Poly[(p-ethynylphenyl)hydrogalvinoxyl] and Its Polyradical Derivative with High Spin Concentration

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ABSTRACT: [4-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-methyl]phenyl]acetylene (6), was synthesized and polymerized to yield a solvent-soluble polyacetylene poly-[[4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phen-yl]acetylene] (5a). The polymer gave its polyradical derivative 5b through the chemical oxidation with active PbO₂. 5b was stable, whose spin concentration could be increased up to 4.8 × 10²³ spins per molar monomer unit. ESR analysis indicated localization of unpaired electrons in the galvinoxyl residue. ESR analysis also suggested an exchange-narrowing and interpolymer dipole–dipole interaction.

Introduction

Stable organic radicals yield bulk paramagnets. Spin ordering at a much lower temperature and antiferromagnetic spin alignment are ascribed to weak intermolecular magnetic interactions derived from relatively long distances between magnetic orbitals and to mutual position in crystal lattice, respectively. For an organic molecule containing multiple radical moieties, a magnetic interaction among them could be expected. Profile and strength of the magnetic interaction depend on the chemical structure connecting the radical moieties.[1,2] E.g. tetrakis-[4-[(3,5-di-*tert*-butyl-4-hydroxypheny)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phenyl]-methane[3] and 1,3-bis[(3,5-di-*tert*-butyl-4-hydroxy-phenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-yli-dene)methyl]benzene[4] were oxidized to give a quintet tetraradical and triplet biradical, respectively, while the biradical derivative of 1,2-bis[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-yli-dene)]ethane was reported to be singlet in the ground state.[5]

If these electronic states can be extended to conjugated polyradicals, a huge spin cluster with magnetic interaction will be realized along one polymer chain. Synthesis of such polyradicals (often called a "high-spin polymer") is one of the most promising approaches to realize molecular-based magnets.[6] Intramolecular magnetic interactions which will be observed in the conjugated polyradicals are delocalization of unpaired spins through the π-conjugation system and/or spin polarization accompanied by spin conduction through the chemical bonds. They are stronger than intermolecular (through space) magnetic interactions working in low molecular weight radicals. The possibility of high-spin states in organic molecules has been discussed by Longuet-Higgins[7] using molecular orbital theory, and some model polyradicals were proposed by Mataga.[8] Modern theory developed by Borden and Davidson[9] and valence bond calculation by Ovchinnikov[10] and Klein[11] described the possibility of high-spin molecules. According to a simple theorem developed by Ovchinnikov,[10] which was also supported by computational examination,[2] the ground-state spin quantum number S for a conjugated π-system with n* α(up)-spin and n° β(down)-spin centers is described as eq 1. When the theorem is applied to

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

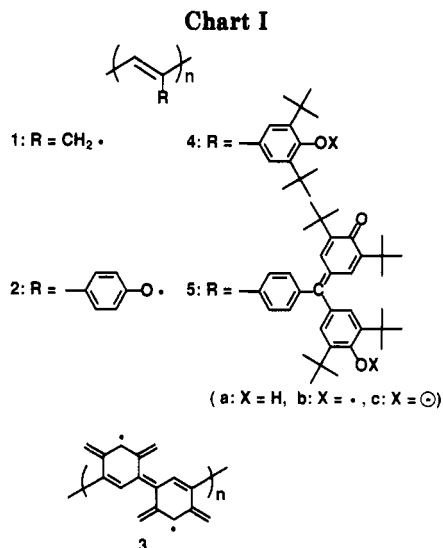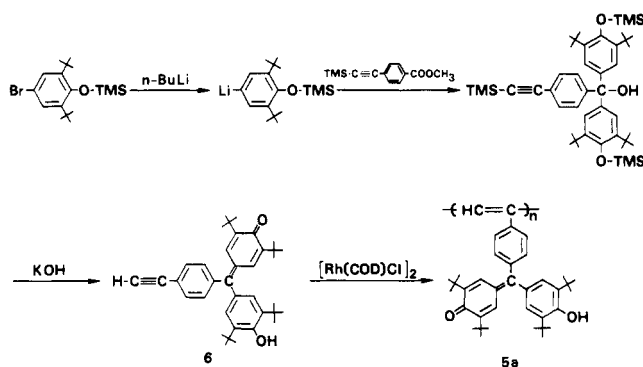conjugated polyenes, polymers of acetylene with a radical

substituent at every carbon atom, can be candidates for the high-spin polymer whose spin multiplicity increases in proportion to its molecular size. Poly(propynyl)[11] (1) and poly(4-ethynylphenoxyl)[10] (2) have been proposed as model systems with spin-delocalized electronic structure.

