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Hyperbranched poly(phenylenevinylene) bearing pendant phenoxys for a high-spin alignment

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2,6-Dibromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene was polymerized in a one-pot reaction using a palladium catalyst, and subsequent hydrolysis and oxidation yielded the hyperbranched poly[(4-(3′,5′-di-*tert*-butyl-4′-ylooxyphenyl)-1,2,(6)-phenylenevinylene)], which three-directionally satisfies both an alternant but non-Kekulé-type π-conjugation and the ferromagnetic connectivity of the unpaired electrons of the pendant phenoxyl. The AFM image, unusually low solution viscosity, and low chemical reactivity of the phenol group indicated the polymer to have a highly branched and globular structure. In spite of the extremely crowded branching, π-conjugation in the polymer skeleton was maintained, as indicated by photoelectron and EPR spectroscopies. The phenoxyl polymer even with a spin concentration of only 0.4 spin per monomer unit displayed an average S value of 3.

Introduction

Synthetic research into high-spin organic molecules using intramolecular through-bond ferromagnetic spin alignment has been exhaustively continued to realize pure organic-derived compounds of unknown magnetism.[1–4] Some of the π-conjugated and alternant, but non-Kekulé-type, organic polymers bearing multiple radical groups (unpaired electrons) as the spin source display ferromagnetic or high-spin ordering, owing to intramacromolecular spin-exchange interaction through the π-conjugated skeleton.[5–13] Their spin-alignment numbers or the spin quantum numbers (S) in the ground state have long been expected to be proportional to the degree of polymerization.[14] In addition, the stability of the high-spin state is also theoretically predicted to be enhanced exponentially by the dimensions of the ferromagnetically spin-connecting π-conjugated skeleton.[15] For example, Rajca *et al.*[16] recently reported the highest recorded value of spin-alignment for pure organic molecules, with the average S over 5000 at low temperatures, by synthesizing two-dimensionally dendric-macrocyclic poly(1,3-phenylenephenylmethine)s, but they lacked chemical stability at room temperature. Bushby *et al.*[5] focused on a triphenylamine radical cation that is stable in ambient conditions and synthesized the networked poly(phenylenephenylaminium cationic radical) with $S = 3$. However, an increase in the molecular size and/or the dimensionality of such radical polymers always accompanies a structural defect or distorted and ineffective π-conjugation. That is, a tradeoff problem remains between the extended π-conjugation and the higher dimensional structure in the polymer framework. (A study of electroconductive and optoelectrical polymers encounter a similar tradeoff.[17,18]) This motivated us to explore the possibility of a hyperbranched polymer obtained by a one-pot reaction of an AB_2 type monomer,[19,20] as a π-conjugated skeleton to ferromagnetically connect spins.

For this purpose, we have designed a hyperbranched phenoxyl polymer, poly[4-(3′,5′-di-*tert*-butyl-4′-ylooxyphenyl)-1,2,(6)-phenylenevinylene] (Chart 1), by extending our previous results[21–25] on the corresponding linear poly(1,2-phenylenevinylene)-based phenoxyl polymers that displayed partial spin-alignment ($S = 2$–4) and sufficient chemical stability. The hyperbranched phenoxyl polymer satisfies both an alternant and non-Kekulé π-conjugated structure, and its ferromagnetic connectivity represented by up–down small arrows in Chart 1, three-directionally requires the ferromagnetic (up) alignment of all of the phenoxyls' spin (represented by a big arrow) within the polymer. (In Chart 1, the big arrow and the small up and down arrows represent the spin on the phenoxyl radical and the direction of the temporarily induced spin density on the carbons, respectively.)

There has been no report on such a hyperbranched, head-to-tail linked, and 1,2,4,6-substituted phenylene polymer, although the dendrimer of a simple poly(1,3,5-phenylenevinylene) with fifth-generation[26–30] and hyperbranched copolymers of phenylene and 1,1-vinylene[31] have been recently synthesized as a new class of π-conjugated polymers. In this paper, we synthesized an asymmetric AB_2 type monomer (2,6-dibromo-4-phenoxyl-precursor substituted styrene) and polymerized the monomer in one-pot *via* the palladium-catalyzed Heck reaction to form the hyperbranched and head-to-tail linked poly(phenylenevinylene). The π-conjugated skeleton of the hyperbranched nano-size polymer is discussed.

Results and discussion

Polymer synthesis

2,6-Dibromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene **6** was synthesized as a three-functional monomer to be linked with head-to-tail bonds *via* the β-phenylation of the styrenic vinyl group with phenyl bromide by the Heck reaction,[32] according to Scheme 1. The 3,5-di-*tert*-butyl-4-acetoxyphenyl group was introduced onto the 4-bromo substituent of 2,4,6-tribromotoluene to produce **5c** *via* preferential coupling with [3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]magnesium bromide using a nickel catalyst[33] to yield **5a**, followed by hydrolysis and acetylation. The methyl group of **5c** was converted to a vinyl group *via* the Wittig reaction[34] to yield **6** (for details see the Experimental section). 4,6-Dibromo-2-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (**10**), the isomer of **6**, was also synthesized *via* the same synthetic procedure.

The sterically very crowded structure of the polymer in Chart 1 first suggested a strong retardation of the polymer formation. The hyperbranched (precursor acetoxy) polymer was synthesized through a simple one-pot reaction of the starting AB_2 type monomer **6**, in the presence of a (tri-*o*-tolylphosphine)-palladium catalyst at 90 °C. Although the polymerization of **6** proceeded more slowly, the molecular weight of the

