Notes

Synthesis and Characterization of Poly(1,3-phenyleneethynylene) with Pendant Nitroxide Radicals

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Introduction

Of the many models proposed for the design of new, organic-based magnetic materials, the polyradical magnets have proven to be one of the most interesting.[1] Our approach to the polyradical magnets has developed along two paths: One is poly(ethynylbenzenes) with pendant stable free radicals,[2,3] and the other is poly(1,3-phenyleneethynylene) with pendant stable free radicals.[4,5] In a previous paper[5] we reported the synthesis and magnetic characterization of poly(1,3-phenyleneethynylene) with pendant nitronyl nitroxides. The magnetic susceptibility measurements of the polyradical, however, showed no presence of significant ferromagnetic interactions among the spins, and this result was ascribed to the lack of sufficient delocalization of the spins to the 1,3-phenylenediethynylene coupling units.

On the basis of this result, we decided to synthesize poly(1,3-phenyleneethynylene) carrying nitroxide radicals instead of nitronyl nitroxides because, in nitroxide radicals, the unpaired electron is more widely delocalized. Since, however, nitroxide radicals are less stable than nitronyl nitroxides, there may be many difficulties in the synthesis of such nitroxide polyradicals. Hence, it is important to establish the synthesis of such polynitroxides. We therefore studied the synthetic approach to a high spin concentration nitroxide pendant poly(1,3-phenyleneethynylene) (3) and found that it is obtained by the Pd-catalyzed polycondensation of *N-tert*-butyl 3,5-diethynylphenyl nitroxide (1) with 5-*tert*-butyl-1,3-diiodobenzene (2). Herein we report the synthesis and characterization of polynitroxide 3.

Results and Discussion

Synthesis of 1. Monomer 1 was synthesized according to the procedures shown in Scheme I. Treatment of 3,5-dibromophenylmagnesium bromide with a 2-methyl-2-nitrosopropane dimer in THF gave *N-tert*-butyl-3,5-dibromo-1-(hydroxyamino)benzene in 77% yield. This (hydroxyamino)benzene was allowed to react with 2 equiv of (trimethylsilyl)acetylene in triethylamine in the presence of $(PPh_3)_2PdCl_2$ and CuI to give *N-tert*-butyl-3,5-bis[(trimethylsilyl)ethynyl]-1-(hydroxyamino)benzene.[6] Detrimethylsilylation was carried out by treatment with K_2CO_3 in methanol, giving *N-tert*-butyl-3,5-diethynyl-1-(hydroxyamino)benzene as colorless prisms in 62% yield after sublimation. Oxidation of this (hydroxyamino)benzene to 1 was encountered with difficulty. Although the oxidation was at first carried out in benzene with PbO_2, the orange nitroxide radical solution turned dark brown during evaporation even at a low temperature, giving nonparamagnetic decomposition products. The solvent was also removed by freeze-drying, but the decomposition of 1 took place similarly. This incomprehensible problem was, however, overcome by the following procedure using THF as the solvent. That is, the (hydroxyamino)benzene was oxidized in THF with PbO_2, and, after filtration, the orange filtrate was concentrated to ca. 2 mL by evaporation at room temperature. After addition of benzene, the solvents were removed by the freeze-drying method, and the residual orange powder was sublimed, giving 1 as red prisms in 85% yield. The purity (spin concentration) determined by ESR was ~88%, which was in satisfactory agreement with that (87%) determined by the magnetic susceptibility measurements performed on a SQUID magnetometer.

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

run	solvent Et_3N–pyridine, mL	yield, %	$\bar{M}_n$[c]	spin concn,[d] spins/g (% spin/repeating unit)
1	7.5:7.5	94	3200	0.85×10^{21} (49)
2	5.0:10.0	93	3000	1.17×10^{21} (67)
3	3.0:12.0	87	3000	1.51×10^{21} (86)

[a] 1, 106 mg (0.50 mmol); 2, 193 mg (0.50 mmol), $(PPh_3)_2PdCl_2$, 17.5 mg (0.025 mmol); CuI, 2.0 mmg (0.011 mmol). [b] Time, 2 h; temperature, 20 °C. [c] Determined by GPC. [d] Determined by ESR spectroscopy.

