N,N-Bis(4-{5-[N,N-bis(4-methoxyphenyl)-N-yloammonio]-2-methylstyryl}phenyl)ammoniumyl Triradical: A Trimer Model of High-Spin Poly[(4-methoxyphenyl-N-yloammonio)-1,2(or 4)-phenylenevinylene-1,2(or 4)-phenylene]

Eiji Fukuzaki, Shigemoto Abe, and Hiroyuki Nishide*

Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555

Received November 28, 2005; E-mail: nishide@waseda.jp

Hyperbranched poly[(4-methoxyphenyl-N-yloammonio)-1,2(or 4)-phenylenevinylene-1,2(or 4)-phenylene], obtained by the polycondensation of N-(4-methoxyphenyl)-N-(4-vinylphenyl)-3-bromo-4-vinylaniline and the subsequent oxidation, three-directionally satisfied the non-Kekulé-type π-conjugation and ferromagnetic connectivity of the unpaired electrons of triarylammoniumyl cationic radicals, and behaved as a high-spin organic polymer even at room temperature. The trimer model compound, N-(4-{5-[N,N-bis(4-methoxyphenyl)amino]-2-methylstyryl}-3-methylphenyl)-N-(4-{5-[N,N-bis(4-methoxyphenyl)amino]-2-methylstyryl}phenyl)-4-methoxyaniline, was synthesized from N-(4-methoxyphenyl)-N-(4-vinylphenyl)-3-methyl-4-vinylaniline. The corresponding ammoniumyl triradical displayed an average S (spin quantum number) value of 3/2, which supported the strong spin-coupling between the unpaired electrons of the ammoniumyl radicals through the π-conjugated and branched phenylenevinylene structure. Head-to-tail linkage and the branched structure of the polymer were also studied by a model reaction of N-(4-methoxyphenyl)-N-(4-vinylphenyl)-3-methyl-4-vinylaniline and bromobenzene.

There is still a strong research interest in the synthesis of purely organic-derived high-spin polymers because they are possible candidates for magnetically active organic materials.[1–7] The high-spin polymers have been synthesized to satisfy non-Kekulé-type and non-disjoint connectivity among the unpaired electrons of the radical moieties through the π-conjugated skeleton of the polymers.[8–17] Chemically stable radical species would facilitate studies of such high-spin polymers. We selected triarylammoniumyl radicals as a favorable source of the unpaired electron, which satisfies both the chemical stability and efficient delocalization of the spin-density for the high-spin alignment.[18–22]

On the other hand, the high-spin polymers have been recently extended to the branched and/or dendritic π-conjugation analogues to enhance the strong spin-alignment through the π-conjugated skeleton.[23–26] For example, Rajca et al. synthesized two-dimensionally dendritic-macrocyclic poly(1,3-phenylenephenylmethine)s and reported a huge magnetic moment corresponding to an S (spin quantum number) > 5000;[11] that is, the unpaired electrons of the radicals multi-directionally and quasi two- or three-dimensionally couple with a high number of the neighboring radicals' unpaired electrons through the branched or dendritic π-conjugation pathway in order to stabilize the high-spin ground state and increase the spin-alignment number. A combination of the multi-directionally extended π-conjugation with a chemically stable radical species such as the triarylammoniumyl radical was expected[27] to provide the possibility of a high-spin polymer as a magnetically active material and possibly raise the temperature range of the high-spin ordering.

Hyperbranched polymerization[28,29] is one of the methods to prepare a highly branched π-conjugation skeleton for the poly-

radical. We have recently succeeded in synthesizing poly[(4-methoxyphenyl-N-yloammonio)-1,2(or 4)-phenylenevinylene-1,2(or 4)-phenylene] (**1**) (Fig. 1), which is the first example of a room temperature high-spin, purely organic polymer.[27] The hyperbranched polyammoniumyl radical **1** was obtained via the one-pot polycondensation of an asymmetric trifunctional ABB′-type monomer, N-(4-methoxyphenyl)-N-(4-vinylphenyl)-3-bromo-4-vinylaniline, and the subsequent oxidation. Usually, hyperbranched polymers are easily prepared via a one-pot polymerization; however, the produced polymers involve irregular structures including unreacted branch points,
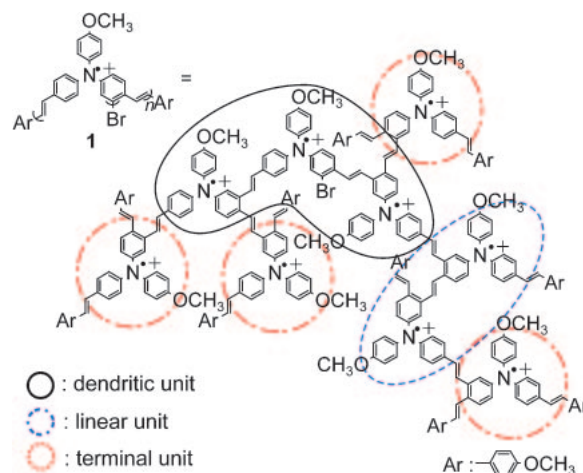

Fig. 1. Structure of the hyperbranched poly[(4-methoxyphenyl-N-yloammonio)-1,2(or 4)-phenylenevinylene-1,2-(or 4)-phenylene] (**1**).

when compared to the analogous dendrimers.[27,28] The magnetic property or the high-spin alignment of the hyperbranched polyradical **1** is presumed to depend upon its branched π-conjugation structure. Characterization of the hyperbranched structure of the high-spin polymer **1** is crucial in order to elucidate the outstanding magnetic property of **1**.

