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Poly[[4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]acetylene] and the Magnetic Property of Its Radical Derivative

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ABSTRACT: [4-(*N*-*tert*-Butyl-*N*-hydroxyamino)phenyl]acetylene (**7**) was synthesized and polymerized to yield a solvent-soluble polyacetylene: poly[[4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]acetylene] (**8**). Oxidation of the polymer gave its radical derivative: the ESR spectrum showed a broad signal only in the $\Delta m_s = \pm 1$ region, and magnetic measurement with a SQUID magnetometer revealed an antiferromagnetic through-space interaction.

Introduction

There has recently been substantial interest in the synthesis of organic π-conjugated polyradicals as potential candidates of molecular-based magnetic materials.[1,2] A series of low-molecular-weight π-conjugated multiradicals have been synthesized and reported to show intramolecular and positively magnetic interactions and to possess maximum spin multiplicity in their ground-state.[3] This kind of magnetic interaction represents ferromagnetism on the molecular level. By designing the macromolecular π-conjugation, the spins are also expected to be magnetically coupled by through-bond or intramolecular interaction in the polyradicals, and a very large spin cluster will be obtained along one polymer chain.

According to a simple theorem proposed by Ovchinnikov,[4] which was also supported and developed by computational examinations,[5] the ground-state spin quantum number S for an alternant π-conjugated molecule is described by[4a]

$$S = (n^* - n)/2 \qquad (1)$$

where n^* and n are the numbers of starred and unstarred centers, respectively. When the theorem is applied to π-conjugated macromolecules such as the polymer of the acetylene containing a π-conjugated built-in radical group, S increases in proportion to the degree of polymerization.

As model polyradicals with such high-spin electronic structure, we have previously synthesized poly[(3,5-di-*tert*-butyl-4-oxyphenyl)acetylene][6] (**1**; Chart I) and poly[[4-[(3,5-di-*tert*-butyl-4-oxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phenyl]acetylene][7] (**2**). Though various other poly(phenylacetylene) derivatives containing radical groups have also been reported,[8–13] no intramolecular high-spin ordering was observed.

We explored an alternative radical group to introduce the polyacetylenic main chain, by comparing ESR spin-coupling constants of the vinylic protons of the corresponding monomeric compounds (Chart II). 2,6-Di-*tert*-butyl-4-vinylphenoxy (**4**) has been reported[14] to be tautomerized to the quinone methide structure and to be easily dimerized. On the other hand, (*p*-vinylphenyl)-galvinoxyl (**5**) gave no vinylic hyperfine structure (hfs) in an ESR study of its solution,[15] indicating that the radical strictly localizes in the galvinoxyl moiety of **5**. A moderate hyperfine structure constant (hfsc) was reported for isolable *tert*-butyl vinylphenyl nitroxide[16] (**6**), representing effective distribution of the spin density throughout the vinyl group. *p*-**6** is superior to *m*-**6** as a monomer structure because of it has larger hfsc on the vinylic protons ($a_{\alpha\text{-H}}$ 1.1, $a_{\beta\text{-H}}$ 1.1) than those of *m*-**6** ($a_{\alpha\text{-H}}$ −0.23, $a_{\beta\text{-H}}$ +0.22). These results suggest that the spin density distributes throughout the π-conjugated polymer chain in poly(phenylacetylene) *para*-substituted with *tert*-butyl nitroxide (**3**). This paper describes the polymerization of [4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]acetylene (**7**), formation of the polyradical derivative **3**, and its magnetic property characterized with ESR and a SQUID magnetometer.