Polycondensation of 1 with 2. The $(PPh_3)_2PdCl_2$–CuI-catalyzed polycondensation of nitroxide 1 with 5-*tert*-butyl-1,3-diiodobenzene (2) was performed as follows according to the usual method:[7] A mixture of 1 equiv of 1 and 2, $^1/_{20}$ equiv of $(PPh_3)_2PdCl_2$ and $^1/_{50}$ equiv of CuI in triethylamine was stirred for 2 h at room temperature and poured into a large excess of methanol to give polynitroxide 3 as a light orange powder in ~100% yield (Scheme II). The spin concentration of 3, however, was 0.76×10^{21} spins/g (43% spin/repeating unit), indicating that a significant decomposition of 1 took place during the polycondensation. To resolve this problem, the stabilities of 1 to the solvent and catalysts used were examined. It was found that 1 was stable to the catalysts (in pyridine) but unstable in triethylamine, regardless of the presence or absence of the catalysts, and a 16% decomposition of 1 was shown by following the double-integrated ESR signal from a solution of 1 in triethylamine for 1 h at room temperature. Since nitroxide 1 was found to be stable in pyridine, the polycondensation of 1 with 2 was performed in a triethylamine–pyridine mixture solvent. As found in Table I, the yields and $\bar{M}_n$ are almost the same in any run, but the spin concentrations are markedly increased from 0.85×10^{21} (49% spin/repeating unit) to 1.17×10^{21} spins/g (67% spin/repeating unit) in going from 1:1 to 1:2 triethylamine–pyridine solvent, and in a 1:4 triethylamine–pyridine solvent it reached 1.51×10^{21} spins/g (86% spin/repeating unit), indicating that no significant decomposition of 1 took place. Polynitroxide 3 was soluble in benzene, dichloromethane, chloroform, THF, ether, DMF, and DMSO but insoluble in methanol.

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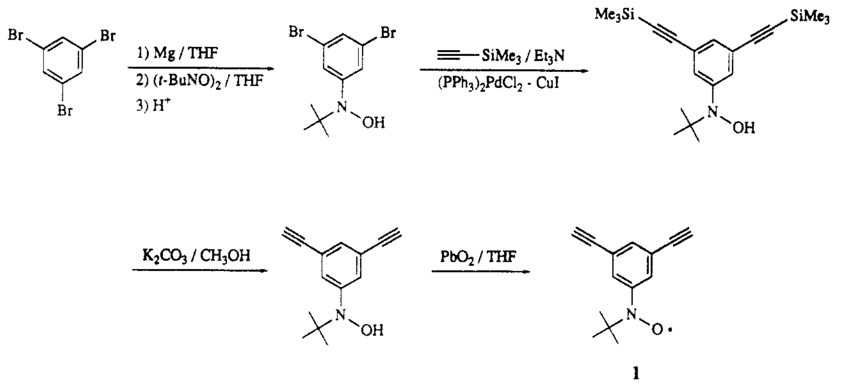
Scheme I



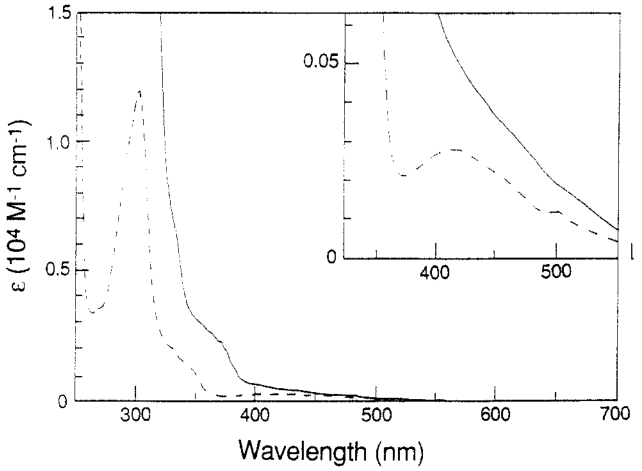


Figure 1. UV–vis spectra of **1** and **3** (run 3 in Table I) in dichloromethane. (- - -) **1**; (—) **3**. The inset shows an expansion of the visible region. ε is corrected for the spin concentration determined by ESR spectroscopy.

