

Synthesis, optical and electrochemical properties of new hyperbranched poly(triphenylamine amide)s

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ABSTRACT

A new triphenylamine-containing AB₂ type monomer with one carboxylic acid and two amino groups, 4-(bis(4-aminophenyl)amino)benzoic acid (**3**), was synthesized and used for the preparation of hyperbranched poly(triphenylamine amide)s. The self-polycondensation of the AB₂ monomer (**3**) afforded hyperbranched poly(triphenylamine amide) with amino end groups. The molecular weight of the hyperbranched poly(triphenylamine amide) was 21,000 Da determined by light scattering. End-capped hyperbranched polyamides were isolated by the chemical modification of unreacted amino groups with various acid chlorides. All the hyperbranched poly(triphenylamine amide)s exhibit excellent solubility in organic solvents such as NMP, DMF, DMSO, and DMAc at room temperature. The viscosities of hyperbranched poly(triphenylamine amide)s are as low as about 0.15 dL/g due to their dendritic structures. Poly(triphenylamine amide)s end-capped with rigid benzene ring have higher thermal stability than those with amino or aliphatic end groups. The photoluminescence of the hyperbranched polyamides is blue-yellow emissions around 430–510 nm. The energy gaps of the hyperbranched poly(triphenylamine amide)s with different end groups are about 2.93 eV and are independent on the end groups, but the HOMO and LUMO energy levels are dependent on the end groups.

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1. Introduction

Dendritic polymers have received considerable attention due to their unique chemical and physical properties [1–7]. Hyperbranched polymers show similar properties to those dendrimers, such as low viscosity, high solubility in organic solvents, and lack of significant entanglement in the solid state. However, hyperbranched polymers are readily synthesized by one-step polymerization of AB_n monomers [1–4]. This is advantageous over the multi-step synthesis of dendrimers because of the rapid production in large quantities. It is also well known that the properties of the dendritic polymers depend on terminal functional groups in addition to backbone structure [1–7]. Therefore, the properties of dendritic polymers can be tuned to some extent by the chemical modification of end functional groups [1–7]. On the other hand, wholly aromatic polyamides are well known as high performance polymers due to their excellent thermal, mechanical and chemical properties [8–10]. However, the rigidity of the backbone and strong hydrogen bonding result in high melting temperatures or glass transition temperatures and limited solubility in most organic solvents. These properties make them generally intractable or

difficult to process, thus restricting their applications in some fields [8–10]. Incorporation of hyperbranched structure to polymers is an approach to overcome the limited solubility of polyamides.

Organic charge transporting materials play an important role in many electrical and optical applications such as organic photoconductors, electroluminescence (EL), and electrochromic devices [11–14]. Especially the family of triphenylamine (TPA) derivatives has attracted intense research interest during the past few decades due to their excellent charge transporting properties as hole transporting materials in thin layer electrooptical devices such as organic light-emitting diodes, solar cells, organic field effect transistors, two-photon lithography, and photorefractive holography [11–20].

Linear polymers containing triphenylamine moiety have also been reported in literatures [11,21,22]. Compared to linear polymers, hyperbranched polymers are alternatively outstanding candidates for scientific and industrial applications due to their unusual chemical and physical properties. It has been reported that electrooptical devices with hyperbranched polymers showed significantly improved stability and efficiency in comparison to linear polymers [23,24]. However, most hyperbranched triphenylamine-containing polymers were prepared by A₂ + B₃ route; only few papers [25,26] discuss on the AB₂ route.

Accordingly, a new triphenylamine-based AB₂ monomer with one carboxylic acid and two amino groups was synthesized for the

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preparation of hyperbranched poly(triphenylamine amide)s. The effects of end functional groups on the physical properties of prepared hyperbranched poly(triphenylamine amide)s were evaluated as well as their optical and electrochemical properties.

2. Experimental

2.1. Materials

The materials, *p*-toluidine (from TCI), potassium permanganate (from J.T. Baker), 4-fluoronitrobenzene (from Acros), cesium fluoride (from Aldrich), acetyl chloride (from Acros), benzoyl chloride (from TCI), 4-nitrobenzoyl chloride (from TCI), 3,5-dinitrobenzoyl chloride (from Acros), hydrazine monohydrate (from Alfa Aesar), 10% palladium on activated carbon (from Merck) were used as received. The solvents, *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) were purchased from TEDIA and tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) were purchased from ECHO. These solvents were purified by distillation over calcium hydride and stored over 4 Å molecular sieves. All acid chlorides were used as received.