Chart I

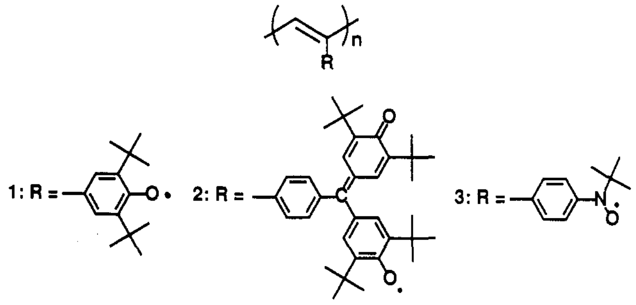
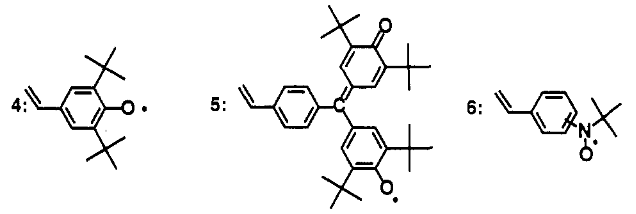


Chart II



Results and Discussion

Synthesis. *N*-*tert*-Butyl-*N*-hydroxyamino-substituted poly(phenylacetylene) was previously synthesized *via* an organometallic coupling reaction of 2-methyl-2-nitrosopropane and poly[(4-bromophenyl)acetylene].[9a] We have synthesized the acetylenic monomer [4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]acetylene (**7**) *via* Scheme I. The acetylene coupling reaction of *p*-iodobromobenzene proceeded selectively at the iodo position by using $Pd(PPh_3)_2Cl_2$.[17] *tert*-Butylhydroxylamine was introduced by coupling the terminally protected acetylene intermediate, [4-[(trimethylsilyl)ethynyl]phenyl]magnesium bromide, with 2-methyl-2-nitrosopropane. Elimination of the trimethylsilyl protecting group yielded **7**.

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Scheme I

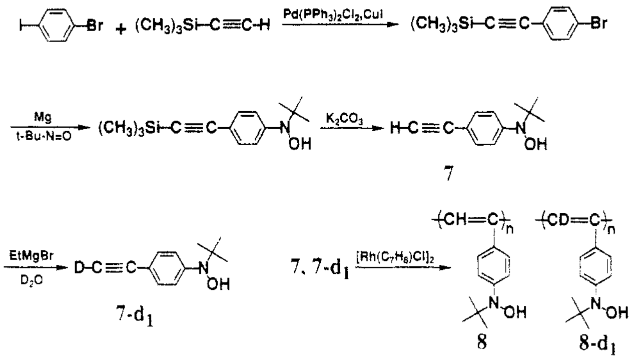

Table I. Polymerization of 7[a]

run	additive	time (h)	yield (%)	$\bar{M}_w/10^4$	$\bar{M}_w/\bar{M}_n$
1		24	85	1.7	3.7
2	$(C_2H_5)_3N$	24	100	1.7	2.2
3	$(C_2H_5)_3N$	1	100	1.7	2.1

[a] [Monomer] = 0.2 M ethanol solution, cat = $[Rh(C_7H_8)Cl]_2$, [cat]/[monomer] = 0.01, $[(C_2H_5)_3N]$ = 2 mM, polymerization temperature 25 °C.

Substituted acetylenes are often polymerized with chlorides of group 5 or 6 transition metals or Rh complexes.[18,19] We polymerized our monomer 7 with $[Rh(C_7H_8)Cl]_2$ (Table I), because a nitrogen-containing monomer often acts as a catalytic poison for metathesis reactions. The polymerization was completed within 1 h in the presence of a small amount of triethylamine. Polymer 8 was obtained as a yellow powder, soluble in THF and benzene/methanol but insoluble in benzene and hexane, due to its polar hydroxyamino group. Prolonged polymerization caused degradation of the polymer, and the molecular weight of the isolated polymer also decreased gradually to $\bar{M}_w$ = ca. 1.7 × 10^4 on standing its solution at room temperature. The solution color also changed during the standing from yellow to brown, suggesting that the polymer degradation is accompanied by cis–trans isomerization (see the next section).

Structural Analysis of the Polymer. The IR spectrum of 8 clearly indicated complete disappearance of the stretching vibrations of the C≡C bond and the ≡CH bond attributed to the acetylenic monomer 7 and appearance of an out-of-plane bending mode of the =CH bond to the polymer chain.