Tyutyulkov discussed the possibility of ferromagnetic interaction in another type of conjugated polyradical where unpaired spins strictly localize within each monomer unit such as polyacetylene with a cyclic pentadienyl structure[12] 3 (Chart I), and pointed out the possibility of an indirect spin coupling mediated by the delocalized π-electron system.

In our previous papers[13–18] we reported the synthesis of poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] (4a)[13] and poly[[4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phe-nyl]acetylene] (5a)[14] and the formation of their polyradical derivatives 4b and 5b through chemical oxidation. Antiferromagnetic interaction was observed in 4b with a spin concentration above 10 mol %, which indicated the possibility of through-bond magnetic interaction which could not be expected for a stable polyradical without π-conjugated linkage between radical centers. While polyradical 4b was regarded as a model of high-spin polymer 2, long-range parallel (ferromagnetic) spin alignment was not realized due to quinone methide formation accompanying the migration of unpaired spin from the side chain phenoxy group to the conjugated polyene main chain.[15,16] Electronic structure of polyradical 5b is interesting because formed unpaired spins localize in the pendant group. Thus polyradical 5b could be regarded as related to model compound 3. This paper describes the synthesis of poly[[4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phenyl]acety-lene] (5a) and magnetic characteristics of its polyradical derivative 5b in connection with their electronic properties.

Results and Discussion

Synthesis of (p-Ethynylphenyl)hydrogalvinoxyl. 2,6-Di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-p-tolyloxy (abbreviated as galvinoxyl) is one of the most stable phenoxy radicals. Galvinoxyl and its derivatives have been synthesized mainly in two ways: extensive oxidation of diphenylmethanes or triphenyl-methanes such as bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-methane[19] and bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-phenylmethane,[20] and oxidation of hydrogalvinoxyl derivatives.[21] Because polyradicals are to be generated by

Chart I

1: R = CH₂ •   4: R = [structure] —OX

2: R = —[ring]—O •   5: R = [structure]—OX

(a: X = H, b: X = • , c: X = ⊖)

[structure 3]

Scheme I

Table I
Polymerization of the Monomer 6[a]

run	cat.	solv	time, h	yield, %	$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n$
1	WCl₆–Ph₄Sn[b]	Bz	72	trace	0.4	2.2
2	[Rh(COD)Cl]₂[c]	THF	24	1	0.4	4.3
3	[Rh(COD)Cl]₂[c]	THF	168	4	2.0	7.9

[a] Polymerization temperature = 40 °C. [b] [Monomer]₀ = 0.2 M, [WCl₆] = [Ph₄Sn] = 30 mM. [c] [Monomer]₀ = 0.2 M, [[Rh(COD)Cl]₂] = 0.3 mM.

polymer reaction, the latter method via one-electron oxidation is preferable to the former often accompanied with degradation during extensive oxidation. Thus we synthesized [4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)meth-yl]phenyl]acetylene (6) via an organometallic synthetic pathway.[21] Methyl-4-[(trimethylsilyl)ethynyl]benzoate[22] was treated with (2,6-di-*tert*-butyl-4-lithiophenoxy)tri-methylsilane, followed by elimination of three protecting trimethylsilyl groups with methanolic KOH (Scheme I).