2.2. Measurements

Infrared (IR) spectra were recorded on a PerkinElmer GX FTIR spectrometer. NMR spectra were recorded using a BRUKER DRX-500 NMR (^1H at 500.13 MHz and ^{13}C at 125.76 MHz). Elemental analyses were made on a Perkin–Elmer 2400 instrument. The inherent viscosity of polyimide was measured by Ubbelohde viscometer. Thermogravimetric data were obtained on a PerkinElmer Pyris 6 TGA under nitrogen or air flowing condition at a rate of $20\text{ cm}^3\text{ min}^{-1}$ and a heating rate of $20\text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetric analysis was performed on a PerkinElmer Pyris DSC 6 under nitrogen flowing condition at a rate of $20\text{ cm}^3\text{ min}^{-1}$ and a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Absorption spectra were measured with a UV 500 UV–Visible spectrometer at room temperature in air. Photoluminescence (PL) spectra were measured with a PerkinElmer LS 55 Luminescence spectrometer. Cyclic voltammetry (CHI model 619A) was conducted with the use of a three-electrode cell in which ITO (the polymer film area was ca. $0.7\text{ cm} \times 0.5\text{ cm}$) was used as a working electrode. The electrochemical cell was composed of a 1-cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and an Ag/AgCl as reference electrode. The absolute molecular weight was determined by light scattering (Malvern 4800 with Autosizer 4700) in DMF at room temperature.

2.3. Synthesis of monomer (Scheme 1)

2.3.1. 4-Nitro-*N*-(4-nitrophenyl)-*N*-*p*-tolylbenzenamine (**1**)

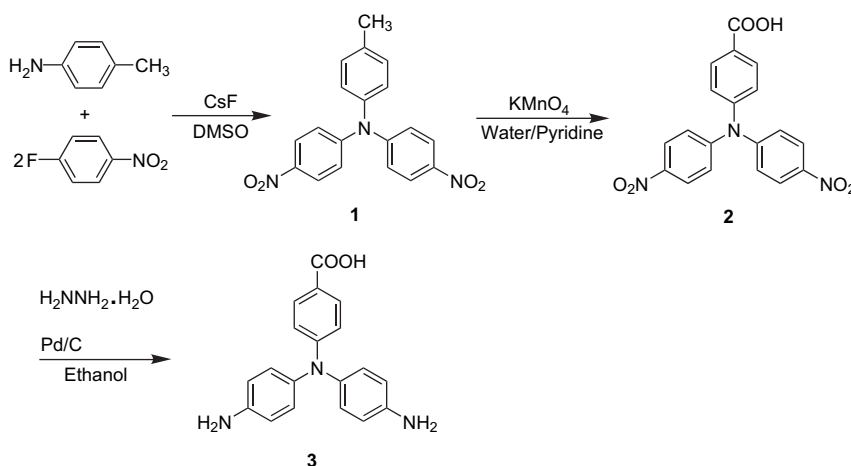
In a 250 mL round-bottomed flask, a mixture of 4.68 g (43 mmol) of *p*-toluidine, 14.58 g of CsF, 12.0 g (86 mmol) of 4-fluoronitrobenzene and 100 mL of DMSO was stirred at $120\text{ }^\circ\text{C}$ for 48 h. Upon cooling, the solution was poured into 1000 mL of water, and the precipitated orange solid was collected by filtration and washed with methanol. The yield of the product was 12 g (79%); m.p. $294\text{ }^\circ\text{C}$ (by DSC); FTIR (KBr, cm^{-1}): 1508 and 1339 (NO_2). Elemental analysis: calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4$: C, 65.32; H, 4.33; N, 12.03, found: C, 65.35; H, 4.35; N, 11.95; ^1H NMR (DMSO- d_6 , ppm): 8.16 (d, $J = 9.06\text{ Hz}$, 4H), 7.30 (d, $J = 8.13\text{ Hz}$, 2H), 7.16 (d, $J = 9.19\text{ Hz}$, 4H), 7.14 (d, $J = 8.26\text{ Hz}$, 2H), 2.33 (s, 3H).

2.3.2. 4-(Bis(4-nitrophenyl)amino)benzoic acid (**2**)

To a 1 L three-necked flask with a mixture of 5 g (14 mmol) compound **1**, 540 mL cosolvent (pyridine/water = 2/1), 66.7 g (0.422 mol) of KMnO_4 was added slowly. The mixture was stirred at $120\text{ }^\circ\text{C}$ for 24 h. The mixture was then filtered to remove MnO_2 and hydrogen chloride was added to afford the crude product. The crude product was recrystallized from acetic acid to afford the pure yellow product **2**; 3.7 g (68%); m.p. $305\text{ }^\circ\text{C}$ (by DSC); FTIR (KBr, cm^{-1}): 1673 (C=O), 1504, 1339 (NO_2). Elemental analysis: calcd. for $\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_6$: C, 60.16; H, 3.45; N, 11.08, found: C, 60.22; H, 3.42; N, 11.20; ^1H NMR (DMSO- d_6 , δ , ppm): 8.19 (d, $J = 9.18\text{ Hz}$, 4H), 7.97 (d, $J = 9.11\text{ Hz}$, 2H), 7.28 (d, $J = 8.53\text{ Hz}$, 2H), 7.25 (d, $J = 9.87\text{ Hz}$, 4H); ^{13}C NMR (DMSO- d_6 , δ , ppm): 166.59, 151.29, 148.51, 142.77, 131.48, 128.07, 125.82, 125.55, 123.57.

