Syntheses and Magnetic Characterization of Poly(1,3-phenyleneethynylene) with Pendant Nitronyl Nitroxide Radicals

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ABSTRACT: The $(PPh_3)_2PdCl_2$–CuI-catalyzed polycondensation of 4,4,5,5-tetramethyl-3-oxido-2-(3,5-diethynylphenyl)-2-imidazolin-1-yloxyl with 5-*tert*-butyl- or 5-hexyl-1,3-diiodobenzene in triethylamine–pyridine at room temperature afforded nitronyl nitroxide pendant poly(1,3-phenyleneethynylene) polyradicals in almost quantitative yields. The polyradicals obtained as a blue powder are soluble in CH_2Cl_2 and $CHCl_3$, partially soluble in THF and DMF, and insoluble in methanol, ether, and common hydrocarbons such as hexane and benzene. The number-average molecular weights ($\bar{M}_n$) determined by GPC are 4300–4800, and the spin concentrations determined by electron spin resonance (ESR) are 1.12×10^{21}–1.33×10^{21} spins/g (82–91% spin/repeating unit). Both the solution (CH_2Cl_2) and powder ESR spectra of the polyradicals consist of a hyperfine-smeared single line, suggesting that spin-exchange narrowing takes place. The magnetic susceptibility (χ) measurements of the polyradicals have been carried out by a SQUID magnetometer in the temperature range 1.8–300 K. The χ^{-1} vs T and χT vs T plots show that the polyradicals are paramagnetic species with a very weak antiferromagnetic coupling ($\theta = -0.6$ K) and that there are no significant ferromagnetic interactions among the spins. The magnetic susceptibility results are discussed in conjunction with the structure of the polyradicals.

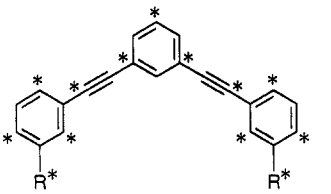
Introduction

The quest for synthetic organic magnetic materials is the focus of current topics in many fields of both pure and applied sciences. One approach exploits topological symmetry of the π-electron network in alternant hydrocarbons, which renders the degeneracy of a singly occupied π-nonbonding orbital unlimited.[1-3] This approach predicts the occurrence of high-spin macromolecules with extremely large spin or organic superparamagnets as well as organic ferromagnets. The profile and strength of the magnetic interaction depend on the chemical structures connecting the spin centers.[4-7]

Standing on this theoretical background, many polyradicals have been prepared by many synthetic routes,[8] and some of them have been claimed to show ferromagnetic behavior from the experimental sides. However, those structures are still unclear, and the reproducibilities in a synthetic sense have been poor in some cases.

As part of a program directed toward the syntheses of ferromagnetic materials, we previously reported two kinds of polyradicals with pendant stable nitronyl nitroxide radicals.[9,10] In this work we synthesized polyradicals **3** by the palladium-catalyzed polycondensation of 4,4,5,5-tetramethyl-3-oxido-2-(3,5-diethynylphenyl)-2-imidazolin-1-yloxyl (**1**) [abbreviated as 2-(3,5-diethynylphenyl) nitronyl nitroxide] with 5-alkyl-substituted 1,3-diiodobenzenes (**2**). Since this polycondensation gives the alternating combination of **1** with **2**, the resulting polyradicals have a structure in which the nitronyl nitroxide units are linked by the *m*-phenylenediethynylene groups. For such a structure of a polyradical we can expect that the polyradicals adopt a planar framework which is favorable to the extensive delocalization of the π-spins. In this paper we report the synthesis of polyradicals **3** and their magnetic characterization.

Chart I



4

R ; Radical site

Results and Discussion

Design of Polyradicals. According to the valence bond theory of topological symmetry of alternant hydrocarbon π-systems,[2] the ground spin states (S) are predicted by eq 1, where n^* is the number of starred atoms and n is the

$$S = (n^* - n)/2 \quad (1)$$

number of unstarred atoms (where adjacent atoms are respectively starred and unstarred, and identically denoted atoms are not adjacent to each other). In Chart I all the atoms in the π-system of **4** are either starred or unstarred according to the starred and unstarred rule. As seen from the chart, n^* is 13 and n is 11, predicting that the ground state of **4** is a triplet. This consideration predicts the intramolecular ferromagnetic interaction among the π-spin centers for polyradicals **3**.

