

## Synthesis and Properties of Hyperbranched Poly(triphenylamine)s Prepared by Palladium Catalyzed C–N Coupling Reaction

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**ABSTRACT:** Hyperbranched poly(triphenylamine)s with various end functional groups were prepared starting from 4,4'-diamino-4''-bromotriphenylamine through palladium catalyzed C–N coupling reaction. The self-polycondensation of the monomer afforded secondary amino groups predominantly. End-capped polymers were isolated by the chemical modification of unreacted amino groups by acid chlorides. The properties of the hyperbranched poly(triphenylamine)s, such as solubility, thermal stability and ionization potential, were dependent on the end functional groups. The hyperbranched poly(triphenylamine)s were examined as a hole transporting material for organic light emitting diodes. The multi-layered device composed of ITO/hyperbranched poly(triphenylamine)/Alq<sub>3</sub>/Mg–Ag showed yellow-green emission derived from Alq<sub>3</sub>. The device performance was improved when the polymer end-capped with alkyl chlorides were used as a hole transporting material. Since the ionization potentials of the hyperbranched polymer with alkyl amide end groups were higher than that with aromatic amide end groups, efficient hole injection from ITO/hyperbranched poly(triphenylamine)/Alq<sub>3</sub> might be achieved to improve the device performance.

**KEY WORDS** Hyperbranched Polymer / Triphenylamine / C–N Coupling / Palladium Catalyst / EL Device /

Dendritic macromolecules, such as dendrimers and hyperbranched polymers deserve much attention from both synthetic and application viewpoints, and are characterized by low viscosity, good solubility and amorphous nature in solid state.<sup>1–11</sup> It is also well-known that the properties of the dendritic macromolecules are dependent on terminal functional groups in addition to backbone structure.<sup>12,13</sup> Therefore, the properties of dendritic macromolecules can be tuned in some extent by the chemical modification of end functional groups. Although multi-step procedures required for the preparation of dendrimers allow the precise control of molecular architecture, one-step process to prepare hyperbranched polymers seems to be attractive for mass production and industrial applications.

Palladium catalyzed condensations are one of the useful propagation reactions for polycondensation. We have previously reported the palladium catalyzed polycondensations to form linear polyamides,<sup>14</sup> polycinnamamides,<sup>15,16</sup> and hyperbranched polyesters.<sup>17</sup> Recently, Buchard and Hartwig have been independently reported palladium catalyzed C–N coupling reactions.<sup>18–22</sup> The reaction conditions required for the palladium catalyzed C–N coupling are apparently much milder in comparison with conventional Ullmann type coupling reactions. Polycondensa-

tions through the amination were also reported by Kanbara,<sup>23–27</sup> Hartwig,<sup>28,29</sup> and Meyer.<sup>30</sup> Among them, Meyer reported linear and hyperbranched *m*-polyanilines through the amination in the presence of BINAP ligand and sodium *t*-butoxide. According to the model reaction for the polymerization, triphenylamine units were rarely formed during the polymerization under the reaction conditions. On the other hand, triphenylamine derivatives are known as one of the key materials for multi-layer organic electroluminescent devices. Shirota reported that dendritic triphenylamine derivatives acted as good hole-transporting materials for electroluminescent devices.<sup>31–34</sup> Linear polymers containing triphenylamine moiety have also been reported in literatures. Generally, high molecular weight amorphous polymers have good thermal stability and low risk for crystallization in comparison with the corresponding monomers. Therefore, hyperbranched poly(triphenylamine)s with high molecular weight might have good thermal and long-term stability and show hole-transporting property owing to extremely extended triphenylamine units.

In this work, we report the synthesis, properties and application of hyperbranched poly(triphenylamine)s through the palladium catalyzed C–N coupling. The monomer, 4,4'-diamino-4''-bromotriphenylamine, contains a triphenylamine moiety and the propagation

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reaction might give additional triphenylamine units in the resulting polymers. The effects of end functional groups on the properties of resulting hyperbranched poly(triphenylamine)s are discussed. Moreover, organic electroluminescent devices are fabricated using the novel hyperbranched polymer as a hole-transport material.

