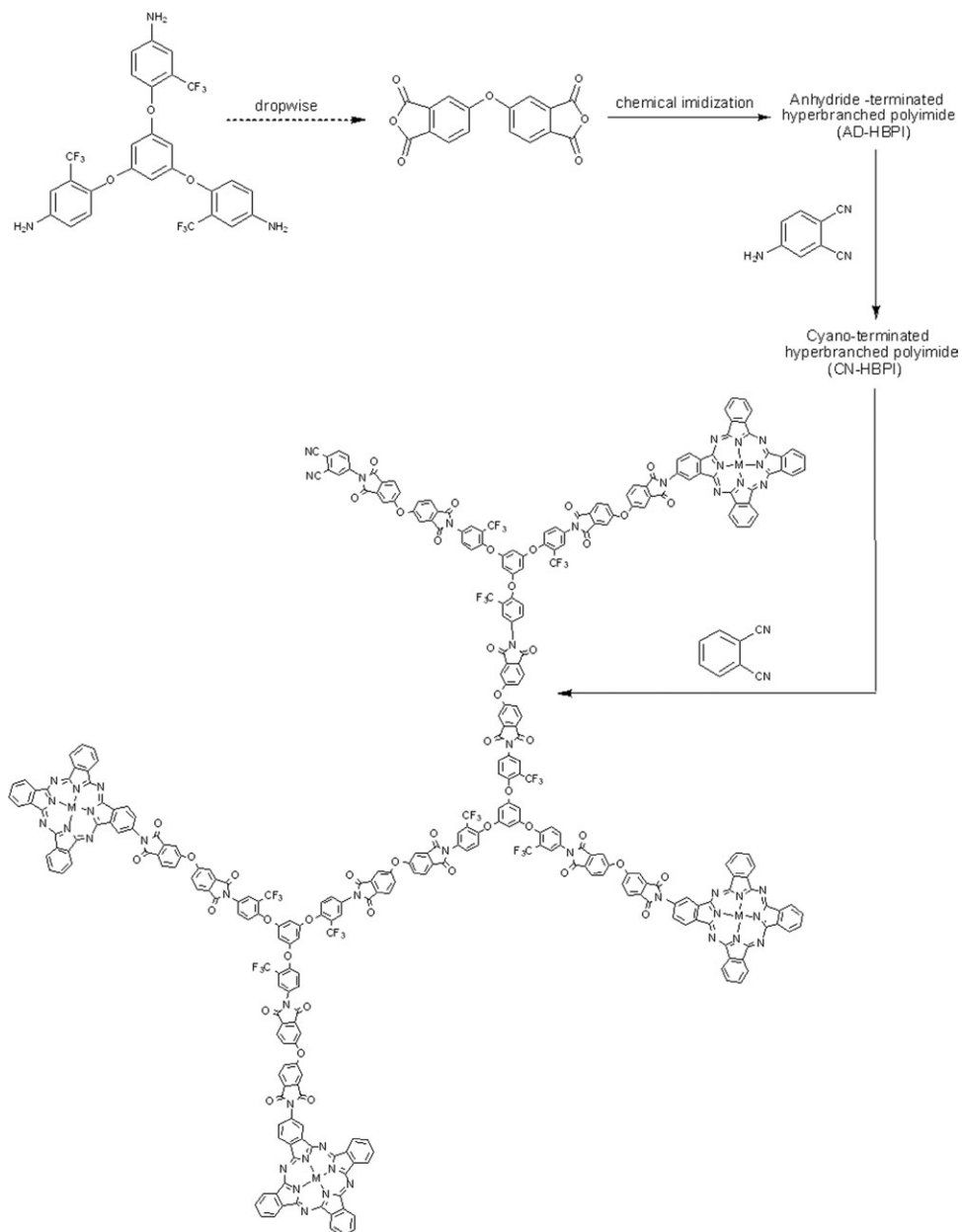
**Synthesis of Cyano-Terminated Hyperbranched Polyimide (CN-HBPI).** AD-HBPI (1.1699 g) was dissolved in 20 mL DMAc in a 50-mL three-necked flask fitted with a nitrogen inlet, a magnetic stirrer, a thermometer, a Dean-Stark trap, and the apparatus was purged with nitrogen. To the mixture a solution of 4-aminophthalonitrile (0.1717 g, 1.2 mmol) in DMAc (5 mL) was added dropwise through a syringe under magnetic stirrer. Toluene (10 mL) was then added, and the reaction mixture was refluxed for 6 h, during which time the water released in the imidization process was removed by distillation as toluene/water azeotrope. After cooling to room temperature, the solution was precipitated from ethanol (200 mL). The product was collected by filtration and dried under vacuum at 80 $^{\circ}\text{C}$  for 24 h.