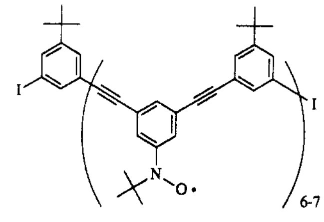
The IR spectrum of **3** showed the complete disappearance of the absorption due to the stretching vibration of the ≡CH bond (3250 cm^{-1}) characteristic of monomer **1** and the appearance of the absorption (weak) due to the stretching vibration of the C≡C bonds (2200 cm^{-1}), confirming the proposed structure illustrated in Scheme II.

The elemental analysis of **3** (run 3 in Table I) (C, 76.80; H, 6.65; N, 3.74; I, 10.38) gives the best agreement with structure **4** (for n = 6: C, 75.77; H, 6.45; N, 3.44; I, 10.40 and for n = 7: C, 76.80; H, 6.53; N, 3.52; I, 9.12) (see Chart I).[8] This elemental result suggests that polyradical **3** is terminated by iodines, in agreement with the IR spectrum of **3** in which there is no absorption due to the stretching vibration of the ≡CH in terminal acetylene. The molecular weight (6–7 repeating units) estimated from the elemental analysis is in relatively good agreement with that determined from GPC (8.8 repeating unit).

UV–Visible Spectra of the Polyradical. The UV–visible spectra of **1** and **3** (run 3 in Table I) were measured using dichloromethane as the solvent. As found in Figure 1, the monomer nitroxide shows λ_{max} at 302 (ε 12000), 416 (280), and 500 nm (121 M^{-1} cm^{-1}). The weak absorptions in the visible region are responsible for the characteristic orange color of nitroxides. In contrast, the UV–visible spectrum of polynitroxide **3** is monotonous and shows no clear absorption peaks above 300 nm. However, a weak broad shoulder found in the visible region 400–550 nm is attributable to the nitroxide group.

ESR Spectra of the Monomer and the Polyradical. The solution and powder ESR spectra of **3** were measured at 20 °C using benzene as the solvent. As found in Figure 2a, the ESR spectrum of **1** consists of three sets of a 1:3:3:1 quartet (a_N = 1.210, a_H = 0.198 mT) with a g value of 2.0061. This splitting pattern is characteristic of 3,5-disubstituted phenyl *tert*-butyl nitroxide, and the mag-

Chart I



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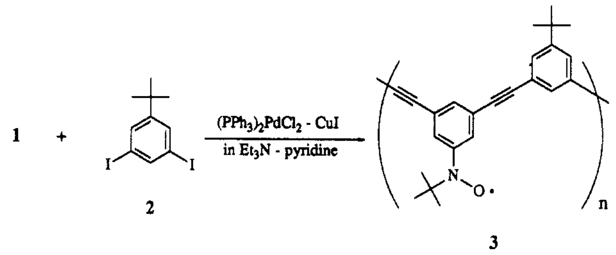
Scheme II



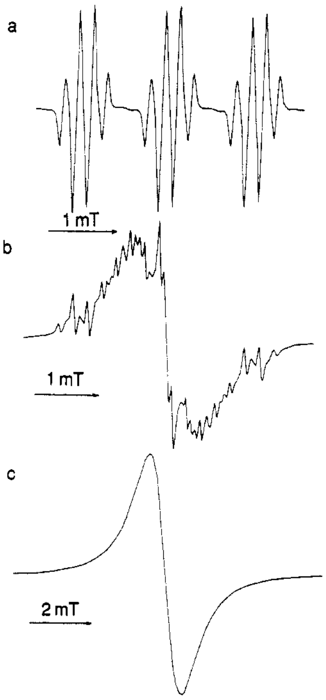


Figure 2. Solution and powder ESR spectra of **1** and **3** (run 3 in Table I) at 20 °C: (a) **1** in benzene; (b) **3** in benzene; (c) **3** in powder.