## EXPERIMENTAL

### Materials

Dimethyl sulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP) were used after distillation under reduced pressure from calcium hydride. 4,4'-Diamino-4''-bromotriphenylamine was prepared from 4-bromoaniline and 1-fluoro-4-nitrobenzene as starting materials, as reported in literatures.<sup>35,36</sup> Tris(dibenzylideneacetone)dipalladium (Pd<sub>2</sub>(dba)<sub>3</sub>), tri-*tert*-butylphosphine (P(*t*-Bu)<sub>3</sub>) and sodium *tert*-butoxide (NaO*t*Bu) were used as received (Aldrich). Tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) was purified by sublimation. Magnesium and silver were used as received. An HPLC-grade chloroform was used as received for film preparation. Other solvents and reagents were used without further purification.

### Model Reaction

A three-necked flask was dried by using a heating gun under nitrogen flow, and then, sodium *tert*-butoxide (1.15 g, 12 mmol), aniline (0.36 mL, 4 mmol), bromobenzene (0.21 mL, 2 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (92 mg, 0.1 mmol) were charged. NMP (15 mL) and P(*t*-Bu)<sub>3</sub> (0.15 mL, 0.6 mmol) were added into the flask *via* syringes. The mixture was heated and stirred at 60°C under nitrogen atmosphere. After a certain period of the reaction, a small amount of the reaction mixture was taken out and poured into methanol. HPLC measurement of the methanol solution was carried out in order to investigate the reaction products.

### Polymerization and End-Capping Reaction

A three-necked flask was dried by using a heating gun under nitrogen flow, and then, sodium *tert*-butoxide (0.80 g, 8.5 mmol), 4,4'-diamino-4''-bromotriphenylamine (0.5 g, 1.4 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (32 mg, 0.035 mmol) were charged. NMP (10 mL) and P(*t*-Bu)<sub>3</sub> (0.05 mL, 0.2 mmol) were added into the flask *via* syringes. The mixture was heated and stirred at 60°C for 48 h under nitrogen atmosphere. After cooling to room temperature, *tert*-butylbenzoyl chloride (2.75 mL, 14.1 mmol), as an end-capping agent, was added into the flask. The mixture was stirred at room temperature for additional 12 h, and then,

poured into methanol (800 mL) containing lithium bromide (0.01 mol L<sup>-1</sup>). The precipitate was recovered by filtration, and was purified by re-precipitation into methanol containing lithium bromide from chloroform solution. The purified polymer was dried *in vacuo* at room temperature for 12 h (polymer **1**). Yield 83%. IR (KBr, cm<sup>-1</sup>): 3038, 2968, 1655, 1609, 1505, 1408, 1364, 1314, 1269, 1196, 1121, 1017, 830, 768, 704, 548. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 9.93 (amide), 7.85, 7.84, 7.70, 7.68, 7.48, 7.26, 7.07, 6.94, 6.85 (aromatic), 1.30, 1.22 (*t*-butyl). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm): 169.20, 164.89, 153.97, 152.15, 144.89, 142.28, 134.67, 133.36, 132.03, 128.76, 127.99, 127.03, 126.11, 124.58, 124.08, 123.84, 122.80, 121.31, 34.18, 34.00, 30.54.

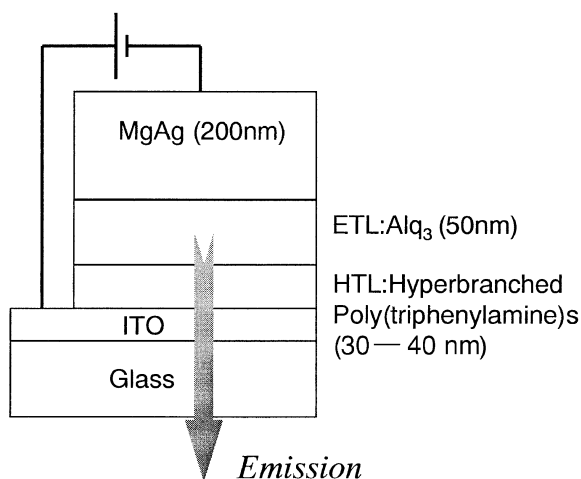
Polymer **2** was prepared in the same manner as polymer **1**. 4-Cyanobenzoyl chloride was used as an end-capping agent instead of *tert*-butylbenzoyl chloride. Yield 94%. IR (KBr, cm<sup>-1</sup>): 3041, 2232, 1661, 1599, 1505, 1408, 1316, 1269, 1179, 1107, 1019, 828, 760, 591, 546. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 10.27 (amide), 8.06, 7.94, 7.71, 7.53, 7.18, 6.99, 6.87 (aromatic).