For poly(phenylacetylene) the IR absorption of the out-of-plane bending mode of =CH can be used to estimate the cis–trans microstructure of the main chain.[20] Although the IR band of the polymer had a shoulder peak at 780 cm^{-1} for 8 after polymerization, the shoulder peak disappeared and the peak at 960 cm^{-1} increased (accompanied by a color change from yellow to brown) after standing for a few weeks or after redissolving–reprecipitating the polymer. These peaks are assigned to the out-of-plane bending mode of the cis and trans =CH bond, respectively. This assignment was supported by the IR spectrum of the selectively deuterated polymer 8-d_1, which was prepared by polymerization of the corresponding monomer 7-d_1. A new IR peak appeared at 520 cm^{-1} believed to be due to 8-d_1.

The hydrogen bond in the polymer contributed to the cis–trans structural isomerization: the cis isomer showed a broad signal at 3265 cm^{-1} similar to that in monomer 7, and the trans one, at 3440 cm^{-1}.

The cis-rich and yellow-colored polymer 8 had a visible absorption maximum (λ_{max}) at 412 nm, which shifted gradually to 455 nm of the trans-rich and brownish polymer. Development of the π-conjugation in poly(phenylacetylene) derivatives has been explained by the steric effect of the substituent groups on the chain-sided phenyl ring.[13] Polymer 8 possessing the extended absorption in the visible region would take a π-conjugation more developed, probably because of its bulky substituent group, than unsubstituted poly(phenylacetylene) which had no absorption maximum in the visible spectrum.

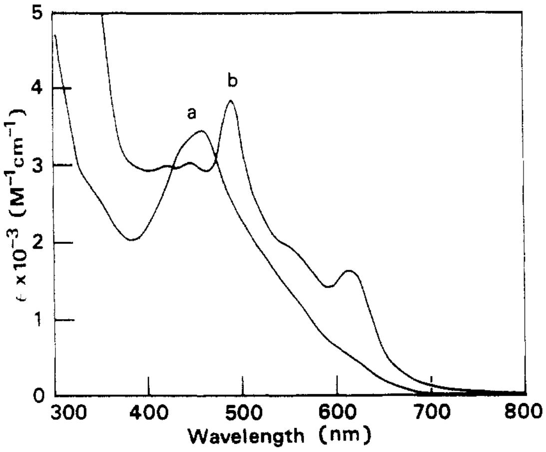

Figure 1. Visible spectra of the polymers in a benzene/methanol (6/1) solution: (a) 8; (b) 3 (spin concentration 66 mol %).

Polyradical Formation. Polymer 8 was easily oxidized, e.g., by active PbO_2, to give the corresponding polyradical 3. An oxygen stream in an alkaline benzene/methanol (=6/1) solution was also effective to yield the polyradical 3. In the IR spectrum the absorption band at 3440 cm^{-1} assigned to the O-H stretching vibration of hydroxylamine disappeared completely.

The solution turned dark brown through the oxidation, with new absorption maxima at 490 and 613 nm ascribed to phenyl nitroxides[21] (Figure 1). This absorption extends to 700 nm, the same as that of 8 before the oxidation, which suggests that the π-conjugation in the main chain develops even after the polyradical formation.

The ESR spectrum of the 3 solution showed a broad signal with three-line hfs attributed to a nitrogen of the *tert*-butyl phenyl nitroxide moiety (Figure 2). The *g* value 2.006 of the spectra indicates the formation of a nitroxy-centered radical. The ESR signal broadened with the degree of oxidation, due to a high local concentration of the radical site along the main chain even in the dilute solution.

Spin concentrations were determined by carefully integrating the ESR signals with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) solutions used as a standard. The spin concentration of 3 could be increased up to ca. 4.2 × 10^{23} spin/molar monomer unit (70 mol %) by the oxidation. This spin concentration is much higher than that of the previously reported similar polyradical (ca. 40 mol %) derived from the precursor obtained by the polymer reaction.[9a]

The polyradical 3 was stable at least under ESR and SQUID measurement conditions. The spin concentration was decreased to half after 7 days in the solution.

