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SYNTHESES OF NITRONYL NITROXIDE AND NITROXIDE POLYRADICALS AND THEIR MAGNETIC CHARACTERIZATION

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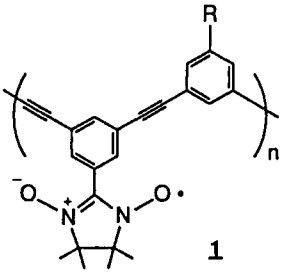
Abstract The present paper describes the syntheses of polyradicals with pendant nitronyl nitroxide (**1**) or nitroxide radicals (**2**) and their magnetic characterization. Polyradical **1** was obtained by the polycondensation of nitronyl nitroxide substituted 3,5-diethynylbenzene with 1,3-diiodobenzenes in Et_3N-pyridine in the presence of $(PPh_3)_2PdCl_2$ - CuI. The spin concentrations were 1.12×10^{21} - 1.33×10^{21} spin/g and the number average molecular weights (M_n) were 4300 - 4800. Polyradical **2** was obtained by the polymerization of *N-tert*-butyl-3-ethynyl-5-*tert*-phenyl nitroxide using a Rh catalyst. The spin concentration of **2** was 2.09×10^{21} spin/g and M_n was 11000. Solution ESR spectra of **1** and **2** were a broad single line, and no hyperfine splittings due to nitrogen and proton nuclei were observed. This is due to the spin-exchange interaction. The SQUID measurements of **1** performed in the temperature range of 300 - 1.8 K showed that polyradical **1** is paramagnetic and there is no significant interaction among the spins. The magnetic characterization of **2** is in progress.

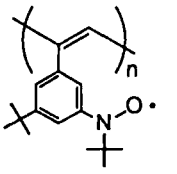
INTRODUCTION

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 singly occupied π-nonbonding orbital unlimited.[1,2] This approach predicts the occurrence of high-spin macromolecules with extremely large spins or organic superparamagnets as well as organic ferromagnets.

Standing on the theoretical background, many polyradicals have been prepared and some of them have been claimed to show ferromagnetic behaviors from the experimental sides.[3] However, there have been severe contradictions and some of those materials have suffered from poor reproducibilities in a synthetic sense. Herein we report the syntheses of polyradicals **1** and **2** and their magnetic characterization.



1

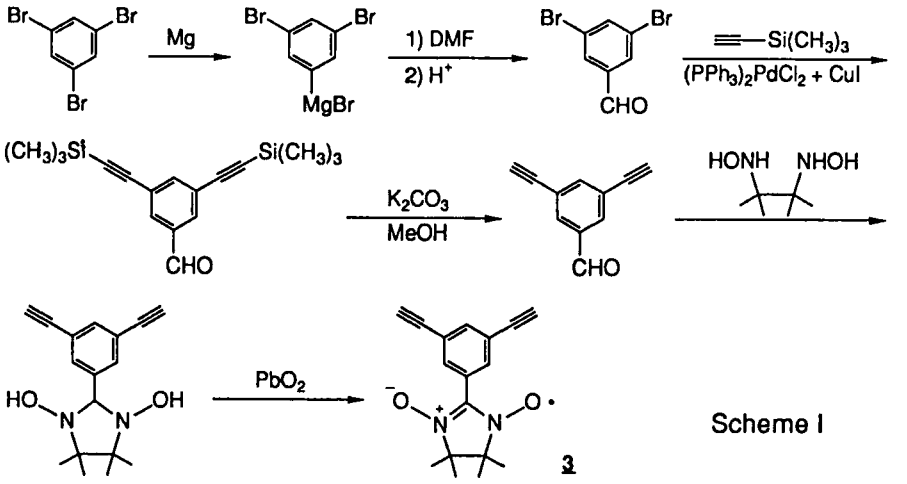


2

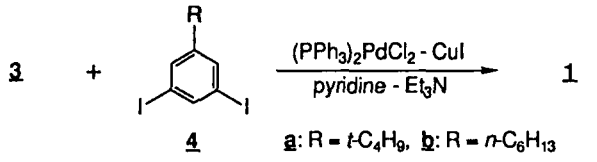
RESULTS AND DISCUSSION

SYNTHESIS OF POLYRADICAL 1

Monomer **3** was prepared according to Scheme I.[4] Palladium catalyzed polycondensation of **3** with 3,5-diiodobenzens **4** was carried out by stirring a mixture of **3**, **4**, $(PPh_3)_2PdCl_2$, and CuI in Et_3N - pyridine at 20 °C under nitrogen (Scheme II).[5] After 2 - 10 h, the mixture was poured into a large excess of methanol to give **1** as a blue powder. The results of the polycondensation are shown in Table I.