Polymer **3** was prepared in the same manner as polymer **1**. 4-Methoxybenzoyl chloride was used as an end-capping agent instead of *tert*-butylbenzoyl chloride. Yield 92%. IR (KBr, cm<sup>-1</sup>): 3041, 2950, 2837, 1647, 1607, 1505, 1406, 1312, 1254, 1175, 1111, 1028, 837, 787, 762, 608, 527. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 9.85 (amide), 7.91, 7.68, 7.31, 7.08, 6.99, 6.87 (aromatic), 3.81, 3.72 (methoxy).

Polymer **4** was prepared in the same manner as polymer **1**. Propionyl chloride was used as an end-capping agent instead of *tert*-butylbenzoyl chloride. Yield 50%. IR (KBr, cm<sup>-1</sup>): 3040, 2979, 2938, 1662, 1601, 1505, 1408, 1377, 1267, 1111, 1073, 1017, 830. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 9.61, 9.57 (amide), 7.52, 7.18, 6.94 (aromatic), 2.27, 2.18, 1.08, 0.97 (propionyl).

Polymer **5** was prepared in the same manner as polymer **1**. Heptanoyl chloride was used as an end-capping agent instead of *tert*-butylbenzoyl chloride. Yield 47%. IR (KBr, cm<sup>-1</sup>): 3040, 2928, 2857, 1661, 1601, 1532, 1505, 1408, 1377, 1318, 1264, 1173, 1107, 1017, 830, 725, 540. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 9.55 (amide), 7.49, 7.12, 6.91 (aromatic), 2.25, 2.15, 1.57, 1.48, 1.27, 1.16, 0.83 (heptanoyl).

Polymer **6** was prepared in the same manner as polymer **1**. Stearoyl chloride was used as an end-capping agent instead of *tert*-butylbenzoyl chloride. Yield 50%. IR (KBr, cm<sup>-1</sup>): 3040, 2924, 2853, 1653, 1601, 1534, 1505, 1466, 1408, 1377, 1317, 1269, 1173, 1111, 831, 722, 544. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 7.40, 2.55 (aromatic), 2.30, 1.63, 1.26, 0.87 (stearoyl).



**Figure 1.** OLED device structure.

### Fabrication of OLED Devices

Figure 1 shows the OLED device structure in this work. Indium-tin-oxide (ITO) substrates were cleaned with detergent, de-ionized water and isopropanol and activated by plasma treatment, as reported in the literature.<sup>37</sup> On the ITO substrate, the polymer film was cast by spin coating (4000 rpm) from the chloroform solution of each end-capped polymer ( $5 \text{ mg mL}^{-1}$ ). The thickness of the spin-coated films was in the range 30–40 nm. After elimination of residual solvent (chloroform) by heating the spin-coated films at  $70^\circ\text{C}$  for 1 h, a 50 nm-thick tris(8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ ) was vacuum vapor deposited ( $5\text{--}8 \times 10^{-6}$  Torr) as an electron transport and an emission layer. Finally, a Mg–Ag alloy cathode (200 nm) was co-deposited by vacuum vapor deposition ( $5\text{--}8 \times 10^{-6}$  Torr, Mg–Ag weight ratio = 10 : 1).

### Measurements

Infrared (IR) spectra were recorded using a Shimadzu FT-IR-8100 Fourier transform infrared spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a JEOL JNM-AL 300 spectrometer. Thermo gravimetric analysis (TGA) was carried out with a Seiko TGA 6200 at a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen. Differential scanning calorimetry (DSC) was carried out with a Seiko DSC 6200 at a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen. Inherent viscosity was measured at  $30^\circ\text{C}$  in DMF ( $0.5 \text{ g dL}^{-1}$ ) containing lithium bromide ( $0.01 \text{ mol L}^{-1}$ ). Gel permeation chromatography (GPC) measurements were carried out with a JASCO HPLC 880PU, polystyrene-divinylbenzene columns (two Shodex KD-806M and KD-802.5) and a Shodex RI-71 refractive index detector. DMF containing  $0.01 \text{ mol L}^{-1}$  of lithium bromide was used as an eluent. HPLC measurements were car-