Syntheses of Polyradicals. Monomer **1** was obtained by our previously reported method.[10] Since this radical was in part decomposed upon the usual recrystallization from hexane–benzene, it was purified by reprecipitation from benzene–hexane at room temperature. The spin concentration of **1** estimated by the electron spin resonance (ESR) spectroscopic method was ~100%. On the other

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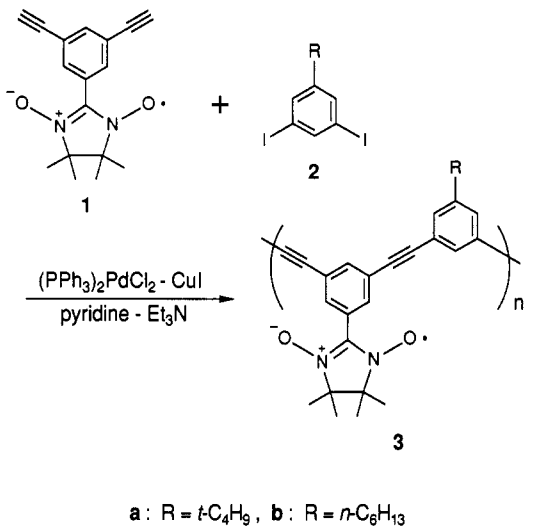
Scheme I



a: R = *t*-C_4H_9, b: R = *n*-C_6H_{13}

Table I. Polycondensation of 1 with 2 Catalyzed by $(PPh_3)_2PdCl_2$–CuI[a,b]

run	monomers[c]	polymer	time, h	yield, mg (%)	M_n[d]	M_w/M_n[d]	spin concn, spins/g[e]
1	1 and **2a**	**3a**	2	206 (~100)	4300	1.8	1.31×10^{21}
2	1 and **2a**	**3a**	5	205 (~100)	4800	2.0	1.33×10^{21}
3	1 and **2a**	**3a**	10	204 (~100)	4800	1.8	1.33×10^{21}
4	1 and **2b**	**3b**	2	221 (~100)	4500	1.8	1.19×10^{21}
5	1 and **2b**	**3b**	5	218 (~100)	4700	1.8	1.12×10^{21}

[a] Solvent, pyridine (6 mL) + triethylamine (6 mL); temperature, 20 °C. [b] $(PPh_3)_2PdCl_2$, 17.5 mg (0.025 mmol); CuI, 2 mg (0.011 mmol). [c] 1, 141 mg (0.50 mmol); **2a**, 193 mg (0.50 mmol); **2b**, 206 mg (0.50 mmol). [d] Determined by GPC. [e] Determined by the ESR spectroscopic method.

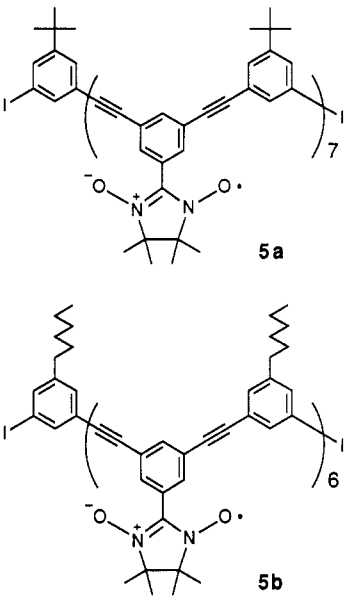
hand, 3,5-diiodo-1-*tert*-butylbenzene (**2a**) and 3,5-diiodo-5-hexylbenzene (**2b**) were prepared from 4-*tert*-butylaniline or 4-hexylaniline via iodination of the ortho positions with ICl, followed by removal of the amino group by the reaction with $NaNO_2$ in H_2SO_4. Repeated chromatographic purification and subsequent distillation gave pure **2** as needle crystals (**2a**) or an oil (**2b**).

