Macromolecules

Folding-Induced Through-Space Magnetic Interaction of Poly(1,3phenyleneethynylene)-Based Polyradicals

Takashi Kaneko,*^{,†,‡,§} Hiromasa Abe,[†] Masahiro Teraguchi,^{†,‡,§} and Toshiki Aoki^{†,‡,§,||}

[†]Graduate School of Science and Technology, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

[‡]Center for Education and Research on Environmental Technology, Materials Engineering, Nanochemistry, Institute of Science and Technology, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

[§]Center for Transdisciplinary Research, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

^{II}Venture Business Laboratory, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

Supporting Information

ABSTRACT: We synthesized poly(1,3-phenyleneethynylene)s bearing galvinoxyl moieties. The absorption ratio of the anion form in 1 M KOH methanol solution between 309 and 294 nm (A_{309}/A_{294}) decreased with increasing degree of polymerization. The wide-angle X-ray scattering of the powder, which was prepared by precipitation in dilute hydrochloric acid solution from the anion form in 1 M KOH methanol solution, showed a crystalline peak at $2\theta = 28^{\circ}$. Polymers in which the chiral diethynyl-1,1'-binaphthyl moiety was inserted into the poly(1,3-phenyleneethynylene) chain were synthesized, and clear Cotton effects were observed in the absorption region of the galvinoxyl anion chromophore in the CD spectra taken in 1 M KOH–MeOH solution, indicating an excess of one-handed folded helical conformation. A relatively strong antiferromagnetic interaction was observed for the polyradicals



prepared by precipitating the anionic form from alkaline methanol solution accompanied with oxidation using aqueous $K_3Fe(CN)_6$ solution. These observations suggest that the relatively strong antiferromagnetic interaction of the polyradicals was caused by the close packing between galvinoxyl radicals induced by the formation of the folded helical structure.

INTRODUCTION

The π -conjugated polymers have attracted much attention as an organic material with various electronic properties. In particular, the magnetic property of π -conjugated polyradicals is one of the most attractive research fields concerning new functional polymer materials.¹⁻⁴ Numerous π -conjugated polymers substituted with pendant radicals have been synthesized and characterized,^{5,6} since ferromagnetic throughbond interaction between the pendant spins was theoretically predicted for regioregular head-to-tail π -conjugated macromolecules possessing conjugated pendant radicals by using simple polyene models and by analogy with other π -conjugated polymers.⁷⁻⁹ Some of them did exhibit the expected ferromagnetic behavior through their π -conjugated back-bone,^{10–27} but the through-space magnetic interaction based on their steric conformation has not been investigated well, except for a few examples.^{28,29} Poly(phenyleneethynylene) (PPE) is one of the most promising backbone structures for magnetic π -conjugated polyradicals, and various PPE-based polyradicals have been investigated.^{30–38} On the basis of molecular topology and spin polarization, regioregular head-totail linked poly(1,4- and 1,2-phenyleneethynylene) (1,4- and 1,2-PPE) structures are required for a ferromagnetic throughbond interaction between the pendant spins. On the other hand, a poly(1,3-phenyleneethynylene) (1,3-PPE) structure is a

cross-conjugated system, and the corresponding polyradicals bearing pendant spins at the 5-position have a disjoint nonbonding molecular orbital based on the theoretical prediction by Borden and Davidson.³⁹ This feature leads to minimized through-bond magnetic interaction between pendant spins, and in fact most of 1,3-PPE-based polyradicals have not shown strong magnetic properties.^{31–33} However, it is wellknown that some 1,3-PPEs can form folded helical conformations depending on their side groups and/or solvent. $^{40-48}$ Some theoretical calculations were performed for the magnetic property related to helical conformation,^{49,50} and it was reported that electron spin resonance (ESR) line broadening was observed by forming a folded helical conformation for oligo(1,3-phenyleneethynylene) bearing TEMPO radicals.⁵¹ In this study, we found a moderately strong through-space magnetic interaction, which was induced by forming the folded helical conformation of 1,3-PPE-based polyradicals bearing galvinoxyl side groups.

Received:November 7, 2012Revised:March 4, 2013Published:March 21, 2013

RESULTS AND DISCUSSION

Synthesis of Polymer 3. As shown in Scheme 1, the diiodobenzene 1 and diethynylbenzene 2 were polymerized in

Scheme 1. Polymerization of 1 and 2 and Formation of Polyradical 3b and Polyanion 3c



the presence of the $Pd(PPh_3)_4$ complex catalysts, and a yellow solid polymer 3a(19mer) was obtained by precipitation from the polymerization mixtures into methanol. The polymerization data for these resultant polymers are summarized in Table 1.

