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Synthesis of Poly(ethynylbenzene) with Pendant Nitroxide Radicals by Rhodium-Catalyzed Polymerization of Ethynylphenyl Nitroxide

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Introduction

The quest for synthetic organomagnetic 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 the 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, some poly(ethynylbenzene)s with pendant stable free radicals such as phenoxy,[3] galvinoxyl,[4] and nitronyl nitroxide[5,6] have so far been synthesized. However, the magnetic investigations of these polyradicals showed that they were paramagnetic, showing there is no significant ferromagnetic interaction among the spins. The results were explained in terms of the low–spin concentration of polyradicals or no sufficient delocalization of the spins onto the conjugated polyene backbone. These disadvantages may be overcome by using poly(ethynylbenzene) with pendant nitroxide radicals. Herein we report the synthesis of poly(ethynylbenzene) with pendant nitroxide radicals (**2**) by Rh-catalyzed polymerization of *N*,5-di-*tert*-butyl-3-ethynylphenyl nitroxide (**1**).

Results and Discussion

Nitroxide monomer **1** was synthesized according to Scheme I. 1,3-Dibromo-5-*tert*-butylbenzene[7] was converted to the corresponding Grignard reagent by treatment with magnesium in THF. The Grignard reagent was then treated with a 2-methyl-2-nitrosopropane dimer to give hydroxyamine **3** in 86% yield.[7] The hydroxyamine was allowed to react with (trimethylsilyl)acetylene in Et_3N in the presence of $(PPh_3)_2PdCl_2$ and CuI, and the coupling compound **4** was obtained in 95% yields. Hydrolysis of **4** was carried out in methanol in the presence of K_2CO_3, and compound **5** was obtained in 89% yield after purification by sublimation. Oxidation of **5** was performed with PbO_2 in benzene, and nitroxide **1** was obtained as reddish microprisms with mp 108–110 °C in 74% yield after sublimation. The formulates of **1** and **5** were confirmed by elemental analyses and the ^1H NMR spectrum (see the Experimental Section).

Polymerization of **1** was performed in anhydrous EtOH–Et_3N with $[Rh(BCHD)Cl]_2$ catalyst (BCHD: bicyclo[2.2.1]-hepta-2,5-diene) under nitrogen according to the procedure reported for substituted ethynylbenzene (Scheme II).[8,9] A homogeneous solution of **1**, Et_3N, and $[Rh(BCHD)Cl]_2$ in anhydrous EtOH was stirred at 20 °C under nitrogen. After ca. 20 min, the polymer precipitation began. The heterogeneous mixture was further stirred for 40–160 min and poured into a large excess of methanol to give **2** as a brick-red powder with a number-average molecular weight ($\bar{M}_n$) of 9200–11 000 in 51–53% yield (see Table I). In the absence of Et_3N, however, the yield was lower (33%) and $\bar{M}_n$ was smaller (5600). When benzene or CH_2Cl_2 was used as the solvent, no polymeric product was obtained. The polymerization of **5** was also attempted in ethanol in the presence of Et_3N, but no polymeric product was obtained. In this case the Rh catalyst may be poisoned by the N–OH group in monomer **1**.

The IR spectrum of **2** showed the complete disappearance of the stretching vibration of the ≡C-H (3200 cm^{-1}) and C≡C bonds (2100 cm^{-1}) characteristic of monomer **1**, and the elemental analysis satisfactorily agrees with the calcuations. The polyradical was soluble in CH_2Cl_2 and $CHCl_3$, partially soluble in THF and benzene, and insoluble in MeOH.

Solution ESR spectra of **1** and **2** are shown in Figure 1. Both ESR spectra were recorded from a dilute degassed solution of **1** or **2** in CH_2Cl_2 at 20 °C. As found in Figure 1, the ESR spectrum of **1** consists of three 1:3:3:1 quartets by the interaction with one nitrogen nucleus and three magnetically equivalent aromatic protons (a_N = 1.32 mT, a_H = 0.219 mT, g = 2.0060). The magnitudes of ESR parameters are typical of planar phenyl *tert*-butyl nitroxide radicals,[10] suggesting a planar conformation of **1** for which considerable delocalization of the unpaired electron onto the phenyl group can be expected.

