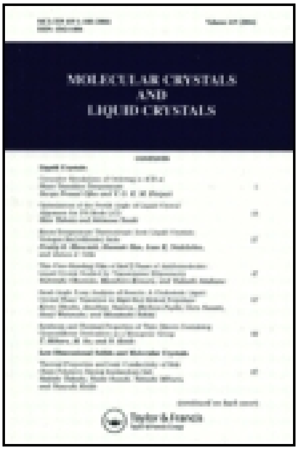

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Synthesis and Magnetic Behavior of Poly(1,3-phenylene)-Based Polyradical Carrying N-tert-Butyl Nitroxide Radicals

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Synthesis and Magnetic Behavior of Poly(1,3-phenylene)-Based Polyradical Carrying *N-tert*-Butyl Nitroxide Radicals

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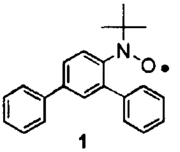
Synthesis and magnetic behavior of poly[6-(*N*-oxy-*tert*-butylamino)biphenyl-3,3'-ylene] (**2**) are described. Polyradical **2** was prepared the Pd-catalyzed polycondensation of *N-tert*-butyl-2,4-dibromoaniline with 1,3-phenylenebis(trimethylene boronate), followed by oxidation with 3-chloroperoxybenzoic acid. The degree of polycondensation determined by SEC was ~18. Polyradical **2** was very stable in both solution and solid state. The spin concentration of **2** determined by ESR was 1.89×10^{21} spins g^{-1} (0.75 spin per repeating unit). The magnetic susceptibility (χ) measurements of **2** carried out with a SQUID magnetometer showed that the magnetic interaction between the unpaired electron spins was antiferromagnetic ($\theta = -0.98$ K). No observation of the ferromagnetic interaction was ascribed to twisting of the nitroxide moiety from the π-conjugated main chain. This twisting was confirmed by the X-ray crystallographic analysis of the monomer model radical **1**.

Keywords: poly(1,3-phenylene); *N-tert*-butyl nitroxide; magnetism; polycondensation

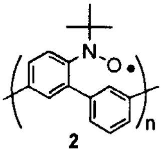
INTRODUCTION

For the study of organic ferromagnets, polymeric polyradicals have attracted much attention. A wide variety of π-conjugated spin systems have been investigated in recent years. Intramolecular spin interaction through π-conjugation is very important for polymer organic ferromagnetism. Topological symmetry of alternant hydrocarbon π-systems has been certified in the studies of 1,3-phenylene connected polycarbenes[1], and many π-conjugated polyradicals have been designed and synthesized based on topological symmetry. Poly(triarylmethyl polyradical)s (Rajca polymers) have been one of successful polyradicals, being in high spin ground states[2]. However, polycarbenes and Rajca polymers have a disadvantage that lack of carbene and radical centers leads to interruption of π-conjugation. Another type of polyradicals were poly(phenylacetylene)-[3], poly(1,3-phenylene ethynylene)-[4], and poly(phenylene vinylene)-based polyradicals[5], which have the radical spins in the side chains. These polyradicals are chemically stable in air at room temperature, but the magnetic interactions between the radical spins are weak.

We have focused on poly(1,3-phenylene)-based polyradical. Poly(1,3-phenylene) is a good ferromagnetic coupler of spins. However, poly(1,3-phenylene)-based polyradicals carrying stable pendant radicals have never been synthesized. We synthesized polyradical **2** carrying *N-tert*-butyl nitroxide radicals and measured its magnetic behavior. Herein we report the results.



1



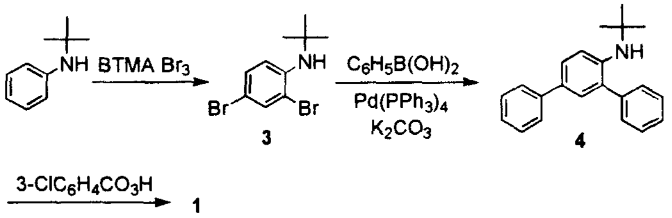
2

RESULTS AND DISCUSSION

Synthesis of Monoradical 1

Monoradical **1** was synthesized according to SCHEME 1. Dibromo **3** was prepared with benzyltrimethylammonium tribromode (BTMA Br$_3$)[6]. Treatment of a mixuture of *N-tert*-butylaniline with BTMA Br$_3$ in CH_2Cl_2–MeOH gave **3** in 93 % yield as a colorless oil, and the Pd-catalyzed cross-coupling reaction of **3** with phenylboronic acid in benzene–H_2O at the reflux temperature for 24 h under nitrogen gave **4** in 85 % yield[7]. Oxidation of **4** was carried out with 3-chloroperoxybenzoic acid. A solution of **4** and 3-chloroperoxybenzoic acid in CH_2Cl_2 was stirred for 30 min at room temperature, and the reaction mixture was chromatographed on silica gel using

CH_2Cl_2–hexane (1 : 5) to give **1** in 70 % yield. Recrystallization of **1** from hexane gave deep red prisms with mp. 94–96 °C. (Elemental analysis : Calcd for $C_{22}H_{22}NO$: C, 83.51; H, 7.01; N, 4.43. Found: C, 83.36; H, 6.71; N, 4.38.). Monoradical **1** was very stable in both solution and solid state over a long period.