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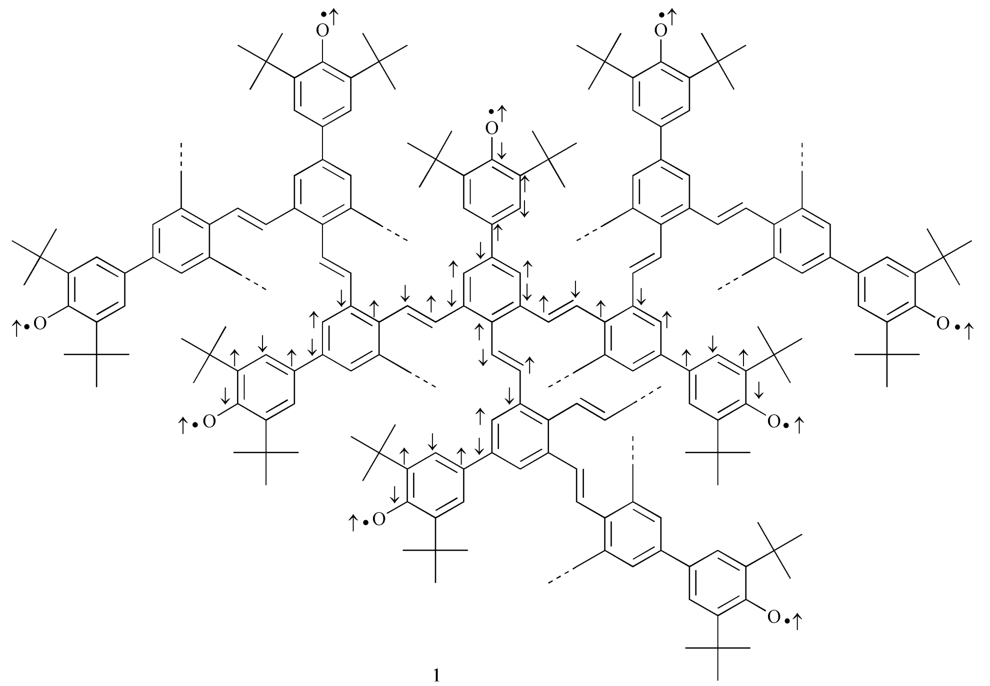

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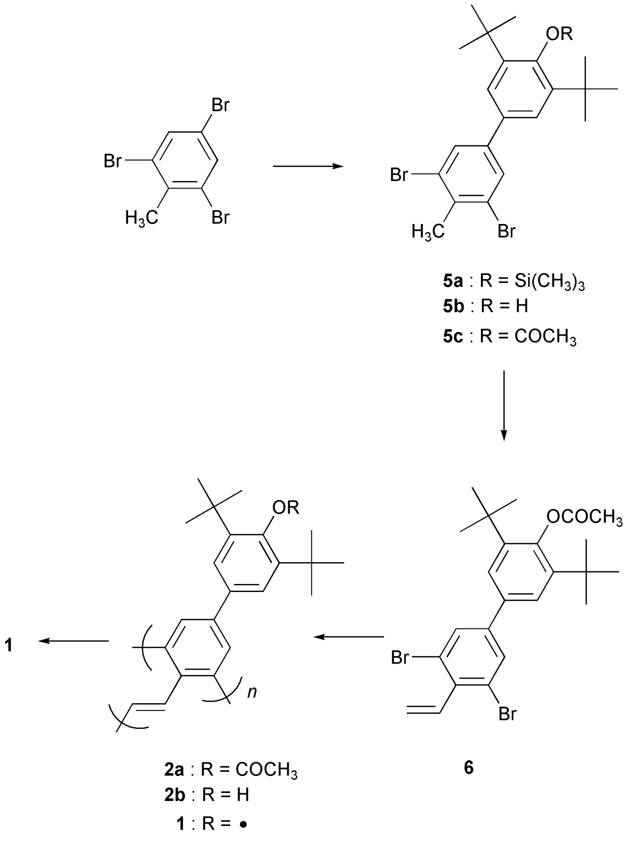
Chart 1



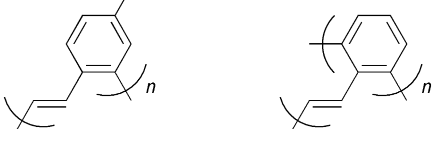
Scheme 1

hyperbranched polymer **2a** (Chart 2) was unexpectedly somewhat higher in comparison with the polymerization of the corresponding two-functional 2-bromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (**7**) which yields the linear polymer **3a** (*e.g.*, $\bar{M}_w = 2.4 \times 10^4$ (degree of polymerization = 56) and = 4.9×10^3 (degree of polymerization = 14) for the hyperbranched and linear polymer, respectively, under the same reaction conditions, see Table 1). The higher molecular weight can probably be ascribed to the three-functionality of the monomer **6** and/or to the high solvent–solubility of the hyperbranched polymer **2a**. The GPC profile of the polymer was unimodal. Further reaction of the isolated polymer with the Pd catalyst resulted in the recovery of the starting polymer. These results exclude a coupling reaction between the oligomers during the polymerization because the surface of the oligomer is occupied by the B group of the AB_2 monomer (the Br group of **6**).

The head-to-tail and *trans*-vinylene linkage structures of polymer **2a** were confirmed by NMR, IR, and fluorescence spectroscopies. Head-to-tail linkage in **2a** was supported by a model reaction of **5a** and styrene using the same Pd catalyst and reaction conditions, which quantitatively yielded 2,6-distyryl-4-(3′,5′-*tert*-butyl-4′-acetoxyphenyl)toluene (for details see the Experimental section). Polymer **2a** was converted to the corresponding hydroxy polymer **2b** after complete elimination of the protecting acetyl group in alkaline solution. The sterically crowded structure of the hyperbranched **2a** retarded the hydrolysis: hydrolysis of **2a** took a long time (24 h) even with a large excess of alkaline solution, while hydrolysis linear **3a** was completed for the with a small excess of alkaline solution after 12 h ([KOH]/[the acetoxy unit] > 50 and = 12 for **2a** and **3a**, respectively).

Hyperbranched structure and π-conjugation

The precursor acetoxy polymer **2a** was obtained as a yellow powder. In spite of its poly(phenylenevinylene) skeleton, the



3 : R = •

4

3a : R = COCH3

3b : R = H

Chart 2

Table 1 Examples of the polymerization,[a] molecular weight, and hydrolysis[b] of the polymers

Monomer/polymers	$[M]_o$/M	Acetoxy polymers Yield (%)	 $\bar{M}_w/10^3$	 $\bar{M}_w/\bar{M}_n$	Hydroxy polymers $\bar{M}_w/10^3$	 $\bar{M}_w/\bar{M}_n$
6/2a/2b	0.1	16	3.1	1.6	3.2	1.5
	0.5	50	24	1.7	24	1.6
7/3a/3b	0.5	68	4.9	1.5	4.9	1.5
8/4	0.5	34	3.8	1.6	—	—
10/11a/11b	0.1	16	4.2	1.3	5.0	1.3

[a] $[Pd(OAc)_2]/[M]_o = 0.1$, $[P(C_6H_4CH_3)_3]/[Pd(OAc)_2] = 2$, $[N(C_2H_5)_3]/[M]_o = 5$. Temp. = 90 °C. Time = 24 h. Yield = methanol insoluble fraction. [b] [KOH]/[acetoxy unit] = 50, time = 24 h (except for **3a**/**3b** = 12 h), temp. = 50 °C.