ESR Spectra of the Polyradical. The ESR spectrum of *tert*-butyl *p*-vinylphenyl nitroxide (*p*-6) has been reported to show a three-split hfs attributed to the nitrogen of the nitroxide group, with additional multisplits due to the seven protons of phenyl and vinyl groups:[16] the spin distributes over the vinyl group. Solution ESR spectrum of the polyradical 3 with low spin concentration also gave hfs attributed to the nitrogen and to some protons of the phenyl ring and/or the main chain (Figure 2a). Though

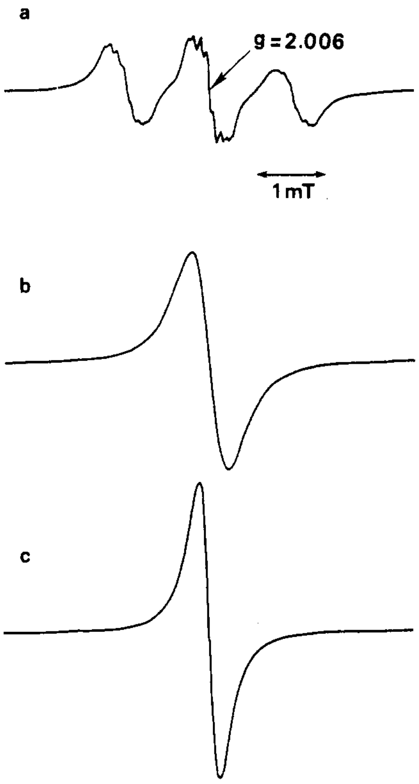

Figure 2. ESR spectra of the polyradical **3** at room temperature: (a) with spin concentration 1 mol % (5×10^{-4} monomer unit mol/L) in benzene/methanol (6/1); (b) with spin concentration 70 mol % (5×10^{-4} monomer unit mol/L) in benzene/methanol (6/1); (c) with spin concentration 60 mol % at the powder state.

a broadening effect of the isotropic nitroxide radicals along the main chain prevented a detailed analysis, the hfs due to the nitrogen at $a_N = 1.2$ mT is comparable to that of *p*-**6** ($a_N = 1.17$ mT), which supports the spin distribution over the phenyl ring and probably over the main chain. For the polyradical **3** with high spin concentration, the spectrum showed a single broad signal only in the $\Delta m_s = \pm 1$ region (Figure 2b), and any forbidden transition at $\Delta m_s = \pm 2$ ascribed to a triplet state was not observed even at 77 K. This result implies that a magnetic coupling leading to a high-spin state is not observed in the polyradical **3**.

The powder ESR spectrum of **3** also showed a single broad signal in the $\Delta m_s = \pm 1$ region. The peak to peak line width (ΔH_{pp}) of the signal for **3** with high spin concentration considerably decreased with temperature from 5 mT at 123 K to 0.4 mT at 293 K, while that of **6** was maintained at 3 mT in this temperature region. This narrowing was not affected even by diluting the sample with diamagnetic polystyrene, but depending on the decreasing of the spin concentration (ΔH_{pp} broadened to 2 mT at 10 mol %). The ΔH_{pp} narrowing was related to a distance narrowing between the radical sites localized along the polymer chain.