The palladium-catalyzed polycondensation of **1** with **2** was performed by stirring a triethylamine–pyridine (1:1) solution containing 1 equiv of **1** and **2**, 1/20 equiv of $(PPh_3)_2PdCl_2$, and 1/50 equiv of CuI at 20 °C under nitrogen[11-13] (Scheme I). The reaction mixtures were homogeneous during the polycondensation. After 2–10 h, the reaction mixtures were poured into a large excess of methanol to give polyradicals **3** as blue powders in almost quantitative yields. The results are summarized in Table I.

In contrast to the insolubility of poly(1,4- and 1,3-phenyleneethynylene)s in common solvents,[12] polyradicals **3** were completely soluble in CH_2Cl_2 and $CHCl_3$, and partially soluble in THF and DMF. However, they were insoluble in methanol, ether, and common hydrocarbons such as benzene and hexane. The instrumental and elemental analyses were performed after purification by reprecipitation from CH_2Cl_2–hexane.

In the IR spectra of the polyradicals the complete disappearance of the absorption due to the stretching vibration of the ≡C—H bond (3250 cm^{-1}) characteristic of monomer **1** and the appearance of the absorption due to the stretching vibration of the C≡C bonds (2200 cm^{-1}) were observed. The gel permeation chromatography (GPC) analyses of **3** performed using $CHCl_3$ and polystyrene as an eluant and a reference, respectively, gave 4300–4800 as the number-average molecular weight ($\bar{M}_n$).

Chart II



The values correspond to 9.3–10.7 repeating units. As seen from Table I, the polycondensation of **1** with **2** was practically completed in 2 h and the further reaction did not bring about a significant increase in $\bar{M}_n$.

The elemental analyses for polyradical **3a** (C, 73.37; H, 6.20; N, 6.44; I, 7.53 for the polyradical of run 1 in Table I) gave the best agreement with structure **5a** (C, 73.16; H, 6.20; N, 6.00; I, 7.77), and those for **3b** (C, 73.78; H, 6.48; N, 5.85; I, 7.89 for the polyradical of run 4 in Table I) gave the best agreement with structure **5b** (C, 73.54; H, 6.88; N, 5.36; I, 8.09) (Chart II). These results suggest that the polyradicals were terminated by iodines in the polycondensation of **1** with **2**, and this is supported by the IR spectra of **3** where the absorption due to the stretching vibration of the ≡C—H in terminal acetylene is not found. The molecular weights estimated from the elemental analyses are considerably lower than those from the GPC results (9.3–10.7 repeating units). A similar result was reported for substituted poly(1,4-phenyleneethynylenes).[11] Since polystyrene used as a reference in the GPC measurements seems to be more flexible than the polyradicals, it is reasonable to think that the GPC measurements tend to give a higher molecular weight for the polyradical samples.

The elemental analyses also showed the presence of an ash of ~2 wt %. The incombustible compounds in the polyradicals seem to be a mixture of inorganic palladium compounds from $(PPh_3)_2PdCl_2$ used as a catalyst. Efforts were made to remove the incombustible compounds by filtration of the polymer solutions or by washing of the polyradicals with a dilute HCl solution (~1 wt %), but they could not be completely removed by such procedures.

ESR Spectra of the Monomer and Polyradical. The solution and powder ESR spectra of **1** and **3** were recorded at 20 °C using dichloromethane as a solvent. As shown in Figure 1a, the ESR spectrum of **1** is split into a 1:2:3:2:1 quintet due to the interaction with two equivalent nitrogen nuclei (a_N = 0.753 mT, g = 2.0066). This ESR pattern is characteristic of 2-aryl nitronyl nitroxide radicals and the a_N and g values are almost similar to those for the nitronyl nitroxides [a_N = 0.738–0.757 mT (in benzene), g = 2.0062–2.0063 (in water)].[14]

In contrast to the well-revolved ESR spectrum of **1**, the solution ESR spectrum of the polyradical consists of a single line (g = 2.0066, ΔH_{pp} = 0.90 mT), even in a dilute solution, and the hyperfine splittings due to the nitrogen

