# Magnetic and Optical Characterization of Poly(ethynylbenzene) with Pendant Nitroxide Radicals

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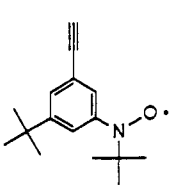
*Received June 30, 1993*

## Introduction

The quest for synthetic organomagnetic materials is the focus of current topics in many fields of both pure and applied sciences.[1] One approach exploits topological symmetry of the $\pi$-electron network in alternant hydrocarbons, which renders the degeneracy of a singly occupied $\pi$-nonbonding orbital unlimited.[2] This approach predicts the occurrence of high spin macromolecules with extremely large spins or organic superparamagnets as well as organic ferromagnets. According to this theoretical principle, a variety of polyradicals have been synthesized and their magnetic characterizations have widely been made. Particularly interesting are poly(ethynylbenzene)s with pendant stable free radicals because high spin concentration and high molecular weight polyradicals of this type can be relatively readily obtained by polymerization of ethynylbenzenes with pendant stable free radicals or by polymerization of ethynylbenzene with pendant radical precursors, followed by oxidation. For example, poly(ethynylbenzene)s with pendant stable phenoxy,[3] galvinoxyl,[4] nitronyl nitroxide radicals,[5-7] trityl,[8] and bis(diphenylene)phenylallyl radicals[9] have been synthesized up to now. The magnetic investigations of these polyradicals, however, have showed that they are paramagnetic and there is no detectable ferromagnetic interaction among the spins. The magnetic results may be explained in terms of the low spin concentrations (phenoxy and trityl polyradicals) or insufficient delocalization/polarization of the spins to the conjugated polyene backbone [nitronyl nitroxide, galvinoxyl, and bis(diphenylene)phenylallyl polyradicals]. It is expected that these disadvantages may be overcome by the syntheses of poly(ethynylbenzene) with pendant nitroxide radicals because in aryl alkyl nitroxides the spin is delocalized over the whole of the molecules. Indeed, for *tert*-butyl 3-vinylphenyl nitroxide the hyperfine splittings due to the vinyl $\alpha$ (−0.023 mT) and $\beta$ protons (+0.023 mT) were observed by NMR.[10,11] We therefore investigated the method of the syntheses of high spin concentration nitroxide polyradicals. It was found that a stable nitroxide monomer, 1, is polymerized



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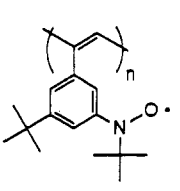

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by the use of a Rh catalyst, without significant decomposition of the nitroxide groups, giving polynitroxide 2 in 30–50% yields.[12] The number average molecular weights determined by GPC are 5600–11000, and the spin concentrations determined by ESR spectroscopy are $2.02 \times 10^{21}$–$2.09 \times 10^{21}$ spins/g (82–85% spin/repeating unit). Herein we report the optical and magnetic characterization of the nitroxide polyradical.

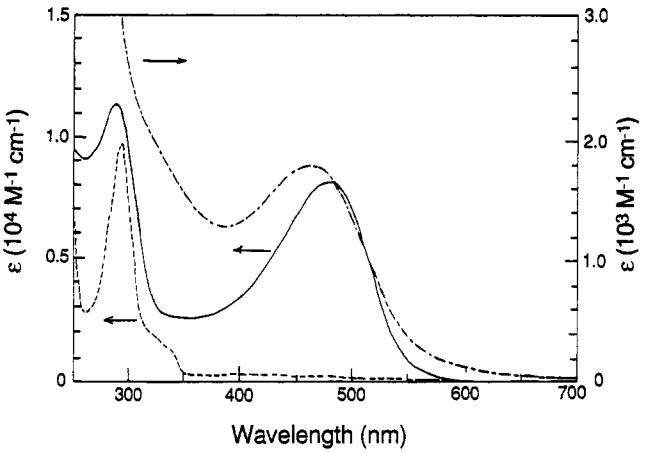
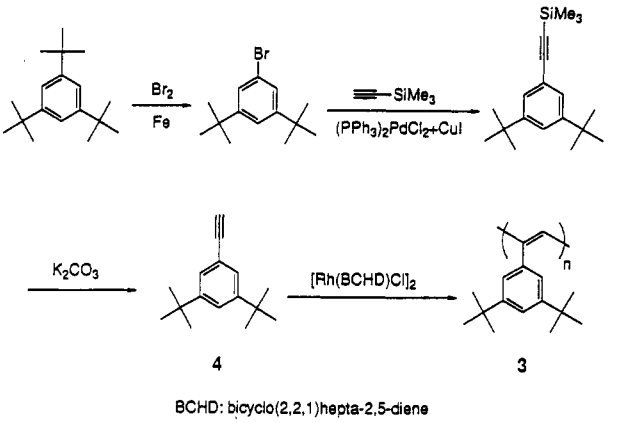



**Figure 1.** UV–visible spectra of **1**–**3** in dichloromethane: (- - -) **1**; (—) **2**; (– - –) **3**. $\epsilon$ of **2** is corrected for the spin concentration determined by ESR spectroscopy.