Table 1. Polymerization of 1 and 2 using $Pd(PPh_3)_4$ catalyst.^{*a*}

no.	[2]/[1]	fraction	yield (%)	$M_{\rm n}^{\ b} \ (\ \times \ 10^3)$	$M_{\rm w}/M_{\rm n}^{\ b}$	DP_n
1	0.9	1^c	95	10	1.8	19 ^f
2	0.5	1^d	17	7.0	1.2	8 ^g
		2^e	9	2.5	1.1	3 ^g

^{*a*}[1]₀ = 0.25 mol/L, [1]₀/[Pd(PPh₃)₄] = 20, [CuI]/[Pd(PPh₃)₄] = 4, THF/NEt₃ = 1:1 (v/v), r.t., 24 h. ^{*b*}Measured by GPC calibrated with polystyrene standard. ^{*c*}Methanol-insoluble fraction. ^{*d*}Methanol-insoluble fraction followed by preparative GPC. ^{*e*}Methanol-soluble fraction followed by preparative GPC. ^{*f*}Based on the monomer unit and estimated from M_n . ^{*g*}Based on the monomer unit and estimated from integration ratio of ¹H NMR.

Polymerization under the initial molar ratio of monomers [2]/[1] = 0.9 gave 3a(19mer) with the average degree of polymerization $(DP_n) = 19$ as predicted theoretically $(DP_n = (1 + [2]/[1])/(1 - [2]/[1]))$. The polymer 3a(19mer) was soluble in tetrahydrofuran (THF), chloroform, and benzene, but insoluble in methanol. On the other hand, polymerization under the initial molar ratio of monomers [2]/[1] = 0.5 gave oligomer 3a(8mer) with $DP_n = 8$ and 3a(3mer) with $DP_n = 3$ from methanol insoluble and soluble fraction, respectively, through separation by preparative GPC.

Helical Folding of Anion Form. UV–vis spectra of 3a in chloroform and benzene show absorption maxima at 420 nm attributed to the side chain hydrogalvinoxyl chromophore⁵² and multiple absorption bands at 250–350 nm attributed to the backbone chromophore (Figure 1). Polymer 3a was converted to the corresponding polyanion 3c by treatment with an alkali methanol solution and exhibited absorption maximum at 604 nm attributed to the galvinoxyl anion chromophore.⁵² Moore and co-workers previously reported that the solvophobically driven folding reaction of oligo(1,3-phenyleneethynylene)s bearing polar tri(ethylene glycol) side chains was confirmed by UV–vis studies; that is, the oligomers in chloroform were present in a random conformation, and the folded helical



Article

Figure 1. UV–vis absorption spectra of **3a**(19mer) in benzene (dotted line) and chloroform (broken line), and **3c**(19mer) (solid line) in 1 M KOH methanol at 20 °C (2.5×10^{-5} M based on the galvinoxyl unit).

conformation was preferred in acetonitrile and was accompanied by a decrease of the absorption at 305 nm.^{40,41} The absorption ratio between 309 and 294 nm (A_{309}/A_{294}) of 3c in 1 M KOH methanol solution decreases with increasing DP_{n} , while A_{309}/A_{294} of 3a in chloroform and benzene are comparable independent of the chain length (Figure 2). It



Figure 2. UV absorption ratio at 294 and 309 nm (A_{309}/A_{294}) versus chain length for **3a** in benzene (open square) and chloroform (open triangle), and **3c** (filled circle) in 1 M KOH methanol at 20 °C (2.5 × 10⁻⁵ M based on the galvinoxyl unit).

was confirmed that the polymer 3c(19mer) in 1 M KOH methanol solution preferred to form the folded helical conformation, while the chain lengths of 3c(8mer) and 3c(3mer) were not long enough to form the folded helical conformation. The population of the folded helical conformation increased at lower temperature, which was supported by the downward deviation of A_{309}/A_{294} values for 3c(19mer) in 1 M KOH methanol solution from trend in A_{309}/A_{294} versus temperature for 3c(8mer) and 3c(3mer) (Figure 3).

The wide-angle X-ray scattering (WAXS) of 3a(19mer) powder which was prepared by evaporation from the benzene solution of 3a(19mer) showed no crystalline peaks (Figure 4a). On the other hand, the WAXS of 3a(19mer) powder, which was prepared by precipitation in dilute hydrochloric acid solution from the anion form 3c(19mer) in 1 M KOH methanol solution, showed a crystalline peak at $2\theta = 28^{\circ}$, and the *d* spacing was calculated using the Bragg equation to be 3.2 Å, which would correspond to a distance consistent with



Figure 3. UV absorption ratio at 294 and 309 nm (A_{309}/A_{294}) versus temperature for **3c**(19mer) (filled circle), **3c**(8mer) (open square) and **3c**(3mer) (open triangle) in 1 M KOH methanol (2.5×10^{-5} M based on the galvinoxyl unit).



Figure 4. WAXS patterns of 3a(19mer) powder (a) prepared by evaporation from the benzene solution and (b) prepared by precipitation in dilute hydrochloric acid solution from the anion form 3c(19mer) in 1 M KOH methanol solution.

aromatic face-to-face stacking (Figure 4b).⁵³ This fact suggested that the folded helical conformation of 3c(19mer) formed in 1 M KOH methanol solution remained for 3a(19mer) powder prepared by precipitation in dilute hydrochloric acid solution.