ried out with a Shodex DS-4 pump, a Shodex C18-5B column, and a Jasco 875-UV detector. Ionization potential of each polymer film was determined by a Riken-Keiki AC-1 photo-emission spectrometer. UV spectra were recorded using a Hitachi U-3200 spectrophotometer. Electron affinity was estimated by the energy gap determined by the edge of UV spectra and the ionization potential. Spin coating was carried out using a Mikasa spinner 1H-D2 spincoater. The thickness of the films was measured by an Alpha-step 500 (KLA-Tencor Japan Ltd.). Current-voltage-luminance characteristics were measured by using a HP4140B (Hewlett Packard Co. Ltd.) electrometer and a BM-7 (Topcom Co. Ltd.) luminance colorimeter. Electroluminescent spectra were obtained by using a Hamamatsu Co. C4196 photonic multi-channel analyzer.

### Computational Methods

Vertical and adiabatic ionization potentials ( $IP_v$  and  $IP_a$ ) were evaluated according to eqs 1 and 2, respectively.

$$IP_v = -(E(A^+) - E(A)) \quad (1)$$

$$IP_a = -(E(A^+) - E(A)) \quad (2)$$




$E(A)$  and  $E(A^+)$  indicate the energies of neutral amine A and its cation radical, respectively, in which the geometries were fully optimized.  $E(A^+(A))$  is that of the cation radical with the optimized geometry of neutral one. Density functional theory calculations were carried out at the B3LYP/6-31G(d) level using a Gaussian 98 program.<sup>38</sup>

## RESULTS AND DISCUSSION

### Model Reaction

According to the literatures about palladium catalyzed C–N coupling reactions, both secondary and tertiary amine units can be formed from the condensation of a primary amine and an aromatic halide. The reaction of aniline and bromobenzene was carried out prior to the polymerization in order to optimize reaction conditions and to investigate the ratio of secondary and tertiary amine compounds in the product. Tris(dibenzylideneacetone)dipalladium ( $\text{Pd}_2(\text{dba})_3$ ), tri-*tert*-butylphosphine ( $\text{P}(t\text{-Bu})_3$ ) and sodium *tert*-butoxide ( $\text{NaO}^t\text{Bu}$ ) were used as a palladium source, a ligand and a base, respectively, which are reported as a good combination to form tertiary amine units from primary amines and aromatic halides in toluene.<sup>25</sup> Aprotic polar solvents, such as DMF, DMAc, NMP, and DMSO, were examined in this work since these solvents often can dissolve aromatic amine polymers. The feed molar ratio (ani-

**Table I.** Preparation and properties of hyperbranched polymers<sup>a</sup>

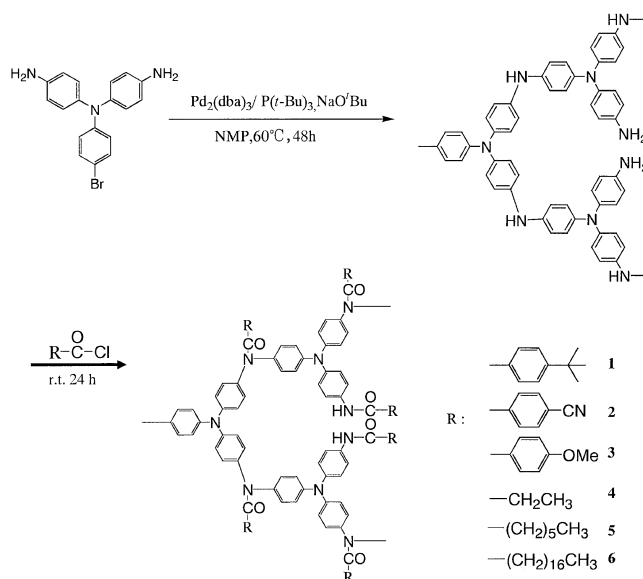
polymer	Yield %	$M_w^b$	$M_w/M_n$	$\eta_{inh}^d$ dL g <sup>-1</sup>	$T_d^e$	$T_g^g$
1 	83	$4.7 \times 10^4$	2.1	0.09	248	—
2 	94	$1.2 \times 10^5$	2.1	0.09	236	—
3 	92	$5.2 \times 10^4$	2.0	0.07	225	—
4 $-\text{CH}_2\text{CH}_3$	50	$5.3 \times 10^4$	1.7	0.08	212	—
5 $-(\text{CH}_2)_5\text{CH}_3$	47	$5.6 \times 10^4$	2.3	0.09	197	152
6 $-(\text{CH}_2)_{16}\text{CH}_3$	50	$1.6 \times 10^{4c}$	1.8	0.08	195	—

