

Synthesis and Characterization of Poly(1,3-phenylene)-Based Polyradical Carrying Cyclic Nitroxides. Observation of Ferromagnetic Interaction

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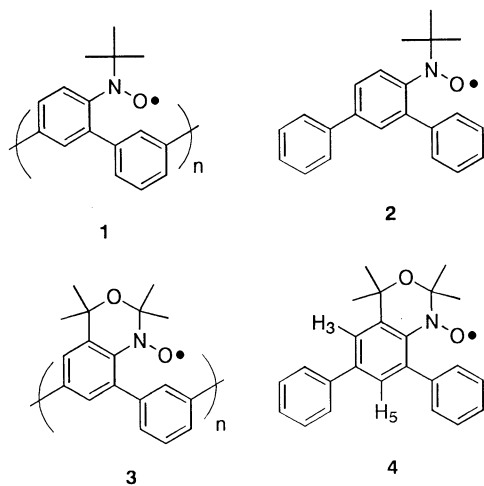
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Organic ferromagnetic polyradicals have attracted much attention.¹ A wide variety of π -conjugated spin systems including poly(phenylacetylene)-,² poly(1,3-phenyleneethynylene)-,³ and poly(phenylenevinylene)-based polyradicals⁴ have been designed based on the rule of the π -topological symmetry and synthesized in recent years.⁵ A previous paper reported the synthesis and magnetic property of **1**.⁶ This was the first example of poly(1,3-phenylene)-based polyradicals. The 1,3-phenylene unit has been shown to be one of the best ferromagnetic couplers by the theoretical studies⁷ and by the magnetic studies on polycarbenes⁸ and poly(triarylmethyl radicals).⁹ Although the spin concentration of **1** was very high (0.82 spin per repeating unit), the magnetic measurements showed weak antiferromagnetic interaction. No observation of ferromagnetic interaction was attributed to the interruption of π -conjugation due to a twisting (68.5°) between the N–O moieties and the poly(1,3-phenylene) backbone, as confirmed by X-ray crystallographic analysis of the corresponding model radical **2**. We therefore prepared poly(1,3-phenylene) carrying cyclic nitroxide radicals, **3**, to overcome this problem. Aromatic cyclic nitroxides are planar in most cases, which makes an extensive delocalization of the unpaired electrons over the whole of radical molecules.¹⁰ Herein we report the synthesis of **3** and its magnetic properties.



EXPERIMENTAL

Measurements

FT-IR spectra were run on a JASCO FT/IR-230 spectrometer. ¹H NMR spectra (400 MHz) were recorded with a JEOL α -400 spectrometer with Me₄Si as the internal reference. ESR spectra were measured with a Bruker ESP 300 spectrometer operated at the X band. Spin concentrations were determined by the double integrated ESR spectra of the sample in benzene. A calibration curve was drawn with 1,3,5-triphenylverdazyl solutions using the same ESR cell and solvent and the same instrument setting as for the sample measurements. Size exclusion chromatography (SEC) was run on a Tosoh 8020 series using TSK-gel G5000HHR, GMulti-poreHXL-M, and GMHHR-L columns calibrated with polystyrene standards, eluting with THF at 40°C. Detection was made with a Tosoh refractive index detector RI8020.

Materials

2,2,4,4-Tetramethyl-1*H*,2*H*,4*H*-3,1-benzoxazine (**6**) was prepared by reaction of methyl anthranilate with MeMgI, and subsequent treatment with acetone based on procedures reported by Rassat *et al.*¹¹

6,8-Dibromo-2,2,4,4-tetramethyl-1*H*,2*H*,4*H*-3,1-benzoxazine (**7**)

To a solution of 5.00 g (26.0 mmol) of **6** in CH₂Cl₂ (150)-MeOH (60 mL) were added 22.2 g (58.0 mmol) of benzyltrimethylammonium tribromide (BTMA Br₃) and 7.0 g (70 mmol) of CaCO₃ powder at room temperature. After the mixture was stirred for 1.5 h, the CaCO₃ powder was removed by filtration and the filtrate was evaporated under reduced pressure. Aqueous 10 wt% NaHSO₃ (120 mL) was added and the mixture was extracted with CH₂Cl₂ and dried (MgSO₄). After filtration and evaporation, the residue was chromatographed on silica gel with benzene to give **7** in 77% yield (7.00 g, 20.1 mmol) as colorless prisms with mp 55–57°C. IR (KBr): 3380 cm⁻¹ (NH); ¹H NMR (400 MHz, in CDCl₃): δ 1.45 (6H, s, CH₃), 1.52 (6H, s, CH₃), 4.48 (1H, s, NH), 7.12 (1H, d, *J* = 2.0 Hz, ArH), 7.44 (1H, d, *J* = 2.0 Hz, ArH). *Anal.* Calcd for C₁₂H₁₅Br₂NO: C, 41.29%; H, 4.33%; N, 4.01%. Found: C, 41.23%; H, 4.17%; N, 3.95%.

