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Regioregular Polythiophene with Pendant Phenoxyl Radicals: A New High-Spin Organic Polymer

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ABSTRACT: Poly[3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene] (**1a**) was regioselectively synthesized via simple oxidative polymerization of 3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene (**2a**) with ferric chloride. Head-to-tail content of **1a** with a molecular weight of $>10^4$ reached 96% by modulating both the polymerization conditions and the purification procedure of the polymer. Visible absorption and fluorescence maxima were bathochromically shifted for both **1a** and poly[3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)thiophene] (**1b**), which suggests an extended π-conjugation, i.e., a regioregular structure. Redox of the phenolate and of the thiophene residue of **1b** was observed reversibly and independently under alkaline conditions. The polyphenoxyl **1** derived from the oxidation of **1b** showed an electrical conductivity of 10^{-5} S cm^{-1}. The polyradical **1** satisfies both an alternant but non-Kekulé-type π-conjugation and ferromagnetic connectivity of the unpaired electrons of the pendant phenoxyls. **1** with a spin concentration of 0.3 spin/unit displayed a spin quantum number (S) value of $^2/_2$ to $^3/_2$, indicating a high-spin ground state and an intramolecular ferromagnetic spin coupling through the polythiophene backbone.

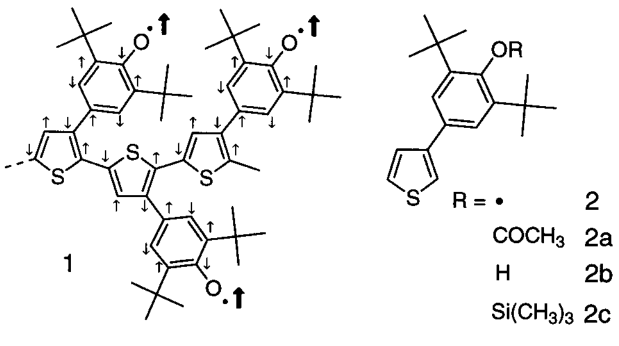
Introduction

Current interest in the synthesis of high-spin organic polyradicals is driven by the possibility of attaining purely organic magnetic molecules based upon intramolecular ferromagnetic interaction.[1,2] On the other hand, multifunctional molecules possessing not only the high-spin property but also an optical and/or an electrical property have been attractive for the past few years.[3] To the best of our knowledge, there has been no trial of organic polymers that are bifunctionally characterized by both high-spin and electrically conductive properties. (A magnetic property has been reported for doped and electrically conductive polyacetylene, polyaniline, and polypyrrole.[4]) Concerning the high-spin polymers, recently, Rajca et al.[5] demonstrated the highest-spin alignment for purely organic molecules, using cross-conjugated polyradicals such as poly(1,3-phenylenephenylmethine)s. In contrast to this approach, another strategy for high-spin molecules has been studied using a π-conjugated and alternant, but non-Kekulé-type, polymer bearing pendant multiple radical groups.[6] Advantages of these pendant-type polyradicals are as follows. (i) The ferromagnetic interaction functions between the pendant unpaired electrons through the π-conjugation. (ii) The high-spin alignment is not sensitive to a spin defect. (iii) A chemically stable radical species can be introduced on a polymer as a pendant group. The resultant polyradical could be isolated and easily handled during the measurement. That is, the π-conjugated and pendant radical-bearing polymers are one of the candidates for realizing the high-spin and electrically conductive polyradicals.

We have synthesized the pendant-type polyradicals based on poly(phenylenevinylene)[6a,e] and poly(phenyleneethynylene) backbones[6f,g] and successfully reported high-spin alignment in these polymers. We concluded that the less sterically hindered or highly planarized polymer conformation (e.g., realized for the poly(1,2-phenylenevinylene)-based polyradicals) favors good π-conjugation, effectively delocalizes spin distribution over the entire polymer, and is essential for the purpose of aligning the pendant spins.[6a] The precursors of these pendant-type polyradicals were synthesized via reductive polycondensation using palladium catalysts. While the palladium-catalyzed polycondensation gave the restrictedly head-to-tail-linked poly(phenylenevinylene)s and poly(phenyleneethynylene)s,[6c] their molecular weight remained below 10^4. Additionally, the corresponding monomers, i.e., asymmetrically radical precursor- and vinyl- or ethynyl-substituted halogenobenzenes, were synthesized via multisteps of tedious processes.