Table 2 Solution viscosity,[a] UV-vis absorption,[b] fluorescence,[c] and ionization threshold (I^{th})[d] of the polymers

Polymer	$M_w/10^3$	Viscosity $[\eta]$/dl g^{-1}	UV-vis abs λ_{max}/nm	 $\varepsilon_{max}/10^4$ dm^3 mol^{-1} cm^{-1}	Fluorescence λ_{em}/nm	 Φ	I^{th}/eV
2a	24	0.031	357	0.80	470	0.12	5.8_8
2b	24		375	0.82	490	0.12	5.8_6
3a	24	0.39	304	1.1	448	0.61	5.8_5
	4.9	0.12	302	1.1			
3b	24		322	1.3	450	0.63	5.8_4

[a] Intrinsic viscosity $[\eta]$, toluene solution at 25 °C. [b] $CHCl_3$ solution. [c] Benzene solution, quantum yield (Φ) normalized with 9,10-diphenylanthracene ($\Phi = 0.84$). [d] Poly(1,2-phenylenevinylene), **4**, and **1** = 6.1_7, 5.6_7 and 5.8_9 eV, respectively. Reference data measured using the same procedure with the same UPS spectrometer for poly(1,4-phenylenevinylene), poly(acetylene) and poly(1,4-phenylene): $I^{th} = 5.2_9$, 5.2_5, and 5.8_3 eV, respectively (from previously reported data:[35, 36] I^{th} = 5.3, 5.2, and 5.8 eV, respectively).

hyperbranched polymer was quite soluble in common solvents such as benzene, THF, and $CHCl_3$. In addition, the solution viscosity of **2a** was one order of magnitude lower in comparison with those of the corresponding linear polymer **3a** (Table 2). Extremely low solution viscosity is one of the characteristics of dendric macromolecules, which is ascribed to a highly branched and globular structure.

The dilute solution of the hyperbranched polymer **2a** was then transferred to a mica surface and subjected to atomic force microscopy (AFM). Although the polymer collapsed on a graphite surface, globular polymers were detectable on the mica (Fig. 1). The globular size corresponds to the molecular weight of the hyperbranched polymer: a horizontal distance of *ca.* 50 nm and a vertical distance of *ca.* 8 nm were estimated for **2a** with a molecular weight of 2.4×10^4, by taking into account the width of the cantilever tip in tapping mode.

UV-vis absorptions of the hyperbranched polymers **2** were broadened but significantly shifted bathochromically, relative to those of the linear polymers **3** (Table 2). The absorptions were not influenced by the solvent species, such as benzene, $CHCl_3$, and acetone. The emission maxima of the fluorescence ascribed to the poly(phenylenevinylene) skeleton were also shifted to longer wavelengths for **2** with a decrease in the quantum yield of the fluorescence in comparison with those for **3**. A cast (solvent-free) film of **3b** was prepared: UV-vis absorption and fluorescence maxima were shifted bathochromically to 390 and 470 nm, respectively, which nearly agreed with those of **2b**. This result suggests that an excitonic interaction causes the bathochromic shifts, that the aromatic rings are closely spaced together in the hyperbranched polymer, and that the π-conjugation of the hyperbranched **2** is similar to that of linear **3**.

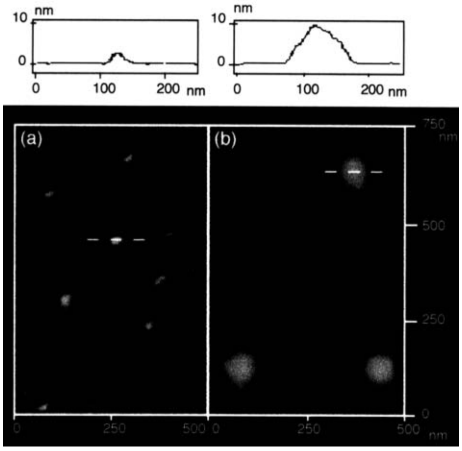


Fig. 1 AFM images (tapping mode) of the hyperbranched polymer **2a** with a moleculer weight of 4.9×10^3 (a) and 2.4×10^4 (b).

The π-conjugated electronic structure of poly(phenylenevinylene)s has been investigated with ultraviolet photoelectron spectroscopy (UPS).[35,36] The ionization threshold (I^{th}) of the hyperbranched polymers **2** was estimated by UPS (Table 2). The I^{th} values of **2** including the phenoxyl polymer **1** were comparable to those of the linear polymers **3**. The I^{th} value of the hyperbranched poly(1,2,(6)-phenylenevinylene) **4** was considerably smaller than that of the linear poly(1,2-phenylenevinylene). These results indicate that the π-conjugation in the poly(phenylenevinylene) skeleton in the hyperbranched polymers **2** and **1** is surprisingly maintained despite the extremely crowded branching structure.

Radical generation and EPR spectra

The hydroxy polymer **2b** was converted to a deeply red-colored phenolate anion of the polymer with a small excess of $(C_4H_9)_4NOH$ in CH_2Cl_2. Quantitative formation of the phenolate anion was detected by complete disappearance of the IR absorption at 3638 cm^{-1} (ν_{O-H}). The anionic solution of **2b** was heterogeneously treated with an aqueous potassium ferricyanide phase to yield phenoxyl polymer **1**. Polymer **1** was also soluble in common solvents. GPC elution curves of the polymers **2b** and **1**, *i.e.*, before and after radical generation, were coincident with each other. Radical generation does not bring about oxidative degradation or cross-linking of the hyperbranched polymer. Polymer **1** was isolated as a deep brownish powder which was chemically persistent at room temperature even in air. For example, the half-life of the radical

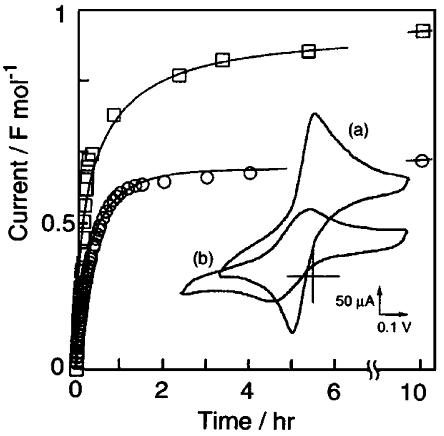


Fig. 2 Controlled potential coulometric oxidation of the phenolate anions of the hyperbranched polymer **2b** (○) and the linear polymer **3b** (□). Inset: cyclic voltammogram of the phenolate anions of the hyperbranched polymer **2b** (a) and **5b** (b), in CH_2Cl_2 with $(n\text{-}C_4H_9)_4NBF_4$ and $(CH_3)_4NOH$.