Postpolymerization of 3a with Chiral Monomer and Formation of One-Handed Helical Conformation. The helical conformation essentially has an asymmetric nature, and the optical activity is induced by an excess of one-handed helical conformation. Moore and co-workers previously reported that an optically active binaphthol derivative inserted into the oligo(1,3-phenyleneethynylene) chain imparted a bias in the twist sense of the helical structure.⁵⁴ As shown in Scheme 2, the diiodo polymer 3a(19mer) and diethynyl binaphthol monomer 4 were polymerized in the presence of the $Pd(PPh_3)_4$ complex catalysts, and a yellow solid polymer 5a was obtained by precipitation from the polymerization mixtures into methanol. The polymerization data for these resultant polymers are summarized in Table 2. Because the polymer 5a had more than twice the molecular weight of the polymer 3a(19mer), 5amostly had the structure in which at least two 3a(19mer) units

Scheme 2. Postpolymerization of 3a with 4 and Formation of Polyradical 5b and Polyanion 5c



Table 2. Postpolymerization of 3a(19mer) with 4 Using Pd(PPh₃)₄ Catalyst^{*a*}

4	$M_{\rm n}$ of 3a (\times $10^4)$	yield ^b (%)	$M_{\rm n}{}^c$ ($\times 10^4$)	$M_{\rm w}/M_{\rm n}^{\ c}$
(R)	1.0	94	2.4	2.4
(S)	1.0	90	2.2	2.4
rac	1.0	97	3.6	

 a [**3a**]₀ = [**4**]₀ = 25 mmol/L, [**4**]₀/[Pd(PPh₃)₄] = 1, [CuI]/ [Pd(PPh₃)₄] = 4, THF/NEt₃ = 1:1 (v/v), room temperature, 24 h. ^bMethanol insoluble fraction. ^cMeasured by GPC calibrated with polystyrene standard.

were connected with the binaphthyl unit. The polymer **5a** was soluble in THF, chloroform, and benzene but insoluble in methanol.

The CD spectra of enantiomeric **5a** obtained by polymerization using (R)-**4** (abbreviated as (R)-**5a**) were measured in chloroform and benzene solution. Clear Cotton effects were observed for (R)-**5a** in the absorption region of the backbone binaphthyl chromophore (300–350 nm), although no induced CD signal appeared in the absorption region of the side chain hydrogalvinoxyl chromophore (420 nm) (Figure 5a). This behavior supports the random conformation of **5a** in chloroform and benzene as well as **3a**.

The polyradical **5b** was obtained by oxidizing the polymer **5a** by treatment of the polymer solution in degassed benzene with fresh PbO₂. The formation of the polyradical was supported by the appearance of the ESR signal at g = 2.0048 accompanied by the decrease of the peak at 420 nm attributed to the hydrogalvinoxyl chromophore and appearance of the peak at 470 nm attributed to the galvinoxyl radical chromophore in UV–vis spectra. However, the folded helical conformation was not observed for (*R*)-**5b** as well as (*R*)-**5a** in benzene because no induced CD signal appeared besides the backbone binaphthyl chromophore (Figure 5b).

On the other hand, the polyanion 5c obtained by dissolution of 5a in 1 M KOH methanol solution showed absorption maximum at 604 nm attributed to the galvinoxyl anion chromophore, and bisignated Cotton effects were observed for (*R*)-5c and (*S*)-5c, which were mirror images of each other, in the absorption region of the galvinoxyl anion chromophore (604 nm) (Figure 5c). The dynamic character of the folded helical conformation for 5c was confirmed by the CD intensities depending on temperature as shown in Figure 6. While (*R*)-5c in methanol with tetrabutylammonium hydroxide showed the bisignated Cotton effects as well as in 1 M KOH methanol solution, addition of benzene to the solution diminished the Cotton effects (Figure 7). This behavior



Figure 5. CD and UV–vis absorption spectra of (a) (R)-**5a** in chloroform, (b) (R)-**5b** (spin concentration = 0.58 spin/galvinoxyl unit) in benzene, and (c) (R)- and (S)-**5c** in 1 M KOH methanol solution at 20 °C (0.25 mM based on the galvinoxyl unit).



Figure 6. CD and UV–vis absorption spectra of (R)-5c at –10, +20, and +50 °C in 1 M KOH methanol solution (0.25 mM based on the galvinoxyl unit).

supports the solvophobically driven folding reaction of 5c because benzene and methanol were good and poor solvents for 5a, respectively.