In this paper, we use polythiophene as the π-conjugated polymer backbone for the pendant-type polyradicals. A phenoxyl radical was selected as the pendant spin source because of its chemical stability and sufficient spin-exchange interaction.[6b] Using the simple spin polarization rule, the molecular connectivity requirement for high spin is schematically shown for a poly(3-oxyphenylthiophene)-based polyradical by the up−down arrows 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). In this study, we expected polythiophene or the poly(1,4-butadienediyl) backbone marked with small up−down arrows to be one of the effective spin-communication pathways for the high-spin polyradical, because poly-

Chart 1



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thiophene is known to possess highly developed and rigid conjugation[7] and to take a relatively planar and less coiling conformation even after the 3-substitution.[7]

There has been substantial interest in polythiophenes that have a large number of potential applications for electrical and optical materials.[8] Among such polythiophenes, regioregular 3-substituted polythiophenes have led to significant improvement of physical properties such as high conductivity, strong luminescence, and self-assembling capability. Head-to-tail-linked or regioselective polymerization has been established by McCullough et al.[9a,b] and Rieke et al.,[9c,d] which was performed via selective metalation at the 5-position of 3-alkyl-2-halogeno- or 2,5-dihalogenothiophene and the following reductive polymerization.

On the other hand, there has been much attention on oxidative polymerization as an atom economical polymer synthesis.[10] We have also reported oxidative polymerization to yield aromatic polymers such as poly(phenylene sulfide)s.[11] The oxidative polymerization proceeds at room temperature with high yield using a simple oxidizing agent or via a metal complex-catalyzed air oxidation. A monomer for the polymerization does not require any removing group in its structure or the polymerization system does not form any byproduct to be removed from the product. Recently, oxidative polymerization of 3-alkylthiophenes using ferric chloride has been successfully reported in preparing regioregular polythiophenes. Andersson et al.[12a] reported a polymerization under diluted condition to yield poly[3-(4-octylphenyl)thiophene] with a head-to-tail content of 94%. Ueda et al.[12b] improved the polymerization conditions for 3-hexylthiophene to yield poly(3-hexylthiophene) with a head-to-tail content of 91%. His group also reported oxovanadium-catalyzed air oxidation to yield poly[3-(4-dodecylphenyl)thiophene] with a head-to-tail content of 91%.[12c]

On the basis of the above-mentioned background, we have synthesized, in this paper, a non-Kekulé-type poly(3-oxyphenylthiophene) **1** via a convenient and regioregular oxidative polymerization of 3-acetoxyphenylthiophene **2a** and have, for the first time, succeeded in observing a high-spin state of the polythiophene-based polyradical **1**. There were two previous papers on the completely same molecular designing and similar synthetic trials of **1**. Yamamoto et al.[13] reported the oxidative and the Ni-catalyzed reductive polymerization of 3-(3′,5′-di-*tert*-butyl-4′-trimethylsiloxyphenyl)thiophene (**2c**) and 2,5-dibromo-3-(3′,5′-di-*tert*-butyl-4′-trimethylsiloxyphenyl)thiophene as the monomer, respectively, but the resultant polythiophenes were not regioregular.[13b] Lahti et al.[1,14] recently reported a similar synthesis using 3-(3′,5′-di-*tert*-butyl-4′-methoxyphenyl)thiophene and 3-(3′,5′-di-*tert*-butyl-4′-methyloxymethoxyphenyl)thiophene and succeeded in obtaining the regioregular polythiophenes. However, molecular weights of the polymers remained low, and Lahti et al. could not achieve to any magnetic measurement of the corresponding polyradicals.[14] In this paper, we found that the acetoxy-protected thiophene monomer **2a** was not deprotected during the oxidative polymerization with ferric chloride, to yield a high molecular weight and high regioregular polythiophene. We discuss also the regioregular polymer structure, alignment of the pendant phenoxyl spins, and other properties based on π-conjugation of this polythiophene.

Experimental Section

3-(3′,5′-Di-*tert*-butyl-4′-acetoxyphenyl)thiophene (2a). 3-Thiopheneboronic acid (Aldrich, 1.5 g, 11.7 mmol) and 4-bromo-2,6-di-*tert*-butylacetoxybenzene (3.49 g, 10.7 mmol) were dissolved in 1,2-dimethoxyethane (22.4 mL). To this solution was added tetrakis(triphenylphosphine)palladium(0) (0.776 g, 0.671 mmol) and 2 N Na_2CO_3 (22.4 mL), and the solution was stirred at 95 °C for 24 h. The organic layer was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. The diethyl ether layer was evaporated, and the crude product was purified by column chromatography on silica gel with a hexane/$CHCl_3$ (1/1) eluent. Recrystallization from hexane gave rhombic crystals of **1**: yield 82%; mp 83.0−83.5 °C. IR (KBr pellet, cm^{-1}): 3098 ($\nu_{\text{thiophene } \beta \text{ C-H}}$), 1755 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$ 600 MHz; ppm): 1.43 (s, 18H, *tert*-butyl), 2.39(s, 3H, $-OCOCH_3$), 7.37−7.42(m, 3H, thiophene), 7.56 (s, 2H, phenyl). ^{13}C NMR ($CDCl_3$, ppm): δ 22.59, 31.41, 35.42, 120.08, 124.72, 125.94, 133.12, 142.64, 142.70, 147.25 (aromatic), 171.0 (acetyl). MS (*m*/*z*): 330 (M^+), calcd for $M = 330.49$. Anal. Calcd for ($C_{20}H_{26}O_2S$): C, 72.7; H, 7.9; S, 9.7. Found: C, 72.2; H, 8.1; S, 9.7.