<sup>a</sup>The monomer (1.4 mmol) was allowed to polymerized in the presence of  $\text{Pd}_2(\text{dba})_3$  (0.035 mmol : 2.5 mol%),  $\text{P}(t\text{-Bu})_3$  (0.21 mmol) and  $\text{NaO}^t\text{Bu}$  (8.5 mmol) in NMP (10 mL) at 60°C for 48 h. <sup>b</sup>Determined by GPC in DMF solution containing LiBr (0.01 mol L<sup>-1</sup>).  $M_w$  and  $M_n$  were calculated based on polystyrene standards. <sup>c</sup>Determined by GPC in THF solution.  $M_w$  and  $M_n$  were calculated based on polystyrene standards. <sup>d</sup>Measured at a concentration of 0.5 g dL<sup>-1</sup> at 30°C in DMF containing LiBr (0.01 mol L<sup>-1</sup>). <sup>e</sup>Determined by TGA at a heating rate of 10°C min<sup>-1</sup> in N<sub>2</sub>. <sup>f</sup> $T_{10}$  was determined by TGA at a heating rate of 10°C min<sup>-1</sup> in N<sub>2</sub>. <sup>g</sup>Determined by DSC at a heating rate of 10°C min<sup>-1</sup> in N<sub>2</sub> on second heating.

line/bromobenzene) was set to be 2/1 in order to imitate the polymerization system using 4,4'-diamino-4''-bromotriphenylamine as a monomer. When the reaction was carried out in NMP at 60°C for 48 h, the complete consumption of bromobenzene and the predominant formation of diphenylamine were observed by HPLC measurements. Triphenylamine was not detected in the reaction mixture under the conditions. A small peak attributed to biphenyl formed as a by-product was also observed. Increasing the reaction temperature caused undesired side reactions, as evidenced by small additional peaks in HPLC measurements. The predominant formation of diphenylamine might be caused by both the effect of high polarity of the solvent and the feed ratio of aniline and bromobenzene (2/1).

### Polymerization

The polymerization of 4,4'-diamino-4''-bromotriphenylamine in NMP in the presence of  $\text{Pd}_2(\text{dba})_3$ ,  $\text{P}(t\text{-Bu})_3$  and  $\text{NaO}^t\text{Bu}$  was carried out at 60°C for 48 h. Hyperbranched poly(triphenylamine) terminated by unreacted amino groups was isolated when the polymerization mixture was poured into methanol containing lithium chloride (0.01 mol L<sup>-1</sup>). The solubility of the resulting polymer in aprotic polar solvents significantly decreased after 2 days, which suggests that the polymer with amino end groups was unstable and was probably sensitive to oxidation. Therefore, the acid chlorides as end-capping agents were added to the polymerization mixture before the isolation, as shown in Scheme 1. Table I summarizes the results of the poly-



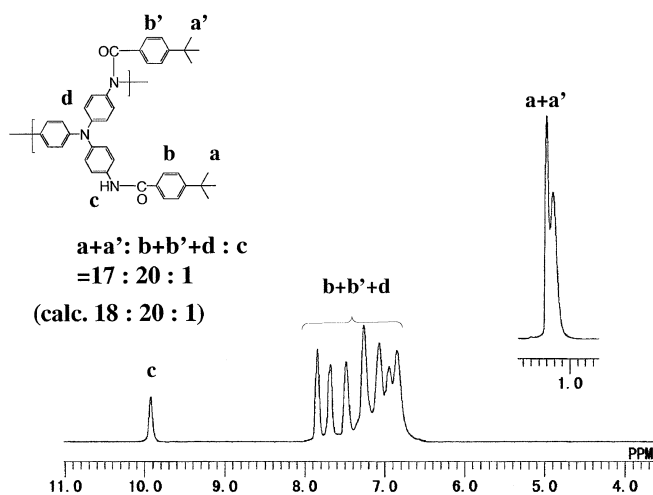
**Scheme 1.** Preparation of hyperbranched poly(triphenylamine)s.