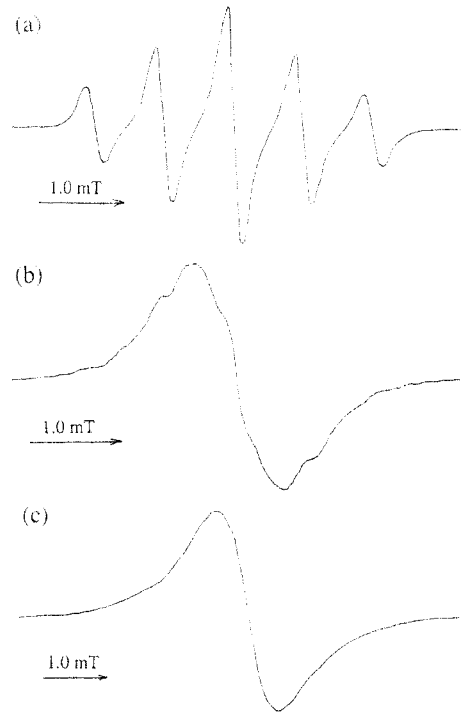


Figure 1. ESR spectra of 1 and 3 (run 1 in Table I) measured at 20 °C: (a) 1 in CH_2Cl_2; (b) 3 in CH_2Cl_2; (c) 3 in solid.

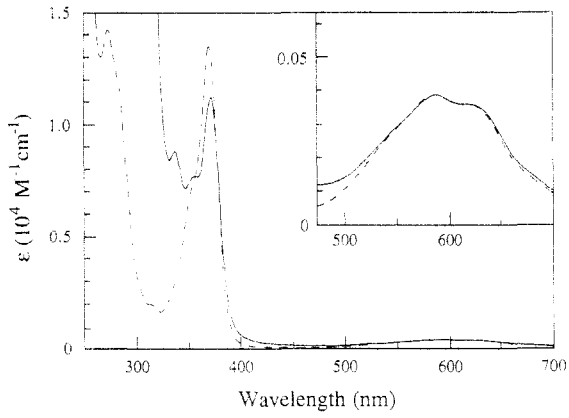


Figure 2. UV–vis spectra of 1 and 3 (run 1 in Table I) in CH_2Cl_2: (- - -) 1; (—) 3. The inset shows an expansion of the visible region.

nuclei are completely masked, as shown in Figure 1b. This hyperfine-smeared spectrum is due to spin-exchange interactions, indicating that the spin concentrations of the polyradicals are sufficiently high. For the powder samples an almost similar single line was observed (g = 2.0070, ΔH_{pp} = 0.99 mT).

The spin concentrations of 3 were estimated by the ESR spectroscopic method using the same ESR cell and solvent and the same ESR instrument settings as for the reference (1,3,5-triphenylverdazyl). The values obtained are 1.31 × 10^{21}–1.33 × 10^{21} spins/g (90–91% spin/repeating unit) for **3a** and 1.12 × 10^{21}–1.19 × 10^{21} spins/g (82–87% spin/repeating unit) for **3b**, showing that no significant decomposition of the nitronyl nitroxide radicals takes place during the polycondensation. As found in Table I the spin concentrations of **3a** are somewhat higher than those for **3b**. This suggests that the nitronyl nitroxide sites are more effectively protected by *tert*-butyl groups than *n*-hexyl groups.

UV–Vis Spectra of the Polyradical. The UV–vis spectra of 1 and 3 are shown in Figure 2. If the nitronyl nitroxides sites interact strongly with the *m*-phenylenediethynylene couplers, observation of bathochromic shifts

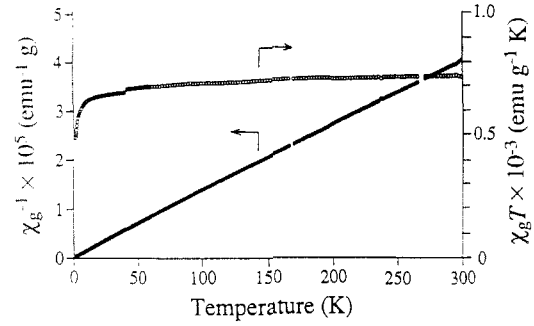


Figure 3. χ^{-1} vs T and χT vs T plots for 3 (run 1 in Table I).