1, estimated by monitoring the EPR signal intensity, was 1.6 days at room temperature.

The phenoxyl polymer **1** was also generated by electrochemical oxidation. The cyclic voltammogram of the phenolate anion of **2b** was recorded reversibly in repeated potential sweeps (inset in Fig. 2). This result means that the phenoxyl polymer is chemically persistent even in solution at room temperature and that radical generation is not accompanied by a subsequent chemical side reaction. Differential pulse voltammetry gave a simple unimodal response even though the polymer involved multiple redox sites. The redox potential (−0.13 V *vs.* Ag/AgCl) almost agreed with those of the monomeric phenolate derivatives (−0.06 and −0.19 V for **5b** and **3b**, respectively).

Coulometric oxidation of the phenolate anion of linear **3b** on a carbon felt electrode indicated approximately stoichiometric oxidation (Fig. 2). Electrolytic EPR spectroscopy supported the formation of the phenoxyl radical. Under the same conditions, oxidation of the phenolate anion of the hyperbranched **2b** was slower than that of **3b** and ceased at a yield of *ca.* 60%. It is believed that the hyperbranched structure retards the oxidation of the inner-embedded phenolate groups.

Fig. 3a shows the EPR spectrum of the hyperbranched phenoxyl polymer **1** at a low spin concentration; the broad but hyperfine spectrum would be attributed to the 5–7 protons of the phenoxyl pendant ring and phenylenevinylene skeleton, which is in contrast to the three-line hyperfine structure of 2,4,6-tri-*tert*-butylphenoxyl ascribed to an unpaired electron localized in the phenoxy ring. The proton hyperfine structure was more clearly observed for the model compound **9** (Fig. 3b), which is simulated by the dashed line by taking into account the skeleton's phenylene and vinylene protons. These EPR results suggest an effectively delocalized spin distribution over the branched skeleton, most likely because of its still π-conjugated structure. The data mentioned above indicate a developed π-conjugation in the poly(phenylenevinylene) skeleton in spite of the sterically very crowded structure of the hyperbranched polymer.

The EPR spectrum of **1** showed a sharp and unimodal signal with increasing spin concentration. $g = 2.0045$ for the signal was ascribed to an oxygen-centered radical. Fig. 3(c) shows a $\Delta M_s = \pm 2$ forbidden transition assigned to a triplet species at $g = 4$ for **1** with a spin concentration of 0.35 spin per monomer unit. The EPR signal in the $\Delta M_s = \pm 2$ region was doubly integrated to give Curie plots (100–6 K, Fig. 3(d)). Although the signal intensity was proportional to the reciprocal of the temperature at higher temperature, the plots deviated upward from linearity in the lower temperature (< 30 K) region. This upward deviation supported the presence of a multiplet state for the phenoxyl polymer **1**.

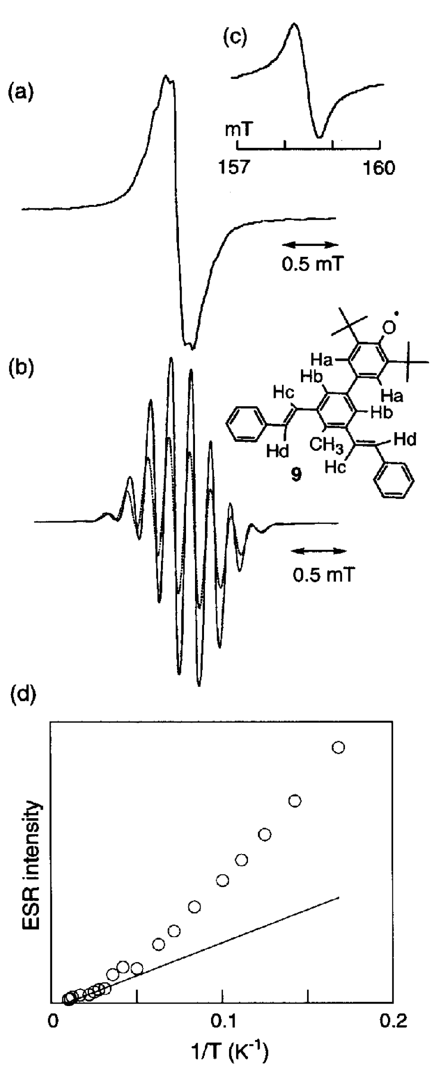


Fig. 3 EPR spectra of the hyperbranched phenoxyl polymer **1**. (a) The solid line at $g = 2.0045$ for **1** with a spin concentration of 0.03 spin per unit in CH_2Cl_2 solution at room temperature. (b) Monoradical of **9** with a spin concentration of 0.10 in benzene solution at $g = 2.0043$; dashed line for simulation with a_H(Ha, Hb) = 0.19, and a_H(Hc, Hd) = 0.04 mT. (c) $\Delta M_s = \pm 2$ spectrum for **1** with a spin concentration of 0.35 in CH_2Cl_2 at 10 K. (d) Curie–Weiss plots (EPR signal intensity *vs.* $1/T$) for **1**.

Magnetization

The magnetization of the phenoxyl polymer **1** in a frozen solution was measured with a SQUID magnetometer.[37] The magnetization (M) plots normalized with the saturated magnetization (M_s) of **1** with a spin concentration of 0.38 are shown to be close to the Brillouin curve for $S = 3$ (closed symbol in Fig. 4). Unfortunately, only *ca.* 40% of the potential spin-sites were successfully oxidized to the phenoxyl radical even after applying heterogeneous oxidation and a variety of conditions in the radical generation step.[38] Coulometric oxidation has suggested that spin concentration may be limited in the radical generation of the hyperbranched polymer (Fig. 2). The average $S = 3$ value for **1** is lower than the degree of polymerization of 63 for this polymer, but it is reasonable considering the spin defect of *ca.* 60%. Fig. 4 also gives the M/M_s plots for the linear phenoxyl polymer **3** with spin concentrations of 0.36 and 0.54: they lie almost on the

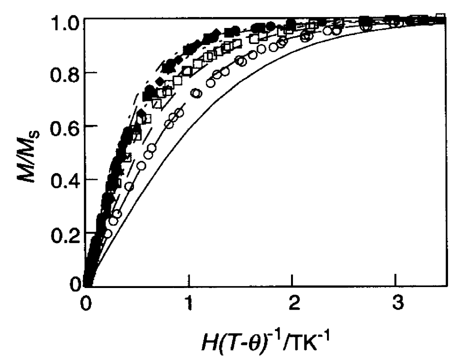


Fig. 4 Normalized plots of magnetization (M/M_s) *vs.* the ratio of magnetic field and temperature ($H/(T-\theta)$) for the hyperbranched phenoxyl polymer **1** with a spin concentration 0.38 spin per unit (●), and for the linear polyradical **3** with a spin concentration 0.36 (○) and 0.54 (□) in frozen CH_2Cl_2 at 1.8–5.0 K. θ is the coefficient of a weak antiferromagnetic interaction. The theoretical curves corresponding to $S = 0.5$ (—), 1, 1.5, 2, 2.5, 3, and 3.5 (- - -) Brillouin functions are also depicted.