merization with various end-capping agents. Hyperbranched poly(triphenylamine)s were isolated in good yield when aromatic acid chlorides were used as end-capping agents. Quantitative end-capping reactions were confirmed by the disappearance of the broad peak around 5 ppm attributed to N–H proton in <sup>1</sup>H NMR measurements. The molecular weight ( $M_w$ ) determined by GPC with polystyrene standards was in the range 1.6–12 × 10<sup>4</sup>, which suggests that the resulting polymers have moderate to high molecular weights. The inherent viscosity measured in DMF for all of the polymers was lower than 0.1 dL g<sup>-1</sup>, which implies that the resulting polymers have low viscosity, similar to other

**Table II.** Solubility of resulting polymers

Polymer	NMP	DMAC DMF	DMSO	CHCl <sub>3</sub>	THF	Ethyl acetate	Hexane	Benzene	Diethyl ether
1	+	+	+	+	+	-	-	-	-
2	+	+	+	-	-	-	-	-	-
3	+	+	+	+-	-	-	-	-	-
4	+	+	+	+-	-	-	-	-	-
5	+	+	+	+	+	-	-	-	-
6	+	-	-	+	+	-	+-	-	+

+ : soluble, +- : partially soluble, - : insoluble.

**Figure 2.** <sup>1</sup>H NMR spectrum of polymer **1**.

hyperbranched polymers in literatures.

The structure of the resulting polymers was investigated by IR, <sup>1</sup>H and <sup>13</sup>C NMR measurements. Figure 2 shows <sup>1</sup>H NMR spectrum and its assignment of polymer **1**. Peaks attributed to amide (9.93 ppm), aromatic (7.9–6.8 ppm) and *t*-butyl (1.30 and 1.22 ppm) protons were observed. Two separated peaks attributed to *t*-butyl group implies that the original hyperbranched poly(triphenylamine) have both primary and secondary amines. The integration of the peaks was almost equal, which indicates that the original polymer have equal amount of primary and secondary amino groups. In other words, secondary amino groups were predominantly formed during the polymerization and the monomer acted as an AB<sub>2</sub> type monomer.<sup>39</sup> The integration ratio of other peaks also supported the proposed structure drawn in Figure 2. It should be pointed out that the structure corresponds to the linear unit and represents the average repeating unit of the resulting polymer. The polymer must contain other repeating units, dendritic and terminal ones, depending on the number of unreacted amino groups in the original unit. <sup>1</sup>H NMR measurements of other polymers (polymer **2–6**) also suggested that the original polymer contained almost equal amount of primary and secondary amino groups.

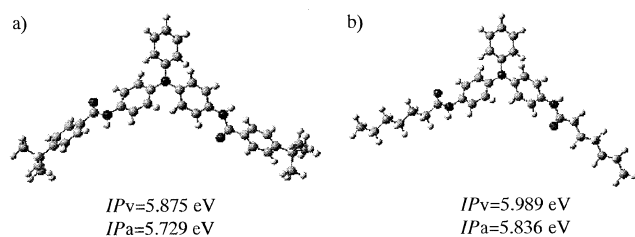
**Table III.** Ionization potential, band gap and electron affinity of polymers

polymer	Ionization potential eV	Band gap eV	Electron affinity eV
1	5.06	3.13	1.93
2	5.60	2.72	2.88
3	5.32	2.88	2.44
4	5.57	3.32	2.25
5	5.53	3.35	2.18
6	5.52	3.35	2.17

#### Properties of Polymers

It is well known that the properties of hyperbranched polymers are influenced by not only the backbone structure but also end functional groups. Table I also shows the effect of end groups on thermal properties. The polymers with aromatic amide end groups showed the onset degradation temperature in the range 225–248°C. The degradation temperature decreased when aliphatic chains were introduced to the end. Only polymer **5** showed a detectable *T<sub>g</sub>* at 152°C by DSC measurement. Solubility of the resulting polymers was also influenced by the nature of end functional groups, as shown in Table II. Most of the polymers were soluble in aprotic polar solvents, such as NMP, DMF, and DMSO. Polymers **1**, **5**, and **6** were even soluble in chloroform and THF. The good solubility in low boiling-point solvents is one of the desired properties for film preparation by spin-coating method.