Formation of Folded Helical Polyradical and Magnetic Property. As mentioned above, the polyradical Sb obtained by oxidizing the polymer Sa in benzene, where the suffix "r" was added to the thus obtained polyradical, i.e., as Sb_r, showed no characteristics for the folded helical conformation. On the other hand, Sb powder was obtained by precipitation from the alkaline methanol solution of Sc accompanied with oxidation using aqueous $K_3Fe(CN)_6$ solution, where the suffix "h" was added to the thus obtained polyradical, i.e., as Sb_h. Unfortunately, the obtained Sb_h powder was practically insoluble in organic solvents, but the formation of polyradical was confirmed by the appearance of the ESR signal at g =2.0048, indicating the formation of the galvinoxyl radical. The organic solvent-insoluble **3b**_h(19mer) was obtained from



Figure 7. CD and UV–vis absorption spectra of (R)-5c in 10% tetrabutylammonium hydroxide methanol/benzene solution at 20 °C (0.25 mM based on the galvinoxyl unit).

3c(19mer) in alkaline methanol solution as well, while 3a(19mer) in benzene was oxidized to give $3b_r(19\text{mer})$, which probably had the random conformation in benzene. The insolubility of $3b_h(19\text{mer})$ and $5b_h$ in organic solvents was probably caused by predominant formation of the dense and rigid helical structure through the oxidation process and/or the entanglement of the polymer chain induced by the folding reaction.

The static magnetic susceptibility (2–100 K at 0.5 T) of 3b(19mer) and 5b powders were measured using a SQUID magnetometer. The $\chi_{mol}T$ versus T plots of $3b_r(19mer)$ and $5b_r$ powders are shown in Figure 8, where χ_{mol} is normalized to



Figure 8. $\chi_{mol}T$ versus *T* plots of $3b_r(19mer)$ (open circle; spin concentration = 0.57 spin/galvinoxyl unit), (*R*)- $5b_r$ (open square; 0.53 spin/galvinoxyl unit) and *rac*- $5b_r$ (open triangle; 0.47 spin/galvinoxyl unit) prepared by evaporation from the benzene solution. Solid line: The Curie–Weiss fitting using $\Theta_w = -0.89, -0.78$, and -0.78 K for $3b_r(19mer)$, (*R*)- $5b_r$, and *rac*- $5b_r$, respectively.

0.375 (S = 1/2) at higher temperature by spin concentration. The $\chi_{mol}T$ versus T data fitted the Curie–Weiss law ($\chi_{mol} = 0.375/(T - \Theta_w)$) with a small Weiss temperature (Θ_w), indicating weak antiferromagnetic interaction as shown in Figure 8. Figure 9 shows the $\chi_{mol}T$ versus T plots of $3b_h(19mer)$ and $5b_h$ powders. Linear fitting of the $1/\chi_{mol}$ versus T data at higher temperature range (100-300 K) gave $\Theta_w = ca. -13$ K (see Figure S16 in the Supporting Information) indicating relatively strong antiferromagnetic interaction, while the $\chi_{mol}T$ versus T plots deviate upward at a lower temperature from the Curie–Weiss relationship. This deviation from the Curie–Weiss law indicates that the magnitude of magnetic interaction between the radicals broadly varied owing to the heterogeneous morphology probably mixing the random conformation, the perturbed helical conformation and the



Figure 9. $\chi_{mol}T$ versus *T* plots of $3\mathbf{b}_h(19\text{mer})$ (open circle; spin concentration = 0.54 spin/galvinoxyl unit), (*R*)- $5\mathbf{b}_h$ (open square; 0.40 spin/galvinoxyl unit) and *rac*- $5\mathbf{b}_h$ (open triangle; 0.54 spin/galvinoxyl unit) prepared by precipitating from alkaline methanol solution of anion form accompanied with oxidation using aqueous $K_3Fe(CN)_6$ solution. Solid line: The Curie–Weiss relation with $\Theta_w = -13$.

folded helical conformation of polyradicals and the various magnetic coupling sets included the partially strong antiferromagnetic coupling.

On the basis of theoretical prediction,³⁹ the through-bond magnetic interaction of 3b(19mer) and 5b would be negligible or weak antiferromagnetic as shown in Figure 10a. In fact, the



Figure 10. (a) Connectivity pattern for 3b(19mer) and 5b, and (b) plausible through-space magnetic interaction between galvinoxyl radials in close proximity induced by the formation of the folded helical structure.

magnetic behavior of $3b_r(19mer)$ and $5b_r$, which had the random conformation in Figure 8, is weak antiferromagnetic, as is that of poly(binaphthyl-6,6'-diylethynylene-1,3-phenyleneethynylene) bearing galvinoxyl side groups, which did not form the folded helical conformation.⁵⁵ That is, the relatively strong antiferromagnetic interaction of $3b_h(19mer)$ and $5b_h$ as shown in Figure 9 is consequently caused by close packing between galvinoxyl radicals induced by the formation of the folded helical structure as shown in Figure 10b.