nitudes of a_N and a_H are typical of aryl *tert*-butyl nitroxides.[9]

In contrast, the solution ESR spectrum of the polynitroxide (run 3 in Table I) (g = 2.0060) is very complex and the hyperfine splittings are poorly resolved (Figure 2b), showing that spin-exchange interaction takes place due to the high spin concentration of 3. This broadening of the ESR spectrum is further enhanced in the powder ESR spectrum (Figure 2c), and the hyperfine structures completely disappear (g = 2.0063, ΔH_{pp} = 0.96 mT).

In conclusion, a high spin concentration (86% spin/repeating unit) nitroxide pendant poly(1,3-phenyleneethynylene) has been obtained by the Pd-catalyzed polycondensation of 1 with 2 in 1:4 triethylamine–pyridine at room temperature. In the extension of this work the syntheses of polyradicals by the Pd-catalyzed polycondensation of 1 with a 3,5-diiodobenzene carrying a nitroxide or nitronyl nitroxide radical are planned. This type of polyradical might be expected as a high spin or superparamagnetic material.[10]

Experimental Section

Measurements. IR spectra were run on a JASCO A-202 spectrophotometer. UV–visible spectra were measured with a Shimadzu UV-240 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL GX-400 spectrometer (400 MHz). Chemical shifts (δ) are expressed in ppm downfield from TMS as an internal standard. GPC was run on a Tosoh GPC 8000 series using Tosoh TSK 2000 + 4000 + 4000 + 6000 columns calibrated with polystyrene standards, eluting THF and monitoring refractive index.

ESR spectra were measured with a Bruker ESP 300 or a JEOL ME-3X spectrometer operated at X-band. The 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 in an aqueous K_2CO_3 solution (a_N = 1.309 mT, g = 2.0055).

The spin concentrations of 1 and 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 benzene. Calibration curves were drawn with solutions of 1,3,5-triphenylverdazyl[11] 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 carried out with a Quantum Design SQUID MPMS2 magnetometer in the temperature range 1.8–300 K. The $1/\chi$ vs T plots of 1 gave a Curie constant of 0.326 emu K mol^{-1} (the theoretical value, 0.375 emu K mol^{-1}). Thus the spin concentration of 1 was determined to be 87%. In the determination of the Curie constant the diamgnetic components were estimated from the Pascal constants.

Materials. 5-*tert*-Butyl-1,3-diiodobenzene (2) was previously prepared by us.[5] The 2-methyl-2-nitrosopropane dimer was purchased from Aldrich was used without purification. The pyridine and triethylamine (purchased from Wako Pure Chem., Inc.) used in the polycondensation were purified by distillation. CuI was of commercial grade.

***N-tert*-Butyl-3,5-dibromo-1-(hydroxyamino)benzene.** 1,3,5-Tribromobenzene (10.0 g, 31.8 mmol) was allowed to react with 1.0 g of Mg in 100 mL of anhydrous THF at reflux temperature under N_2. To this Grignard solution was added dropwise with stirring a solution of 2.0 g (11.5 mmol) of the 2-methyl-2-nitrosopropane dimer in 20 mL of anhydrous THF. After 1 h, saturated NH_4Cl was added at 0 °C and the organic layer was extracted with ether (2 × 100 mL). The combined ether extract was washed with brine, dried ($MgSO_4$), and evaporated, and the residue was crytallized from hexane to give *N-tert*-butyl-3,5-dibromo-1-(hydroxyamino)benzene as colorless prisms with mp 119–121 °C in 77% yield (5.68 g, 17.6 mmol); ^{1}H NMR ($CDCl_3$) δ 1.14 (s, *t*-Bu, 9 H), 5.90 (s, NOH, 1H), 7.30 (s, *o*-H, 2 H), 7.40 (s, *p*-H, 1 H).