3-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)thiophene (2b). A THF solution (75.3 mL) of **2a** (8.3 g, 0.23 mmol), methanol (37.7 mL), and 10 N HCl (11.7 mL) was stirred at room temperature for 12 h. After the removal of methanol, the solution was extracted with ether. The crude product was purified using a silica gel column with a hexane/$CHCl_3$ (3/1) eluent. Recrystallization from hexane gave needle crystals of **3b** (6.0 g): yield 91%; mp 109.0−110.5 °C. IR (KBr pellet, cm^{-1}): 3622 (ν_{O-H}), 3082 ($\nu_{\text{thiophene } \beta \text{ C-H}}$). ^1H NMR ($CDCl_3$, 600 MHz, ppm): $\delta = 1.48$ (s, 18H, *tert*-butyl), 5.23 (s, 1H, OH), 7.29−7.36 (m, 3H, thiophene), 7.39 (s, 2H, phenyl). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 30.27$, 34.39, 118.72, 123.45, 125.77, 126.61, 127.53, 136.15, 143.37, 153.26. MS (*m*/*z*): 288 (M^+), calcd for $M = 288.45$. Anal. Calcd for ($C_{18}H_{24}OS$): C, 75.0; H, 8.4; S, 11.1. Found: C, 74.8; H, 8.3; S, 10.9.

3-(3′,5′-Di-*tert*-butyl-4′-trimethylsiloxyphenyl)thiophene (2c). **2c** was prepared as in the literature.[13b]

Polymerization. Ferric chloride (0.589 g, 3.63 mmol) was suspended in a $CHCl_3$ solution (45.4 mL) of **2a** (0.30 g, 0.908 mmol). The resulting dark green mixture was stirred for 24−200 h at −30 °C to room temperature under nitrogen. The reaction mixture was poured into methanol, and the deep red precipitate was collected and washed several times with water and methanol. The precipitate was dissolved in $CHCl_3$ and poured again into methanol. The deep red precipitate was washed with hot methanol, acetone, and hexane using a Soxhlet extractor and redissolved in hot CH_2Cl_2. The CH_2Cl_2 solution was poured into methanol to give the purified polymer of **1a**: yield 62%. IR (KBr, cm^{-1}): 1765 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$, 600 MHz, ppm): δ 1.34 (s, 18H, *tert*-butyl), 2.35 (s, 3H, $-OCOCH_3$), 6.92 (s, 1H, thiophene), 7.27 (s, 2H, phenyl). ^{13}C NMR ($CDCl_3$, ppm): δ 22.26, 31.49, 35.52, 127.45, 129.50, 131.18, 132.30, 134.37, 139.88, 142.43, 147.46, 170.92. Anal. Calcd for $(C_{20}H_{24}O_2S)_n$ ($n = 100$): C, 73.1; H, 7.3; S, 10.5. Found: C, 72.7; H, 7.2; S, 10.0.

The molecular weight of the polymer was measured by GPC (Tosoh LS-8000 polystyrene-gel column, THF eluent at 40 °C, polystyrene calibration).

Poly[3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)thiophene] (1b). **1a** (160 mg) was dissolved in a slight amount of THF. It was suspended in DMSO (47 mL), and 2.5 N KOH (3.0 mL) was added. The solution was stirred at 45 °C for 12 h under a nitrogen atmosphere and neutralized with 1 N HCl. The product was extracted with $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. The organic layer was evaporated and the solution poured into methanol to yield a deep red powder of **1b** (126 mg): yield 90%. IR (KBr, cm^{-1}): 3639 (ν_{O-H}). ^1H NMR ($CDCl_3$, 600 MHz, ppm): δ 1.39 (s, 18H, *tert*-butyl), 5.22 (s, 1H, OH), 6.86 (s, 1H, thiophene), 7.13 (s, 2H, phenyl). ^{13}C NMR ($CDCl_3$, ppm): δ 30.37, 34.40, 125.99, 126.59, 129.35, 130.08, 135.76, 140.30, 144.90, 153.52. Anal. Calcd for $(C_{18}H_{22}OS)_n$ ($n = 110$): C, 75.5; H, 7.7; S, 11.2. Found: C, 75.8; H, 7.6; S, 11.0.

Oxidation. A small excess of (n-C_4H_9)$_4$NOH was added to a toluene solution (2 mL) of **1b** (12.2 mg, 20 unit mmol/L), and the solution was stirred for 0.5 h under a nitrogen atmosphere. The solution was then vigorously stirred with 1 mL 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 the phenoxyl radical formation. The organic layer was washed with water and dried over anhydrous sodium sulfate to give a solution of **1**.

Electrochemical Measurements. A voltammetric investigation was carried out in CH_2Cl_2 in the presence of 0.1 M (n-C_4H_9)$_4$NBF$_4$ as a supporting electrolyte and a small amount of (n-C_4H_9)$_4$NOH as an alkaline material with a platinum working electrode using a function generator (Nikko Keisoku NPG-3) and a potentiogalvanostat (NPGS-301) at a scan rate from 100 to 25 mV.