CONCLUSION

We synthesized 1,3-PPEs bearing galvinoxyl moieties. The folded helical conformation is preferred for the anion form in alkaline methanol solution owing to the solvophobic interaction, and the corresponding polyradical precipitates were obtained by oxidation using aqueous $K_3Fe(CN)_6$ solution. The static magnetic susceptibility of the polyradical thus obtained exhibited a relatively strong antiferromagnetic behavior compared with the weak antiferromagnetic behavior of the polyradical, which was prepared by evaporating solvent from the benzene solution of the polyradicals followed by drying in vacuum. This fact suggests that the relatively strong antiferromagnetic interaction of the polyradicals was caused by close packing between galvinoxyl radicals induced by the formation of the folded helical structure. This finding will lead to the development of new polyradicals with electronic, magnetic, and chiroptical properties through the fusion with optically active helical polymers and the control of hierarchical structures.

EXPERIMENTAL SECTION

Materials. The monomer 2^{37} and $4^{56,57}$ were synthesized according to the literature procedures. Tetrakis(triphenylphosphine)-palladium (0) (Pd(PPh₃)₄) (Aldrich Co.) was used without further purification. Other conventional reagents were used as-received or purified by conventional methods.

(3,5-Diiodophenyl)hydrogalvinoxyl (1). To a solution of 1,3,5triiodobenzene (12 g, 27 mmol) in ether (180 mL) was added n-butyl lithium in hexane (17.5 mL, 28 mmol, 1.6 M) under nitrogen at -70 °C. The mixture was stirred for 30 min, and a solution of 4,4'diacetoxy-3,3',5',5-tetra-tert-butylbenzophenone (14 g, 27 mmol) in ether (180 mL) were added. The mixture was stirred at -70 °C for 2 h and at room temperature for another 1 h. It was neutralized with dilute aqueous hydrochloric acid, and extracted with ether. The extract was dried over anhydrous sodium sulfate, solvent was evaporated, and then the residue was recrystallized from hexane to give α, α -bis(3,5-di-tertbutyl-4-acetoxyphenyl)-3,5-diiodobenzyl alcohol (9.3 g, 11 mmol) as colorless crystals. Yield: 41%. Mp 209-210 °C. ¹H NMR (CDCl₃, 270 MHz; ppm): δ 7.97 (t, 1H, J = 1.4 Hz, ArH), 7.70 (d, 2H, J = 1.4 Hz, ArH), 7.22 (d, 2H, J = 2.4 Hz, ArH), 6.99 (d, 2H, J = 2.4 Hz, ArH), 2.68 (s, 1H, OH), 2.33 (s, 6H, -CH₃), 1.28 (s, 18H, C(CH₃)₃), 1.23 (s, 18H, C(CH₃)₃). ¹³C NMR (CDCl₃; ppm): δ 170.68, 150.90, 147.23, 143.51, 142.13, 141.82, 141.64, 136.24, 126.25, 125.86, 94.08, 81.27, 35.71, 35.62, 31.50, 31.42, 22.73. IR (KBr pellet; cm⁻¹): 3582 $(\nu_{\rm O-H})$, 1763 $(\nu_{\rm C=O})$. The obtained compound (8.5 g, 10 mmol) was dissolved in DMSO (100 mL) under a nitrogen atmosphere, and then aqueous 5 M KOH (60 mL) was added to the solution. The mixture was stirred at 80 °C for 12 h, cooled to room temperature, and neutralized with aqueous 4 N hydrochloric acid. The organic product was extracted with chloroform, washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated, and then the residue was recrystallized from hexane to give (3,5-diiodophenyl)hydrogalvinoxyl (1) (6.1 g, 8.2 mmol) as reddish orange crystals. Yield 82%, mp 223–224 °C. ¹H NMR (CDCl₃, 270 MHz; ppm): δ 8.11 (t, 1H, J = 1.0 Hz, ArH), 7.59 (d, 2H, J = 1.0 Hz, ArH), 7.18 (d, 1H, 1.8 Hz, ArH (quinoid)), 7.02 (d, 1H, 1.8 Hz, ArH (quinoid)), 6.99 (s, 2H, ArH), 5.57 (s, 1H, OH), 1.43 (s, 18H, C(CH₃)₃), 1.27 (s, 18H, C(CH₃)₃). ¹³C NMR (CDCl₃; ppm): δ 185.86, 155.65, 147.38, 147.29, 145.09, 144.56, 140.08, 135.48, 132.11, 131.33, 130.49, 129.84, 129.69, 93.87, 35.43, 35.42, 34.50, 30.36, 29.72, 29.59. IR (KBr pellet; cm⁻¹): 3630 (ν_{O-H}), 1584 ($\nu_{quinoid}$). Anal. Calcd for C₃₅H₄₄I₂O₂: C, 56.0; H, 5.9; I, 33.8. Found: C, 56.3; H, 5.9; I, 33.6.