is expected. As found in Figure 2, monomer 1 gives absorption maxima at 273 (ε 14 200), 368 (13 500), 586 (390), and 620 nm (370), while polyradical 3 gives absorption maxima at 371 (ε 11 200), 586 (388), and 620 nm (365). As can be seen from the comparison of the UV–vis spectra, the spectroscopic results indicate that there is no strong electronic interaction between the nitronyl nitroxide chromophores and the *m*-phenylenediethynylene couplers.

Magnetic Susceptibility Measurements. The magnetic susceptibility (χ) measurements of polyradicals 3 were performed on a SQUID magnetometer in the temperature range 1.8–300 K. The diamagnetic contribution from the samples was estimated from the Pascle diamagnetic constants.

Figure 3 shows the χ^{-1} vs T and χT vs T plots of polyradical 3. The χ^{-1} vs T plots gave a straight line characteristic of paramagnetic species with a very weak antiferromagnetic interaction (Θ = −0.6 K), and the χT vs T plots gave a curve which is horizontal above ~15 K and goes down below ~15 K. These SQUID results indicate that the polyradical is a paramagnetic species of S = 1/2 with a very weak antiferromagnetic interaction which becomes prominent only at very low temperatures. The other 3 also showed almost the same magnetic behavior. On the basis of the magnetic susceptibility measurements, it is concluded that in the polyradicals there is no appreciable amount of the ferromagnetic interaction among the spins.

Conclusions

π-Conjugated nitronyl nitroxide polyradicals have been synthesized by the palladium-catalyzed polycondensation of 2-(3,5-diethynylphenyl) nitronyl nitroxide with 5-alkyl-substituted 1,3-diiodobenzenes. The polyradicals obtained possess high spin concentrations of 1.12 × 10^{21}–1.33 × 10^{21} spins/g (corresponding to 82–91% spin/repeating unit). The ESR spectra of the polyradicals consist of a hyperfine-smeared single line, indicating that a spin-exchange interaction takes place. Although the polyradicals possess high spin concentrations and satisfy the π-topological symmetry requirement for inducing ferromagnetic interactions among the π-spins, the magnetic susceptibility measurements show that there is no appreciable amount of the ferromagnetic interaction among the spins in the polyradicals. This is ascribable to the following two points: (1) the spin is less delocalized from the nitronyl nitroxide sites to the *m*-phenylenediethynylene couplers and (2) the distances between one spin center and the neighboring ones are too long for inducing the ferromagnetic coupling among the spins. Quite recently, Iwamura *et al.* reported that in 4 (R = N:) there was no significant interaction among the nitrenes.[15] On the basis of the results in our and Iwamura *et al.*'s works, we think that, if the distances among the spins become much shorter and the incorporated free radicals

have an extensively delocalized electron spin, the corresponding polyradicals may exhibit ferromagnetic interaction among the spins. The syntheses of such polyradicals are under way.

Experimental Section

Measurements. IR spectra were run on a JASCO A-202 spectrophotometer. UV–vis spectra were measured with a Shimadzu UV-240 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL GX-400 spectrometer (400 MHz); chemical shits (δ) are expressed in parts per million downfield from TMS as an internal standard. GPC was run on a Tosoh GPC 8000 series using Shodex K-800Y + K-805L + K-805L columns calibrated with polystyrene standards, eluting $CHCl_3$ and monitoring the refractive index.

ESR spectra were measured with a Bruker ESP 300 or JEOL ME-3X spectrometer operated at the X-band. Sample solutions in ESR cells were degassed by three freeze–pump–thaw cycles using a high vacuum system, and the cells were sealed off. Hyperfine splitting constants (a) and g values were determined by simultaneous measurements with a dilute Fremy's salt in aqueous K_2CO_3 solution (a_N = 1.309 mT, g = 2.0055).