ESR. ESR spectra were taken using a JEOL JES-TE200 ESR spectrometer with 100 kHz field modulation. The spin concentration of each sample was determined on the basis of the assumption of $S = {}^1/_2$ by careful integration of the ESR signal standardized with that of a TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) solution.

Magnetic Measurement. The toluene solutions of the phenoxyl polymer were immediately transferred to a diamagnetic capsule after the oxidation. The samples diluted with diamagnetic polystyrene were also prepared as described previously.[6a] Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured 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 (<10 ppm) was determined by Honda-Owen plots and subtracted from the overall magnetization. Diamagnetic susceptibility ($\chi_{\rm dia}$) of the sample solution and the capsule was estimated by the Curie plots of magnetic susceptibility.[15] The corrected magnetization data were fitted to Brillouin functions using a self-consistent version of the mean-field approximation.

Other Measurements. Thermal analyses were performed over a temperature range from 25 to 600 °C for thermogravimetry and over a temperature range of −50 to 550 °C with a heating rate of 8 °C/min for differential scanning calorimetry with a Seiko DSC 5200. The intrinsic viscosity of the toluene solution of polymer was measured at 25 °C using an Ubbelohde viscometer. Electrical conductivity was measured on the pressed pellets by a four-probe technique.

Results and Discussion

Oxidative Polymerization and Polymer Characterization. A 2,6-di-*tert*-butyl-4-acetoxyphenyl group was introduced on the 3-position of the thiophene ring via Suzuki coupling reaction[16] to almost quantitatively give 3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene (**2a**) as the monomer (Scheme 1). **2a** was oxidatively polymerized with 4 equiv of ferric chloride in a dilute chloroform solution (5−20 mM) and at low temperature (−30 °C to room temperature) for 24−200 h. The reaction mixture was poured into methanol, and the precipitated polymer was washed with water and methanol to remove the ferric ion. The polymer was reprecipitated in methanol, washed with hot methanol, acetone, and hexane, successively, using a Soxhlet extractor according to the procedure of Trznadel et al.,[17] and reprecipitated from dichloromethane to methanol. Poly(3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene) (**1a**) was obtained as bright red-orange powders. This purification completely dedoped the polymer and removed ferric chloride from the product (both Fe and Cl <0.001%; no Fe^{3+} signal in ESR). The polymer was soluble in common solvents such as chloroform, benzene, and THF.

Scheme 1

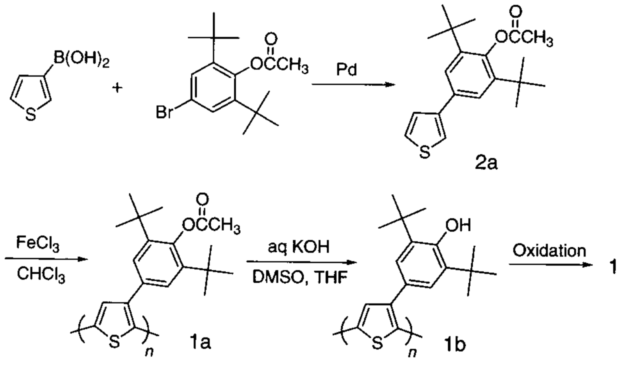

Table 1. Oxidative Polymerization of 3-(3′,5′-Di-*tert*-butyl-4′-acetoxyphenyl))thiophene (2a) and Molecular Weight,[a] Polydispersity,[a] and Head-to-Tail[d] Content of the Polythiophene (1a)

run	monomer concn (mM)	temp (°C)	time (h)	yield (%)	$M_n{}^a/10^4$	$M_w/M_n{}^a$	HT[b] (%)
1	100	50	5	81	9.2	2.9	69
2	100	r.t.	24	78	6.8	1.9	80
3	20	r.t.	24	84	14.4	1.7	83
4	5	r.t.	24	69	4.2	1.8	87
5	20	−5	150	86	8.2	1.9	89
6	20	−30	200	66	7.1	1.8	92
7	5	−30	200	62	3.3	1.7	96
8[c]	100	r.t.	24	63	0.14	1.2	
9[d]	5	−30	200	84	2.9	1.8	90
10[e]	5	−30	200	0			

[a] Average molecular weight and ratio of the number- and weight-average molecular weight measured by GPC. [b] Head-to-tail content determined with ^1H NMR of the thiophene β-proton. [c] Polymerization of **2c**. [d] Polymerization of 3-hexylthiophene. [e] Polymerization of **2b**.

The molecular weight of the polymer **1a** was more than 10^4. The polymerization of **2a** proceeded more effectively than that of the previously reported TMS-protected corresponding monomer **2c**: the latter gave only an oligomer also in this experiment (run 8 in Table 1). It was suggested that the TMS group of **2c** was deprotected with ferric chloride during the polymerization and that the phenolic **2b** significantly retarded the polymerization.