Brillouin curves for $S = 1$ and 2, respectively. By comparing these magnetization data, it can be concluded that the hyperbranched skeleton acts as an effective π-conjugated coupler of the pendant spins.

Conclusion

Hyperbranched poly(1,2,(6)-phenylenevinylene) bearing 4-substituted phenol groups have been synthesized. π-Conjugation was maintained in spite of the highly branched polymer skeleton. The phenoxyl polymer **1** with only a spin concentration of 0.4 gave an average spin state of $S = 3$, which suggests that a higher spin alignment could be realized by optimization of the radical generation step. The molecular approach to the study of mesoscopic phenomena such as molecular recognition and magnetism is now at the stage that it can be applied to large molecules with multiple interacting entities through to a nanosize molecules with added complexities. Our results suggest that a hyperbranched but still π-conjugated poly(phenylenevinylene) is an effective backbone structure that could be used for the preparation of a purely organic-based electronic and/or magnetic material with a high dimensional structure that could display nanoscopic properties.

Experimental

Synthesis

2,6-Dibromo-4-(3′,5′-di-*tert*-butyl-4′-trimethylsiloxyphenyl)toluene (5a). The Grignard solution (THF, 156 cm^3) of (4-bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (29 g, 81 mmol) was added to the cooled THF solution (60 cm^3) of 2,4,6-tribromotoluene[39] (22.2 g, 68 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride (81.5 mg), and the mixture was refluxed for 3 h. The reaction was quenched with 2 M HCl (84 cm^3) and then extracted with ether. The extract was washed with water, dried, evaporated, and then purified by silica gel column separation with hexane elution. It was recrystallized from hexane to give a pale yellowish needle crystal of 2,6-dibromo-4-(3′,5′-di-*tert*-butyl-4′-trimethylsiloxyphenyl)toluene (**5a**) (17.4 g): yield 49%. Mp 145 °C; IR (KBr pellet/cm^{-1}) 1255 (ν_{Si-C}), 914 (ν_{Si-O}); δ_H ($CDCl_3$) 0.40 (s, 9H, Si-CH_3), 1.23 (s, 18H, tert-butyl), 2.60 (s, 3H, CH_3), 7.48 (s, 2H, phenyl), 7.84 (s, 2H, phenyl); δ_C ($CDCl_3$) 3.87, 18.35, 23.38, 35.10, 120.54, 125.68, 125.77, 134.79, 139.64, 140.79, 143.61, 154.36; MS (m/z) 524, 526, 528 (M^+, $M^+ + 2$, $M^+ + 4$), calcd for M = 526.4. Anal. Calcd for $C_{24}H_{34}OBr_2Si$: C, 54.8; H, 6.5; Br, 30.4. Found: C, 54.6; H, 6.3; Br, 30.2%.

2,6-Dibromo-4-(3′,5′-*tert*-butyl-4′-hydroxyphenyl)toluene (5b). Methanol (53 cm^3) and 10 M HCl (19 cm^3) were added to the THF solution (105 cm^3) of **5a** (17.4 g, 33 mmol), and the resulting solution was stirred at room temperature for 3 h. After the removal of methanol, the solution was extracted with ether. The crude product was purified using a silica gel column with hexane–$CHCl_3$ (1 : 1) eluent. Recrystallization from hexane gave a needle crystal of 2,6-dibromo-4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)toluene (**5b**) (9.0 g): yield 60%. Mp 178 °C; IR (KBr pellet/ cm^{-1}) 3626 (ν_{O-H}); δ_H ($CDCl_3$) 1.5(s, 18H, *tert*-butyl), 2.6 (s, 3H, CH_3), 5.3 (s, 1H, OH), 7.3 (s, 2H, phenyl), 7.7 (s, 2H, phenyl); δ_C ($CDCl_3$) 23.32, 31.27, 34.50, 123.80, 125.50, 129.47, 130.55, 134.95, 136.55, 142.73; MS (*m*/*z*) 452, 454, 456 (M^+, $M^+ + 2$, $M^+ + 4$), calcd for $M = 454.2$. Anal. Calcd for ($C_{21}H_{26}OBr_2$): C, 55.5; H, 5.8; Br, 35.2. Found: C, 55.4; H, 5.6; Br, 35.1%.

2,6-Dibromo-4-(3′,5′-*tert*-butyl-4′-acetoxyphenyl)toluene (5c). Compound **5b** (9.0 g, 20 mmol) was suspended in acetic anhydride (70 cm^3) and was stirred in the presence of a few drops of perchloric acid at room temperature for 15 h. After the addition of excess water, the product was filtered off and extracted with ether and purified by column separation (hexane–$CHCl_3$ (1 : 1) eluent). Recrystallization from hexane gave 2,6-dibromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)toluene (**5c**) (7.5 g): yield 76%. Mp 154 °C; IR (KBr pellet/cm^{-1}) 1763 ($\nu_{C=O}$); δ_H ($CDCl_3$) 1.39 (s, 18H, *tert*-butyl), 2.17 (s, 3H, CH_3), 2.37 (s, 3H, $COCH_3$), 7.41 (s, 2H, phenyl), 7.67 (s, 2H, phenyl); δ_C ($CDCl_3$) 22.63, 23.36, 31.47, 35.60, 125.18, 125.43, 130.49, 135.35, 135.81, 142.03, 143.14, 143.19, 170.94; MS (*m*/*z*) 494, 496, 498 (M^+, $M^+ + 2$, $M^+ + 4$), calcd for $M = 496.3$. Anal. Calcd for ($C_{23}H_{28}O_2Br_2$): C, 55.7; H, 5.7; Br, 32.2. Found: C, 55.6; H, 5.6; Br, 32.%1.

2,6-Dibromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (6). *N*-Bromosuccinimide (3.4 g, 20 mmol) and α,α'-azobisisobutyronitrile (a few mg) were suspended in a CCl_4 solution (28 cm^3) of **5c** (7.5 g, 15 mmol) and refluxed until succinimide floated on the solution. The mixture was cooled and filtered off. After evaporation, benzene (32 cm^3) and triphenylphosphine (4.2 g, 16 mmol) were added to it and stirred at 50 °C for 5 h. Excess reactants were removed on a silica gel column with hexane–$CHCl_3$ (1 : 1) eluent, and the residue was eluted with methanol. Freeze-drying of the methanol solution gave the phosphonium salt (11.2 g): yield 88%.