Ionization potential, band gap and electron affinity of the polymers are summarized in Table III. Band gap was calculated from the edge of UV absorption spectrum. Electron affinity was calculated from the deduction of the band gap from the ionization potential. Polymer **1** showed fairly low ionization potential, similar to other triphenylamine derivatives. Polymer **2**, end-capped with *p*-cyanobenzoyl chloride, showed the highest ionization potential, which is probably due to electron withdrawing effect by the cyano group. The polymers end-capped with alkyl chlorides (Polymer **4–6**) have similar ionization potential at *ca.* 5.5 eV, which are higher than that of polymer **1**. Ionization poten-



**Figure 3.** Optimized structure and ionization potential of the model compound for polymer **1** (a) and **6** (b).

**Table IV.** Performance characteristics of the EL devices

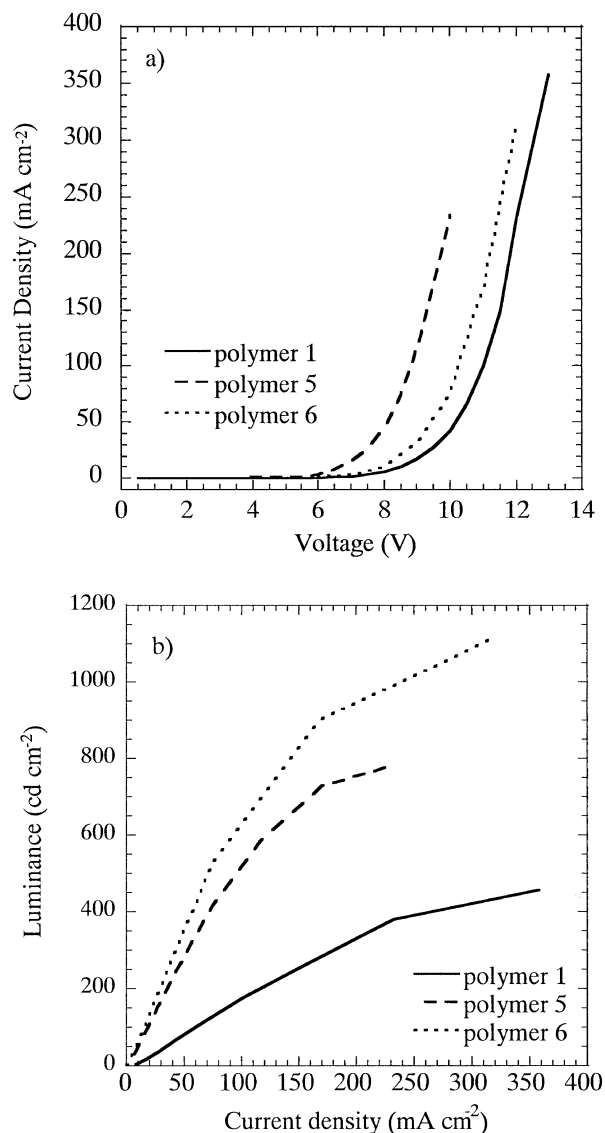
Material for HTL	Turn on voltage V	Maximum luminance cd m <sup>-2</sup>	Current efficiency <sup>a</sup> cd A <sup>-1</sup>	Luminous efficiency <sup>a</sup> lm W <sup>-1</sup>
Polymer 1	7.0	460	0.17	0.050
Polymer 5	6.0	780	0.51	0.19
Polymer 6	6.5	1110	0.63	0.19

<sup>a</sup>At a current density of 100 mA cm<sup>-2</sup>.

tial was also evaluated by molecular orbital calculation (Gaussian 98) for model compounds based on 4,4'-diaminotriphenylamine, as shown in Figure 3.  $IP_v$  was calculated based on the optimized geometry of the neutral model compound, whereas the geometry of the cation radical was fully optimized for the calculation of  $IP_a$ . Both  $IP_v$  and  $IP_a$  for the model compound end-capped with *n*-heptanoyl chloride were higher in comparison with the model end-capped with *t*-butylbenzoyl chloride. Therefore, the calculation data support the fact that the ionization potentials of polymer **4–6** were higher than that of polymer **1**. To the best of our knowledge, this is the first example for the change in ionization potential depending on the end functional groups of the hyperbranched polymer. Other electronic properties (band gap and electron affinity) were also influenced by the end functional groups. All of absorption spectra for resulting polymers broadened and shifted toward longer wavelength in comparison with the absorption spectrum for the monomer. Polymer **2** and **3** showed smaller band gaps, which correspond to the broad absorption spectra. Similar band gaps in the range 3.1–3.4 eV were calculated for other polymers. The small electron affinity for polymer **1** is mainly caused by the small ionization potential. It is clear that polymer **4**, **5**, and **6** showed similar ionization potential, band gap and electron affinity. In other words, the electronic properties of these polymers was independent on the length of the alkyl chain of the end-capping agent.