The regioregular or head-to-tail-linked polymer structure of **1a** was characterized by NMR spectroscopies. The ^1H and ^{13}C NMR spectra of polythiophenes provide sensitive probes of the substitution pattern in the polymer backbone.[18] Parts a and b of Figure 1 are typical examples of aliphatic and aromatic regions in ^1H and ^{13}C NMR spectra of **1a**. Two major strong singlet ^1H NMR signals (Figure 1a) at 6.92 and 7.27 ppm were assigned to the β-protons of the thiophene and phenyl protons, respectively. In the previous literature,[18a,c] the most intense peak at the highest field in the aromatic region has been attributed to a head-to-tail−head-to-tail configuration. Therefore, the signal at 6.92 ppm was ascribed to the head-to-tail linked β-thiophene proton, while very weak signals from 6.94 to 7.02 ppm were to other linkages. The content of the head-to-tail linkage of the thiophene units was calculated on the basis of the integration of these β-protons, e.g., 96% for the polymer obtained by run 7 (Table 1). The ^{13}C NMR spectrum (Figure 1b), on the other hand, simply showed eight signals in the aromatic region (ascribed to carbons of the phenyl and thiophene ring), which supports the high regioregularity of the polymer.

COSY, HMQC, and HMBC experiments on **1a** were applied to support the high regioregularity.[19] The carbon

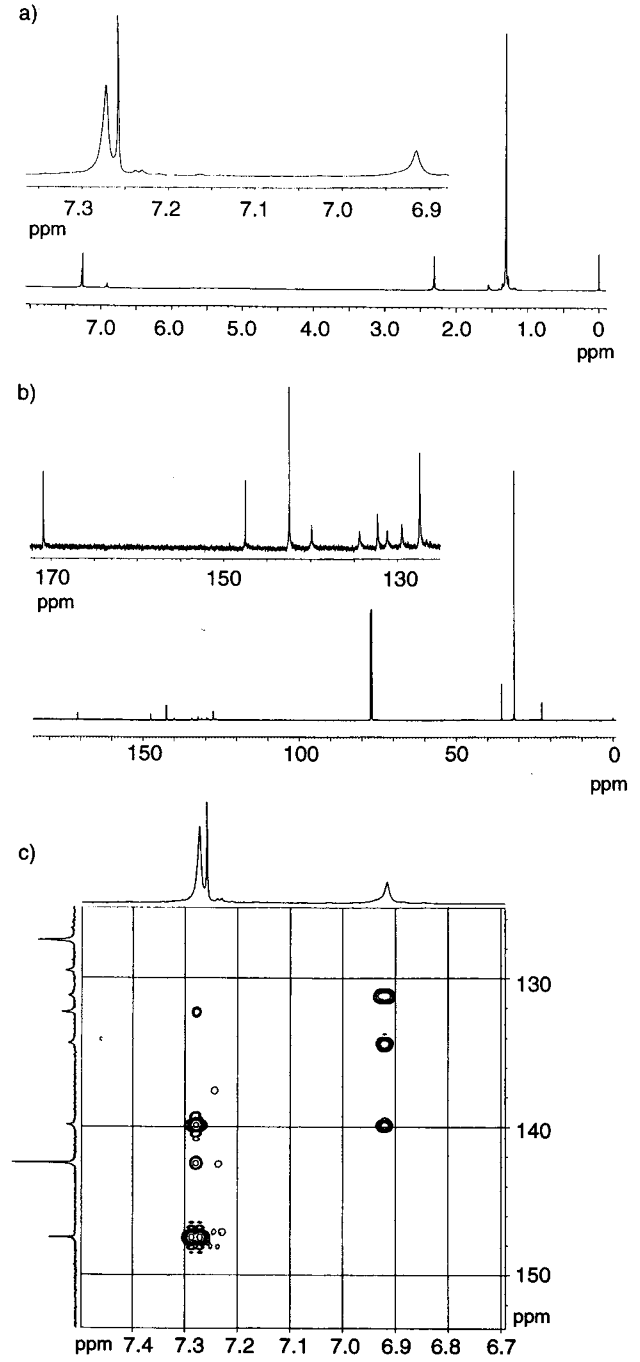

Figure 1. Whole and expanded aromatic region in ^{1}H (a) and ^{13}C NMR (b) spectra and HMBC spectrum of aromatic region (c) of **1a** (600 MHz in $CDCl_3$).

(129.5 ppm) directly bonded to the head-to-tail linked β-thiophene proton (6.92 ppm) was only found in the coupled HMQC spectrum of **1a**. The other three signals derived from the thiophene carbon at δ 130.1, 135.8, and 140.3 were detected in the HMBC experiment (Figure 1c). This indicates that the β-proton of thiophene reflects long-range correlations with almost all the related thiophene carbons. The head-to-tail content was also examined by integration of the signals at 5.21 (strong) and 5.22 ppm (very weak) of the hydroxy group of **1b** obtained below.