**Synthesis of Metallophthalocyanine-Terminated Hyperbranched Polyimide (MPC-HBPI).** CN-HBPI (0.6472 g), phthalonitrile (0.2305 g, 1.8 mmol), the corresponding metal chloride (0.6 mmol), and ammonium molybdate (0.1 g) were dissolved in 25 mL of quinoline in a 50-mL three-necked flask equipped with a nitrogen inlet, a mechanical stirrer, a thermometer and a condenser. The reaction mixture was heated to 210–220 $^{\circ}\text{C}$  for 6–8 h. The mixture became dark. After cooling to room temperature, the solution was poured into a mixture of 50 mL of methanol and 3 mL of hydrochloric acid (36%) under vigorous stirring. The precipitated particles were washed with acetone, ethanol, and water. Then the precipitate was collected by filtration and extracted by chloroform with a Soxhlet's extractor. The chloroform solution was concentrated and precipitated in methanol. The product was dried at 110 $^{\circ}\text{C}$  for 24 h. In this work, copper, zinc, and nickel chloride were used.

## RESULTS AND DISCUSSION

### Synthesis of Triamine Monomer

The triamine monomer TFAPOB was synthesized by the reaction of phloroglucinol with 3-(2-trifluoromethyl-4-chloronitrobenzene) in the presence of  $\text{K}_2\text{CO}_3$ , followed by the reduction of the

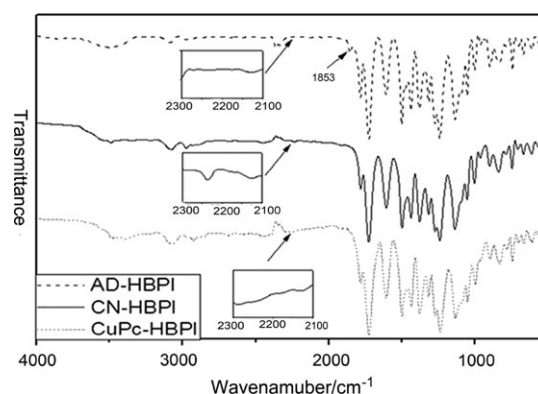


**Scheme 2.** Synthesis of metallophthalocyanines-terminated hyperbranched polyimide (MPC-HBPI).

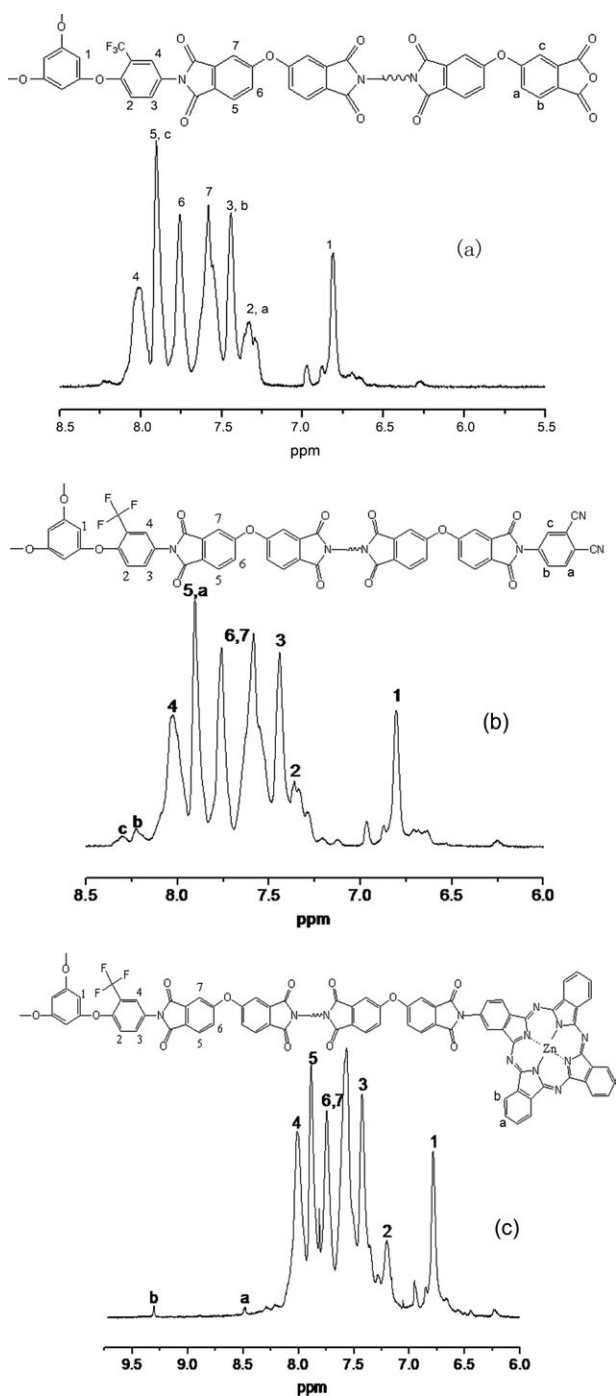
trinitro compound with Fe/HCl. The synthesis route is shown in Scheme 1. The structure of the TFAPOB was confirmed by mass spectrometry, FTIR and  $^1\text{H-NMR}$  spectroscopy.