Polymerization. Typical procedure was described as follows. The monomer 1 (1.5 g, 2.0 mmol), 2 (0.98 g, 1.8 mmol), tetrakis-(triphenylphosphine)palladium (0) (0.12 g, 0.10 mmol), and copper iodide (0.076 g, 0.40 mmol) were placed in a Schlenk tube equipped with a three-way stopcock, a rubber septum, and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. THF (4.0 mL) and triethylamine (4.0 mL) were transferred to the tube, and the solution was stirred at room temperature for 24 h. The solution was treated with aqueous 3 N hydrochloric acid, extracted with chloroform, washed with saturated

saline, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by precipitation from chloroform into methanol to yield the polymer **3a** as yellow powder. The yield and the molecular weight are given in Table 1, no. 1. ¹H NMR (CDCl₃, 270 MHz; ppm) δ 7.91 (br, 2H, ArH), 7.68 (br, (*m*-2)H, ArH), 7.62 (br, 2H, ArH), 7.38 (br, (2*m*-2)H, ArH), 7.20 (br, *m*H, ArH), 7.00 (br, 3*m*H, ArH), 5.53 (s, *m*H, OH), 1.39 (s, 18*m*H, *tert*-butyl), 1.26 (s, 9*m*H, *tert*-butyl), 1.21 (s, 9*m*H, *tert*-butyl). IR (KBr, cm⁻¹): 3630 (ν_{O-H}), 2957–2870 (ν_{C-H}), 1610 ($\nu_{quinoid}$).

Postpolymerization. Typical procedure was described as follows. The monomer 3a (0.40 g, 0.040 mmol), 4 (0.020 g, 0.040 mmol), tetrakis(triphenylphosphine)palladium(0) (0.046 g, 0.040 mmol), and copper iodide (0.030 g, 0.16 mmol) were placed in a Schlenk tube equipped with a three-way stopcock, a rubber septum, and a Tefloncoated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. THF (1.6 mL) and triethylamine (1.6 mL) were transferred to the tube, and the solution was stirred at room temperature for 24 h. The solution was treated with aqueous 3 N hydrochloric acid, extracted with chloroform, washed with saturated saline, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by precipitation from chloroform into methanol to yield the polymer as yellow powder. The yield and the molecular weight are given in Table 2. ¹H NMR (CDCl₃, 270 MHz; ppm) δ 8.04 (br, 2H, ArH in 4), 7.85 (br, 2H, ArH in 4), 7.68 (br, mH, ArH in 3a), 7.38 (br, 2mH, ArH in 3a), 7.21 (br, mH, ArH in 3a), 7.00 (br, 3mH, ArH in 3a), 5.53 (s, mH, OH), 3.75-3.94 (m, 4H, CH₂ in hexyloxy), 1.39 (m, 18mH, tert-butyl), 1.26 (s, 9mH, tert-butyl), 1.20 (s, 9mH, tert-butyl), 0.88 (br, 12H, CH₂ in hexyloxy), 0.72 (t, 6H, J = 6.9 Hz, CH₃ in hexyloxy). IR (KBr, cm⁻¹): 3630 $(\nu_{\rm O-H})$, 2957–2870 $(\nu_{\rm C-H})$, 1609 $(\nu_{\rm quinoid})$.

Oxidation. The polyradicals were prepared by chemical oxidation of the corresponding hydroxyl precursors with PbO_2 or $K_3Fe(CN)_6$ under nitrogen in a glovebox as follows.

Oxidation Using PbO_2 . A degassed benzene solution of the hydroxyl precursor (1 mM per galvinoxyl unit) was treated with 20 equiv of recently prepared PbO_2 and was vigorously stirred for 1 h. After filtration, the solution was used for spectroscopic measurement. The powder sample was prepared by evaporating the solvent and by drying in vacuo, and was used for spectroscopic and magnetic measurement.

Oxidation Using $K_3Fe(CN)_6$. A degassed 1 M KOH methanol solution of the anion form (1 mM per galvinoxyl unit) was treated with 100 equiv of aqueous $K_3Fe(CN)_6$ solution (0.1M) to form precipitates. After vigorously stirring for 0.5 h, the precipitates were washed with water thoroughly and then with methanol. The obtained precipitates were dried in vacuo, and were used for ESR and magnetic measurement.

ESR Spectroscopic Measurement. Solutions for ESR experiments were prepared under nitrogen in a glovebox and placed in quartz tubes sealed with septa and Parafilm. ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with 100 kHz field modulation in the X-band frequency region. Signal positions were calibrated against an external standard of Mn^{2+}/MgO (g = 1.981). The spin concentrations of each sample were determined by careful double integration of the ESR signal calibrated with that of the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) standard solution.

Magnetic Measurement. The powder samples were contained in a diamagnetic capsule. The static magnetic susceptibility was measured from 2 to 300 K in a field of 0.5 T using a Quantum Design MPMS-XL1 SQUID magnetometer. $\chi_{mol}T$ versus T data were corrected for diamagnetism of the sample and the capsule, where the diamagnetism of the sample and the capsule was determined from the theoretical calculation using the Pascal, Gallais, and Labarre method⁵⁸ and from SQUID measurements, respectively.