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6,8-Diphenyl-2,2,4,4-tetramethyl-1H,2H,4H-3,1-benzoxazine (8)

To a solution of 1.75 g (5.00 mmol) of **7** in 75 mL of benzene were added a solution of 1.85 g (15.0 mmol) of phenylboronic acid in 7.5 mL of EtOH, 15 mL of aqueous 2 M K₂CO₃, and 0.35 g (0.30 mmol) of Pd(PPh₃)₄. The resulting heterogeneous mixture was purged with N₂ and gently refluxed for 24 h with stirring under N₂. After cooling, the organic layer was separated, and the aqueous layer was extracted with benzene. After the combined organic layers were dried (MgSO₄) and evaporated under reduced pressure, the residue was chromatographed on silica gel with benzene to give **8** in 76% yield (1.30 g, 3.79 mmol) as colorless needles with mp 150–151°C. IR (KBr) 3370 cm⁻¹ (NH); ¹H NMR (400 MHz, in CDCl₃): δ 1.41 (6H, s, CH₃), 1.65 (6H, s, CH₃), 4.23 (1H, s, NH), 7.25–7.32 (3H, m, ArH), 7.41 (3H, t, *J* = 7.8 Hz, ArH), 7.47–7.48 (4H, m, ArH), 7.58 (2H, d, *J* = 8.3 Hz, ArH). *Anal.* Calcd for C₂₄H₂₅NO: C, 83.93%; H, 7.34%; N, 4.08%. Found: C, 84.10%; H, 7.32%; N, 4.02%.

6,8-Diphenyl-2,2,4,4-tetramethyl-1H,2H,4H-3,1-benzoxazin-1-oxyl (4)

To a solution of 0.10 g (0.30 mmol) of **8** in 20 mL of CH₂Cl₂ was added 0.16 g of 3-chloroperoxybenzoic acid and the mixture was stirred for 30 min under N₂. After evaporation under reduced pressure, the residue was chromatographed on alumina gel with benzene–ethyl acetate (5 : 1), giving pure **4** in 78% (0.80 g, 0.22 mmol). Recrystallization from MeOH gave **4** as red prisms with mp 151–153°C. *Anal.* Calcd for C₂₄H₂₄NO₂: C, 80.42%; H, 6.75%; N, 3.91%. Found: C, 80.20%; H, 6.71%; N, 3.85%.

Pd-Catalyzed Polycondensation of 7 with 10

To a solution of 2.09 g (6.00 mmol) of **7** in 62.4 mL of tetrahydrofuran (THF) were added 1.92 g (7.80 mmol) of **10**, 62.4 mL of aqueous 1 M K₂CO₃, 8.67 g (31.2 mmol) of Bu₄NCl, and 0.42 g (0.36 mmol) of Pd(PPh₃)₄. The resulting heterogeneous mixture was purged with N₂ and gently refluxed for three days with stirring under N₂. After cooling, the organic layer was extracted with benzene, and the benzene extract was washed with aqueous 5 wt% NaCN and brine, and dried (MgSO₄). After evaporation under reduced pressure, the residue was reprecipitated from THF (30)-MeOH (300 mL) and THF (30)-hexane (300 mL) to give **11** in 60% yield (0.95 g, 3.58 mmol) as a colorless powder. IR (KBr) 3380 cm⁻¹ (NH); ¹H NMR (400 MHz, in CDCl₃): δ 1.40 (6H, s, CH₃), 1.62 (6H, s, CH₃), 4.29 (1H, br s, NH), 7.34–7.69 (6H, m, ArH); SEC (THF) *M_n* = 4000 (*n* = 15.1), *M_w*/*M_n* = 1.35. *Anal.* Calcd for (C₁₈H₁₉NO)_{*n*}: C, 81.47%; H, 7.22%; N, 5.28%, Br, 1.34%. Found: C, 81.16%; H, 7.09%; N, 5.15%; Br, 1.34%.