In contrast to the well-resolved ESR spectrum of **1**, that of **2** consists of a hyperfine-smeared single line (g = 2.0061) with a peak-to-peak line width of 0.84 mT, even in a dilute solution. This hyperfine-smeared spectrum is due to spin-exchange interactions, indicating that the spin concentration of the polyradical is sufficiently high.

The spin concentrations of monomer **1** and polyradical **2** were determined 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).[11] The values obtained were 2.32×10^{21} spins/g for **1** and 2.09×10^{21} spins/g for **2**. From the values the purity of **1** and the spin concentration per repeating unit of **2** were estimated to be 94% and 85%, respectively. Thus it was shown that no significant decomposition of the spin sites took place during the polymerization process. Interestingly, the polyradical was very stable over long periods at room temperature. The magnetic susceptibility measurements of polyradicals **2** are under way.

Experimental Section

Measurements. IR spectra were run on a Jasco A-202 spectrophotometer. ^1H NMR spectra were recorded with a JEOL GX-400 spectrometer (400 MHz); chemical shifts (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 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 **1** and **2** were determined by the double-integrated ESR spectra of the sample solutions (0.87×10^{-4}–1.83×10^{-4} M) in CH_2Cl_2. Calibration curves were drawn with the 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.

Materials. $[Rh(BCHD)Cl]_2$ was purchased from Aldrich. Anhydrous ethanol was obtained by distillation from $Mg(OEt)_2$. Triethylamine was used after it was passed through a short alumina column and subsequently distilled.

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Scheme I

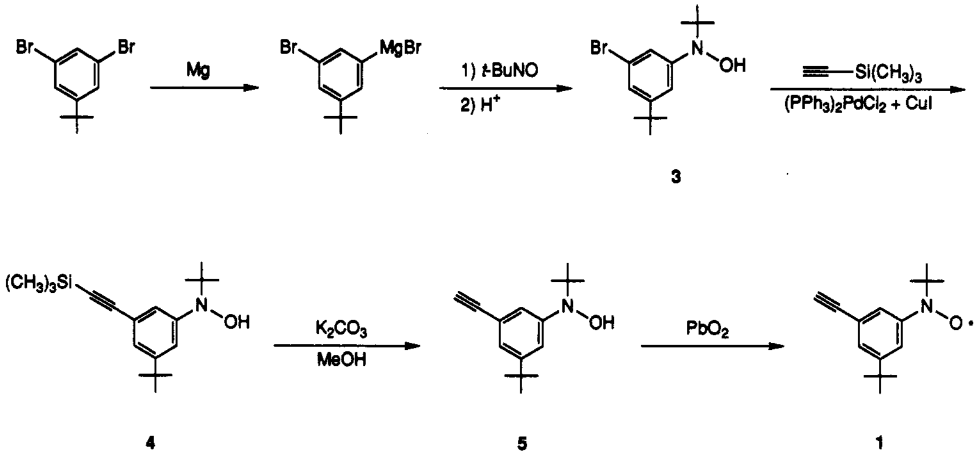
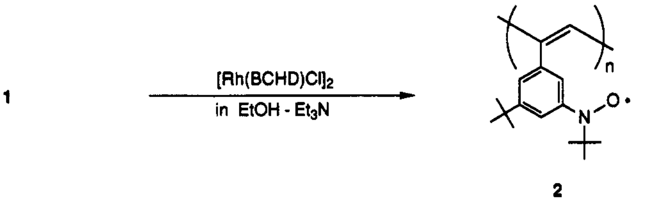


Table I. Results of Rh-Catalyzed Polymerization of 1 and 5[a]

run	monomer[b]	solvent[c]	Et$_3$N, mmol	time, h	yield, %	$\bar{M}_n$[d]	M_w/M_n[d]	spin concn,[e] ×10^{-21} (spins/g, (%)[f])
1	1	EtOH	0.82	1	51	9200	3.6	2.09 (85)
2	1	EtOH	0.82	3	53	11000	3.2	2.09 (85)
3	1	EtOH	0	3	33	5600	4.8	2.02 (82)
4	1	benzene	0.82	3	0			
5	1	CH$_2$Cl$_2$	0.82	3	0			
6	5	EtOH	0.82	3	0			

[a] [Rh(BCHD)Cl]$_2$, 0.41 × 10^{-2} mmol; temperature, 20 °C. [b] 0.41 mmol. [c] 4.0 mL. [d] Determined by GPC. [e] Determined by ESR. [f] The values refer to the percent spin concentration per repeating unit.