### Synthesis and Properties of Anhydride-Terminated Hyperbranched Polyimide (AD-HBPI)

The synthesis and characterization of AD-HBPI had been described in detail by Gao et al.<sup>20</sup> The anhydride-terminated hyperbranched polyimide (AD-HBPI) was synthesized by the reaction between TFAPOB and 4,4'-oxydiphthalic anhydride (ODPA), as shown in Scheme 2. The synthesis route was similar to the conventional two-step method for the synthesis of linear polyimides, but a different monomer addition order and molar ratios of the dianhydride monomer and triamine monomer resulted in different hyperbranched polymers, as reported in the

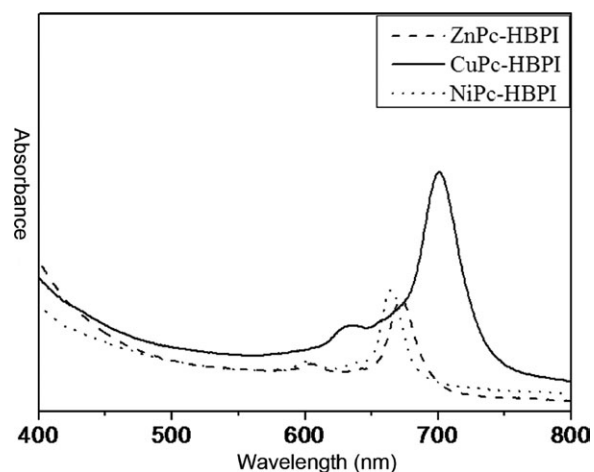


**Figure 1.** FTIR spectrum of AD-HBPI, CN-HBPI, ZnPc-HBPI.



**Figure 2.**  $^1\text{H-NMR}$  spectrum of AD-HBPI (a), CN-HBPI (b), ZnPc-HBPI (c).

literature.<sup>18,21</sup> In this paper, we added TFAPOB to ODPA with a monomer molar ratio of 1:2 (the molar ratio between the amino and anhydride groups in the monomers was 3:4) to get the anhydride-terminated polymers. The chemical structure of AD-HBPI was confirmed by FTIR and  $^1\text{H-NMR}$ . In the IR spectra, the bands at 1784 ( $\text{C=O}$  asymmetrical stretching), 1726 ( $\text{C=O}$  symmetrical stretching), and  $1379\text{ cm}^{-1}$  ( $\text{C-N}$  stretching) are the characteristic absorption bands of polyimides. However, no characteristic band of polyamic acid (around 1



**Figure 3.** UV-visible absorption spectra of MPC-HBPIs in  $\text{CHCl}_3$ .

$680\text{ cm}^{-1}$ ) is identified. In addition, the bands around  $1853\text{ cm}^{-1}$  are attributed to the stretching of  $\text{C=O}$  of the terminal anhydride groups in the AD-HBPI. The bands at  $1136\text{ cm}^{-1}$  are the characteristic absorption bands of  $\text{—CF}_3$ , and the bands at  $1240\text{ cm}^{-1}$  are attributed to  $\text{—O—}$ . These results indicate that the polyimides are well imidized (Figure 1).