The phosphonium salt (11.2 g, 13 mmol) was suspended in 25% formaldehyde (190 cm^3) and 5 M NaOH (20 cm^3) was added dropwise. The mixture was stirred for 1 h and extracted with ether. The crude product was purified using a silica gel column with hexane–$CHCl_3$ (1 : 1) eluent. Recrystallization from hexane gave 2,6-dibromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (**6**) (4.9 g): yield 72%. Mp 139 °C; IR (KBr pellet/cm^{-1}) 1765 ($\nu_{C=O}$), 1631 ($\nu_{C=C}$); δ_H ($CDCl_3$) 1.36 (s, 18H, *t*-butyl), 2.35 (s, 3H, $COCH_3$), 5.19, 5.38 (d, 2H, $CHCH_2$), 6.51 (dd, 1H, $CHCH_2$), 7.41 (s, 2H, phenyl), 7.75 (s, 2H, phenyl); δ_C ($CDCl_3$) 22.67, 31.58, 35.57, 120.70, 122.39, 124.32, 127.85, 132.41, 134.17, 135.88, 142.27, 144.53, 147.46, 170.87; MS (*m*/*z*) 506, 508, 510 (M^+, $M^+ + 2$, $M^+ + 4$), calcd for $M = 508.3$. Anal. Calcd for ($C_{24}H_{28}O_2Br_2$): C, 56.7; H, 5.6; Br, 31.4. Found: C, 56.7; H, 5.5; Br, 31.2%.

2,6-Dibromostyrene (8). *N*-Bromosuccinimide (5.0 g, 28 mmol) and α,α′-azobisisobutyronitrile (a few mg) were suspended in a CCl_4 solution (36 cm^3) of 2,6-dibromotoluene (5.0 g, 20 mmol) and refluxed until succinimide floated on the solution. The mixture was cooled and filtered off. After evaporation, benzene (40 cm^3) and triphenylphosphine (5.0 g, 19 mmol) were added, and stirred at 50 °C for 3 h.

Excess reactants were removed on a silica gel column with hexane–$CHCl_3$ (1 : 2) eluent, and the residue was eluted with methanol. Freeze-drying of the methanol solution gave the phosphonium salt (5.1 g): yield 43%.

The phosphonium salt (5.1 g, 8.7 mmol) was suspended in 25% formaldehyde (44 mL) and 5 M NaOH (13 cm^3) was added dropwise. The mixture was stirred for 1 h and extracted with ether. The crude product was purified using a silica gel column with hexane eluent to give 2,6-dibromostyrene as a yellowish viscous oil (0.9 g): yield 36%. IR (cm^{-1}) 1631 ($\nu_{C=C}$); δ_H ($CDCl_3$) 5.66, 5.68 (d, 2H, CHC*H*$_2$), 6.63 (dd, 1H, C*H*CH$_2$), 6.95 (dd, 1H, phenyl), 7.54 (d, 2H, phenyl); δ_C ($CDCl_3$) 122.67, 123.59, 129.13, 131.80, 132.22, 135.22; MS (*m*/*z*) 260, 262, 264 (M^+, M^+ + 2, M^+ + 4), calcd for M = 261.9.

4,6-Dibromo-2-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (10). Compound **10** is an isomer of **6** and was synthesized *via* the same synthesis procedure and polymerized to yield the hyperbranched poly(2-substituted-1,4,(6)-phenylenevinylene) (**11**). **10**: Mp 117 °C; IR (KBr pellet/cm^{-1}) 1765 ($\nu_{C=O}$), 1630 (ν_{O-H}); δ_H ($CDCl_3$) 1.4 (s, 18H, *tert*-butyl), 2.4 (s, 3H, CH_3), 5.6 (d, 1H, CHC*H*$_2$), 5.7 (d, 1H, CHC*H*$_2$), 6.7 (dd, 1H, C*H*CH$_2$), 7.2 (s, 2H, phenyl), 7.4 (s, 1H, phenyl), 7.8 (s, 1H, phenyl); δ_C ($CDCl_3$) 22.7, 30.9, 31.5, 35.6, 120.7, 122.4, 132.4, 134.2, 134.3, 135.8, 136.5, 142.3, 144.5, 147.5, 170.9; MS (*m*/*z*): 506, 508, 510 (M^+, M^+ + 2, M^+ + 4), calcd for M = 508.3. Anal. Calcd for ($C_{24}H_{28}O_2Br_2$): C, 56.7; H, 5.6; Br, 31.4. Found: C, 56.9; H, 5.5; Br, 31.2%.

Polymerization

Palladium acetate (66 mg, 0.30 mmol) and tri-*o*-tolylphosphine (180 mg, 0.59 mmol) were added to a DMF solution (3.9 cm^3) of **6** (1.0 g, 3.4 mmol) and triethylamine (1.0 g, 9.9 mmol). The solution was heated at 90 °C for 24 h. The mixture was separated using a polystyrene gel column with $CHCl_3$ as eluent and was purified by reprecipitation from $CHCl_3$ in methanol to yield the polymer (**2a**) as a yellow powder (0.50 g): yield 50%. The molecular weight of the polymer was measured by light-scattering molecular weight analysis (Tosoh LS-8000). IR (KBr pellet/cm^{-1}) 1765($\nu_{C=O}$), 968 ($\delta_{trans HC=CH}$); δ_H ($CDCl_3$) 1.35 (s, 18H, *tert*-butyl), 2.35 (s, 3H, -$OCOCH_3$), 6.72–7.74 (m, 4H, Ar). Anal. Calcd for $C_{24n}H_{27n+1}Br_{n+1}O_{2n}$ (n = 56): C, 67.2; H, 6.3; Br, 19.0. Found: C, 67.3; H, 6.3; Br, 18.6%. Examples of the yield and the molecular weight under different polymerization conditions are given in Table 1.