This paper describes the synthesis of the key model compound of the high-spin polymer **1** or the trimer of **1**, *N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}-3-methylphenyl)-*N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}phenyl)-4-methoxyaniline (**2**), from *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) and *N,N*-bis(4-methoxyphenyl)-3-bromo-4-methylaniline (**4**), and its quartet high-spin property or the effective spin-coupling through the designed π-conjugation. The branched structure and degree of branching of the hyperbranched polymer **1** are also discussed in this paper based on the model reaction of *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) and bromobenzene using the same Pd-catalyzed condensation conditions for the formation of **1**.

Results and Discussion

The trimer model compound, *N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}-3-methylphenyl)-*N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}phenyl)-4-methoxyaniline (**2**), was synthesized by coupling of *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) with *N,N*-bis(4-methoxyphenyl)-3-bromo-4-methylaniline (**4**) using the palladium(II) acetate-tri-*o*-tolylphosphine catalyst (Scheme 1). **2** was characterized by NMR, IR, and UV–vis spectroscopies. 42 Carbons in the ^{13}C NMR spectrum were ascribed to the asymmetric structure of **2** composed of three triarylamine moieties and two stilbene bridges. The large coupling constant of the vinylenes in the ^{1}H NMR spectrum ($J = 16$ and 16 Hz) and the IR absorption at $\delta_{C-H} = 963$ cm^{-1} indicated the *trans*-vinylene structure for the two stilbene bridges. The UV–vis absorption ($\lambda_{max} = 302$, 387 nm) and fluorescence ($\lambda_{em} = 502$ nm) suggested a developed π-conjugation in **2**.

Cyclic voltammetry of the trimer model compound **2** showed reversible redox waves at 0.72 and 0.84 V (Fig. 2a). Two oxidation peaks were also observed at 0.70 and 0.85 V
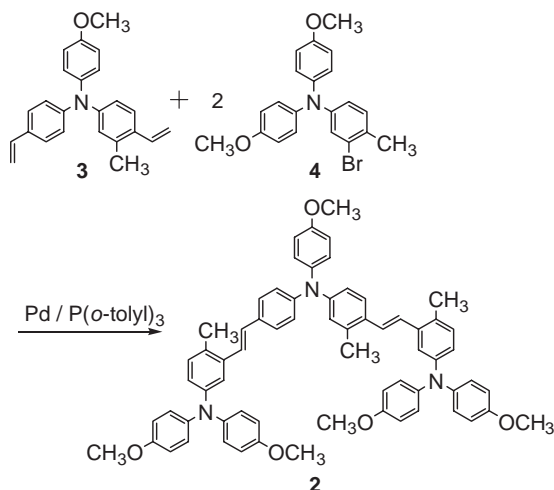
using differential pulse voltammetry ($i_{p1}/i_{p2} = 2$; peak current (i_{p1}, i_{p2}) at 0.70 and 0.85 V are 18 and 9.4 μA). The first and second oxidation waves involved two- and one-electron processes, respectively. The rotating disc voltammetry for the oxidation of **2** also revealed a two-step oxidation current ($i_{l1}/(i_{l2} - i_{l1}) = 2$; diffusion current ($i_{l1}$, i_{l2}) at 0.83 and 1.1 V are 60 and 90 μA). These results suggested that the outer two amine moieties, *N*-(4-methylphenyl)bis(methoxyphenyl)amines, were oxidized prior to the inner *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline unit.

The triamine **2** was chemically oxidized to the ammoniumyl cation triradical **2**$^+$ with an equivalent amount of thianthreniumyl tetrafluoroborate in an acidic mixed solvent of trifluoroacetic acid, trifluoroacetic anhydride, and dichloromethane (vol l7/2/81) (Scheme 2). Upon the oxidation of **2**, the solution color turned deep purple. The ESR spectrum of the **2**$^+$ solution had a narrow unimodal signal ($g = 2.0029$) without any absorption at $g = 2.008$ ascribed to the oxidizing agent of the thianthrene radical. The half-life of the triradical **2**$^+$ was estimated by the ESR signal intensity to be ca. 1 week at room temperature.

The content of the ammoniumyl cation radical or spin concentration (spin per amine site) in the chemically formed **2**$^+$
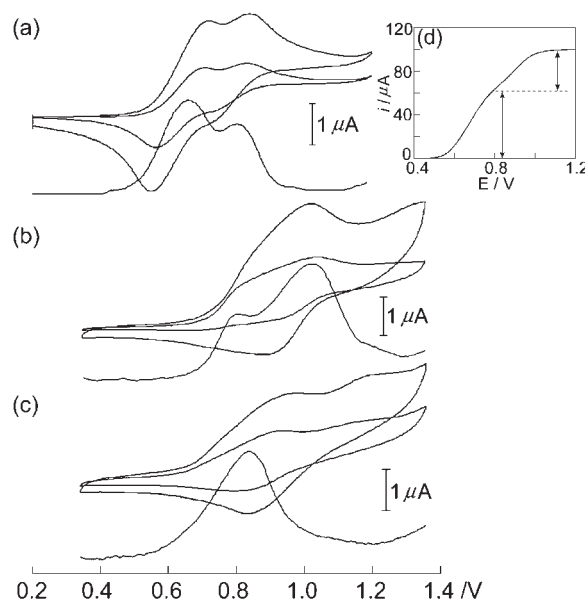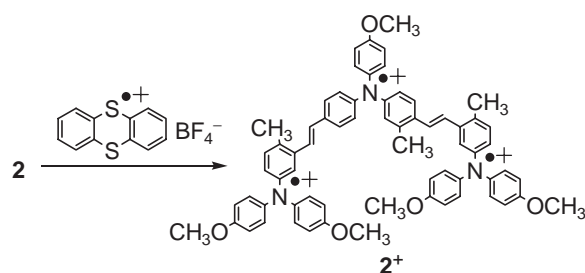
Fig. 2.   Cyclic and differential pulse voltammograms of the trimer model compound **2** (a), the hyperbranched polymer **6** with DP = 12 (b), **6** with DP = 4 (c), and rotating disk voltammogram of **2** in CH$_2$Cl$_2$ with 0.1 M (C$_4$H$_9$)$_4$NBF$_4$.