Scheme I



Scheme II

Table I. Polycondensation of **3** with **4** catalyzed by $(PPh_3)_2PdCl_2$ - CuI[a,b]

monomers[c]	polymer	time, h	yield, mg (%)	M_n[d]	spin conc., spins/g[e]
3 and **4a**	**1a**	2	206 (~100)	4300	1.31×10^{21}
3 and **4a**	**1a**	5	205 (~100)	4800	1.33×10^{21}
3 and **4a**	**1a**	10	204 (~100)	4800	1.33×10^{21}
3 and **4b**	**1b**	2	221 (~100)	4500	1.19×10^{21}
3 and **4b**	**1b**	5	218 (~100)	4700	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]**3** 141 mg (0.50 mmol), **4a** 193 mg (0.50 mmol), **4b** 206 mg (0.50 mmol). [d]Determined by GPC. [e]Determined by the ESR spectroscopic method.

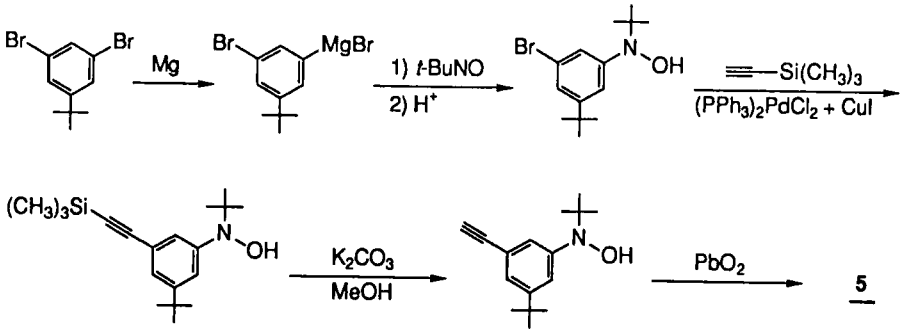
As found in Table I, the yields of **1** are quantitative. The IR spectra showed the complete disappearance of the absorption due to the stretching vibration of the ≡C-H bond (3250 cm^{-1}) characteristic of monomer **3**, confirming the structure of **1**. The polyradicals are soluble in $CHCl_3$ and CH_2Cl_2, partially soluble in THF and DMF, and insoluble in benzene and methanol. The number average molecular weights (M_n) determined by GPC were in the range of 4300 - 4800.

SYNTHESIS OF POLYRADICAL 2

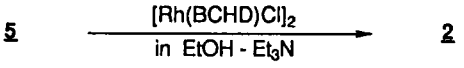
Nitroxide monomer **5** was prepared according to Scheme III. Polymerization of **5** was performed in Et_3N-ethanol with $[Rh(BCHD)Cl]_2$ catalyst (BCHD: bicyclo[2,2,1]hepta-2,5-diene) at 20 °C under nitrogen according to the

procedure reported for substituted phenylacetylene (Scheme IV), [6,7] and **2** was obtained as a reddish orange powder in 53 - 75 % yields.

The IR spectrum of **2** showed the complete disappearance of the absorption due to the stretching vibrations of the ≡C-H (3200) and C≡C (2100 cm^{-1}) characteristic of monomer **2**. The polyradical is soluble in CH_2Cl_2 and $CHCl_3$, partially soluble in THF and benzene, and insoluble in MeOH. The value of M_n of the polyradical determined by GPC was 11000.