Scheme II



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

1,3-Dibromo-5-*tert*-butylbenzene. This compound was obtained from 4-*tert*-butylaniline according to the method reported by Iwamura et al.[7] Purification was performed by column chromatography (silica gel, hexane) and subsequent distillation [108–109 °C (4.5 mmHg)]. On standing, it solidified to give colorless needles with mp 31 °C.

***N*,5-Di-*tert*-butyl-*N*-hydroxy-3-bromoaniline (3).** This compound was obtained by a procedure similar to that of Iwamura et al.[7] Thus, a mixture of 3.10 g (10.6 mmol) of 1,3-dibromo-5-*tert*-butylbenzene and 0.30 g of Mg in 30 mL of anhydrous THF was gently refluxed and then stirred for 1 h at room temperature. After cooling with ice water, 0.67 g (3.84 mmol) of a 2-methyl-2-nitrosopropane dimer in 5 mL of anhydrous THF was added, and the resulting mixture was stirred for 1 h at room temperature. Then, aqueous NH$_4$Cl (excess) was added at 0 °C, and the mixture was extracted twice with ether. The combined ether extract was dried (MgSO$_4$) and evaporated, and the residue was column chromatographed on silica gel (Waco gel, C-200) using benzene as the eluant to give 3 in 86% yield (1.99 g, 6.60 mmol) as an orange oil, which solidified on standing at room temperature: mp 65–68 °C (lit.[7] mp 73–76 °C); ^{1}H NMR (CDCl$_3$) δ 1.12 (s, *t*-Bu, 9 H), 1.26 (s, *t*-Bu, 9 H), 6.35 (br s, OH, 1 H), 7.04 (t, *J* = 1.83 Hz, aromatic, 1 H), 7.24 (t, *J* = 1.83 Hz, aromatic, 1 H), 7.30 (t, *J* = 1.83 Hz, aromatic, 1 H).

***N*,5-Di-*tert*-butyl-*N*-hydroxy-3-[(trimethylsilyl)ethynyl]-aniline (4).** A mixture of 1.99 g (6.6 mmol) of 3, 0.33 g of (PPh$_3$)$_2$PdCl$_2$, and 0.04 g of CuI was stirred at room temperature for 1 h under nitrogen, and a solution of 0.70 g (7.1 mmol) of (trimethylsilyl)acetylene in 3 mL of Et$_3$N was added. After the resulting mixture was stirred at the reflux temperature for 4 h, it was cooled and filtered with a Buchner funnel. The filtrate was evaporated, and the residue was column chromatographed on silica gel with benzene as the eluant to give 4 as a colorless solid in 95% yield (2.00 g, 6.30 mmol): mp 174–176 °C; ^{1}H NMR (CDCl$_3$) δ 0.25 (s, SiMe$_3$, 9 H), 1.10 (s, *t*-Bu, 9 H), 1.26 (s, *t*-Bu, 9 H), 6.52 (s, OH, 1 H), 7.12 (t, *J* = 1.83 Hz, aromatic, 1 H), 7.23 (d, *J* = 1.83 Hz, aromatic, 1 H), 7.24 (d, *J* = 1.83 Hz, aromatic, 1 H).