Polymerization. Substituted acetylenes are reported to be polymerized with chlorides of group 5 or 6 transition metals[23] or Rh complexes[24] to give polyacetylenes with high molecular weight. Our acetylene monomer 6 was po-lymerized with WCl₆–Ph₄Sn and with [Rh(COD)Cl]₂ (COD = 1,5-cyclooctadiene) (Table I), but was not with WCl₆ or MoCl₅, suggesting a poisoning effect of the phenolic hydroxy group and/or carbonyl group against these metathesis catalysts. While addition of triethyl-amine to the Rh(I) catalyst was reported to form long-lived propagation species,[25] a distinct positive effect on the yield or molecular weight of the polymer was not observed in our experiment. The polymerization pro-ceeded very slowly: [Rh(COD)Cl]₂ gave polymer with the
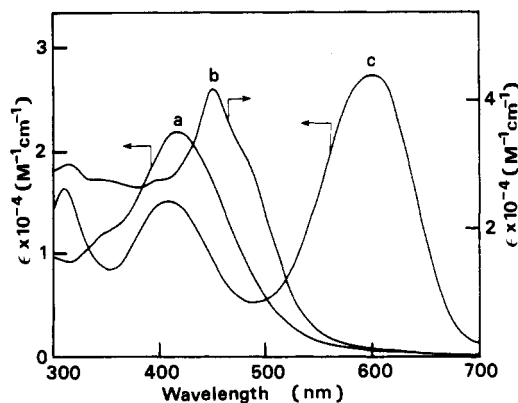
Figure 1. Visible spectra of the polymers: (a) polymer 5a in CH₂Cl₂; (b) polyradical 5b in benzene (spin concentration 56 mol %); (c) polyanion 5c in methanol. ε of 5b was corrected using spin concentration by ESR spectroscopy.

yield of only 4% even after 7 days, and the monomer could be recovered from the residual solution. It is in contrast to phenylacetylene[23] and (3,5-di-*tert*-butyl-4-acetoxyphe-nyl)acetylene[15] which were polymerized with WCl₆ to give a polymer with molecular weight 10⁴ in the yields of 100 and 52% after 24 h, respectively. This is probably due to a very bulky substituent of 6 at the para position. Polymer 5a was obtained as a dark red powder irrespective of the catalyst. Polymer 5a was soluble in organic solvents, such as CHCl₃, benzene, tetrahydrofuran, acetone, and alco-hols, but insoluble in aliphatic hydrocarbons. Poly(phe-nylacetylene) (PPA) is reported to be almost benzene-soluble and methanol-insoluble. Solubility of the polymer 5a in alcohols can be explained by the presence of polar phenolic hydroxy group and/or carbonyl group.

Structural Analysis of the Polymers. IR spectrum of the polymer 5a clearly indicated complete disappearance of the stretching vibration of the C≡C bond and ≡C—H bond characteristic of the monomer 6. In the polymer spectra, the sharp absorption at 3635 cm⁻¹ attributed to the sterically hindered phenolic hydroxy group and the strong one at 1630–1610 cm⁻¹ attributed to quinoid structure remained after the polymerization. In ¹H and ¹³C NMR spectra, peaks assignable to the ethynyl group, i.e., δ 3.21 (s, 1 H, ≡CH) in ¹H NMR and δ 83.5 (C≡C—H), 78.2 (C≡C—H) in ¹³C NMR, completely disappeared. These data support the polymer structure represented as 5a.

The UV–vis spectrum (Figure 1) of 5a shows a strong maximum at 420 nm (in CH₂Cl₂, log ε = 4.3) due to the presence of a quinoid chromophore of the hydrogalvinoxyl residue similar to that of monomer 6. This absorption extends to 600 nm, which is ca. 30 nm longer than that of 6, indicating the presence of some π-conjugation along the main chain.

The ionization potential of 5a evaluated from the ultraviolet photoelectron spectroscopy (UPS) was 5.9 eV, which was higher than that of PPA (5.7 eV).[18] These values indicated the presence of π-conjugation along the poly-acetylene main chain whose mean length was not as long as that of PPA. The degree of π-conjugation in poly-(phenylacetylene)s has been explained by the steric effect of substituents over the side-chain group.[18] Steric repul-sion between the very bulky substituents in 5a may deform the planarity along the polyacetylene main chain, leading to a decrease in the mean conjugation length.

Formation of the Polyradical. Polymer 5a was converted to the corresponding polyanion 5c and poly-radical 5b after the treatment with an alkali and an oxidizing agent, respectively. In the methanolic solution