**Scheme I**




BCHD: bicyclo(2,2,1)hepta-2,5-diene

## Results and Discussion

The UV–visible spectrum of polynitroxide **2** was measured in dichloromethane, together with nitroxide monomer **1** (Figure 1). While **1** gives the absorption maxima at 292 ($\epsilon$ 9750) and 387 nm (278), **2** gives those at 287 ($\epsilon$ 11 400) and 478 nm (8190), there being a large difference in the visible region. Recently, Masuda et al. reported that poly(ortho-substituted ethynylbenzene)s gave a broad absorption maximum around 500 nm, which is a much longer wavelength than that of poly(ethynylbenzene) ($\lambda_{max}$ < 300 nm).[13] Also, Nishide et al. reported that such a broad absorption was observed for poly(3,5-di-*tert*-butyl-4-(hydroxyethynyl)benzene) (450 nm, log $\epsilon$ = 3.6), and they accounted for this absorption in terms of the extended backbone conjugation caused by reduction of the mixing of the $\pi$ orbitals between the polyene backbone and the phenyl rings, which is the result from the restricted bond rotation between the polyene backbone and the phenyl ring and/or crowded packing of the chain-sided substituent.[3] If this is true, poly(3,5-di-*tert*-butylethynylbenzene) (**3**) should also give such a broad absorption around 500 nm. To confirm this one, 3,5-di-*tert*-butylethynylbenzene (**4**) was prepared from 1,3,5-tri-*tert*-butylbenzene according to the procedures shown in Scheme I and polymerized by a Rh catalyst in ethanol containing a small amount of triethylamine. Since **3**, which was obtained as a reddish

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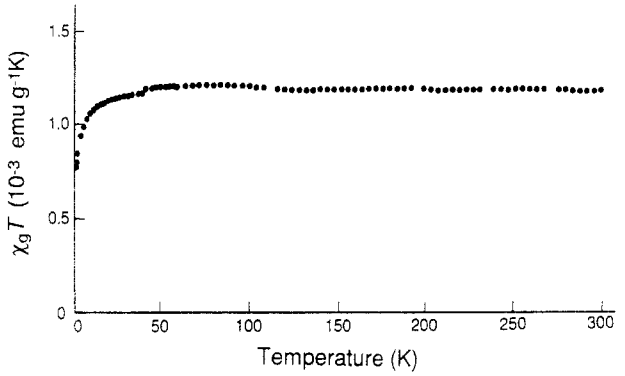


**Figure 2.** $\chi T$ vs $T$ plot of **2**.

brick powder in 26% yield, was partially soluble in dichloromethane, the soluble part was used for the UV–visible measurements. As shown by Figure 1, **3** gives an absorption maximum at 463 nm ($\epsilon$ 1770), which is close to that of **2** (478 nm). From the optical results it is likely that nitroxide polyradical **2** adopts a conformation twisted between the conjugated polyene backbone and the phenyl ring.

The magnetic susceptibility measurements of polyradical **2** (spin concentration $2.09 \times 10^{21}$ spins/g) were carried out with a SQUID magnetometer in the temperature range 1.8–300 K. The diamagnetic contribution from the sample was estimated from the Pascal diamagnetic constants.

When the magnetic interactions among the electron spins are smaller than the energy of the thermal fluctuation $\kappa T$, the magnetic susceptibility $\chi$ is expressed by eq 1,

$$\chi = \frac{N\mu_B{}^2 g^2 J(J+1)}{3\kappa} \frac{1}{T-\theta} \tag{1}$$

where $N$ is Avogadro's number, $\mu_B$ is the Bohr magneton, $g$ is the Lande factor, $J$ is the total angular momentum quantum number, and $\theta$ is the Weiss temperature. If the orbit angular momentum is neglected, $J$ can be replaced with the spin quantum number $S$, and eq 1 is written as eq 2, where $N\mu_B{}^2 g^2 S(S+1)/3\kappa$ is called the Curie constant $C$.

$$\chi = \frac{N\mu_B{}^2 g^2 S(S+1)}{3\kappa} \frac{1}{T-\theta} \tag{2}$$

$$\frac{1}{\chi} = \frac{T-\theta}{C} \tag{3}$$

The $1/\chi$ vs temperature plots in the temperature range 1.8–300 K gave a linear curve with the Curie constant of $1.26 \times 10^{-3}$ emu K $g^{-1}$ and the Weiss temperature ($\theta$) of $-1.0 \pm 0.3$ K. The spin concentration of this polynitroxide derived from this Curie constant, providing that $S = {}^1/_2$, is $2.02 \times 10^{21}$ spins/g (82% spin/repeating unit), which is in good agreement with the previous value ($2.09 \times 10^{21}$ spins/g) determined by ESR spectroscopy.