2.3.3. 4-(Bis(4-aminophenyl)amino)benzoic acid (**3**)

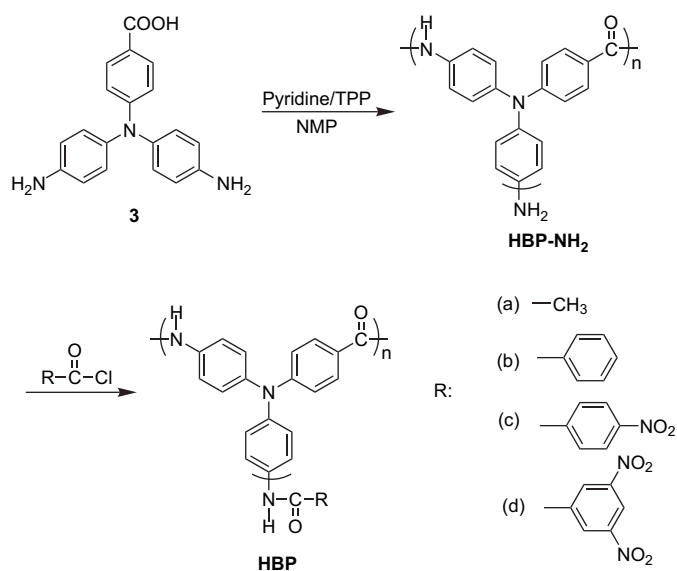
In a 250 mL three-necked flask, a mixture of 3.0 g (7.9 mmol) nitro compound **2**, 0.09 g 10% Pd/C and 85 mL of ethanol was added. A solution of hydrazine monohydrate (6.6 mL) in ethanol (13.2 mL) was added slowly at $50\text{ }^\circ\text{C}$ and the solution was refluxed with stirring for 24 h. The mixture was then filtered to remove Pd/C and dried by using rotation vapor to afford the crude product. The crude product was recrystallized from THF to afford the desired monomer. The yield of the yellow-green product **3** was 2.2 g (86%); m.p. $245\text{ }^\circ\text{C}$ (by DSC); FTIR (KBr, cm^{-1}): 2700–3400 (OH), 1660 (C=O) and 3459, 3374 (NH_2). Elemental analysis: calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$: C, 71.46; H, 5.37; N, 13.16, found: C, 71.40; H, 5.29; N, 13.20; ^1H NMR (DMSO- d_6 , ppm): 7.60 (d, $J = 8.78\text{ Hz}$, 2H), 6.87 (d, $J = 7.02\text{ Hz}$, 4H), 6.55 (d, $J = 8.47\text{ Hz}$, 4H), 6.49 (d, $J = 7.29\text{ Hz}$, 2H), 5.09 (s, 4H); ^{13}C NMR (DMSO- d_6 , ppm): 168.30, 152.55, 145.43, 134.79, 130.44, 127.92, 121.13, 114.85, 114.03.



Scheme 1. Synthesis of AB_2 monomer, 4-(bis(4-aminophenyl)aminobenzoic acid (**3**)).

2.4. Preparation of polymers (Scheme 2)

In a flask, 5.0 g (15.6 mmol) of 4-(bis(4-aminophenyl)amino)benzoic acid (**3**) was dissolved in 21 mL of NMP, then 4 mL of pyridine and 4 mL of triphenylphosphite were charged into the flask. The solution was heated to 100 °C and stirred under nitrogen atmosphere for 3 h. After the temperature decreased to room temperature, the solution was slowly poured into 800 mL of methanol containing 0.1 wt% lithium chloride (0.1 wt% LiCl/CH₃OH), and yellow-green precipitated polymer (**HBP-NH₂**) was washed by refluxing methanol under nitrogen atmosphere and collected by filtration. The product was dried overnight at room temperature under vacuum, giving 4.5 g: 90% yield. IR (KBr, cm⁻¹): 1650 (C=O).



Scheme 2. Preparation of hyperbranched poly(triphenylamine amide)s.