Other Measurements. IR spectra were obtained using a Shimadzu FTIR 8100 spectrometer. NMR (¹H, ¹³C) spectra were measured using a JEOL GSX-270 (270 MHz) spectrometer. Average molecular weights (M_n and M_w) were evaluated by GPC calibrated by polystyrene standard at 25 °C on THF eluent using Jasco Liquid Chromatograph instruments with PU-2080, DG-2080-53, CO-2060,

UV2070, CD-2095, and polystyrene gel columns (Shodex KF-807L). CD and UV–vis absorption spectra were recorded using a Jasco J-720WI Spectropolarimeter with a peltier controller for temperatures at –10 to +50 °C (a quartz cell of 1 mm path length; sample concentration = 0.1–1 mM based on the galvinoxyl unit), and were analyzed using the associated J-700 software. UV–vis absorption spectra were recorded on a Jasco Ubest V-550 UV–vis spectrometer with a peltier controller for temperatures at –10–50 °C (a quartz cell of 10 mm path length; sample concentration = 2.5×10^{-5} M based on the galvinoxyl unit). The wide angle X-ray scattering measurements were performed using a Rigaku Geigerflex with a graphitemonochromatized Cu K α radiation, which was supplied at 40 kV and 20 mA.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra of 1, 3a(19mer), 3a(8mer), 3a(3mer), (*R*)-5a and (*S*)-5a; UV-vis absorption spectra of 3a and 3c for Figure 2 and 3; CD and UV-vis absorption spectra of (*R*)-5a in benzene; ESR spectra of (*R*)-5b; molecular mechanics modeling of 3c; and $1/\chi_{mol}$ versus *T* plots of 3b_h(19mer), (*R*)-5b_h and *rac*-5b_h. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kanetaka@gs.niigata-u.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research (B) (No. 24310081) from JSPS and by a Grant for the Promotion of Niigata University Research Projects.

REFERENCES

(1) Magnetic Properties of Organic Materials; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; Vol. 279.

(2) *Molecular Magnetism: New Magnetic Materials*; Itoh, K., Kinoshita, M., Eds.; Kodansha and Gordon & Breach: Tokyo and Amsterdam, 2000.

- (3) Rajca, A. Chem. Rev. 1994, 94, 871.
- (4) Rajca, A. Chem.-Eur. J. 2002, 8, 4834-4841.
- (5) Aoki, T.; Kaneko, T.; Teraguchi, M. Polymer 2006, 47, 4867.
- (6) Nishide, H. Adv. Mater. 1995, 7, 937.
- (7) Ovchinnikov, A. A. Theor. Chim. Acta 1978, 47, 297.
- (8) Yamaguchi, K.; Toyoda, Y.; Fueno, T. Synth. Met. 1987, 19, 81.
- (9) Lahti, P. M.; Ichimura, A. S. J. Org. Chem. 1991, 56, 3030.
- (10) Kaneko, T.; Toriu, S.; Kuzumaki, Y.; Nishide, H.; Tsuchida, E. Chem. Lett. **1994**, 2135.

(11) Nishide, H.; Kaneko, T.; Toriu, S.; Kuzumaki, Y.; Tsuchida, E. Bull. Chem. Soc. Jpn. **1996**, 69, 499.

(12) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Yamaguchi, K. J. Am. Chem. Soc. 1995, 117, 548.

(13) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Lahti, P. M. J. Am. Chem. Soc. **1996**, 118, 9695.

(14) Takahashi, M.; Nakazawa, T.; Tsuchida, E.; Nishide, H. *Macromolecules* **1999**, *32*, 6383.

(15) Nishide, H.; Takahashi, M.; Takashima, J.; Tsuchida, E. Polym. J. 1999, 31, 1171.

(16) Nishide, H.; Maeda, T.; Oyaizu, K.; Tsuchida, E. J. Org. Chem. 1999, 64, 7129.

(17) Miyasaka, M.; Yamazaki, T.; Tsuchida, E.; Nishide, H. *Macromolecules* **2000**, 33, 8211.

(18) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. J. Am. Chem. Soc. 2001, 123, 5942.