***N-tert*-Butyl-3,5-diethynyl-1-(hydroxyamino)benzene.** To a solution of 4.0 g (12.4 mmol) of *N-tert*-butyl-3,5-dibromo-1-(hydroxyamino)benzene, 0.434 g of $(PPh_3)_2PdCl_2$, and 0.047 g of CuI in 80 mL of Et_3N was added 1.93 g (28.3 mmol) of (trimethylsilyl)acetylene. After the mixture was refluxed with stirring for 4 h under N_2, it was cooled and filtered. The filtrate was evaporated under reduced pressure, and the residue was column chromatographed on silica gel (Wakogel C-200) with benzene as the eluant to give *N-tert*-butyl-3,5-bis[(trimethylsilyl)ethynyl]-1-(hydroxyamino)benzene as a colorless powder.

The (hydroxyamino)benzene was dissolved in 200 mL of methanol, and 0.3 g of K_2CO_3 was added. After the mixture was stirred for 3 h at room temperature, methanol was evaporated under reduced pressure and 100 mL of CH_2Cl_2 was added. The organic layer was washed with 5% $NaHCO_3$ and water and dried ($MgSO_4$). After filtration, the filtrate was evaporated under reduced pressure, and the residue was sublimed at 94 °C (1 Torr) to give *N-tert*-butyl-3,5-diethynyl-1-(hydroxyamino)benzene as colorless prisms with mp 120–121 °C in 62% yield (1.65 g, 7.74 mmol); IR (KBr) 3280 ($\nu_{\equiv CH}$), 3200 (ν_{OH}), 2980 ($\nu_{t\text{-Bu}}$), 2100 ($\mu_{C\equiv C}$), 1580 cm^{-1} (ν_{Ph}); ^{1}H NMR ($CDCl_3$) δ 1.12 (s, *t*-Bu, 9 H), 3.05 (s, ≡CH, 2 H), 6.13 (s, NOH, 1 H), 7.34 (s, *o*-H, 2 H), 7.36 (s, *p*-H, 1 H). Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 79.22; H, 7.23; N, 6.63.

***N-tert*-Butyl 3,5-Diethynylphenyl Nitroxide (1).** The (hydroxyamino)benzene (0.20 g, 0.94 mmol) was dissolved in 15 mL of THF and stirred. After 2.0 g of K_2CO_3 and 2.0 g of PbO_2 were added, the mixture was stirred for 30 min. After filtration, the filtrate was concentrated to ca. 2 mL under reduced pressure to leave a red oil. This oil was diluted with ca. 20 mL of benzene, and the solvent was removed by the freeze-drying method. The resulting orange powder was sublimed at 70 °C (1 Torr) to give 1 as red prisms with mp 89–91 °C in 85% yield (0.17 g, 0.80 mmol); IR (KBr) 3250 ($\nu_{\equiv CH}$), 2980 ($\nu_{t\text{-Bu}}$), 2120 ($\nu_{C\equiv C}$), 1590 cm^{-1} (ν_{Ph}); UV–visible (CH_2Cl_2) λ_{max} 302 (ϵ 12 000), 416 (280), 500 nm (121 M^{-1} cm^{-1}); ESR (benzene) a_N = 1.210, a_H (3 H) = 0.198 mT, g = 2.0061. Anal. Calcd for $C_{14}H_{14}NO$: C, 79.22; H, 6.65; N, 6.60. Found: C, 78.89; H, 6.81; N, 6.18.

Typical Procedure for Polycondensation of 1 with 2. In a two-necked flask were placed 193 mg (0.50 mmol) of 2, 17.5 mg of $(PPh_3)_2PdCl_2$, 2 mg of CuI, and 3.0 mL of Et_3N, and the flask was charged with N_2. After 106 mg (0.50 mmol) of 1 in 12.0 mL of pyridine was added through a double septum with a syringe, the resulting mixture was stirred at room temperature (20 °C) for 2 h and poured into a large excess of methanol to give polynitroxide 3 as an orange powder, which was collected by filtration and dried in vacuum. The results are summarized in Table I.

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