The head-to-tail content of the polythiophene (summarized in Table 1) increased for the polymerization of a more diluted monomer concentration and at lower temperature. The polymerization of 5 mM **2a** at −30 °C yielded the polythiophene **1a** with a molecular weight of 3.3×10^4 and a head-to-tail content of 96%. A control polymerization of 3-hexylthiophene under the same polymerization and purification conditions (run 9 in Table 1) gave a polymer with head-to-tail content of 90%. The high head-to-tail content of **1a** is considered to be caused by the aromatic and bulky 3-substituent: the 3,5-di-*tert*-butyl-4-acetoxyphenyl group; the aromatic substituent localizes the cationic radical on the 5-position of the thiophene and enhances the coupling selectivity with the electronegative 2-position of 3-substituted thiophene.[12a]

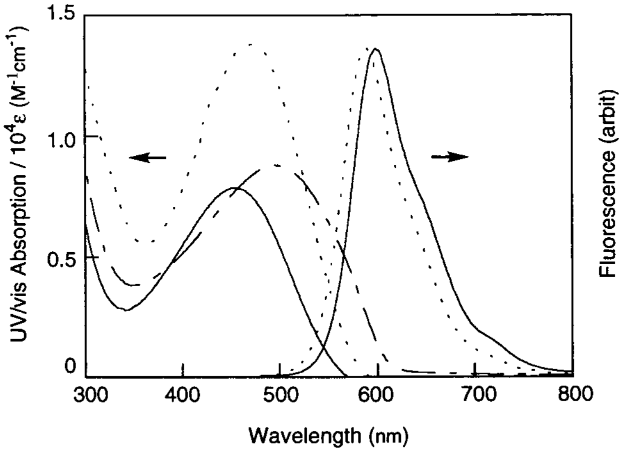

Figure 2. UV−vis absorption and fluorescence spectra of the acetoxy polymer **1a** in $CHCl_3$ solution (—) and solid state (- • -) and of the hydroxy polymer **1b** (- - -) in $CHCl_3$ solution (λ_{ex} = 470 nm).

The **1a** polymer was converted to the corresponding hydroxy polymer **1b** after complete elimination of the protecting acetyl group in alkaline solution.

The thermal decomposition temperature was estimated to be 496 and 430 °C for **1a** and **1b**, respectively, under N_2 atmosphere by TG-DTA analysis. DSC thermograms of **1a** and **1b** gave the glass transition temperature (T_g) at 5 and 0 °C, respectively, which were comparable with the previously reported $T_g = -10$ °C for poly(3-octylthiophene).[20]

Intrinsic viscosity of the solution **1a** (molecular weight estimated by GPC = 7.1×10^4) was 0.51 dL/g, which corresponded to the molecular weight of $(3.3-4.8) \times 10^4$ for poly(3-alkylthiophene).[21]

Fluorescence. The UV−vis absorption and fluorescence spectra of the polythiophenes **1a** and **1b** in chloroform solution are shown in Figure 2. The UV−vis absorption maximum was 460 and 470 nm for **1a** and **1b**, respectively, which were much longer than that of the previously reported **1b** (the oligomer prepared from the polymerization of **2c**; 426 (shoulder), 395 nm[11b]). It is known[9c] that the absorption of regioregular poly(3-alkylthiophene)s is bathochromically shifted by ca. 30 nm from that of the corresponding regiorandom one and is located at ca. 450 nm. The absorptions of **1a** and **1b** at longer wavelengths suggest an extended π-conjugation caused by both high molecular weight and regioregular structure.

The UV−vis absorption of **1a** was further shifted for the film state (λ_{max} = 493 nm). This bathochromic shift is consistent with that of the previously reported regioregular poly(3-(4-octylphenyl)thiophene) (from 467 nm in the chloroform solution to 493 nm in the film),[12a] which suggests a more planar conformation of **1a** in the solid state than that in the solution.

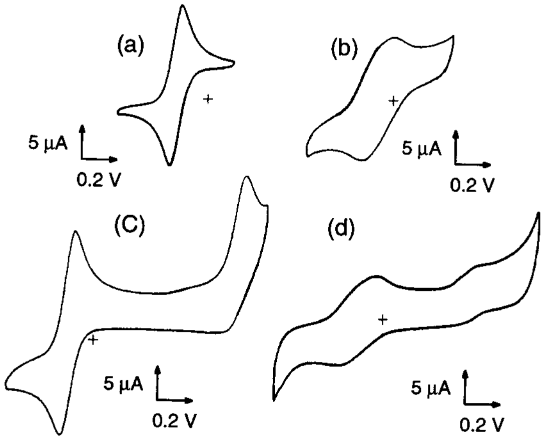

Figure 3. Cyclic voltammograms for the phenolate anion **2b** (a) and (c) and for **1b** (b) and (d) in CH_2Cl_2 with 0.1 M $(C_4H_9)_4NBF_4$ and $(n\text{-}C_4H_9)_4NOH$ (scanning rate = 50 mV/s).