The spin concentrations of the polyradicals were determined by the double integration of the ESR spectra from the sample solutions (0.87×10^{-4}–1.83×10^{-4} M) in CH_2Cl_2. Calibration curves were drawn with solutions of 1,3,5-triphenylverdazyl[16] at 0.85×10^{-4}–2.33×10^{-4} M using the same ESR cell and solvent and the same instrument settings as for the sample measurements.

The magnetic susceptibility measurements were performed on a Quantum Design SQUID MPM2 system in the temperature range 1.8–300 K. The diamagnetic contribution (-5.60×10^{-7} emu g^{-1}) of the sample was estimated from the Pascale diamagnetic constants.

Materials. The preparation of 4,4,5,5-tetramethyl-3-oxido-2-(3,5-diethynylphenyl)-2-imidazolin-1-yloxyl (1) was previously reported by us.[10] The pyridine and triethylamine used in the polycondensation were purified by the usual method, and commercial grade CuI was used without purification.

3,5-Diiodo-1-*tert*-butylbenzene (2a). To a mechanically stirred solution of 9.0 g (60.3 mmol) of 4-*tert*-butylaniline in 7 mL of concentrated HCl and 70 mL of H_2O was added dropwise over 2 h at room temperature a solution of 25.0 g (154 mmol) of ICl in 20 mL of concentrated HCl and 80 mL of H_2O. After completion of the addition, the resulting mixture was stirred for 1 h, and 200 mL of $CHCl_3$ was added. The mixture was then neutralized with 3 N NaOH, and the organic layer was separated, washed with aqueous sodium thiosulfate and water, and dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was column chromatographed on silica gel (Wako gel, C-200) with 1:1 benzene–hexane as an eluant to give 4-*tert*-butyl-2,6-diiodoaniline as a colorless oil. This oil crystallized upon addition of small amounts of ethanol.

The oil was dissolved in 140 mL of ethanol and cooled to 0 °C. After 3 mL of concentrated H_2SO_4 was added dropwise, 9.3 g of $NaNO_2$ was added, as fast as possible, at room temperature, and the mixture was refluxed for 1 day. Ethanol was then evaporated, and the residue was neutralized with 2 N NaOH. The organic products were extracted with $CHCl_3$ (50 mL × 2), the combined $CHCl_3$ extract was washed with water, dried ($MgSO_4$), and evaporated, and the residue was column chromatographed three times on silica gel (Wako gel, C-200) with hexane as an eluant to give pure **2a** as an oil. This oil was further purified by distillation (124 °C/1 Torr). On standing, the oil solidified to colorless prisms: mp 47–49 °C; yield 8.9 g (38%); ^{1}H NMR ($CDCl_3$) δ 1.27 (s, *t*-Bu, 18 H), 7.65 (s, *o*-H, 2 H), 7.86 (s, *p*-H, 1 H). Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.12; H, 3.13. Found: C, 30.76; H, 3.00.

3,5-Diiodo-1-hexylbenzene (2b). By the same procedure as for **2a**, **2b** was prepared from 13.0 g (73.3 mmol) of 4-hexylaniline. Column chromatographic separation and subsequent distillation (164 °C/1 Torr) gave 7.2 g (24%) of **2b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.86–2.49 (m, *n*-Hex, 9 H), 7.47 (s, *o*-H, 2 H), 7.85 (s, *p*-H, 1 H). Anal. Calcd for $C_{12}H_{16}I_2$: C, 34.81; H, 3.89. Found: C, 34.56; H, 3.70.

Polymerization. In a two-necked flask were placed 0.50 mmol of **2**, 17.5 mg of $(PPh_3)_2PdCl_2$, 2 mg of CuI, and 6 mL of triethylamine. After the air was replaced with nitrogen, a solution of 141 mg (0.50 mmol) of **1** in 6 mL of pyridine was added, and the mixture was stirred at room temperature (20 °C) for 2–10 h. The reaction mixture was then poured into a large excess of methanol (100 mL), and the blue powder precipitated was collected by filtration and dried in vacuum. The polyradicals were purified by reprecipitation from CH_2Cl_2–hexane.

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