2.4.1. End-capping of polyamide **HBP-NH₂**

A typical experimental procedure for the end-capping of **HBP-NH₂** to form **HBP-a** is as follows:

A mixture of 0.5 g of **HBP-NH₂**, 0.25 mL (3 mmol) of acetyl chloride, and 2.52 mL of NMP was stirred at 0 °C for 2 h and for another 4 h under nitrogen atmosphere at room temperature, and then poured into 100 mL of methanol containing 0.1 wt% LiCl to precipitate the product (**HBP-a**). The product was filtered, washed with refluxing methanol, and dried overnight at room temperature under vacuum. IR (KBr, cm⁻¹): 1655 (C=O, amide), 3296 (NH, amide).

The other end-capping reaction was carried out in the same manner to afford **HBP-b**, **HBP-c**, and **HBP-d** using benzoyl chloride, 4-nitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, respectively, as end-capping reagents. IR (KBr, cm⁻¹): 1650 (C=O, amide), 3300 (NH, amide) for **HBP-b**; 1651 (C=O, amide), 3401 (NH, amide), 1505 and 1346 (NO₂) for **HBP-c**; and 1669 (C=O, amide), 3262 (NH, amide), 1505 and 1344 (NO₂) for **HBP-d**.

3. Results and discussion

3.1. Monomer synthesis

The synthesis of the triphenylamine-based novel AB₂ type monomer, 4-(bis(4-aminophenyl)amino)benzoic acid (**3**) having one carboxylic acid and two amino groups, is shown in Scheme 1. The AB₂ monomer was prepared from *p*-toluidine and

fluoronitrobenzene via nucleophilic reaction in the presence of cesium fluoride to afford dinitro compound (**1**), followed by oxidation of the methyl group and reduction of the nitro groups. The FTIR spectrum of dinitro compound **1** showed characteristic bands of the nitro group at 1339 and 1508 cm⁻¹ and methyl groups at 2800–3100 cm⁻¹. After oxidation of methyl group in the dinitro compound (**1**) by KMnO₄, a characteristic peak at 1673 cm⁻¹ for the carboxylic group was observed on FTIR spectrum, indicating that the methyl group has been oxidized to afford compound (**2**). Reduction of the compound (**2**) in ethanol with hydrazine monohydrate in the presence of catalytic amount of palladium on activated carbon at 70 °C produced the AB₂ monomer (**3**). The structures of AB₂ monomer (**3**) and the intermediates were confirmed by elemental analysis, IR and NMR spectra. The characteristic absorptions of the nitro group at 1339 and 1508 cm⁻¹ disappeared and new absorptions at 3374 and 3459 cm⁻¹ (N–H stretching) appeared. The ¹H and ¹³C NMR spectra of the new AB₂ monomer (**3**) are shown in Fig. 1. In ¹H NMR spectrum (Fig. 1A), a singlet broad peak at 5.09 ppm due to amino proton was observed. Two doublets at 6.48 (peak d) and 7.60 (peak e) ppm are peculiar to the carboxylic acid attached phenylene protons. Two doublets at 6.55 (peak c) and 6.87 (peak b) ppm are peculiar to the amino groups attached phenylene protons. Usually, carboxylic acid exists as stable hydrogen-bonded dimers and shows up from 10 to 13 ppm as a very broad singlet. In this case, the singlet is so broad that it is hardly observed. However, the ¹³C NMR spectrum (Fig. 1B) exhibits nine features in the range of 114.0–168.3 ppm for each carbon atom. The peak at 168.3 ppm is attributed to the carbon on the carboxylic acid. The FTIR spectrum of the AB₂ monomer (**3**) shows peaks at 1660 cm⁻¹ for carbonyl group and at 3459, 3374 cm⁻¹ for amino groups, which confirmed the supposed AB₂ monomer structure. Elemental analysis, IR and NMR spectra clearly confirmed that the AB₂ monomer (**3**) synthesized herein is consistent with the proposed structure.

3.1.1. Polymerization

The self-polymerization of AB₂ monomer, 4-(bis(4-aminophenyl)amino)benzoic acid (**3**), was carried at 100 °C for 3 h in NMP in the presence of triphenyl phosphite and pyridine. The triphenylamine-based hyperbranched polyamide with unreacted amino groups was isolated when the polymerization mixture was poured into methanol containing lithium chloride (1 × 10⁻² mol/L). The molecular weight determined by light scattering was 2.1 × 10⁴ Da, which suggests that the amino-terminal hyperbranched polyamide has high molecular weight. The terminal amino groups of the hyperbranched polyamide were end-capped by using various acid chlorides as end-capping agents to get poly(triphenylamine amide)s with different terminal groups as shown in Scheme 2. The result of the polymerization with various end-capping acid chlorides is summarized in Table 1. Triphenylamine-based hyperbranched polyamides were isolated in good yields when aromatic acid chlorides were used as end-capping agents. The yield of **HBP-a** polymer end-capped by acetyl chloride is rather lower than all the other samples due to partial soluble property in methanol, which was used as precipitated solvent. Quantitative end-capping reactions were confirmed by the disappearance of the broad peak at around 5 ppm, which is attributed to N–H proton in ¹H NMR measurements. The inherent viscosities measured in DMAc for the amino-terminal poly(triphenylamine amide) and end-capped hyperbranched polyamides were 0.15–0.16 dL g⁻¹, which implies that the resulting polymers have low viscosity due to the unique dendritic structures, similar to other hyperbranched polymers in literatures [1–7]. However, the inherent viscosity of these hyperbranched polyamides is higher than the inherent viscosity (about 0.1 dL g⁻¹) of similar hyperbranched poly(triphenylamine)s prepared from 4,4'-diamino-4''-bromotriphenylamine through