Scheme 1.

Scheme 2.

E. Fukuzaki *et al.*
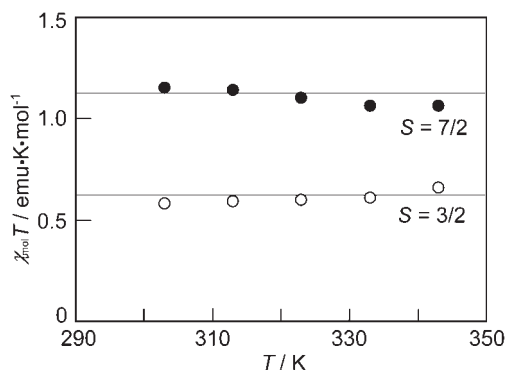
Bull. Chem. Soc. Jpn. Vol. 79, No. 6 (2006)   955

Fig. 3. $\chi_{mol}T$ vs T plots for the triradical 2^+ (spin concentration $= 0.95$) (○) and the polyradical **1** with DP $= 12$ (spin concentration $= 0.65$) (●). The $\chi_{mol}T$ values were estimated by the NMR shift method.

was chemically determined by the titration of 2^+ with the iodide ion of tetrabutylammonium iodide (a chemical quenching or reduction of the radical with the reductant I$^-$).[30,31] The spin concentration based on the titration was 0.90 for 2^+ (hereinafter, the given spin concentration is based on the iodometric titration of the sample).

The magnetic susceptibility (χ_{mol}) of the radical 2^+ was measured using the NMR shift method based on the Evans equation.[32,33] The susceptibility was estimated by taking the mean of the peak shifts for a concentration series of the standard peak of cyclohexane in the deuterated C_6D_6 solution. The $\chi_{mol}T$ value for 2^+ at room temperature (303 K) was 0.64 (0.625 for the theoretical value of spin quantum number (S) = 3/2). The susceptibility for 2^+ was measured in the high temperature range between 303 and 343 K (Fig. 3). The high-spin and triplet state of the triradical 2^+ was maintained even at the high temperature of 343 K (70 °C). The magnetization of 2^+ in a frozen acidic medium was measured by SQUID. The magnetization normalized with saturated magnetization (M/M_s) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$) plots for 2^+ with a spin concentration of 0.72 were very close to the theoretical Brillouin curve for $S = 2/2$ (The spin concentration remained around 0.7 during sample preparation for SQUID measurement). The $\chi_{mol}T$ value vs T plots agreed with the theoretical value of 0.50 for $S = 2/2$ and was almost constant in the temperature range of 20–150 K.

These magnetization data of the ammoniumyl radical 2^+ indicate the chemical stability of the ammoniumyl radical 2^+ and a strong spin-exchange interaction through the branched and π-conjugated phenylenevinylene structure, which support a stable high-spin polymer formation by utilizing the ammoniumyl polyradical combined with the phenylenevinylene skeleton.

In a previous paper,[27] we synthesized the hyperbranched and head-to-tail linked poly(phenylenevinylene), poly[(4-methoxyphenyl-N-amino)-1,2(or 4)-phenylenevinylene-1,2(or 4)-phenylene] (**6**), and reported the room temperature high-spin state for the corresponding ammoniumyl polyradical **1** (Scheme 3). The ^{1}H NMR spectra of **6** were carefully studied in this investigation. The peaks in the range of 5.4–5.0 ppm that resulted from the uncapped polymer could be ascribed to the two terminal vinyl groups of the polymer **6** (Fig. 4). The inte-
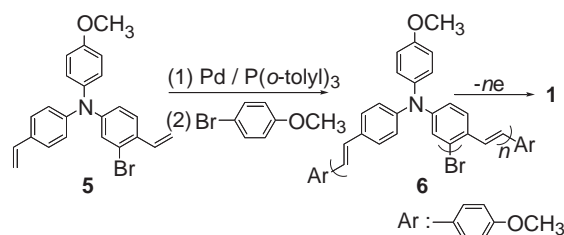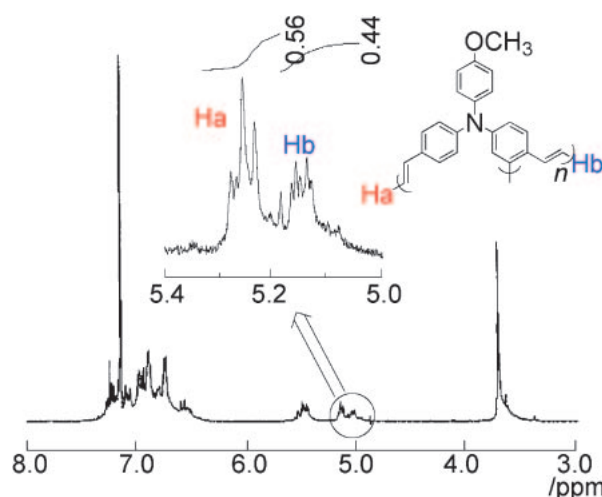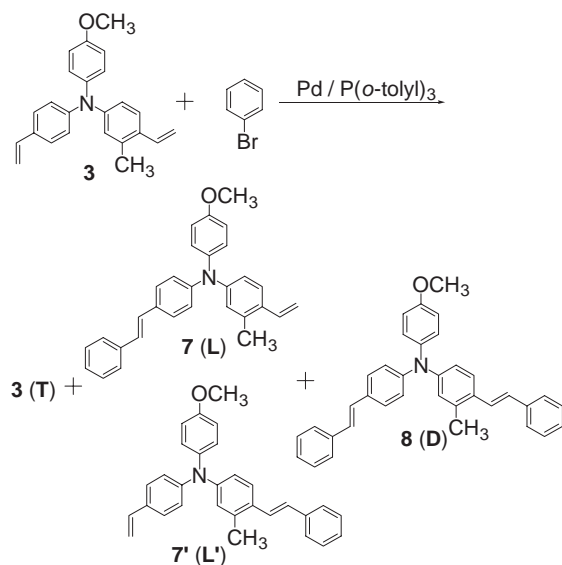