Oxidation of 11

To a solution of 0.10 g of **11** in 30 mL of CH₂Cl₂ was added 0.10 g of 3-chloroperoxybenzoic acid, and the mixture was stirred for 30 min under N₂. The resulting solution was washed with aqueous 10 wt% Na₂CO₃ and brine and dried (MgSO₄). After filtration, the filtrate was poured into a large excess of hexane, and the light red powder deposited was collected by filtration and

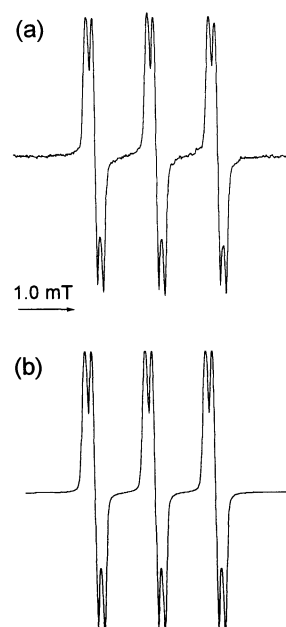


Figure 1. ESR spectra of radical **4** in benzene; (a) observed spectrum and (b) computer-simulation.

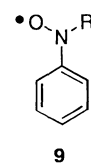
dried *in vacuo* to give **3** in 37% yield (0.040 g) as a light red powder.

RESULTS AND DISCUSSION

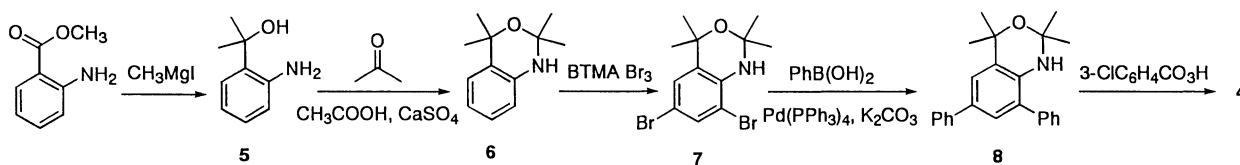
Synthesis of Model Radical 4

Model radical **4** was prepared according to Scheme 1.¹¹ Methyl anthranilate was treated with methylmagnesium iodide (excess) to give **5** as a colorless oil in 77% yield, and treatment of **5** with acetone (excess) in the presence of CaSO₄ gave **6** as colorless oil in 85% yield. Bromination of **6** with BTMA Br₃ gave **7** in 82% yield,¹² and Pd-catalyzed cross-coupling reaction of **7** with phenylboronic acid gave **8** in 75% yield.^{13,14} The oxidation of **8** with 3-chloroperoxybenzoic acid (~70% purity) in CH₂Cl₂ gave **4** as red prisms in 78% yield. This radical was stable for a long period without decomposition.

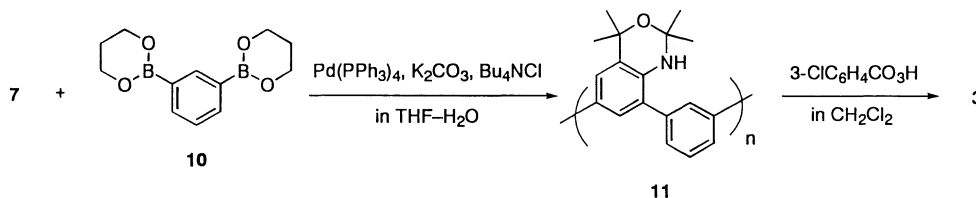
The ESR spectrum of **4** measured at 20°C using benzene as the solvent is shown in Figure 1. The 1 : 1 : 1 triplet splitting by the interaction with nitrogen is further split into 1 : 2 : 1 triplets by the interaction of two protons. Computer simulation of the spectrum gave *a_N* = 1.06 and *a_H* = 0.11 mT (2H) (*g* = 2.0055), and the two protons were assigned to H₃ and H₅. The proton hyperfine coupling constants are nearly equal to those of planar nitroxide radicals. For instance, *a_{m-H}* for **9a** is 0.11 mT (benzene) (*a_N* = 1.18, *a_{o- and p-H}* = 0.32 mT) and *a_{m-H}* for **9b** is 0.091 mT (benzene) (*a_N* = 1.11, *a_{o- and p-H}* = 0.32 mT).¹⁵ It is therefore strongly suggested that **4** has a planar structure.



a: R = CH₃CH₂-
b: R = CH₂=CH(CH₃)-C(CH₃)₂-



Scheme 1.



Scheme 2.