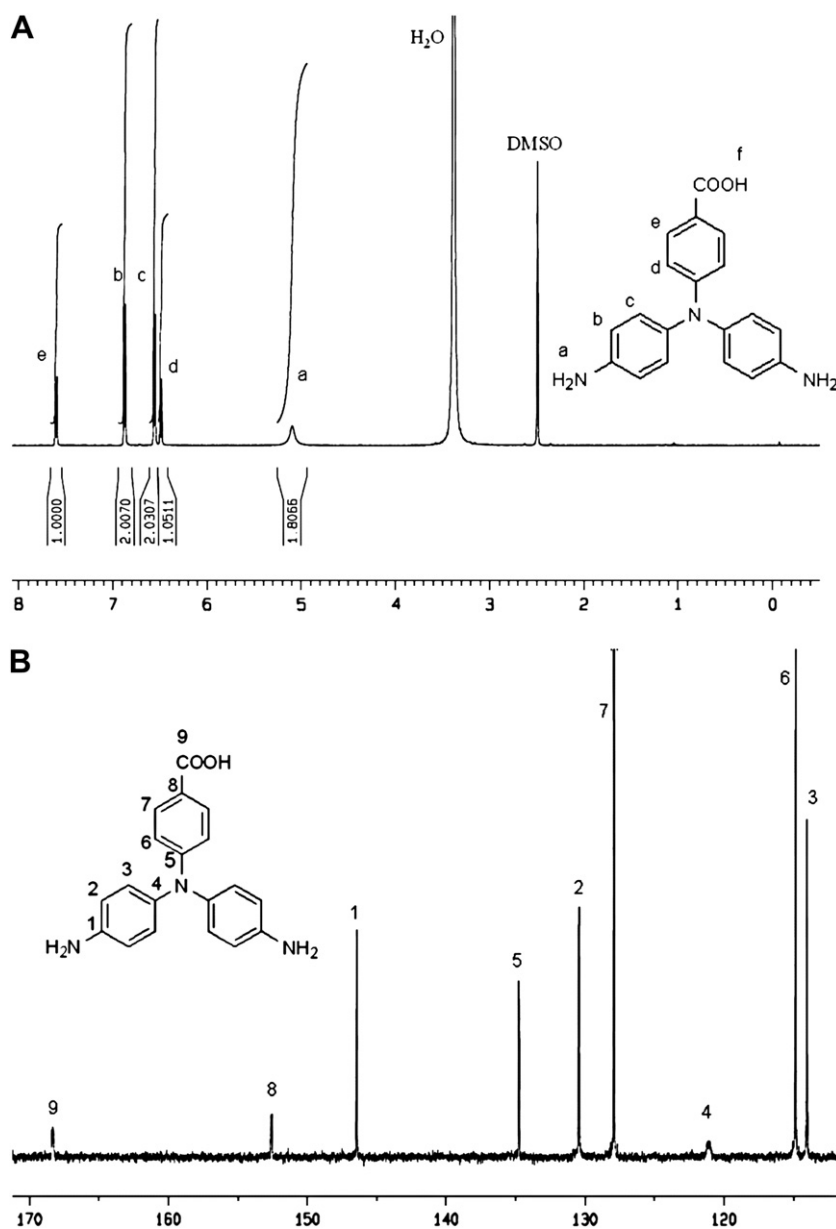


Fig. 1. (A) ^1H NMR and (B) ^{13}C NMR spectra of the AB_2 monomer 3.

Table 1
Yields and inherent viscosities of hyperbranched polyamides

Polymer code	Yield (%)	Inherent viscosity ^a (dL/g)
HBP-NH ₂	90	0.15
HBP-a	77	0.16
HBP-b	93	0.16
HBP-c	92	0.15
HBP-d	94	0.15

^a Measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30 °C.

palladium catalyzed C–N coupling reaction [22] maybe due to the amide hydrogen bonding.