Scheme 3.

Fig. 4. ^{1}H NMR spectrum of the uncapped polymer **6**.

gral ratio of the two vinyl groups was almost unity, indicating a highly branched polymer structure (a favorable reaction of either vinyl group yields a linear-type polymer). Bromine was detected in less than 2 wt % from the elemental analysis.

The head-to-tail linkage and the branched structure in the polymer **6** were studied by examining a model reaction (Scheme 4) of N-(4-methoxyphenyl)-N-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) and bromobenzene using the same Pd catalyst and condensation reaction conditions. The model reaction with the feed molecular ratio of bromobenzene/ **3** = 1 gave the unreacted terminal unit **3**, linear units, N-(4-methoxyphenyl)-N-(3-methyl-4-vinylphenyl)-4-styrylaniline (**7**) and N-(4-methoxyphenyl)-N-(4-vinylphenyl)-3-methyl-4-styrylaniline (**7′**), and the dendritic unit N-(4-methoxyphenyl)-N-(4-styrylphenyl)-3-methyl-4-styrylaniline (**8**), as shown in Scheme 4. The reaction mixture was separated into three fractions by HPLC on a polystyrene-gel column, and the fractions were analyzed by FAB-mass and ^{1}H NMR spectroscopies. The FAB-mass peaks $[(m/z)$ 341, 417, and 493 (M$^+$)] of the three fractions agreed with the molecular mass of the unreacted terminal unit **3**, the linear units **7** and **7′**, and the dendritic unit **8**, respectively. The two linear units in the second fraction could not be separated into **7** and **7′**. In the ^{1}H NMR spectra of the two linear units, **7** and **7′**, the integral ratio of the vinyl groups decreased in comparison with the ratio for the starting **3** after the reaction. The vinyl group disappeared in the ^{1}H NMR spectrum of the dendritic unit **8** and was converted into the stilbene structure.

The reaction mixture of the model reaction was analyzed by NMR to estimate the degree of branching of **6** under this poly-

Scheme 4.
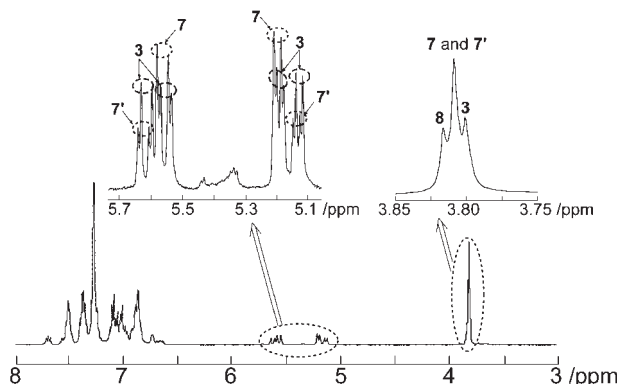
Fig. 5. ^{1}H NMR spectrum of the reaction mixture for the model reaction used to determine the DB.

condensation condition (Fig. 5). The NMR spectrum of the reaction mixture gave multiple peaks in the range of 5.7–5.1 and 3.8 ppm, which were ascribed to the vinyl and methoxy groups of each reactant, the terminal unit **3** (T), the linear units **7** and **7′** (L and L′), and the dendritic unit **8** (D). The integral ratio of the vinyl (linear (L + L′)/terminal (T) = 2.02/1) and the methoxy groups (dendritic (D)/linear (L)/terminal (T) = 0.91/2.08/1) revealed a predominant formation of the dendritic unit **8** in comparison with those of the linear units **7** and **7′**. The degree of branching (DB = (D + T)/(L + D + T) ≈ 2T/(L + 2T))[34–36] was estimated to be 0.50 and 0.48 based on the vinyl and methoxy groups, respectively. These results indicated that the polymer **6** was formed with a highly branched structure under these experimental conditions.