Figure 2a shows the  $^1\text{H-NMR}$  spectrum of AD-HBPI in  $\text{DMSO-d}_6$ . The bands around 6.8, 7.33–7.44, and 8.01 ppm are attributed to the phenyl hydrogen 1, 2, 3, and 4 of the TFAPOB residues. The peaks in the range of 7.58–7.91 ppm can be attributed to the resonance absorption of the phenyl hydrogen 7, 6, and 5 of the ODPA residues. The signals of protons a, b, and c appear at  $\delta$  7.3, 7.4, and 7.9, respectively, and overlap with protons 2, 3, and 5.

### Synthesis and Properties of Cyano-Terminated Hyperbranched Polyimide (CN-HBPI)

CN-HBPI was synthesized by the condensation between AD-HBPI and 4-aminophthalonitrile, as shown in Scheme 2. The chemical structure of CN-HBPI was proved by IR and  $^1\text{H-NMR}$ . The IR spectra show characteristic absorption bands of  $\text{—CN}$ ,  $\text{—C=O}$  (asymmetrical stretching),  $\text{—C=O}$  (symmetrical stretching),  $\text{—C—N}$ ,  $\text{—O—}$  and  $\text{—CF}_3$  at 2233, 1784, 1726, 1379, 1240, and  $1136\text{ cm}^{-1}$ , respectively, which suggests that CN-HBPI has been obtained successfully (Figure 1).

Figure 2b shows the signal assignments of  $^1\text{H-NMR}$  spectrum of CN-HBPI in  $\text{DMSO-d}_6$ . The bands around 6.8, 7.34–7.44, and 8.03 ppm are attributed to the phenyl hydrogen 1, 2, 3, and 4 of the TFAPOB residues. The peaks in the range of 7.58–7.91 ppm can be attributed to the resonance absorption of the phenyl hydrogen 7, 6, and 5 of the ODPA residues. And the bands

**Table I.** UV-Vis Absorption and Color of MPC-HBPIs in  $\text{CHCl}_3$

Polymer	$\lambda_{\text{uv}}$ (nm)	Color (in $\text{CHCl}_3$ )
CuPc-HBPI	672	Brown
ZnPc-HBPI	701	Dark green
NiPc-HBPI	665	Green



**Table II.** The Solubility of the Polymers in Different Organic Solvents

Polymer	Solvents							
	DMF	DMAc	DMSO	NMP	THF	CHCl <sub>3</sub>	Acetone	Ethanol
AD-HBPI	+	+	+	+	+	–	+	–
CN-HBPI	+	+	+	+	+	–	+	–
CuPc-HBPI	+	+	+	+	+	+	–	–
ZnPc-HBPI	+	+	+	+	+	+	–	–
NiPc-HBPI	+	+	+	+	+	+	–	–

(+, soluble; –, insoluble; DMF: *N,N*-Dimethylformamide; DMAc, *N,N*-Dimethylacetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl pyrrolidone; THF, tetrahydrofuran; CHCl<sub>3</sub>, chloroform.

around 7.9, 8.2, and 8.3 ppm can correspond to the three protons near –CN group.

### Synthesis and Properties of Metallophthalocyanine-Terminated Hyperbranched Polyimide (MPc-HBPI)

The metallophthalocyanine-terminated hyperbranched polyimide (MPc-HBPI) was prepared from the condensation of CN-HBPI, phthalonitrile and the corresponding metal chloride, as shown in Scheme 2.

In the IR spectra of CuPc-HBPI, the bands at 1784 cm<sup>-1</sup> (C=O asymmetrical stretching), 1726 cm<sup>-1</sup> (C=O symmetrical stretching), and 1379 cm<sup>-1</sup> (C–N stretching) are the characteristic absorption bands of polyimides. The absence of the characteristic absorption bands of –CN at 2233 cm<sup>-1</sup> suggests the reaction of cyano group of the polymer end have been reacted fully. Other IR spectra of MPc-HBPI are similar (Figure 1).

Figure 2c shows the <sup>1</sup>H-NMR spectrum of ZnPc-HBPI, in which the signals of protons *a* and *b* appear at δ 8.5 and 9.3, respectively, as broad peaks. Because protons *a* and *b* are not very close to the core of the large metal complex ring, the downfield shift effect of the metal-complex ring on the chemical shifts of protons *a* and *b* is not significant. However, the ring current affects the conjugated system, so the chemical shifts of protons *a* and *b* are high because of the low content of the metallophthalocyanine, the signal intensities of protons *a* and *b* are weak.