Synthesis and Characterization of **3**

Polyradical **3** was prepared according to Scheme 2. The palladium-catalyzed cross-coupling reaction of **7** and **10**¹⁶ in the presence of Bu_4NCl and K_2CO_3 in H_2O -THF at reflux temperature for 3 days under N_2 gave **11** as a colorless powder in 47% yield. Polymer **11** was soluble in benzene, ethyl acetate, CHCl_3 , CH_2Cl_2 , and THF, but insoluble in hexane and MeOH. The number average molecular weight (M_n) of **11** determined by SEC with THF as the eluant using polystyrene standards was 4000, corresponding to 15.1 repeating units.

The ^1H NMR spectrum of **11** were measured using CDCl_3 as solvent. Although the aliphatic region was simple, the aromatic region was complex, indicating three connections between the **3** unit and 1,3-phenylene unit (head-to-tail, head-to-head, and tail-to-tail). However, this does not bring about serious problem for occurrence of ferromagnetic coupling between the radical spins through the 1,3-phenylene coupler, though the head-to-head connection may give some steric congestion.

Elemental analysis of **11** showed the presence of 1.34% of Br, indicating polycondensation is in part terminated by the unit of **7**. Although the observed values (C, 81.16; H, 7.09; N, 5.15; Br, 1.34%) are in incidental agreement with the values (C, 81.47; H, 7.22; N, 5.28) calculated as $(\text{C}_{18}\text{H}_{19}\text{NO})_n$, the values obtained, taking the presence of Br of 1.34% into account, are C, 80.38; H, 7.12; N, 5.21%. Therefore, there is a small deviation of 0.78% from the calculation for C, attributable to the influence of the polymer end structure.

Oxidation of Polymer **11**

Oxidation of **11** was carried out with 3-chloroperoxybenzoic acid in CH_2Cl_2 . To a colorless CH_2Cl_2 solution of **11** was added 3-chloroperoxybenzoic acid and the mixture was stirred at room temperature for 30 min under N_2 . After filtration, the filtrate was poured into a large excess of hexane to give **3** as a light red powder in 37% yield. The polyradical was soluble in benzene, CH_2Cl_2 , CHCl_3 , and THF, but insoluble in hexane, acetone, and MeOH.

The IR spectrum showed the complete disappearance of the peak due to NH observed in that of **11**, and the number average molecular weight determined by SEC was 4120, which agrees with that of **11**. This indicates that no significant cleavage or bridging of the polymer

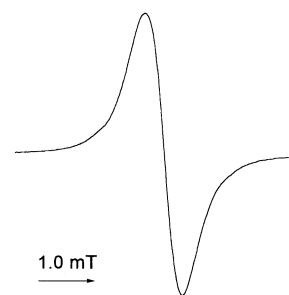
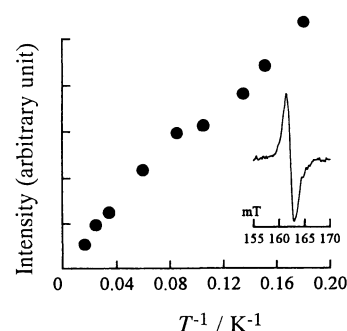
Figure 2. EPR spectrum of **3** in benzene.

Figure 3. Plots of intensity of absorption due to $\Delta M_s = 2$ forbidden transition against T^{-1} . Inset shows ESR spectrum of **3** in toluene glass matrix in the 160 mT region.

chain occurred during oxidation with 3-chloroperoxybenzoic acid.

The spin concentration of **3** determined by ESR was 1.61×10^{21} spins g^{-1} , corresponding to 0.75 spin per repeating unit. Spin concentration was constant in the solid state for a long time at room temperature.

ESR Spectra of **3** in Solution and Toluene Glass Matrix

The ESR spectrum of **3** in benzene is shown in Figure 2. In contrast to that of **4**, the hyperfine structures were smeared out and a singlet line with a peak-to-peak linewidth of 0.64 mT ($g = 2.0056$) was observed. This can be simply accounted for by exchange narrowing. This phenomenon is often observed when the spin concentrations of polyradicals are high.

To detect $\Delta M_s = 2$ forbidden transition an ESR spectrum of **3** in toluene glass matrix was measured at ~ 163 mT. As found in the inset of Figure 3, a clear absorption peak due to the $\Delta M_s = 2$ forbidden transition

was observed at 5.5–60 K. The signal intensity *vs.* T^{-1} plots gives a linear relationship, as found in Figure 3, indicating that **3** is in part at least in a triplet ground state (or both the triplet and singlet are nearly degenerated). The intramolecular magnetic interaction through the π -conjugation is thus ferromagnetic. This is the first observation of ferromagnetic interaction for poly(1,3-phenylene)-based polyradicals.

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