Cyclic voltammetry of the polymer **6** (Fig. 2b) showed a redox wave with the oxidation peak at 1.0 V and the redox peak separation of 120 mV at a sweep rate of 100 mV s^{-1}. On the other hand, the cyclic voltammogram for **6** with the lower molecular weight of 1700 (degree of polymerization = 4) (Fig. 2c) gave the unimodal oxidation wave at 0.9 V. The oxidation potential of the amine moieties of the hyperbranched polymer **6** probably increased with the molecular weight of **6**,

because a Coulomb repulsion between the ammoniumyl cationic radical in the branched and crowded phenylenevinylene skeleton decreases the progress of the ammoniumyl cation formation.

The hyperbranched polymer **6** was chemically oxidized to the corresponding ammoniumyl polyradical **1** with an equivalent amount of thianthreniumyl tetrafluoroborate. χ_{mol} of the polyradical **1** was measured by the NMR shift method. The $\chi_{mol}T$ value, 0.99, for sample **1** with DP = 12 and a spin concentration of 0.65 at 25.6 °C (299 K) corresponded to $S = 6/2$. The high-spin state of the polyradical **1** was maintained even at the high temperature of 303–343 K (Fig. 3) as well as that of the triradical **2**$^+$.

These results suggested that a multiplet state was observed for the triradical **2**$^+$ and the polyradical **1** even at room temperature based on the very strong spin-exchange interaction between the unpaired electrons for **1** through the highly hyperbranched and π-conjugated poly(phenylenevinylene) skeleton.

Experimental

Synthesis.   4-[*N*-(4-Formylphenyl)-*N*-(4-methoxyphenyl)-amino]-2-methylbenzaldehyde: 4-Bromo-2-methylbenzaldehyde (1.93 g, 9.68 mmol), [Pd$_2$(dba)$_3$] (dba: dibenzylideneacetone) (101 mg, 0.110 mmol), BINAP: 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (206 mg, 0.330 mmol), and Cs$_2$CO$_3$ (4.30 g, 13.2 mmol) were added to a 18 mL toluene solution of 4-[(4-methoxyphenyl)amino]benzaldehyde (2.00 g, 8.80 mmol) in a 50 mL ampule. The ampule was degassed, sealed, and heated to 100 °C for 72 h. The resulting mixture was poured into aqueous ammonium chloride, followed by extraction with chloroform, and then the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, purification by chromatography with a silica-gel column and chloroform/ethyl acetate = 9/1 as the eluent gave 4-[*N*-(4-formylphenyl)-*N*-(4-methoxyphenyl)amino]-2-methylbenzaldehyde as a brown oil (1.31 g, Yield 43%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 10.10 (s, 1H, formyl), 9.85 (s, 1H, formyl), 7.75 (d, $J = 8.8$ Hz, 2H, aryl), 7.68 (d, $J = 8.5$ Hz, 1H, aryl), 7.15 (d, $J = 8.8$ Hz, 2H, aryl), 7.12 (d, $J = 9.0$ Hz, 2H, aryl), 7.01 (d, $J = 2.3$ Hz, 1H, aryl), 6.94 (d, $J = 9.0$ Hz, 2H, aryl), 6.92 (d, $J = 2.3$ Hz, 1H, aryl), 3.84 (s, 3H, methoxy), and 2.56 (s, 3H, methyl); ^{13}C NMR (CDCl$_3$, 500 MHz) δ 190.6, 190.2, 157.9, 152.0, 150.9, 142.3, 137.8, 133.5, 131.0, 130.5, 128.9, 128.7, 124.4, 121.7, 119.6, 115.3, 55.3, and 19.6; IR (KBr pellet): 2932 (ν_{ArC-H}), 1594 ($\nu_{C=O}$), and 1243 cm^{-1} (ν_{C-O-C}); Mass: calcd for M 345.4, found (m/z) 345 (M$^+$). Found: C, 76.4; H, 5.6; N, 4.1%. Calcd for C$_{22}$H$_{19}$NO$_3$: C, 76.5; H, 5.5; N, 4.1%.

N-(4-Methoxyphenyl)-N-(4-vinylphenyl)-3-methyl-4-vinylaniline (3):   Methyltriphenylphosphonium bromide (6.21 g, 17.4 mmol) was placed in a Schlenk tube, and then dried under vacuum for 1 h. THF (4.2 mL) was added, and the mixture was stirred for 10 min at room temperature. A 1.58 M hexane solution (5.40 mL) of butyllithium (8.69 mmol) was slowly added to the THF suspension, and then the suspension was stirred for 30 min. A 5.3 mL of THF solution of 4-[*N*-(4-formylphenyl)-*N*-(4-methoxyphenyl)amino]-2-methylbenzaldehyde (600 mg, 1.74 mmol) was slowly added, and the mixture was stirred for 19 h. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, purification by chromatography with a silica-gel column and hexane/chloroform = 4/1 as the eluent gave *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) as a