Because of the paramagnetic copper and nickel ions, a valuable <sup>1</sup>H NMR spectrum could not be supplied. However, the UV-vis absorption spectrum could support to the chemical structure of MPc-HBPIs. The UV-vis absorption spectra of MPc-HBPIs in chloroform solution are shown in Figure 3. It is evident that strong absorption band in the visible range exist for ZnPc-HBPI, whereas they are moderate for CuPc-HBPI and NiPc-HBPI. The absorption bands of the three polymers in chloroform solution are in a range from 665 to 701 nm. The maximum values of the absorption of the three polymers are presented in Table I. The above analysis suggested successful introduction of phthalocyanine group into the polymer end.

### Solubility and Thermal Property of the Polymers

The solubility of synthesized polymers was tested in various organic solvents and the results are summarized in Table II. AD-HBPI and CN-HBPI have excellent solubility in solvents such as

DMSO, DMAc, DMF, NMP, THF, and acetone, etc. MPc-HBPIs also show good solubility in common solvents like DMSO, DMAc, NMP, and CHCl<sub>3</sub>, etc. These polymers containing metallophthalocyanine were found to be colored as expected. The colors of the polymers in chloroform solution are listed in Table I. The molecular weights of HBPIs were determined by GPC and the results are summarized in Table III. From this table, it is evident that the number average molecular weights of the AD-HBPI and CN-HBPI are 19,300 and 21,000, respectively. The MPc-HBPI number average molecular weights vary from 25,300 to 31,800, and the polydispersity values of the Pc-HBP vary from 2.92 to 3.11.

The thermal properties of the polymers are shown in Table III. The thermal behaviors were evaluated by DSC at a heating rate of 20°C/min under nitrogen. The glass transition temperature (*T*<sub>g</sub>) of the polymers were in the range of 216–225°C. The glass transition temperature (*T*<sub>g</sub>) of CN-HBPI (221°C) was higher than the *T*<sub>g</sub> of AD-HBPI (216°C), because of the introduction of CN as a highly polar group. It will results in the increase of intermolecular interactions, causing the difficulties in fragment movement. The thermal stability was evaluated by TGA at a heating rate of 10°C/min under nitrogen. The 5 wt % weight loss temperature of the polymers varied from 440 to 543°C, and the 10 wt % weight loss temperatures varied from 498 to

**Table III.** Molecule Weight and Thermal Properties of the Polymers

Polymer	<i>M</i> <sub>n</sub> <sup>a</sup>	Polydispersity <sup>b</sup>	<i>T</i> <sub>g</sub> <sup>c</sup> (°C)	<i>T</i> <sub>d</sub> <sup>d</sup> (5%) (°C)	Char yield <sup>e</sup> (%)
AD-HBPI	19300	2.38	216	543	51.94
CN-HBPI	21000	2.43	221	520	51.70
CuPc-HBPI	25300	2.92	219	487	55.80
ZnPc-HBPI	30700	3.11	217	440	52.05
NiPc-HBPI	31800	3.02	225	474	53.82

<sup>a</sup>The number average molecular weights.

<sup>b</sup>Weight average molecular weights(*M*<sub>w</sub>)/Number average molecular weights(*M*<sub>n</sub>).

<sup>c</sup>Baseline shift in the second heating DSC traces, with a heating rate of 20°C/min in nitrogen.

<sup>d</sup>Temperature at 5% weight loss were recorded by TGA at a heating rate of 10°C/min in nitrogen.

<sup>e</sup>Residual weight (%) when heated to 800°C.

569°C, indicating that the polymers exhibited a good thermal stability.

## CONCLUSIONS

A series of novel fluorinated hyperbranched polyimides end-capped with metallophthalocyanines were synthesized via the reactions of 1,3,5-tris(2-trifluoromethyl-4-aminophenoxy)benzene (TFAPOB) ( $B_3$ ), as a “core” molecule, 4,4'-oxydipthalic anhydride (ODPA) as a  $A_2$  monomer, and metallophthalocyanines as an end-capping reagent. The obtained MPC-HBPIs show high glass transition temperatures and high thermal stability. These polyimides containing metallophthalocyanine units possess good solubility in common solvents, and they show strong optical absorption in the visible region.

## ACKNOWLEDGMENTS

This work was supported by Jilin Provincial Science and Technology Development Project of China (20116021).

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