The structure of the resulting polymers was investigated by IR, ^1H NMR and ^{13}C NMR measurements. Fig. 2A shows ^1H NMR spectrum of hyperbranched polyamide HBP-NH₂. Peaks attributed to amide (9.8–10.0 ppm), aromatic (6.4–7.8 ppm) and amino (5.0 ppm) protons were observed. The amide groups divided into many peaks, because the amide could be affected by the neighbor repeating units, which could be dendritic, linear and terminal

groups. After the amino end groups of HBP-NH₂ being modified by acid chlorides, the amino groups at 5.0 ppm disappeared, indicating that the amino groups have been modified. Fig. 2B shows ^1H NMR spectrum of hyperbranched polyamide HBP-c modified by *p*-nitrobenzoyl chloride. The peaks at 10.1 and 10.6 ppm attributed to the amide formed in polymerization and that formed in the modification of end amino groups, respectively. The amide peak at 10.1 ppm is not divided into many peaks as HBP-NH₂ did. Because after being modified, all repeating units in the polymer are similar to dendritic units. The disappearance of the characteristic peak of amino groups and the appearance of a new characteristic peak of amide indicate that the modification was carried out successfully.

3.2. Properties of polymers

It is well known that the properties of hyperbranched polymers are influenced not only by the backbone structure but also by the end functional groups [1–7]. The effects of end groups on solubility, thermal, and electrochemical properties were studied. The

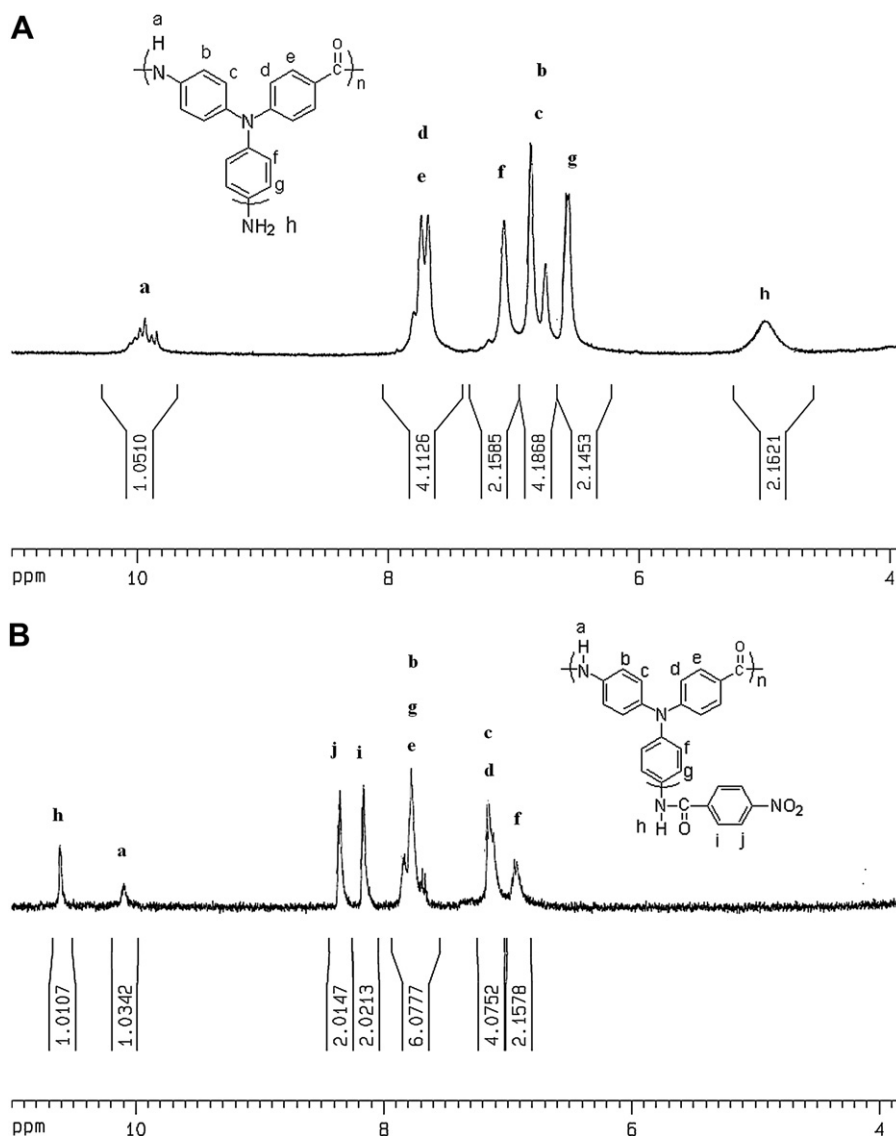


Fig. 2. ^1H NMR spectra of (A) **HBP-NH₂** and (B) **HBP-c**.

solubility of the hyperbranched polyamides with different end groups is shown in Table 2. All poly(triphenylamine amide)s are soluble at room temperature in aprotic solvents such as NMP, DMAc, DMF and DMSO and soluble or partially soluble in pyridine, THF and chloroform on heating. The excellent solubility results from their dendritic structures [1–7].