with excess KOH **5a** yielded the dark green **5c** (λ_{max} in nm [log ϵ]: 600 [4.3], 412 [4.2], 310 [4.2]). Careful oxidation of **5a** with active PbO_2 in benzene under oxygen-free atmosphere gave a deep brownish solution. The sharp absorption at 450 nm increased with the enhancement in ESR signal intensity, and the molar extinction coefficients for polyradical **5b** were log ϵ = 4.3 (Figure 1). These λ_{max} values correspond to those of the low molecular weight phenylgalvinoxyl anion and radical species.[4] It was reported that hydrogalvinoxyl derivatives with bulky substituents such as 2-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]-2-methylpropane and 1-[(3,5-di-*tert*-butyl-4-hydroxy-phenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]-tricyclo[3.3.1.1^{3,7}]decane were oxidized to show absorption maxima around 650 nm similar to the 2,4,6-tri-*tert*-butylphenoxy radical.[26] **5b** had no maxima in the region, which indicates that the electronic state of substituted phenylgalvinoxyl is the same as that of low molecular weight phenylgalvinoxyl even in the very crowded structure along the polymer chain.

Spin concentrations were determined by careful integration of the ESR signal at ΔM_s = ±1 and by iodometric titration. The spin concentrations agreed with each other: e.g. spin concentrations of **5b** obtained by a lower and higher oxidation were 13 and 76 mol % from ESR and 14 ± 1 and 75 ± 2 mol % from the iodometry, respectively. Spin concentration can be controlled by oxidative conditions up to ca. 80 mol % in both solution and the solid state.

Infrared spectra of galvinoxyl radicals give a strong band at ca. 1570 cm^{-1} attributed to the oxygen radical[4,27] instead of four intense absorption bands in the carbonyl region (1630–1610 cm^{-1}) of corresponding hydrogalvinoxyl. In **5b** with oxidation, a strong absorption at 1575 cm^{-1} attributed to the phenoxy radical appeared while an absorption in the carbonyl region and a sharp absorption assigned to ν_{OH} at 3635 cm^{-1} decreased. GPC curves of **5b** were almost the same as those of **5a**, which supports the fact that oxidation does not bring about oxidative degradation or cross-linking of the main chain.

In the solution ESR spectrum of **5b** with a spin concentration of 6 mol %, a broad hyperfine structure at a *g* value of 2.0044 was observed due to the magnetic interaction of an unpaired electron with four equivalent protons (Figure 2a). The spectra become broader with an increase in the spin concentration and coalesce to a single broad line (Figure 2b), which is unchanged even in the dilution solution of the **5b** (Figure 2c). This can be explained by a high local concentration of the radical site along the main chain even in the dilute solution.

The ionization threshold of **5b** from UPS was 6.1 eV irrespective of the spin concentratioin, and almost agreed with that of **5a**. This indicates that the polyradical formation hardly influences the electronic state of the polyene chain.

ESR Spectra in the Solid State. The powder ESR spectra of **5b** in the ΔM_s = ±1 region showed a single broad absorption whose *g* value was 2.0044 + 0.0002. Forbidden transition at ΔM_s = ±2 corresponding to the triplet state was not observed at 77 K, implying that magnetic coupling leading to a high spin state does not work in polyradical **5b**. The peak to peak line width (ΔH_{pp}) of polyradical **5b** with a spin concentration of 23 mol % is slightly increased with a lowering of the temperature (Figure 3): from 5.6 G at 293 K to 6.0 G at 118 K. On the other hand considerable broadening below 220 K was observed for **5b** with 77 spin mol %.
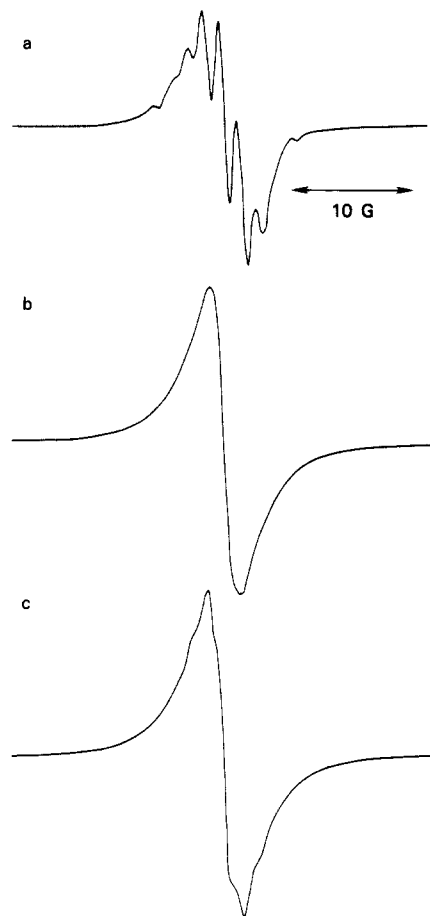