Poly[4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-1,2,(6)-phenylenevinylene] (2b). Compound **2a** (1.0 g) was dissolved in a small amount of THF. To its suspension in DMSO (274 cm^3) was added 2.5 M KOH (18 cm^3). The solution was stirred at 50 °C for 24 h, and neutralized with 1 M HCl. The product was extracted with $CHCl_3$ and poured into methanol. Reprecipitation from $CHCl_3$ to methanol gave a yellow powder of **2b** (0.25 g): yield 25%, IR (KBr pellet/cm^{-1}) 3638 (ν_{O-H}), 960 ($\delta_{trans HC=CH}$); δ_H ($CDCl_3$) 1.38 (s, 18H, *tert*-butyl), 5.40 (s, 1H, OH), 6.72–7.61 (m, 4H, Ar). Anal. Calcd for $C_{22n}H_{25n+1}O_nBr_{n+1}$ (n = 63): C, 68.5; H, 6.5; Br, 21.0. Found: C, 71.1; H, 6.5; Br, 19.7%.

Poly(1,2,(6)-phenylenevinylene) (4). 2,6-Dibromostyrene was polymerized with the Pd catalyst, and the polymer was purified in the same manner as described above: yield 45%. IR (KBr pellet/cm^{-1}) 968 ($\delta_{trans HC=CH}$); δ_H ($CDCl_3$) 6.78–7.60 (m, 5H, phenyl). Anal. Calcd for $C_{8n}H_{5n+1}Br_{n+1}$ (n = 21): C, 51.9; H, 2.7; Br, 45.3. Found: C, 51.9; H, 2.6; Br, 45.0%.

2,6-Distyryl-4-(3′,5′-*tert*-butyl-4′-acetoxyphenyl)toluene (9a). Compound **5a** (0.2203 g, 0.44 mmol) was reacted with styrene (0.23 g, 2.2 mmol) using the Pd catalyst in completely the same manner as for the polymerization of **6**. The product was purified using a silica gel column with hexane–$CHCl_3$ (1 : 1) eluent: yield 85%. IR (KBr pellet/cm^{-1}) 1765 ($\nu_{C=O}$), 960 ($\delta_{trans HC=CH}$); δ_H ($CDCl_3$) 1.42 (s, 18H, *tert*-butyl), 2.18 (s, 3H, CH_3), 2.36 (s, 3H, $COCH_3$), 7.19–7.78 (m, 18H, Ar); δ_C ($CDCl_3$) 22.70 (CH_3), 31.44, 35.45 (*tert*-butyl), 124.60, 126.46, 126.64, 127.30, 127.46, 128.13, 128.27, 128.65, 128.72, 128.78, 128.96, 134.31, 137.48, 142.67 (Ar), 171.10 (Ac). The 14 peaks based on aromatic carbons were assigned to the small letter numbers 3, 6, 9, 10, 12, 14, 13, 8, 4, 5, 11, 7, 2 and 1, respectively, in structure **9a** in Chart 3. MS (*m*/*z*) : 542 (M^+), calcd for M = 542.8.

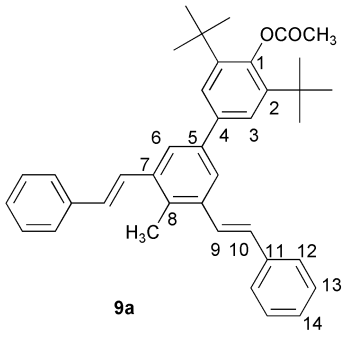


Chart 3

Linear poly[4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-1,2-phenylenevinylene] (**3b**) was synthesized as in the previous papers.[21,22]

Poly(1,2,(6)-phenylenevinylene) (4). 2,6-Dibromostyrene was polymerized with the Pd catalyst, and the polymer was purified in the same manner as described above: yield 45%. IR (KBr pellet/cm^{-1}) 968 ($\delta_{trans HC=CH}$); δ_H ($CDCl_3$) 6.78–7.60 (m, 5H, phenyl). Anal. Calcd for $C_{8n}H_{5n+1}Br_{n+1}$ (n = 21): C, 51.9; H, 2.7; Br, 45.3. Found: C, 51.9; H, 2.6; Br, 45.0%.

AFM

5 mL of the hyperbranched polymer **2a** solution (10 μM) was placed on freshly cleaved mica. After 1 min, excess fluid was carefully blotted off using filter paper and air-dried. AFM measurements were carried out using a Digital Instruments Nanoscope III in the tapping mode under ambient conditions. Silicon cantilevers (length 125 mm, width 30 mm, thickness 3–5 mm) with a spring constant between 17 and 64 N m^{-1} and a resonance frequency in the range 240–400 kHz were used. Resonance peaks in the frequency response of the cantilever were selected in the range between 280 and 320 kHz for the tapping mode oscillation. The scanning rate was usually 1.0 Hz. Imaging was performed by displaying the amplitude signal and the height signal, simultaneously.

Electrochemical measurements

The voltammetric investigation was carried out in CH_2Cl_2 in the presence of 0.1 M $(n\text{-}C_4H_9)_4NBF_4$ as the supporting electrolyte and a small amount of $(CH_3)_4NOH$ as the alkaline solution with a platinum working microelectrode using a function generator (Nikko Keisoku NFG-3) and a potentio-galvanostat (NPGS-301). The differential pulse voltammetry technique was also used since it permits the greatest resolution of the signals associated with consecutive redox events, whose potential is not very distant (an arbitary function generator Hokuto Denko HB-105 and potentiostat/galvanostat HA-501G). For coulometry, a large carbon felt electrode was used with a digital coulomb meter (Nikko Keisoku NDCM-1) under the application of 0.7 V (*vs.* Ag/AgCl). All the electrochemical experiments were carried out in the absence of oxygen.

Oxidation

(i) A small excess of $(n\text{-}C_4H_9)_4NOH$ was added to a CH_2Cl_2 solution (2 cm^3) of **2b** (12.2 mg, 20 monomer unit mmol L^{-1}) and stirred for 1 h in a glove box. The solution was then vigorously stirred with 1 cm^3 of aqueous $K_3Fe(CN)_6$ (0.16 g, 12 equiv. to the phenolate) at room temperature. The solution rapidly turned greenish brown after 10–20 min, which was ascribed to phenoxyl radical formation. The organic layer was washed with water and dried over anhydrous sodium sulfate to give a solution of **1**. (ii) All procedures were performed under high vacuum. A small excess of $(n\text{-}C_4H_9)_4NOH$ was added to a CH_2Cl_2 solution (2 cm^3) of **2b** (12.2 mg, 20 monomer unit mmol L^{-1}) and solvent was removed after complete generation of the polyanion. Subsequently a solution of ferrocenium hexafluorophosphate (1.05 equiv. to the polymer) was added to the solid polyanion at 195 K. The oxidation process was kept at a low temperature for 6 h. The sample (solid or liquid) for measurement was prepared by keeping the tube under vacuum.