Scheme III



BCHD ; bicyclo[2,2,1]hepta-2,5-diene

Scheme IV

ESR SPECTRA

ESR spectra recorded from a dilute solution of **1**, **2**, **3**, and **5** in CH_2Cl_2 are shown in Figure 1. The ESR spectrum of **3** is split into a 1 : 2 : 3 : 2 : 1 quintet due to the interaction with two equivalent nitrogen nuclei (a_N = 7.53 G, g = 2.0066). This ESR pattern is characteristic of 2-aryl nitronyl nitroxide radicals.[8] The ESR spectrum of **5** consists of three 1 : 3 : 3 : 1 quartets with an equivalent intensity by the interaction with one nitrogen nucleus and three aromatic protons (a_N = 13.2, a_H = 2.19 G, g = 2.0060).

In contrast to the well resolved ESR spectra of **3** and **5**, those of **1** and **2** show only a broad single line and the corresponding hyperfine splittings are

completely masked by a line broadening. The broadening of the ESR lines is due to spin-spin exchange interaction, indicating a high spin concentration of the polyradicals.

The spin concentrations of **1** and **2** were determined from the double integration of the solution ESR spectra which were obtained by 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 1.12×10^{21} - 1.33×10^{21} spin/g for **1** and 2.09×10^{21} spin/g for **2**, showing that 85 - 88 % of the spins survive during the polymerization processes.

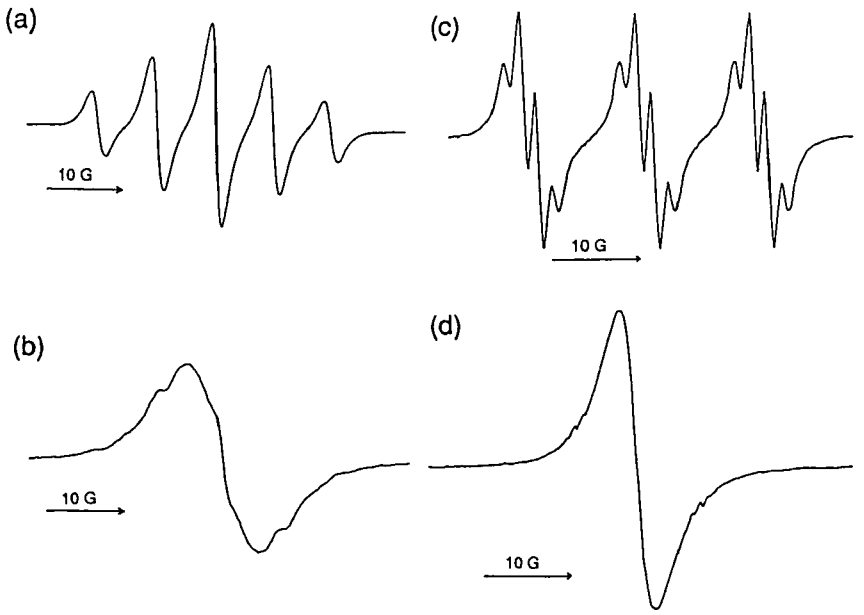


FIGURE 1. ESR spectra of **1**, **2**, **3**, and **5** in CH_2Cl_2. (a) **3**; (b) **1**; (c) **5**; (d) **2**.

UV-VIS Spectra

The UV-Vis spectra of **1, 2, 3**, and **5** were measured in CH_2Cl_2, and those of **2** and **5** are shown in Figure 2. The absorptions of **1** (λmax: 371 and ~600 nm) were very similar to those of **3** (λmax: 368 and ~600 nm), and expected bathochromic shifts were not found. On the other hand, the UV-Vis spectrum [λmax 287 (ε 9680) and 478 nm (6960)] of **2** is different from that of **5** [λmax 292 (ε 9750) and 387 nm (278)], as found in Figure 2. That is, the strong

absorption at 478 nm is not found in the UV-Vis spectrum of **5**. A similar absorption was not also found in that of poly(phenylacetylene) itself. Previously, Masuda *et al.* reported that poly(ortho-substituted phenylacetylene)s have a strong absorption around 500 nm.[9] This is obviously due to the steric effects from the ortho-substituents. Since polyradical **2** bears two bulky groups (per the repeating unit) at the meta positions, a similar situation is expected. Detailed optical spectroscopic investigations are in progress.