Figure 2. Solution ESR spectra of polyradical **5b** in benzene at room temperature. Spin concentration (mol %): (a) 6 (0.5 monomer unit mol/L); (b) 74 (0.5 monomer unit mol/L); (c) 74 (0.0005 monomer unit mol/L).
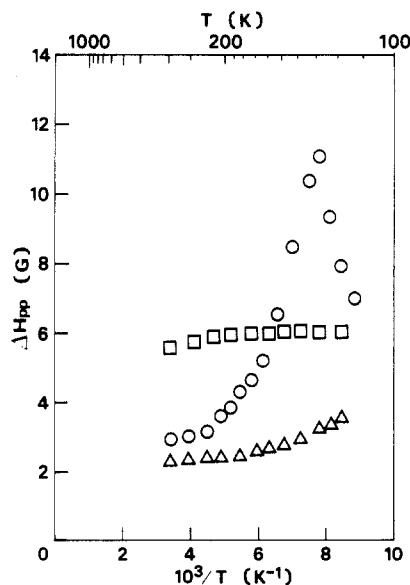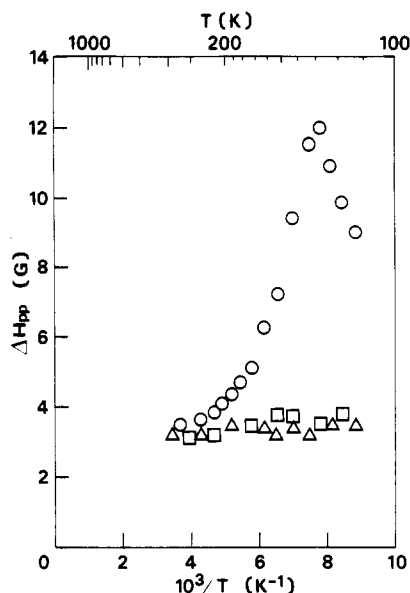

Figure 3. Temperature dependence of peak to peak line width (ΔH_{pp}) of polyradical **5b**. Spin concentration (mol %): (O) 77; (△) 56; (□) 23.

To clarify the narrowing and broadening observed in polyradical **5b** with high spin concentration and to distinguish intra- and interpolymer interaction, dilutions of **5b** are carried out using diamagnetic polystyrene (Figure 4). When **5b** is dispersed in polystyrene, the increase in ΔH_{pp} at low temperature disappears, indicating that broadening is explained by dipole–dipole interaction between polymer chains. On the other hand, there is no

Figure 4. Temperature dependence of peak to peak line width (ΔH_{pp}) of polyradical **5b** diluted with polystyrene. Spin concentration (mol %): (O) 80; (△) 76 (PSt:**5b** = 10:1); (□) 83 (PSt:**5b** = 100:1).

change in ΔH_{pp} at room temperature, suggesting that the exchange narrowing is an intrapolymer interaction. ΔH_{pp} of powder phenylgalvinoxyl showed no anomalous broadening in the measured temperature region (5.5 G at 293 K, 5.7 G at 118 K). These observations support the notion that the relative position of galvinoxyl radicals along the polymer chain accelerates the spin exchange which is not observed in low molecular weight systems. The reason of decrease in ΔH_{pp} below 130 K observed in polyradical **5b** with higher spin concentration (Figure 3) is still uncertain.

Magnetic Interaction. In hypothetical polyradical **3**, magnetic interaction between chain-sided unpaired spins is mediated by the delocalized π-electron system along the main chain even if direct through-bond exchange interaction is negligible.[12] From the experimental results described above, distinct through-bond magnetic interaction leading to ferromagnetic spin ordering could not be observed in polyradical **5b** even at high spin concentration. Reasons for these unexpected results are as follows: (a) The spin density at the phenyl ring is not enough to mediate the spin alignment from the galvinoxyl residue to the polyacetylene main chain. (b) π-conjugation along the main chain is not developed enough to bring about an effective exchange interaction at finite temperature. Either reason a or b or both may occur in polyradical **5b**. As pointed out for hypothetical polyradical **3**, the magnitude of the exchange interaction reaches a maximum when the energy gap vanishes.[12] Due to these unfavorable effects, through-bond magnetic interaction was not realized in **5b** while the interchain dipole interaction was observed at higher spin concentration.