Magnetic Property of the Polyradical. Magnetization and static magnetic susceptibility of the polyradical **3** was measured with a SQUID magnetometer at 2–120 K. If a function of the magnetic field and temperature (H/T) is sufficiently small, the magnetic susceptibility conforms to Curie–Weiss law (eq 2). Equation 2 is modified to eq 3.

$$\chi = C/(T - \theta) \tag{2}$$

$$1/\chi = (1/C)T - \theta/C \tag{3}$$

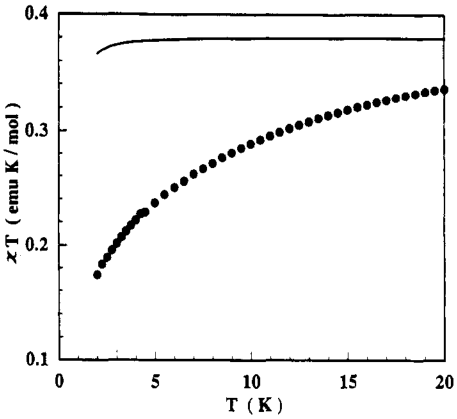

Figure 3. Magnetic susceptibility of the polyradical **3** with spin concentration 65 mol %. The solid line is the theoretical curve at $S = {}^1/_2$. The molar magnetic susceptibility was corrected with the spin concentration.

Table II. Magnetic Parameters of the Polyradical

spin conc (SQUID) (spin/molar monomer unit)	spin conc (ESR) (spin/molar monomer unit)	Curie const (emu·K/mol)	Weiss const (K)
3.9×10^{23}	3.4×10^{23}	0.21	−3.3

For polyradical **3** with high spin concentration (65 mol %), the reciprocal of magnetic susceptibility, $1/\chi$, was linear in T as required by the Curie–Weiss law, because H/T was small enough in the region of 20–120 K under 1 T of the magnetic field. The Curie constant (C) and the Weiss constant (θ) were determined from eq 3 (Table II), where C is represented by

$$C = Ng^2\mu_B{}^2S(S + 1)/3k \tag{4}$$

Under the assumption of $S = {}^1/_2$, N corresponds to spin numbers per molar monomer unit when χ is standardized by a molar monomer unit. The spin concentration was determined from the C value and agreed with that estimated by integrating the ESR signal (Table II).

χT vs T plots of the polyradical **3** with high spin concentration are shown in Figure 3. At low temperature these plots deviate downward from the theoretical curve which was calculated from

$$\chi T = (M/H)T = [Ng\mu_B SB_J(a)/H]T \tag{5}$$

where $B_J(a)$ is the Brillouin function and $a = Sg\mu_B H/kT$.

The negative deviation of the χT vs T plots means an antiferromagnetic interaction between the unpaired electrons, giving $\theta = -3.3$ K. This negative θ value is larger than the previously reported $\theta = -1.5$ K for the similar polyradical poly[2-(*p*-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline 1-oxide 3-oxyl] (**9**).[9b] The chain-sided radical moiety of **3** is less bulky than that of **9**. The unpaired electron of **3** is localized in the NO group in comparison with that of **9**. Thus it is assumed that the radical moieties or the unpaired electrons of **3** easily approach each other and cause a through-space and antiferromagnetic interaction between the unpaired electrons.

The magnetization plots of **3** are shown in Figure 4. The magnetization plot of the neat **3** powder at 2 K is not saturated even at 7 T and deviates downward from the theoretical curve of $S = {}^1/_2$. This deviation was reduced for the magnetization plots of **3** diluted with diamagnetic polystyrene. This suggests that an interpolymer interaction contributes the antiferromagnetic interaction in **3** rather than an interaction between the radical sites of the intrachain.

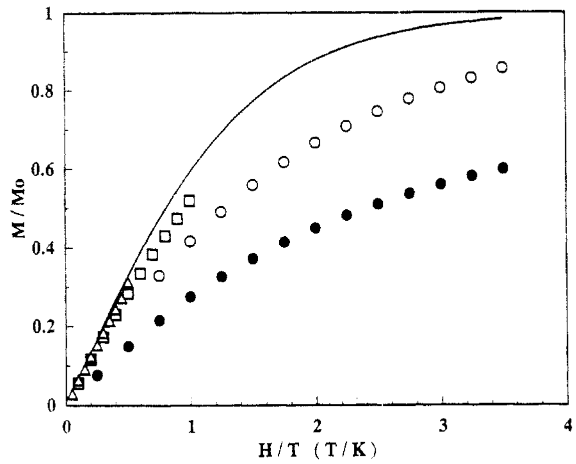

Figure 4. Magnetization curves of the polyradical 3 and 3 diluted with polystyrene at a spin concentration of 40 mol %. Temperature: (●) 2 K (3 neat); (○) 2 K (3/PSt = 1/250); (□) 5 K (3/PSt = 1/250); (△) 10 K (3/PSt = 1/250). The solid line is the theoretical curve at $S = {}^1/_2$.