yellow oil (397 mg, Yield 67%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.36 (d, $J = 8.2$ Hz, 1H, aryl), 7.26 (d, $J = 8.0$ Hz, 2H, aryl), 7.06 (d, $J = 8.8$ Hz, 2H, aryl), 6.97 (d, $J = 8.8$ Hz, 2H, aryl), 6.87 (dd, $J = 11, 17$ Hz, 1H, vinyl), 6.85–6.83 (m, 4H, aryl), 6.65 (dd, $J = 11, 18$ Hz, 1H, vinyl), 5.61 (d, $J = 18$ Hz, 1H, vinyl), 5.55 (d, $J = 17$ Hz, 1H, vinyl), 5.19 (d, $J = 11$ Hz, 1H, vinyl), 5.13 (d, $J = 11$ Hz, 1H, vinyl), 3.80 (s, 3H, methoxy), and 2.24 (s, 3H, methyl); ^{13}C NMR (CDCl$_3$, 500 MHz) δ 156.3, 147.7, 147.2, 140.4, 136.4, 136.3, 134.1, 131.2, 130.7, 127.4, 127.0, 126.0, 124.4, 122.6, 120.8, 114.8, 113.3, 111.7, 55.5, and 19.8; IR (KBr pellet): 1242 cm^{-1} (ν_{C-O-C}); Mass: calcd for M 341.5, found (m/z) 341 (M$^+$). Found: C, 84.2; H, 5.7; N, 4.0%. Calcd for C$_{24}$H$_{23}$NO: C, 84.4; H, 6.8; N, 4.1%.

***N,N*-Bis(4-methoxyphenyl)-3-bromo-4-methylaniline (4):** 2-Bromo-4-iodotoluene (4.84 g, 16.3 mmol), [Pd$_2$(dba)$_3$] (170 mg, 0.185 mmol), BINAP (346 mg, 0.556 mmol), and sodium *t*-butoxide (2.14 g, 22.2 mmol) were added to a 30 mL of toluene solution of bis(4-methoxyphenyl)amine (2.00 g, 8.80 mmol) in a 50 mL of ampule. The degassed ampule was heated to 100 °C and stirred for 72 h. The resulting mixture was poured into aqueous ammonium chloride, followed by extraction with chloroform, and then the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, purification by chromatography with a silica-gel column and hexane/chloroform = 1/1 as the eluent gave *N,N*-bis(4-methoxyphenyl)-3-bromo-4-methylaniline (**4**) as a white powder (3.02 g, Yield 51%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.43 (s, 1H, aryl), 7.25 (d, $J = 8.4$ Hz, 4H, aryl), 7.17 (d, $J = 8.6$ Hz, 1H, aryl), 7.04 (d, $J = 8.6$ Hz, 1H, aryl), 7.02 (d, $J = 8.4$ Hz, 4H, aryl), 3.92 (s, 6H, methoxy), and 2.52 (s, 3H, methyl); ^{13}C NMR (CDCl$_3$, 500 MHz) δ 155.7, 147.7, 140.3, 130.6, 129.0, 126.0, 124.8, 123.9, 119.6, 114.5, 54.9, and 19.8; IR (KBr pellet): 2932 (ν_{ArC-H}) and 1240 cm^{-1} (ν_{C-O-C}); Mass: calcd for M 398.3, found (m/z) 398 (M$^+$). Found: C, 63.4; H, 5.0; N, 3.4%. Calcd for C$_{21}$H$_{20}$BrNO$_2$: C, 63.3; H, 5.1; N, 3.5%.

Model Reaction: Bromobenzene (4.60 mg, 29.3 µmol), palladium(II) acetate (0.13 mg, 0.58 µmol), tri-*o*-tolylphosphine (0.72 mg, 2.4 µmol), lithium chloride (12.4 mg, 0.293 mmol), and triethylamine (7.15 mg, 70.3 µmol) were added to a 0.15 mL of *N,N*-dimethylformamide solution of *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) (10.0 mg, 29.3 µmol) in a 5 mL of ampule. The degassed ampule was heated to 100 °C and stirred for 48 h. The resulting mixture was poured into aqueous ammonium chloride, followed by extraction with chloroform, and then the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the mixture was analyzed by NMR in CDCl$_3$.

***N*-(4-Methoxyphenyl)-*N*-(4-styrylphenyl)-3-methyl-4-styrylaniline (8):** ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.51–6.85 (m, 13H, aryl), 7.38 (d, $J = 8.4$ Hz, 2H, aryl), 7.31 (d, $J = 18$ Hz, 1H, vinylene), 7.25 (d, $J = 19$ Hz, 1H, vinylene), 7.10 (d, $J = 8.8$ Hz, 2H, aryl), 7.03(2) (d, $J = 19$ Hz, 1H, vinylene), 7.02(7) (d, $J = 8.4$ Hz, 2H, aryl), 6.90 (d, $J = 18$ Hz, 1H, vinylene), 3.82 (s, 3H, methoxy), and 2.33 (s, 3H, methyl); IR (KBr pellet): 2932 (ν_{ArC-H}), 1241 (ν_{C-O-C}), and 961 cm^{-1} (δ_{ArC-H}); Mass: calcd for M 493.6, found (m/z) 494 (M$^+$).

***N*-(4-{5-[*N,N*-Bis(4-methoxyphenyl)amino]-2-methylstyryl}-3-methylphenyl)-*N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}phenyl)-4-methoxyaniline (2):** *N,N*-Bis(4-methoxyphenyl)-3-bromo-4-methylaniline (**4**) (583 mg, 1.46 mmol), palladium(II) acetate (6.60 mg, 0.0293 mmol), tri-*o*-tolylphosphine (35.7 mg, 0.117 mmol), lithium chloride (61.9 mg, 1.46 mmol), and triethylamine (355 mg, 3.51 mmol) were added to a