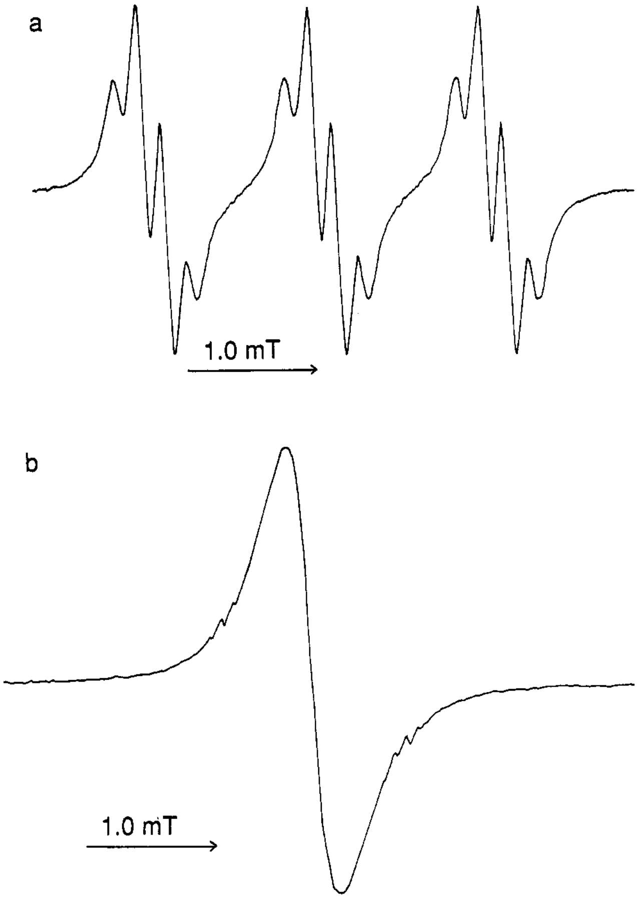


Figure 1. ESR spectra 1 (a) and 2 (b) in dichloromethane at 20 °C.

***N*,5-Di-*tert*-butyl-*N*-hydroxy-3-ethynylaniline (5).** A mixture of 4 (2.00 g, 6.30 mmol) in 80 mL of MeOH was warmed to ~40 °C to dissolve 4 completely and then cooled to room temperature. After 0.6 g of K_2CO_3 was added, the mixture was stirred at room temperature for 5 h and concentrated to 20 mL under reduced pressure. Dichloromethane (50 mL) was then added, and the CH_2Cl_2 layer was washed with water and dried ($MgSO_4$). Filtration and evaporation gave an orange solid, which was sublimed at ~80 °C (1 mmHg) to give **5** as colorless microprisms in 89% yield (1.37 g, 5.58 mmol): mp 129–130 °C: IR (KBr) 3240 (≡CH), 3200 (OH), 2950–2850 (*t*-Bu), 2100 cm^{-1} (C≡C); ^{1}H NMR ($CDCl_3$) δ 1.12 (s, *t*-Bu, 9 H), 1.27 (s, *t*-Bu, 9 H), 3.01 (s, ≡CH, 1 H), 6.09 (s, OH, 1 H), 7.18 (t, J = 1.83 Hz, aromatic, 1 H), 7.24 (d, J = 1.83 Hz, aromatic, 1 H), 7.27 (d, J = 1.83 Hz, aromatic, 1 H). Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.03; H, 9.26; N, 5.70.

***N*,5-Di-*tert*-butyl-3-ethynylphenyl Nitroxide (1).** To a solution of 100 mg (0.41 mmol) of **5** in 20 mL of benzene were added 1.0 g of K_2CO_3 and 1.0 g of PbO_2. The mixture was stirred for 30 min at room temperature and filtered. The solvent was removed by freeze-drying, and the resulting orange powdery crystals were sublimed ~65 °C (1 mmHg) to give **1** as orange microprisms in 74% yield (74 mg, 0.30 mmol): mp 108–110 °C; IR (KBr) 3200 (≡CH), 2950–2850 (*t*-Bu), 2100 (C≡C), 1580, 1560, 1460, 1415, 1395, 1365, 1350, 1280, 1260, 1240, 1220, 1190, 915, 870, 840, 755, 720, 690, 575 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 292 (ϵ 9750), 387 nm (278); ESR (CH_2Cl_2) a_N 1.32 mT, a_H 0.219 mT, g 2.0060. Anal. Calcd for $C_{16}H_{22}NO$: C, 76.64; H, 9.08; N, 5.70. Found: C, 78.86; H, 9.24; N, 5.70.

Polymerization of 1. A typical procedure of the Rh-catalyzed polymerization of **1** is as follows: a mixture of 0.100 g (0.41 mmol) of **1**, 1.89 mg (0.41 × 10^{-2} mmol) of $[Rh(BCHD)Cl]_2$, and 0.12 mL (0.82 mmol) of Et_3N in 4 mL of anhydrous EtOH was stirred at room temperature for 1–3 h under nitrogen, and the polymerization mixture was poured into a large excess of methanol to give polyradical **2** as a brick-red powder in 51–53% yield. The results of the polymerization are summarized in Table I. IR (KBr): 2950–2850 (*t*-Bu), 1590, 1480, 1460, 1420, 1390, 1360, 1240, 1200, 880, 870, 840, 800, 755, 720, 705, 580 cm^{-1}. Anal. Calcd for $(C_{16}H_{22}NO)_n$: C, 78.64; H, 9.08; N, 5.73. Found: C, 78.37; H, 9.01; N, 5.58.

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