Though many π-conjugated polyradicals have been synthesized by using poly(phenylacetylene) as their main chain bearing phenyl-substituted radical moieties, any ferromagnetic interactions predicted by theoretical studies by Ovchinnikov[4] and other workers[22] have not yet been achieved. 3 had been more expected to yield a ferromagnetic spin ordering because of the spin distribution effect over the phenyl ring and chemical stability of its nitroxide radical center. But we observed only the antiferromagnetic through-space and interchain interaction for 3. Poly(phenylacetylene)-based polyradicals probably involve some problems in their chemical structure. Torsion in the polyene main-chain and/or twisted phenyl radical moieties would inhibit extended conjugative spin coupling throughout the polymer. Computational study is desirable on the electronic structure of the π-conjugated polyradicals, taking into account their steric structure.

Experimental Section

4-Bromo-1-[(trimethylsilyl)ethynyl]benzene. Ethynyltrimethylsilane (4.9 g, 50 mmol) was added to a solution of 1-bromo-4-iodobenzene (14.1 g, 50 mmol) in triethylamine, followed by the addition of bis(triphenylphosphine)palladium(II) chloride (0.35 g, 0.5 mmol) and of copper(I) iodide (0.095 g, 0.5 mmol) under a nitrogen atmosphere. The solution was stirred for 15 h at room temperature to give triethylamine hydroiodide precipitate. The mixture was filtered off, and the filtrate was evaporated, then extracted with ether, and washed with saturated aqueous ammonium chloride. After drying over anhydrous sodium sulfate, the ether solution was evaporated and purified by column chromatography on silica gel (hexane). It was recrystallized from methanol to give 9.84 g of 4-bromo-1-[(trimethylsilyl)ethynyl]benzene (yield 77%); mp 60–61 °C (lit.[23] mp 62 °C); IR (KBr pellet, cm^{-1}) 2960, 2900 (ν_{CH_3}), 2160 ($\nu_{C\equiv C}$), 1250 (ν_{SiC}).

***tert*-Butyl-[4-[(trimethylsilyl)ethynyl]phenyl]hydroxylamine.** A two-necked flask was charged with magnesium (0.60 g, 26 mmol), which was heated and dried under a rapid stream of nitrogen. After the flask was cooled at room temperature, 4-bromo-1-[(trimethylsilyl)ethynyl]benzene (6.33 g, 25 mmol) in 17 mL of THF was added under a nitrogen atmosphere. The mixture was stirred and refluxed for 3 h to give Grignard reagent. It was cooled at room temperature, treated with 2-methyl-2-nitrosopropane (2.61 g, 30 mmol) in 17 mL of THF, and then stirred for 1 h. Saturated aqueous ammonium chloride was added to the reaction mixture and then extracted with ether. After the ether layer was dried over anhydrous sodium sulfate, it was recrystallized from methanol to give 3.99 g of *tert*-butyl-[4-[(trimethylsilyl)ethynyl]phenyl]hydroxylamine (yield 61%); mp 162–165 °C; IR (KBr pellet, cm^{-1}): 3240 (ν_{OH}), 2970, 2900 (ν_{CH_3}), 2160 ($\nu_{C\equiv C}$), 1250 (ν_{SiC}).