2.2 mL of *N,N*-dimethylformamide solution of *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)-3-methyl-4-vinylaniline (**3**) (249 mg, 0.73 mmol) in a 5 mL of ampule. The degassed ampule was heated to 100 °C and stirred for 24 h. The resulting mixture was poured into aqueous ammonium chloride, followed by extraction with chloroform, and then the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, purification by chromatography with a silica-gel column and hexane/chloroform = 4/1 as the eluent, and HPLC with a polystyrene-gel column gave *N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}-3-methylphenyl)-*N*-(4-{5-[*N,N*-bis(4-methoxyphenyl)amino]-2-methylstyryl}phenyl)-4-methoxyaniline (**2**) as a yellow solid (64.3 mg, Yield 9.0%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.41 (d, $J = 8.2$ Hz, 1H, aryl), 7.31 (d, $J = 7.6$ Hz, 1H, aryl), 7.21 (s, 1H, aryl), 7.17 (s, 1H, aryl), 7.11 (d, $J = 16$ Hz, 1H, vinylene), 7.07–6.76 (m, 13H, aryl), 7.03(1) (d, $J = 8.9$ Hz, 8H, aryl), 7.02(6) (d, $J = 16$ Hz, 1H, vinylene), 6.88 (d, $J = 16$ Hz, 1H, aryl), 6.81 (d, $J = 8.9$ Hz, 8H, aryl), 6.71 (d, $J = 16$ Hz, 1H, vinylene), 3.78 (s, 15H, methoxy), 2.33 (s, 6H, methyl), and 2.22 (s, 3H, methyl); ^{13}C NMR (CDCl$_3$, 500 MHz) δ 156.4, 155.4, 155.3, 147.4, 147.0, 146.9(4), 146.9(0), 141.5, 141.4, 140.2, 137.7, 137.2, 136.9, 131.2, 131.0, 130.9, 130.7, 129.4, 128.7, 128.6, 127.6, 127.4, 127.3, 126.4, 126.3, 125.8, 125.7, 124.7, 124.4, 122.7, 121.5, 121.1, 120.9, 119.0, 118.9, 114.8, 114.6, 114.5, 55.5, 21.1, 20.0, and 19.2; IR (KBr pellet): 1241 (ν_{C-O-C}) and 963 cm^{-1} (δ_{ArC-H}); UV–vis (dichloromethane) $\lambda_{max} = 387$ and 302 nm; fluorescent (dichloromethane) $\lambda_{em} = 502$ nm ($\lambda_{ex} = 424$ nm); Mass: calcd for M 976.2, found (m/z) 976 (M$^+$). Found: C, 81.4; H, 6.2; N, 4.3%. Calcd for C$_{66}$H$_{61}$N$_3$O$_5$: C, 81.2; H, 6.3; N, 4.3%.

The synthesis of the hyperbranched poly[(4-methoxyphenyl-*N*-amino)-1,2(or 4)-phenylenevinylene-1,2(or 4)-phenylene] and the iodometric titration of the ammoniumyl radical have been described in a previous paper.[27]

Other Materials. Tetrabutylammonium tetrafluoroborate and potassium hexacyanoferrate(III) were purified by recrystallization. All solvents were purified by distillation just before use. All other reagents were used as received.

Oxidations.   Oxidation of the Hyperbranched Polymer 6: A 11.9 mM thianthreniumyl tetrafluoroborate solution (0.208 mL) of the acidic mixture (dichloromethane/trifluoroacetic acid (TFA)/trifluoroacetic anhydride (TFAA) = 97/0.6/2.6 v/v) was slowly added to a 40.9 µL TFA solution of the polymer **6** (1.00 mg), and stirred for 5 min at room temperature. The reaction mixture turned from yellow to deep purple due to the newly formed polyradical **1**. The resulting mixture was transferred to an ESR tube (2 mm quartz) or an NMR tube (2 mm glass).

Oxidation of the Trimer Model Compound 2: A 11.9 mM thianthreniumyl tetrafluoroborate solution (0.271 mL) in an acidic mixture (dichloromethane/TFA/TFAA = 97/0.6/2.6 v/v) was slowly added to a 53.3 µL TFA solution of **2** (1.00 mg, 3.07 µmol), mol), then stirred for 5 min at room temperature. The reaction mixture turned from yellow to deep purple as the polyradical **2**$^+$ was produced. The resulting mixture was transferred to an ESR tube (2 mm quartz), an NMR tube (2 mm glass), or a diamagnetic capsule for the SQUID measurement.

Electrochemical Measurements. Voltammetric investigations were carried out for the samples with a 1 mM/radical unit in a dichloromethane solution of 0.1 M tetrabutylammonium tetrafluoroborate using a BAS 100B/W electrochemical analyzer (BAS, Inc., Tokyo). Platinum working and Ag/AgCl reference electrodes were used. The formal potential of the ferrocene/ferrocenium couple was 0.43 V vs this reference electrode.

ESR Spectroscopy.   The ESR spectrum was recorded by a JEOL JES-2XG ESR spectrometer. The signal positions were calibrated against an external standard of Mn^{2+}/MgO ($g = 1.981$).

NMR Magnetic Susceptibilities Measurement.   The prepared solution of the radical 2^+ or **1** was diluted with the acidic mixture ($CH_2Cl_2/TFA/TFAA = 81/17/2\,v/v$) to 9.5, 6.3, and 3.2 mM solutions. A slight amount of cyclohexane was added to the radical solution for reference. The diluted solution was transferred to a thin NMR tube (2 mm). The thin NMR tube was placed in the center of a thick standard NMR tube (a 5 mm glass tube) filled with a solution of C_6D_6 and 2 vol % cyclohexane. The chemical shift of cyclohexane for each polyradical solution (9.5, 6.3, and 3.2 mM) was measured. The peak shift was calibrated with a blank solution. The $\chi_{mol}T$ value was calculated from the frequency separation ($\Delta\nu$) of cyclohexane between the internal reference (the radical solution) and the external reference. The NMR tube for high temperature measurement was sealed to prevent solvent evaporation.