Figure 2 shows the $\chi T$ vs $T$ plots of the polyradical. As found in the figure, the $\chi T$ values are approximately constant above ca. 30 K, which indicates that this polynitroxide is paramagnetic. At low temperatures below ca. 30 K, a downward turn of the curve is observed which indicates weak antiferromagnetic interactions among the spins. Thus the SQUID data indicate that this polynitroxide is a paramagnetic species showing weak antiferromagnetic interactions at very low temperatures.

In conclusion, the present magnetic susceptibility results reveal that the nitroxide polyradical shows no appreciable ferromagnetic interactions among the spins in spite of the high spin concentration of the polyradical. This may be explained in terms of the twisted conformation of the nitroxide polyradical which prevents the large delocalization/polarization of the spin to the polyene backbone. Another possible explanation for the result is that, owing to the meta substitution of the nitroxide groups, there is no sufficient delocalization/polarization of the spins to the polyene backbone to induce the ferromagnetic interactions among the spins. To overcome these problems, the following points should be improved: (1) planarity of polyradical frameworks; (2) sufficient delocalization/polarization of the spins to the polyene backbone or couplers.

## Experimental Section

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer. UV–visible spectra were measured with a Shimadzu UV-2200 spectrophotometer. $^1$H NMR spectra were recorded with a JEOL GX-400 spectrometer (400 MHz); chemical shifts ($\delta$) are expressed in parts per million downfield from TMS as an internal standard.

Magnetic susceptibility ($\chi$) measurements were carried out on a Quantum Design SQUID MPMS2 magnetometer in the temperature range 1.8–300 K. The diamagnetic contribution of the sample was estimated from the Pascal diamagnetic constants.

3,5-Di-*tert*-butylbromobenzene was obtained by the reaction of tri-*tert*-butylbenzene with $Br_2$ in the presence of iron powder according to the reported method.[14]

**3,5-Di-*tert*-butyl[(trimethylsilyl)ethynyl]benzene (3).** A mixture of 2.0 g (7.3 mmol) of 3,5-di-*tert*-butylbromobenzene, 0.37 g of $(PPh_3)_2PdCl_2$, and 0.05 g of CuI in 30 mL of triethylamine was stirred for 1 h at room temperature under nitrogen. After a solution of 1.04 g (10.6 mmol) of (trimethylsilyl)acetylene in 3 mL of $Et_3N$ was added, the resulting solution was refluxed for 4 h under nitrogen with stirring. After filtration, the filtrate was evaporated under reduced pressure and the residue was column chromatographed on silica gel (Wako gel, C-200) with hexane as an eluant to give **3** in 96% yield (2.01 g, 7.0 mmol) as yellow prisms. Mp: 135–137 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.26 (s, $SiMe_3$, 9 H), 1.31 (s, *t*-Bu, 18H), 7.31 (d, $J$ = 1.8 Hz, aromatic, 2H), 7.37 (t, $J$ = 1.8 Hz, aromatic, 1H).

**3,5-Di-*tert*-butyl-1-ethynylbenzene (4).** Compound **3** (1.96 g, 6.8 mmol) was dissolved in 200 mL of methanol. After 0.60 g of $K_2CO_3$ was added, the mixture was stirred for 5 h under nitrogen and concentrated to 50 mL by evaporation. After water (200 mL) was added, the product was extracted with $CH_2Cl_2$. The $CH_2Cl_2$ extract was washed with a 5% $NaHCO_3$ aqueous solution and water, dried ($MgSO_4$), and evaporated, and the residue was sublimed at ~55 °C/1 mmHg to give **4** in 82% yield (1.20 g, 5.6 mmol) as light yellow prisms. Mp: 85–86 °C (lit.[15] 87–88.5 °C). IR (KBr): 3270 ($\nu_{\equiv C-H}$), 2950 ($\nu_{t\text{-Bu}}$), 2100 ($\nu_{C\equiv C}$), 1590 cm$^{-1}$ ($\nu_{Ph}$). $^1$H NMR ($CDCl_3$): $\delta$ 1.31 (s, *t*-Bu, 9 H), 3.02 (s, $\equiv$C—H, 1H), 7.35 (d, $J$ = 1.8 Hz, aromatic, 2H), 7.42 (t, $J$ = 1.8 Hz, aromatic, 1 H). Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.38; H, 10.32.

**Polymerization of 4.** A mixture of 90 mg (0.42 mmol) of **4**, 3.8 mg ($8.2 \times 10^{-3}$ mmol) of $[Rh(BCHD)Cl]_2$, and 0.1 mL of $Et_3N$ in 4 mL of anhydrous EtOH was stirred for 1 h under nitrogen at room temperature. The polymerization mixture was then poured into a large excess of hexane to give poly(3,5-di-*tert*-butyl-1-ethynylbenzene) (**5**) in 26% yield as a reddish brick powder. IR (KBr): 2950 ($\nu_{t\text{-Bu}}$), 1590 cm$^{-1}$ ($\nu_{Ph}$).

**Acknowledgment.** This work was supported (in part) by the Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No. 228/04242220) from the Ministry of Education, Science, and Culture, Japan.

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