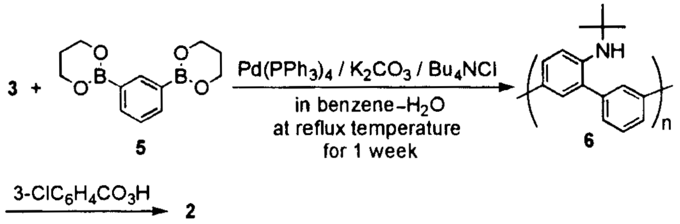


SCHEME 1

Synthesis of Polymer 6

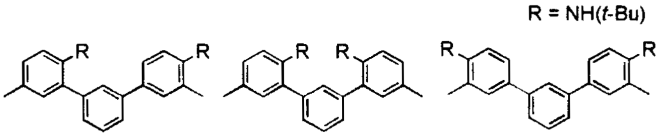
Polymer **6** was prepared by the Pd-catalyzed polycondensation of **3** with 1,3-phenylenebis(trimethylene boronate) (**5**) (SCHEME 2)[8]. A mixture of **3**, **5**, $Pd(PPh_3)_4$, K_2CO_3, and Bu_4NCl was refluxed in benzene–H_2O under nitrogen for a week. The organic layer was then separated and concentrated, and the residue was chromatographed on silica gel. In the above reaction Bu_4NCl functions as a phase transfer catalyst. Elution with benzene gave low molecular weight materials containing catalysts and elution with ethyl acetate gave polymer **6**. The polymer was reprecipitated from CH_2Cl_2–hexane to give a light yellow powder in 18 % yield. Polymer **6** was soluble in ordinary organic solvents such as benzene, $CHCl_3$, CH_2Cl_2, and THF, but insoluble in methanol, hexane, and acetone.

The molecular weight of **5** was determined by SEC (size exclusion chromatography) with polystyrene standard in THF. When the mole ratio of **5** to **3** was 1.3–1.5, the molecular weight of the polymer was the highest (4070). The polycondensation of **3** with **5** was also carried out in toluene, DME, or DMF (100 °C), but the molecular weight of the polymer was lower than in benzene. Furthermore, the polycondensation of *N-tert*-butyl-2,4-diiodeaniline with **5** was carried out, but the molecular weight of the polymer was lower.



SCHEME 2

Both the ^{1}H and ^{13}C NMR spectra of **6** were complicated in the aromatic region, suggesting that **6** has three kinds of connection between monomers: head-to-tail, head-to-head, and tail-to-tail (FIGURE 1). However, this is not an important problem for magnetic behavior of **2** because topological symmetry indicates that all these connections give intramolecular ferromagnetic interaction of spins. However, the head-to-head connection may give the amount of steric strain, reducing the effective π-conjugation.



head-to-tail head-to-head tail-to-tail

FIGURE 1. Three kinds of connection between monomers in **6**.

Oxidation of 6

Oxidation of **6** was carried out with 3-chloroperoxybenzoic acid in the same manner as for **1** (SCHEME 2). A solution of **6** and 3-chloroperoxybenzoic acid in CH_2Cl_2 was stirred for 30 minutes at room temperature, and the mixture was washed with aqueous Na_2CO_3 (10 %) and brine, and dried. After concentration, the residue was reprecipitated from CH_2Cl_2–hexane to give **2** as a light red powder in 50 % yield. Polyradical **2** was soluble in typical organic solvents as well as **6**. The IR spectrum of **2** indicated complete disappearance of the peak due to NH.

The spin concentration of **2** was determined by ESR. When the mole ratio of 3-chloroperoxybenzoic acid to **6** was 1.5 or 2.0, the spin concentration was 0.75 spin per repeating unit, which was the highest value. The SEC curve was almost identical with that of **6**, indicating that no polymer chains were cleaved or bridged during the oxidation.

ESR Spectra of 1 and 2

The benzene solution ESR spectra of **1** and **2** were measured at room temperature (FIGURE 2). Monoradical **1** showed a 1:1:1 triplet peak with a_N = 1.48 mT at g = 2.0061 (FIGURE 2(a)), and no hyperfine coupling due to any protons on the benzene ring was observed. On the other hand, the ESR spectrum of **2** was a singlet broad peak at g = 2.0061 (FIGURE 2(b)), indicating that exchange narrowing occurred because of high spin concentration of **2**.

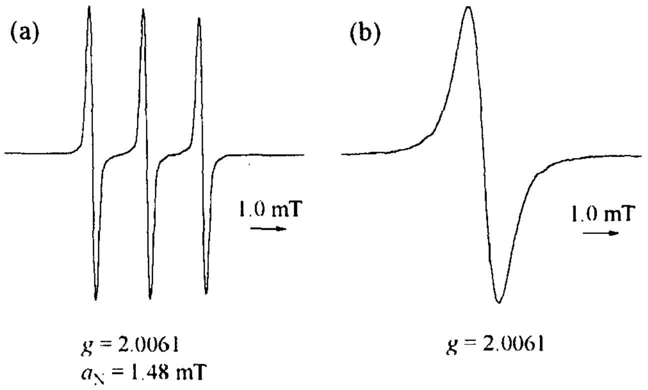


FIGURE 2 ESR spectra of **1** and **2** in benzene at 20 °C. (a) **1**; (b) **2**.