Under UV irradiation, the polythiophenes **1a** and **1b** strongly fluorescence an orange color. The fluorescence maxima at 595−600 nm were also bathochromically shifted more than the previously reported **1b** (λ_{em} = 540−570 nm).[13b] The fluorescence intensity was proportional to the **1a** concentration for the dilute solution, but it significantly decreased beyond 0.3 mM. It was considered that the rodlike polymer **1a** aggregates at the higher concentration to quench the fluorescence. This result suggests that in solution the regioregular polythiophene chain adopts a more rodlike conformation based on its longer conjugation length in comparison with the regiorandom polymer.

The strong fluorescence of **1b** vanished after the phenoxyl radical generation. However, the fluorescence almost recovered to the initial intensity after a 1 week passage or the disappearance of the radical. This means that the radical generation on the pendant group does not cause any degradation of the polythiophene backbone.[22]

Polyradical Formation and Its Electrochemistry. Cyclic voltammograms of **1b** and **2b** in alkaline dichloromethane showed reversible oxidation and reduction peaks in the repeat potential sweep at room temperature (Figure 3a,b), which suggests chemical stability of the oxidized species (phenoxyl radical) of **1**. The redox potential (vs Ag/AgCl) was observed at −0.10 and −0.08 V for **2b** and **1b**, respectively. UV spectroscopy on the solution of **2b** under application of 0.1 V gave the visible absorption at λ_{max} = 553 nm (shoulder 600 nm for **1**), which was ascribed to the phenoxyl radical generation. The radical formation was also supported by the appearance of the ESR signal. The redox potential of **1b** (−0.08 V) was comparable with that of the pheoxyl (−0.13 V) pendantly substituted on the poly(phenylenevinylene) backbone.[6a]

A more anodic sweep of the monomeric thiophene derivative **2b** displayed only an oxidation wave (peak: 0.96 V) of the thiophene (without any reduction wave). This suggests that the thiophene moiety was oxidized and electrolytically polymerized on the electrode (Figure 3c).

On the contrary, a redox wave was observed, in addition to the phenolate−phenoxyl redox couple, at the anodic potential region for the polymer **1b** (Figure 3d), which suggests a reversible redox reaction of the thiophene moiety of **1b**. Each redox wave of the thiophene moiety and the phenoxyl group were independent. This means that it is possible to selectively oxidize the phenol groups using an appropriate oxidizing reagent without further oxidation of the polythiophene backbone.

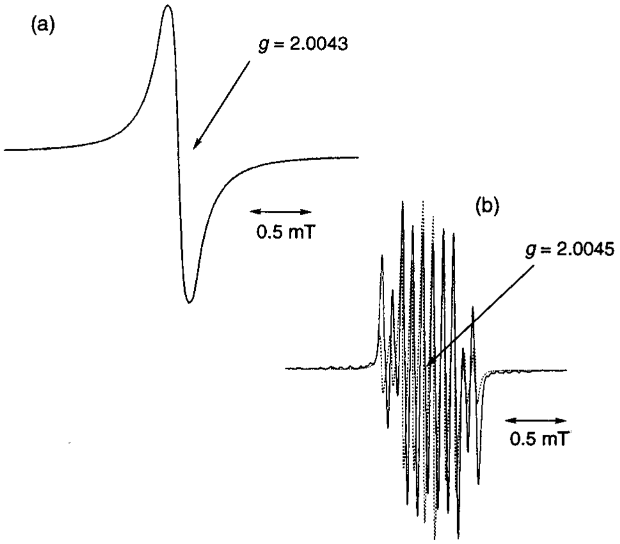

Figure 4. ESR spectra of the radical in 0.5 M toluene solution at room temperature. **1** with spin concentration = 0.28 spin/unit (a), **2** with spin concentration = 0.42 (b); the dashed line for the simulation.

ESR and Magnetic Properties of the Polyradical. The hydroxy precursor of **1b** was dissolved in toluene containing a small excess of tetra-*n*-butylammonium hydroxide and was oxidized heterogeneously with an aqueous solution of potassium ferricyanide (III). The ESR spectrum of the polyphenoxyl radical **1** gave a sharp and unimodal signal at $g = 2.0043$ (Figure 4a). The corresponding monoradical **2** (Figure 4b) showed a hyperfine structure at $g = 2.0045$ caused by the interaction with five protons of the phenyl and the thiophene ring (a_H = 0.172, 0.165, and 0.083 mT) (Lahti et al.[23] reported a better simulation for **2**). This indicates a delocalized spin distribution onto the thiophene moiety and suggests an effective spin interaction through the thiophene backbone.