The effect of end groups on thermal properties of the polymers is shown in Table 3. The TGA curves of these polymers in nitrogen and air atmospheres are shown in Fig. 3. The polymers with

aromatic amide end groups showed the 5% degradation temperature in the range 270–338 °C in air. The thermal stability of these hyperbranched poly(triphenylamine amide)s is higher than the similar hyperbranched poly(triphenylamine)s [22]. It may result from the hydrogen bonding of amide groups in the hyperbranched polyamides. The uncapped polymer **HBP-NH₂** and aliphatic end-capped polymer **HBP-a** exhibited lower 5% degradation

Table 2
Solubility of hyperbranched poly(triphenylamine amide)s

Polymer code	Solubility ^a						
	THF	NMP	DMAc	DMF	DMSO	Pyridine	CHCl ₃
HBP-NH₂	+-	++	++	++	++	+	+-
HBP-a	+-	++	++	++	++	+	+-
HBP-b	+-	++	++	++	++	+	+-
HBP-c	+-	++	++	++	++	+	+-
HBP-d	+-	++	++	++	++	+	+-

NMP: *N*-methyl-2-pyrrolidinone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethylsulfoxide; THF: tetrahydrofuran.

^a Solubility: ++, soluble at room temperature; +, soluble on heating at 70 °C; +-, partially soluble on heating at 70 °C.

Table 3
Thermal properties of hyperbranched polyamides

Polymer code	T_g^a (°C)	T_{d5}^b (°C)		T_{d10}^b (°C)		Char yield ^c (%)	
		In N ₂	In air	In N ₂	In air	In N ₂	In air
HBP-NH₂	- ^d	250	270	327	364	28	0
HBP-a	- ^d	299	306	369	360	62	0
HBP-b	- ^d	333	338	409	388	40	4
HBP-c	- ^d	316	330	392	380	65	0
HBP-d	- ^d	320	317	369	358	58	0

^a Glass transition temperature (T_g) measured by DSC at a heating rate of 10 °C min⁻¹.

^b Decomposition temperature recorded on TGA at a heating rate of 20 °C min⁻¹. T_{d5} and T_{d10} indicate 5 and 10% weight loss, respectively.

^c Char yield (%) at 800 °C.

^d The glass transition temperature of polymer was not observed.

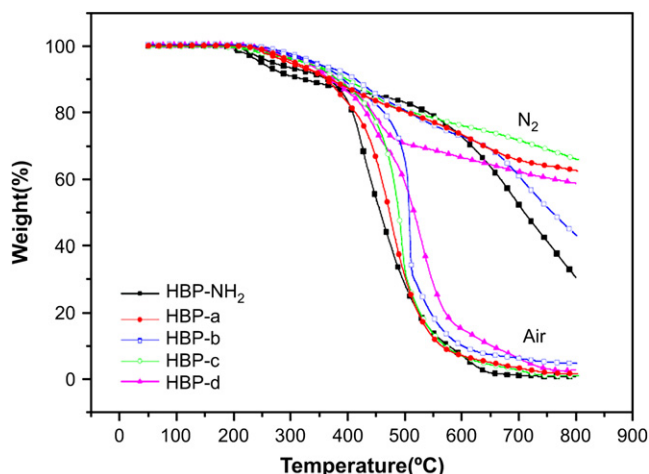


Fig. 3. TGA curves of the resulting poly(triphenylamine amide)s in nitrogen and air atmospheres.

temperatures at 270 and 306 °C, respectively. No glass transition temperature (T_g) was detected for the all hyperbranched polyamides by DSC measurement at the range of -100 to 250 °C.

The optical properties of the hyperbranched polyamides were evaluated by UV absorption and PL emissions and were summarized in Table 4. The maximum absorptions of hyperbranched polyamides with different end groups are at 354–358 nm and the onset of absorption is at 421–425 nm. The photoluminescence emits at 433–505 nm depending on the end groups. Poly(triphenylamine amide) with strong electron-withdrawing *p*-nitrobenzene end groups exhibits shortest emissions (433 nm), the one with strong electron-donating amino end groups exhibits longest emission (505 nm). The absorptions are similar but emission wavelengths are different for the different end-capped hyperbranched poly(triphenylamine amide)s. It means that the end groups do not affect the band gaps of the triphenylamine-containing hyperbranched polyamides but affect the emissions.