Magnetic Behavior of Polyradical 2

Magnetic susceptibility of **2** was measured by SQUID at 1.8–300 K. The χ–T

and χT–T plots are shown in FIGURE 3. The χT–T plot of **2** showed a downward turn in the temperature region below 30 K, indicating that magnetic interaction is antiferromagnetic. The χ–T plot was analyzed with the Curie–Weiss law, and the Curie and Weiss constants were determined to be $C = (1.29 \pm 0.01) \times 10^{-3}$ emu g^{-1} K and $\theta = -0.98 \pm 0.01$ K, respectively. From the Curie constant, the spin concentration was estimated to be 0.82 spin per repeating unit. This value is in good agreement with that estimated by ESR.

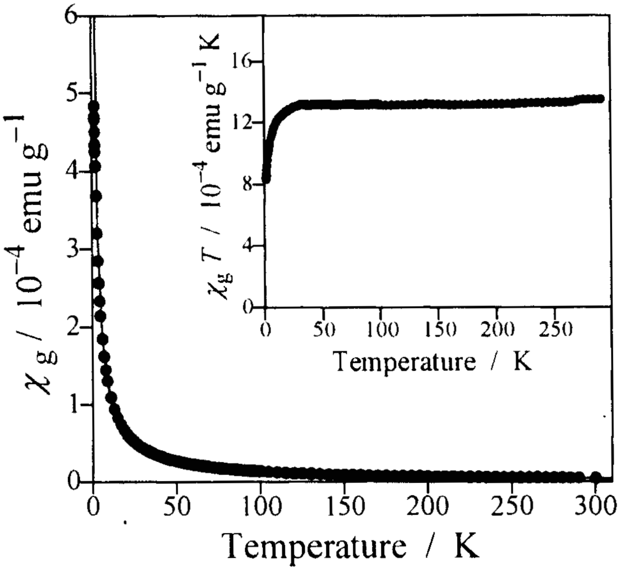
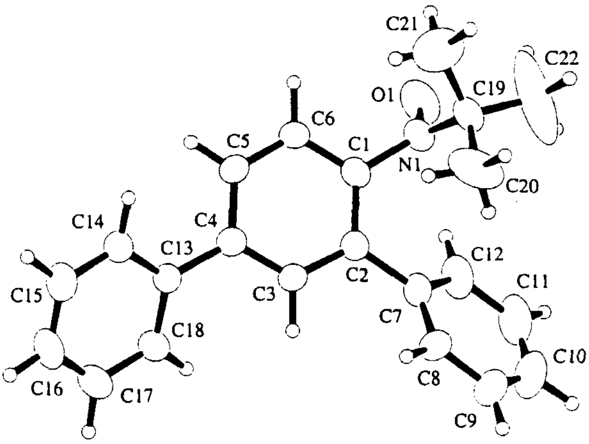


FIGURE 3 χ–T and χT–T plots spectra of **2**. The solid line is calculated by the Curie–Weiss law.

X-Ray Crystallographic Analysis of 1

Since no ferromagnetic interaction between the radical spins through the π-bond was observed for **2**, the structure of monoradical **1** was investigated by X-ray crystallographic analysis. ORTEP drawing of **1** is shown in FIGURE 4.

The dihedral angles between plane A (C1–C6) and plane B (C7–C12), A and C (C13–C18), and A and D (C1–N1–O1) were 45.4, 28.5, and 68.0°, respectively. Because the dihedral angle between A and D is large, the unpaired electron would be localized at the N–O moiety. This is in agreement with the relatively large a_N value of **1**. Therefore, intramolecular interaction between the radical spins seems to be very weak.



Dihedral angle between planes
A–B : 45.4°
A–C : 28.5°
A–D : 68.0°

plane A : C1~C6
plane B : C7~C12
plane C : C13~C18
plane D : C1–N1–O1

FIGURE 4 ORTEP drawing of **1**.

In order to solve this problem of the dihedral angle, cyclic structures as shown in FIGURE 5 are required to induce ferromagnetic interaction between the radical spins through the π-conjugation. Synthesis of poly(1,3-phenylene)-based polyradical carrying cyclic nitroxide radicals shown in FIGURE 5 are in progress.

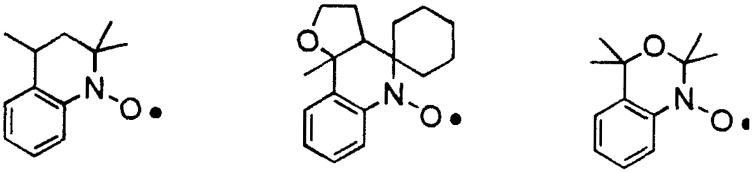


FIGURE 5 Cyclic nitroxide radicals.

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