Magnetic measurement

Prepared phenoxyl polymer **1** was immediately transferred to a diamagnetic capsule or a quartz tube after the oxidation. Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured to be from 0.1 to 7 T at 1.8, 2.0, 2.5, 3, and 5 K. The static magnetic susceptibility was measured from 2 to 200 K at a field of 0.5 T. Ferromagnetic magnetization ascribed to impurities (<1 ppm) was determined by the Honda–Owen plots and subtracted from the overall magnetization. Diamagnetic susceptibility (χ_{dia}) of the sample solution and the capsule was estimated by Curie plots of magnetic susceptibility.[37] The corrected magnetization data were fitted to Brillouin functions using a self-consistent version of the mean field approximation.

Spectroscopic measurements

EPR spectra were recorded on a JEOL JES-TE200 EPR spectrometer with 100 kHz field modulation. Spin concentrations of each sample were determined by double integration of the EPR signal standardized with that of the 2,2,6,6-tetramethylpiperidine 1-oxide solution. UPS spectra were recorded on a UPS spectrometer (Riken Keiki AC-1). The polymer thin films were prepared by casting the CH_2Cl_2 solutions on a glass plate. I^{th} was estimated in a manner analogous to that described in ref. 35. NMR, IR, UV-vis, fluorescence and mass spectra were measured on a JEOL NMR JMM-LA500, a JASCO FT/IR-5300, a Shimadzu UV-2000, Hitachi F-4500, and Shimadzu GC-MS QP-5050 spectrometer, respectively. Intrinsic viscosities were determined at 25 °C in toluene using an Ubbelohde viscometer.

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References and notes

1 *Magnetic Properties of Organic Materials*, ed. P. M. Lahti, Marcel Dekker Inc, New York, 1999.
2 *Molecular Magnetism*, ed. K. Ito and M. Kinoshita, Kodansha, Tokyo and Gordon and Breach, Amsterdam, 2000.
3 *Magnetism: Molecules to Materials II*, ed. J. S. Miller and M. D. Drillon, Wiley-VCH, Weinheim, 2001.
4 J. A. Crayston, J. N. Devine and J. C. Walton, *Tetrahedron*, 2000, **56**, 7829.
5 R. J. Bushby, D. R. MaGill, K. M. Ng and N. Taylor, *J. Mater. Chem.*, 1997, **7**, 2343.
6 L. Viadel, J. Carilla, E. Brillas, A. Labarta and L. Juliá, *J. Mater. Chem.*, 1998, **8**, 1165.
7 H. Oka, T. Tamura, Y. Miura and Y. Teki, *J. Mater. Chem.*, 1999, **9**, 1227.
8 A. Rajca, J. Wongsriratanakul, S. Rajca and R. Cerny, *Angew. Chem., Int. Ed.*, 1998, **37**, 1229.
9 K. K. Anderson and D. A. Dogherty, *Adv. Mater*, 1998, **10**, 688.
10 C. Xie and P. M. Lahti, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 779.
11 A. Rajca, S. Rajca and J. Wongsriratanakul, *J. Am. Chem. Soc.*, 1999, **121**, 6308.
12 M. Miyasaka, T. Yamazaki, E. Tsuchida and H. Nishide, *Macromolecules*, 2000, **33**, 8211.
13 H. Oka, T. Tamura, Y. Miura and Y. Teki, *J. Mater. Chem.*, 2001, **11**, 1364.
14 N. Mataga, *Theor. Chim. Acta*, 1968, **10**, 372.
15 N. N. Tyutyulkov and S. C. Karabunarliev, *Chem. Phys.*, 1987, **112**, 293.
16 A. Rajca, J. Wongsriratanakul and S. Rajca, *Science*, 2001, **294**, 1503.
17 J. Roncali, *Chem. Rev.*, 1997, **97**, 173.
18 Q.-T. Zhang and J. M. Tour, *J. Am. Chem. Soc.*, 1997, **119**, 9624.
19 Y. H. Kim, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 1685.
20 M. Jikei and M. Kakimoto, *Prog. Polym. Sci.*, 2001, **26**, 1233.
21 H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida and K. Yamaguchi, *J. Am. Chem. Soc.*, 1995, **117**, 548.
22 H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida and P. M. Lahti, *J. Am. Chem. Soc.*, 1996, **118**, 9695.
23 H. Nishide, T. Ozawa, M. Miyasaka and E. Tsuchida, *J. Am. Chem.Soc.*, 2001, **123**, 5942.
24 H. Nishide, M. Miyasaka and E. Tsuchida, *Angew. Chem., Int. Ed.*, 1998, **37**, 2400.
25 H. Nishide, M. Miyasaka and E. Tsuchida, *J. Org. Chem.*, 1998, **63**, 7399.
26 H. Meier and M. Lehmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 643.
27 S. K. Deb, T. M. Maddux and L. Yu, *J. Am. Chem. Soc.*, 1997, **119**, 9079.
28 E. Díez-Barra, J. C. García-Martínez and J. Rodríguez-López, *Tetrahedron Lett.*, 1999, **40**, 8181.
29 M. Halim, J. N. G. Pillow, I. D. W. Samuel and P. L. Burn, *Adv. Mater*, 1999, **11**, 371.
30 H. Meier, M. Lehmann and U. Kolb, *Chem. Eur. J.*, 2000, **6**, 2462.
31 T. M. Londergan, Y.-J. You, M. E. Thompson and W. P. Weber, *Macromolecules*, 1998, **31**, 2784.
32 R. F. Heck, *Org. React.*, 1982, **27**, 345.
33 K. Tamao, K. Sumitani, Y. Kiso, M. Zenbayashi and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1958.
34 G. Maerkl and A. Merz, *Synthesis*, 1973, 295.
35 K. Seki, *Optical Techniques to Characterize Polymer Systems*, ed. H. Baessler, Elsevier Science, Amsterdam, 1989, p. 115.
36 T. Kaneko, E. Ito, K. Seki, E. Tsuchida and H. Nishide, *Polym. J.*, 1996, **28**, 182.
37 For example, $\chi_{dia} = -1.12 \times 10^{-7}$ emu for **1** given in Fig. 4, which almost agrees with the χ_{dia} value calculated by Pascal's solvent constant. $\chi_{dia} = -1.24 \times 10^{-8}$ emu for the diamagnetic capsule to hold the sample solution.
38 In order to improve the result, we also used homogeneous oxidizing reagents such as ferrocenium hexafluorophosphate. However, the SQUID measurement gave only $S = 2.5$ and a spin concentration of 0.31.
39 R. Nevile and A. Winther, *Ber.*, 1880, **13**, 975.