The values of HOMO and LUMO depending on the end functional groups of the triphenylamine-based hyperbranched polyamides were investigated by cyclic voltammogram (CV). Fig. 4 shows the cyclic voltammogram of hyperbranched poly(triphenylamine amide)s with different end groups coated on an ITO glass substrate in acetonitrile containing 0.1 M TBAP at scanning rate of 0.1 V/s. The redox was assumed to occur at the nitrogen atom of the triphenylamine groups. The energy levels of the HOMO and LUMO of the investigated hyperbranched polyamides can be estimated from the oxidation onset (E_{onset}) and the onset absorption wavelength of the UV–vis spectra. The results are listed in Table 4. For example, the E_{onset} value for HBP-NH₂ has been determined as 0.8 V vs Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc⁺)

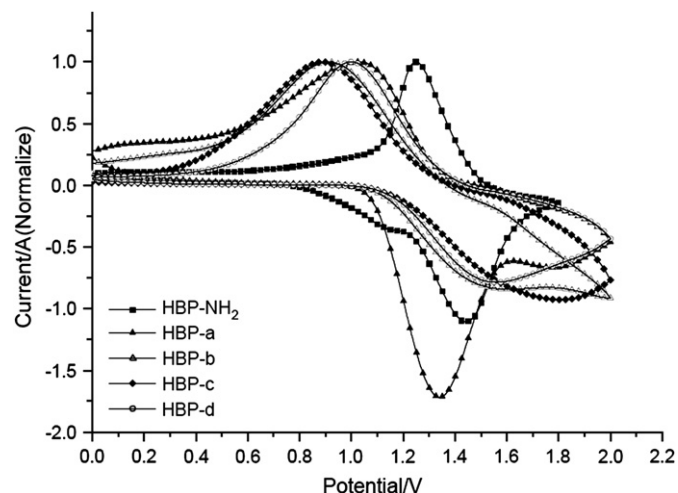


Fig. 4. Cyclic voltammogram of hyperbranched poly(triphenylamine amide)s with different end groups coated on an ITO glass substrate in acetonitrile containing 0.1 M TBAP. Scanning rate = 0.1 V/s.

redox E_{onset} (Fc/Fc⁺) is 0.61 V vs Ag/AgCl in acetonitrile. Assuming that the HOMO energy level for the Fc/Fc⁺ stand is 4.8 eV with respect to the zero vacuum level [27], the HOMO energy level for HBP-NH₂ has been evaluated to be -4.99 eV. The energy gaps of the hyperbranched poly(triphenylamine amide)s with different end groups are about 2.93 eV which are independent on the end groups. However, the HOMOs and LUMOs of hyperbranched poly(triphenylamine amide)s depend on the end groups. The hyperbranched polyamide with amino end groups showed fairly high HOMO and LUMO values. Polymer HBP-NH₂ with electron-donating amino groups showed the highest HOMO and LUMO values. Polymer HBP-c, end-capped with *p*-nitrobenzoyl chloride, showed the lowest HOMO and LUMO values, which is probably due to electron withdrawing effect by the *para*-nitro group.

4. Conclusion

In the present study, a triphenylamine-based amino-terminal hyperbranched poly(triphenylamine amide) was successfully prepared from a new triphenylamine-based AB₂ monomer having one carboxylic acid and two amino groups, 4-(4,4'-diamino-triphenylamine)-2,6-bis(4-methylphenyl)pyridine (**3**). The reactive amino end groups of the hyperbranched polyamide could be end-capped by various acid chlorides. All the hyperbranched polyamides exhibited excellent solubility and inherent viscosities as low as 0.15 dL/g. The band gaps of the hyperbranched polyamides are at around 2.93 eV and their HOMOs and LUMOs are at the range of 4.99–5.34 and 2.07–2.42 eV, respectively, depending on the end groups. These characteristics indicate that the HOMOs and LUMOs as well as other physical properties of these polymers are adjustable by the end functional groups.

Acknowledgment

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Table 4
Optical and electrochemical properties of hyperbranched polyamides

Polymer code	$\lambda_{\text{abs,max}}^a$ (nm)	$\lambda_{\text{abs,onset}}^a$ (nm)	λ_{pl}^b (nm)	Energy gap ^c (eV)	HOMO ^d (eV)	LUMO ^e (eV)
HBP-NH ₂	358	425	505	2.92	-4.99	-2.07
HBP-a	356	423	498	2.93	-5.23	-2.30
HBP-b	354	421	493	2.95	-5.29	-2.34
HBP-c	358	425	433	2.92	-5.34	-2.42
HBP-d	356	423	481	2.93	-5.34	-2.41

^a UV–vis absorption measurements in DMAc (10^{-4} M) at room temperature.

^b PL spectra measurements in DMAc (10^{-4} M) at room temperature.

^c The data were calculated by the equation: energy gap = $1240/\lambda_{\text{onset}}$.

^d The HOMO energy levels were calculated from cyclic voltammetry and were referred to ferrocene (4.8 eV).

^e LUMO = HOMO – energy gap.

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