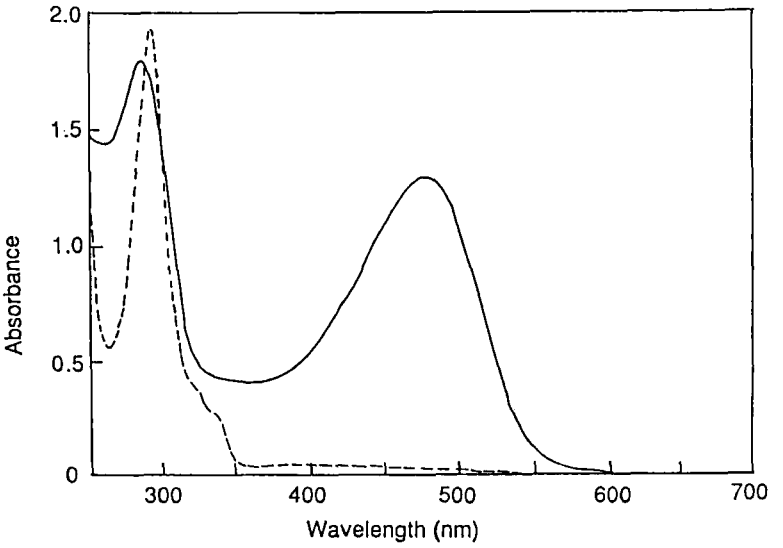


FIGURE 2. UV-Vis spectra of **2** and **5**. (——) : **2** (0.216 mmol L^{-1}); (------): **5** (0.198 mmol L^{-1}).

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The magnetic susceptibility measurements were performed with a QUANTUM DESIGN SQUID MPM2 in the temperature range of 1.8 - 300 K. The diamagnetic contributions from the sample were estimated from the Pascale diamagnetic constants. The χ^{-1} vs T plots of **1** gave a linear line characteristic of paramagnetic species with a very weak antiferromagnetic interaction (θ = -0.6 K). As found in Figure 3, the $T\chi$ vs T plots are horizontal and curve downward around 15 K, showing that there is no ferromagnetic coupling among the spins. The magnetic characterization of **2** is in progress.

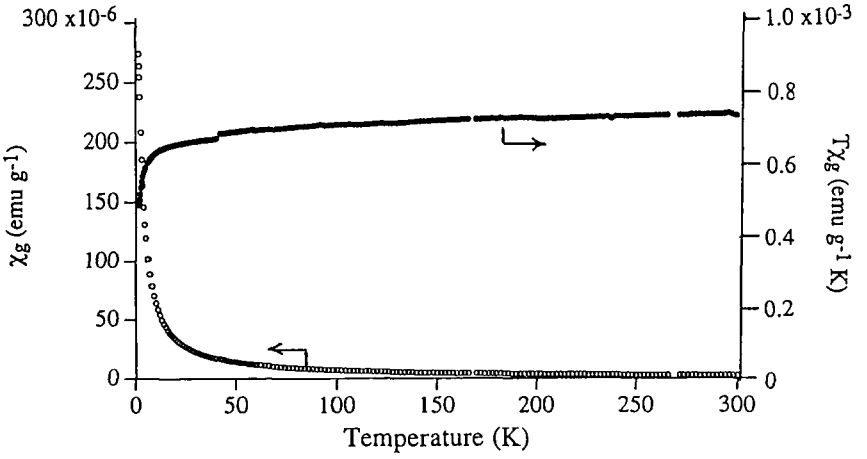


FIGURE 3. χ_g vs T and $T\chi_g$ vs T plots of polyradical **1**.

CONCLUSIONS

Polyradicals **1** and **2** were obtained by the Pd catalyzed polycondensation of **3** with **4** or by the Rh catalyzed polymerization of **5**. The polyradicals had high spin concentrations of 1.12 x 10^{21} - 1.33 x 10^{21} (for **1**) or 2.09 x 10^{21} spins/g (for **2**). The SQUID measurements showed that polyradical **1** is paramagnetic, showing no significant amount of the interaction among the spins. On the other hand, polyradical 2 showed an irreversible transition of magnetic behavior. The detailed study is under way. The failure in inducing ferromagnetic interactions among the spins for polyradical **1** can be ascribable to the less delocalization of the spins from the nitronyl nitroxide sites onto the *m*-phenylenediethynylene couplers.[10] The syntheses of other types of polyradicals are in progress.

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