- (19) Kaneko, T.; Matsubara, T.; Aoki, T. Chem. Mater. 2002, 14, 3898.
- (20) Kaneko, T.; Makino, T.; Miyaji, H.; Teraguchi, M.; Aoki, T.; Miyasaka, M.; Nishide, H. J. Am. Chem. Soc. **2003**, *125*, 3554.
- (21) Kaneko, T.; Makino, T.; Miyaji, H.; Onuma, A.; Teraguchi, M.; Aoki, T. *Polyhedron* **2003**, *22*, 1845.
- (22) Murata, H.; Takahashi, M.; Namba, K.; Takahashi, N.; Nishide, H. J. Org. Chem. **2004**, *69*, 631.
- (23) Murata, H.; Yonekuta, Y.; Nishide, H. Org. Lett. 2004, 6, 4889.
 (24) Itoh, T.; Jinbo, Y.; Hirai, K.; Tomioka, H. J. Am. Chem. Soc. 2005. 127, 1650.
- (25) Kaneko, T.; Onuma, A.; Ito, H.; Teraguchi, M.; Aoki, T. Polyhedron 2005, 24, 2544.
- (26) Fukuzaki, E.; Nishide, H. J. Am. Chem. Soc. 2006, 128, 996.
- (27) Oka, H.; Kiyohara, Y.; Kouno, H.; Tanaka, H. Polyhedron 2007, 26, 2059.
- (28) Murata, H.; Miyajima, D.; Nishide, H. *Macromolecules* **2006**, *39*, 6331.
- (29) Kaneko, T.; Katagiri, H.; Umeda, Y.; Namikoshi, T.; Marwanta, E.; Teraguchi, M.; Aoki, T. *Polyhedron* **2009**, *28*, 1927.
- (30) Sasaki, S.; Iwamura, H. Chem. Lett. 1992, 1759.
- (31) Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 3698.
- (32) Miura, Y.; Ushitani, Y. Macromolecules 1993, 26, 7079.
- (33) Miura, Y.; Issiki, T.; Ushitani, Y.; Teki, Y.; Itoh, K. J. Mater. Chem. 1996, 6, 1745.
- (34) Shultz, D. A.; Hollomon, M. G. Chem. Mater. 2000, 12, 580.
- (35) Meurs, P. J.; van Janssen, R. A. J. J. Org. Chem. 2000, 65, 5712.
- (36) Akita, T.; Koga, N. Polyhedron 2001, 20, 1475.
- (37) Wautelet, P.; Turek, P.; Moigne, J. Le Synthesis 2002, 2002, 1286.
- (38) Kaneko, T.; Yoshimoto, S.; Hadano, S.; Teraguchi, M.; Aoki, T. Polyhedron 2007, 26, 1825.
- (39) Borden, W. T.; Davidson, E. R. J. Am. Chem. Soc. 1977, 99, 4587.
- (40) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. Science **1997**, 277, 1793.
- (41) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. J. Am. Chem. Soc. 1999, 121, 3114.
- (42) Prince, R. B.; Brunsveld, L.; Meijer, E. W.; Moore, J. S. Angew. Chem., Int. Ed. 2000, 39, 228.
- (43) Lahiri, S.; Thompson, J. L.; Moore, J. S. J. Am. Chem. Soc. 2000, 122, 11315.
- (44) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. Chem. Rev. 2001, 101, 3893.
- (45) Inoue, M.; Teraguchi, M.; Aoki, T.; Hadano, S.; Namikoshi, T.; Marwanta, E.; Kaneko, T. *Synth. Met.* **2009**, *159*, 854.
- (46) Liu, R.; Shiotsuki, M.; Masuda, T.; Sanda, F. *Macromolecules* **2009**, *42*, 6115.
- (47) Banno, M.; Yamaguchi, T.; Nagai, K.; Kaiser, C.; Hecht, S.; Yashima, E. J. Am. Chem. Soc. **2012**, *134*, 8718.
- (48) Suzuki, S.; Ishiwari, F.; Nakazono, K.; Takata, T. Chem. Commun. 2012, 48, 6478.
- (49) Nath, K.; Taylor, P. L. Mol. Cryst. Liq. Cryst. 1991, 205, 87.
- (50) Yoshizawa, K.; Hoffmann, R. Chem.—Eur. J. 1995, 1, 403.
- (51) Matsuda, K.; Stone, M. T.; Moore, J. S. J. Am. Chem. Soc. 2002, 124, 11836.
- (52) Gierke, W.; Harrer, W.; Kirste, B.; Kurreck, H.; Reusch, J. Z. Naturforsch. **1976**, 31b, 965.
- (53) The *d* spacing 3.2 Å was shorter than typical aromatic face-to-face stacking (\sim 3.4 Å). Solvophobic effects probably shrank the face-to-face distance to be a modeling structure as shown in Figure S15 (Supporting Information).
- (54) Gin, M. S.; Yokozawa, T.; Prince, R. B.; Moore, J. S. J. Am. Chem. Soc. 1999, 121, 2643.
- (55) Kaneko, T.; Abe, H.; Namikoshi, T.; Marwanta, E.; Teraguchi, M.; Aoki, T. *Synth. Met.* **2009**, *159*, 864.
- (56) Ma, L.; Hu, Q.-S.; Musick, K. Y.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1996**, *29*, 5083.

(57) Ma, L.; Hu, Q.-S.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1997**, *30*, 204.

(58) Gupta, R. R. In Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology; Hellwege, K.-H., Hellwege, A. M., Eds.; New Series, Group II: Atomic and Molecular Physics 16; Springer-Verlag: Berlin, 1986; Vol. 16: Diamagnetic Susceptibility.