The magnetization and static magnetic susceptibility (χ_{mol}) of the polyphenoxyl radical **1** with a spin concentration of 0.3 spin/unit were measured using a SQUID magnetometer. The inset in Figure 5 shows the $\chi_{mol}T$ plots for **1**, which deviated upward at low temperature from the theoretical value ($\chi_{mol}T = 0.375$) for $S = {}^1/_2$ and revealed a ferromagnetic interaction in the polyradical **1**. The **1** sample diluted with diamagnetic polystyrene yielded a stronger ferromagnetic deviation than that of the neat sample because the dilution minimized an antiferromagnetic and probably intermolecular interaction. The spin-exchange coupling constant (J) of the intramolecular spin alignment (or a force to align spins) through the polythiophene backbone was estimated by curve fitting the $\chi_{mol}T$ vs T data to the equation derived from a linear triradical system including a biradical and a monoradical.[15] The fitting gave $2J = 73\ \mathrm{cm}^{-1}$ for **1**, which was larger than that of the corresponding poly(phenylenevinylene)-based phenoxyl ($2J = 50\ \mathrm{cm}^{-1}$).[6a] Such a strong exchange interaction is probably ascribed to the shorter π-conjugated pathway distance between the pendant unpaired electrons in comparison with the poly(phenylenevinylene)-based polyradicals.

The normalized magnetization plots (Figure 5) of the polyradical **1** with a spin concentration of 0.3 were close

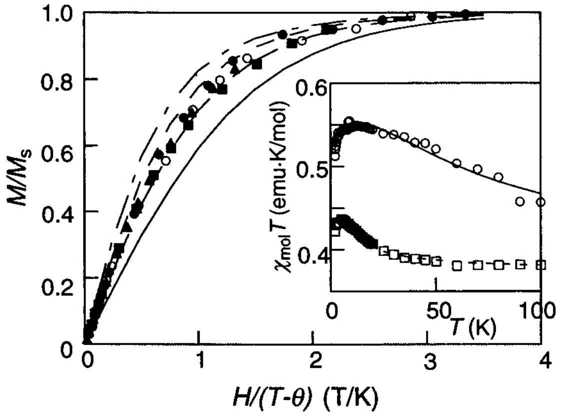

Figure 5. Normalized plots of magnetization (M/M_s) vs the ratio of magnetic field and temperature ($H/(T-\theta)$) for the polyradical **1** with spin concentration = 0.3 spin/unit in toluene at $T = 1.8$ K (○), 2.0 K (●), 2.5 K (■), and 3 K (▲) and the theoretical curves corresponding to the $S = {}^{1}/_{2}, {}^{2}/_{2}, {}^{3}/_{2}$, and ${}^{4}/_{2}$ Brillouin functions. Inset: $\chi_{mol}T$ vs T plots of **1** diluted with a polystyrene-diluted sample (○) and of neat **1** sample (□) (solid line is the theoretical curve calculated using eq in ref 16 for $2J = 73$ cm^{-1}, $\theta = -0.15$ K, $x_1 = 0$, $x_2 = 0.51$, $x_3 = 0.49$).

to the Brillouin curves for ${}^{2}/_{2}$ and ${}^{3}/_{2}$ at low temperature, indicating a high-spin ground state of the polythiophene-based polyradical **1**.

Lahti et al.[1,14] discussed the effects of a structural defect of **1b** using computer simulation. They described that the regioregularly substituted pendant groups enhance the planarity of the polythiophene backbone but that the regioirregular head-to-head linkage causes a large thiophene−thiophene torsion of 56°−58° and also increases the torsional angle between the phenyl ring and the thiophene backbone. The simulation suggests that the spin delocalization is prevented at the head-to-head-linked moiety. This regioirregular head-to-head linkage present at less than 4% in **1** of this experiment, which does not cancel out the ferromagnetic spin alignment established in the regioregular head-to-tail-linked part of the polymer. Unfortunately, only ca. 30% of the potential spin sites were successfully oxidized to the polyphenoxyl radical **1**; the average S value of ${}^{2}/_{2}$ to ${}^{3}/_{2}$ for **1** is considered to be reasonable by taking into account the spin defect of ca. 70%. The S value could be expected to be enhanced with the spin concentration.

Electrical Conductivity. The pristine polymers were almost electrical insulators (conductivity below 10^{-6} S cm^{-1}). After doping with iodine **1a** and **1b** showed a conductivity of 5.2×10^{-4} and 4.2×10^{-4} S cm^{-1}, respectively. On the other hand, the polyradical **1** itself showed 3.8×10^{-5} S cm^{-1}. It would be interesting to dope onto the polythiophene backbone of the polyradical, which provides a model of a ferromagnetic conductor.

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(15) For example, $\chi_{dia} = -3.78 \times 10^{-8}$ emu for **1**. $\chi_{mol}T = (N_A g^2 \mu_B{}^2 T)/(k(T-\theta))[x_3\{1 + \exp(-2J/kT) + 10\exp(J/kT)\}/12\{1 + \exp(-2J/kT) + 2\exp(J/kT)\} + x_2/(3 + \exp(-2J/kT)) + x_1/4]$, where x_1, x_2, and x_3 are the fraction of the doublet, the triplet, and the quartet, respectively ($x_1 + x_2 + x_3 = 1$). μ_B and θ are the Bohr magneton and the Weiss constant: Vleck, J. H. V. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: London, 1932.

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