SQUID Measurement.   The magnetization and static magnetic susceptibility were measured by a Quantum Design MPMS-7 SQUID magnetometer. The sample solution was transferred to a diamagnetic capsule. The static magnetic susceptibility was measured from 1.8 to 200 K in a 0.5 T field. The magnetization was measured from 0.5 to 7 T at 1.8, 2, 2.5, and 5 K. The quality of the ferromagnetic impurities and diamagnetic susceptibility of the matrix and the capsule were determined by the Honda–Owen and Curie plots, respectively, and were subtracted from the measured magnetization.

Other Measurements.   The ^1H and ^{13}C NMR spectra were recorded by a JEOL NMR 500 Λ. The ^1H and ^{13}C chemical shifts were referenced to TMS and the signals in the deuterated solvent. The IR, mass, and UV–vis spectra were measured with JASCO FT/IR-410, Shimadzu GC-MS 17A, and JASCO V-550 spectrometers. The molecular weight of the polymer was measured by GPC using a Tosoh LS-8000 (polystyrene gel, THF eluent, polystyrene calibration). An LC-918 chromatograph (Japan Analytical Industry Co.) was used for the HPLC separation.

Supporting Information

Data of the NMR shift measurement and SQUID. This material is available free of charge on the web at http://www.csj.jp/journal/bcsj/.

References

1   K. Itoh, *Pure Appl. Chem.* **1978**, *50*, 1251.
2   H. Iwamura, N. Koga, *Acc. Chem. Res.* **1993**, *23*, 34.
3   A. Rajca, *Chem. Rev.* **1994**, *94*, 871.
4   *Magnetic Properties of Organic Materials*, ed. by P. M. Lahti, Marcel Dekker, New York, **1999**.
5   *Molecular Magnetism*, ed. by K. Itoh, M. Kinoshita, Kodansha-Wiley, Tokyo and Amsterdam, **2000**.
6   A. Rajca, *Chem. Eur. J.* **2002**, *8*, 4834.
7   A. Rajca, *Adv. Phys. Org. Chem.* **2005**, *40*, 153.
8   K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **1995**, *117*, 5550.
9   H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, P. M. Lahti, *J. Am. Chem. Soc.* **1996**, *118*, 9695.
10   Y. Miura, H. Oka, Y. Teki, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 385.
11   A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503.
12   T. Kaneko, T. Matsubara, T. Aoki, *Chem. Mater.* **2002**, *14*, 3898.
13   T. Kaneko, T. Makino, H. Miyaji, M. Teraguchi, T. Aoki, M. Miyasaka, H. Nishide, *J. Am. Chem. Soc.* **2003**, *125*, 3557.
14   L. M. Field, P. M. Lahti, *Chem. Mater.* **2003**, *15*, 2861.
15   A. Rajca, J. Wongsriratanakul, S. Rajca, *J. Am. Chem. Soc.* **2004**, *126*, 6608.
16   S. Rajca, A. Rajca, J. Wongsriratanakul, P. Butler, S. Choi, *J. Am. Chem. Soc.* **2004**, *126*, 6972.
17   E. Fukuzaki, N. Takahashi, S. Imai, H. Nishide, A. Rajca, *Polym. J.* **2005**, *37*, 284.
18   S. Sasaki, M. Iyoda, *Mol. Cryst. Liq. Cryst.* **1995**, *272*, 175.
19   T. D. Selby, S. C. Blackstock, *J. Am. Chem. Soc.* **1995**, *121*, 7152.
20   F. E. Goodson, S. I. Hauck, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 7527.
21   A. Ito, Y. Ono, K. Tanaka, *Angew. Chem., Int. Ed.* **2000**, *39*, 1072.
22   K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, H. Chiba, *Nature* **2002**, *415*, 509.
23   A. Rajca, S. Utamapanya, *J. Am. Chem. Soc.* **1993**, *115*, 10688.
24   M. M. Wienk, R. A. J. Janssen, *J. Am. Chem. Soc.* **1997**, *119*, 4492.
25   R. J. Bushby, D. Gooding, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1069.
26   H. Nishide, M. Nambo, M. Miyasaka, *J. Mater. Chem.* **2002**, *12*, 3578.
27   E. Fukuzaki, H. Nishide, *J. Am. Chem. Soc.*, **2006**, *128*, 996.
28   M. Jikei, M. Kakimoto, *Prog. Polym. Sci.* **2001**, *26*, 1233.
29   B. Voit, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.
30   N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877.
31   L. Eberson, B. Larsson, *Acta Chem. Scand., Ser. B* **1987**, *41*, 367.
32   D. F. Evans, *J. Chem. Soc.* **1959**, 2003.
33   F. A. Cotton, C. A. Murillo, X. Wang, *Inorg. Chem.* **1999**, *38*, 6294.
34   C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4583.
35   D. S. Thompson, L. J. Markoski, J. S. Moore, *Macromolecules* **1999**, *32*, 4764.
36   L. J. Markoski, D. S. Thompson, J. S. Moore, *Macromolecules* **2002**, *35*, 1599.