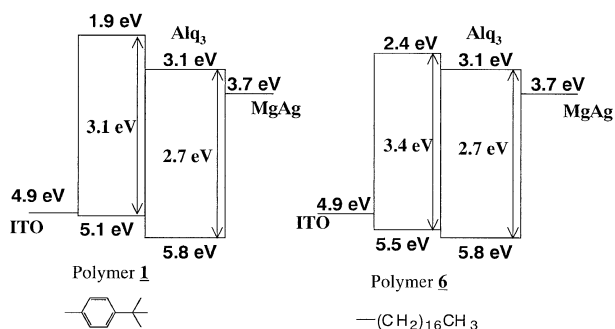
#### EL Device Properties

EL devices were fabricated onto an ITO substrate, as shown in Figure 1. Polymer **1**, **5**, and **6** were examined as a hole transport layer because of the good solubility in chloroform. Tris(8-hydroxyquinoline) alu-



**Figure 4.** Relationship between applied voltage, current density and luminance of the devices.

minum (Alq<sub>3</sub>) was used as an electron transport and an emission layer. Relationship between applied voltage, current density and luminance of the devices are shown in Figure 4. Turn-on-voltages of polymer **5** and **6** were lower than that of polymer **1**. Above the voltage, yellow-green emission was observed for all devices. The emission spectra centered at 540 nm were consistent with Alq<sub>3</sub> emission, and therefore, the formation of exciplex can be negligible. Figure 4b clearly showed that the better luminance was achieved when polymer **5** or **6** was used as a hole transport layer. The device performance is summarized in Table IV. It is clear that the device performance was influenced by the structure of the end functional groups of the hole transport layer. The maximum luminance of 1110 cd m<sup>-2</sup> was achieved when polymer **6** was used. The efficiencies of polymer **5** and **6** were much better than that of polymer **1**. The energy diagram for the devices, shown in Figure 5,



**Figure 5.** Energy band diagrams of the EL devices using polymer **1** and **6**.

might explain the difference. According to the measurements of ionization potential, the energy difference between Alq<sub>3</sub> and polymer **1** is estimated to be 0.7 eV. The ionization potential of polymer **6** is higher than that of polymer **1**, and therefore, the energy difference between Alq<sub>3</sub> and polymer **6** is small (0.3 eV). The small energy difference could cause the efficient hole injection from ITO electrode to Alq<sub>3</sub>. It should be pointed out that the device performance in this work is not as good as other EL devices such as ITO/TPD/Alq<sub>3</sub>/Mg–Ag device.<sup>40</sup> Contamination of impurities during the polymerization and polydispersity of the polymers are possible reasons for lowering the device performance.

## CONCLUSIONS

Hyperbranched poly(triphenylamine)s were prepared through the C–N coupling reaction catalyzed by palladium complex. Secondary amino groups were predominantly formed during the polymerization, which is consistent with the result for the model reaction. End functional groups of the hyperbranched poly(triphenylamine)s gave influence on the properties, such as solubility, thermal stability, glass transition temperature and ionization potential. The hyperbranched poly(triphenylamine)s acted as a hole transporting material for the EL device composed of Alq<sub>3</sub> as an electron transport and an emission layer and ITO and Mg–Ag electrodes. The device performance was improved when the polymer end-capped with alkyl chlorides (polymer **5** or **6**) was used as a hole transport layer. The improved performance might be caused by the smaller energy gap between the polymer and Alq<sub>3</sub>.

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  39. If tertially amino groups were formed during the polymerization, the amount of primary amino groups would be increased due to the feed ratio of the functional groups.
  40. The device composed of ITO, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), Alq<sub>3</sub> and Mg–Ag was fabricated for the control experiment. The maximum luminance and luminous efficiency was 17230 cd m<sup>-2</sup> and 1.2 lm W<sup>-1</sup>, respectively.