[4-(*N-tert*-Butyl-*N*-hydroxyamino)phenyl]acetylene (7). *tert*-Butyl-[4-[(trimethylsilyl)ethynyl]phenyl]hydroxylamine (2.61 g, 10 mmol) was dissolved in 30 mL of methanol and 30 mL of benzene; then potassium carbonate (0.5 g) dissolved in 30 mL of methanol was added and stirred for 12 h at room temperature under a nitrogen atmosphere. Saturated aqueous ammonium chloride was added to the reaction mixture and extracted with ether. After the ether layer was dried over anhydrous sodium sulfate, it was recrystallized from methanol to give 1.29 g of [4-(*N-tert*-butyl-*N*-hydroxyamino)phenyl]acetylene as a yellow crystal (yield 68%); mp 134–135 °C; ^{1}H-NMR ($CDCl_3$, ppm): δ 7.4 (d, 2H, Ph), 7.2 (d, 2H, Ph), 6.7 (s, 1H, –NOH), 3.1 (s, 1H, ≡CH), 1.1 (s, 9H, $-C(CH_3)_3$); IR (KBr pellet, cm^{-1}): 3280 ($\nu_{\equiv CH}$), 3240 (ν_{OH}), 2970 (ν_{CH_3}), 2100 ($\nu_{C\equiv C}$), 1605 (ν_{Ph}). Anal. Calcd for ($C_{12}H_{15}NO$): C, 76.1; H, 8.0; N, 7.4. Found: C, 75.7; H, 8.0; N, 7.4.

[4-(*N-tert*-Butyl-*N*-hydroxyamino)phenyl]acetylene-d_1. Ethylmagnesium bromide (12 mL, 1.0 M) in THF was added to 8 (0.946 g, 5 mmol) in 50 mL of absolute ether, and the solution was stirred for 10 h. The solvent was evaporated, and 10 mL of deuterium oxide was added and stirred for a few minutes. After neutralizing with 9.2 mL of 5% deuterium chloride, the organic layer was extracted with ether and dried over anhydrous sodium sulfate. Recrystallization from hexane gave 0.3 g of deuterated 8 (yield 31%): mp 122–123 °C; IR (KBr pellet, cm^{-1}): 3230 (ν_{OH}), 2970 (ν_{CH_3}), 2580 ($\nu_{\equiv CH}$), 2180 ($\nu_{C\equiv C}$), 1605 (ν_{Ph}).

Polymerization. $[Rh(C_7H_8)Cl]_2$ was added to the ethanol solution of 7 as the polymerization catalyst under a nitrogen atmosphere. The polymerization conditions were given as a footnote of Table I. The precipitate was washed with ethanol and then dried in vacuo. It was redissolved in THF and reprecipitated in hexane. IR (KBr pellet): 3265 (ν_{OH}), 780 ($\delta_{C=CH}$). Anal. Calcd for ($C_{12}H_{15}NO$): C, 76.1; H, 8.0; N, 7.4. Found: C, 74.5; H, 7.9; N, 7.2.

Oxidation. A 10-equiv excess of active PbO_2 was added to the benzene/methanol (6/1) solution of 8, and the mixture was well stirred in the dark. After filtration the solution was freeze-dried.

The solution of polyradical 3 was added to a benzene solution of a certain amount of purified polystyrene (molecular weight 1.7×10^5) and stirred thoroughly for 1 h, to gave the samples diluted with diamagnetic polystyrene. The spin concentration of these diluted samples was unchanged compared with that before dilution.

Measurement. IR, UV–vis, and ^{1}H-NMR spectra were measured with a Jasco FT/IR-5300, Shimadzu UV-2100, and JEOL FX-90Q spectrometer, respectively. The molecular weight of the polymer was estimated by GPC (polystyrene gel column, eluent THF, polystyrene calibration).

ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with a 100-kHz field modulation. The spin concentration of each sample was determined both by careful integration of ESR signal by using those of the TEMPO solution as standard and by magnetization assuming $S = {}^1/_2$ with a SQUID magnetometer.

Magnetization and static magnetic susceptibility was measured with a Quantum Design MPMS SQUID magnetometer. The powder sample was contained in a diamagnetic capsule.

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