Conclusion. Poly(phenylacetylene) with hydrogalvinoxyl as a pendant group was newly synthesized, and chemically oxidized to give a polyradical with a spin concentration up to 4.8 × 10²³ spins per monomer unit. Solution ESR spectra indicated that unpaired electrons were localized in the galvinoxyl pendant group. Exchange narrowing was observed for **5b** as the spin concentration increased. There was also dipole–dipole interaction between polymer chains. Ferromagnetic spin ordering could not be observed even at a spin concentration of 80 mol % due to the strictly localized unpaired electron without effective mediation through the delocalized π-electron

system. The electronic structure of **5b** is quite different from that of **4b** where antiferromagnetic interaction was observed even at a low spin concentration of ca. 10 mol %, which was caused by the delocalization of the unpaired electron through the main chain. It is considered that polyradical **4b** and **5b** have two extreme electronic natures, delocalized mainly along the main chain and strictly localized electronic structure, respectively. At present it is necessary to reduce the highly distorted angle between the conjugated main chain and chain-sided radical groups and to distribute the spin density throughout the polymer chain for realizing effective spin conduction.

Experimental Section

Materials. 4-Bromo-2,6-di-*tert*-butylphenol[28] and methyl-4-[(trimethylsilyl)ethynyl]benzoate[22] were prepared by literature methods. [Rh(COD)Cl]₂, WCl₆, Ph₄Sn, and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were used as received. Solvents were purified in the usual manners.

(4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane. This compound was prepared from 4-bromo-2,6-di-*tert*-butylphenol according to the literature[29] using bis(trimethylsilyl)acetamide: colorless crystal (yield 86%); mp 144–145 °C (lit.[21] 146 °C).

[4-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]phenyl]acetylene (6). To the suspension of 7.9 g (0.022 mol) of bromotrimethylsilane in THF cooled to –70 °C under nitrogen atmosphere was slowly added 16 mL of 1.5 M *n*-BuLi (0.024 mol). After the solution was completed, it was stirred for about 15 min. Then *N,N,N′,N′*-tetramethylethylenediamine (5 mL) and 2.3 g (0.01 mol) of methyl benzoate in THF (15 mL) were added in that order, and the solution was stirred for 2 h at –70 °C accompanying the color change from clear to orange. The solution was warmed to room temperature and was stirred for 2 h. The resulting reddish brown solution was reacted with excess KOH aqueous solution overnight to form a dark bluish solution. Saturated NH₄Cl solution was added, evaporated, and extracted with ether. After drying over Na₂SO₄, ether was evaporated to give a crude material. It was recrystallized from hexane or acetic acid, affording 2.32 g of **6** as bright orange crystals (yield 44%); mp 244 °C. Anal. Calcd for (C₃₇H₄₆O₂): C, 85.0; H, 8.9. Found: C, 84.8; H, 9.2. ¹H NMR (CDCl₃, Me₄Si standard, ppm): δ 7.70–7.02 (m, 8 H, phenyl and quinoid), 5.50 (s, 1 H, hydroxy), 3.21 (s, 1 H, ≡C—H), 1.40 (s, 18 H, *tert*-butyl), 130 (s, 9 H, *tert*-butyl), 1.22 (s, 9 H, *tert*-butyl). ¹³C NMR (CDCl₃, Me₄Si standard, ppm): δ 83.5 (C≡CH), 78.2 (C≡CH). IR (KBr pellet, cm⁻¹): 3635 (ν_{OH}), 3300 ($\nu_{≡CH}$), 2100 ($\nu_{C≡C}$). Mass spectrum (*m/e*): 522.19 (M⁺); calcd for *M* = 522.74.

Polymerization. To a monomer solution was added polymerization catalyst under nitrogen atmosphere (polymerization conditions are listed in Table I). The solution was concentrated and purified by reprecipitation in hexane and gel permeation chromatography. IR (KBr pellet, cm⁻¹): 3635 (ν_{OH}), 730 ($\delta_{C—CH}$). ¹H NMR (THF-d_8, Me₄Si standard): δ around 1.0–1.4 (*tert*-butyl), 6.0–7.5 (phenyl, quinoid, methine). $\nu_{≡CH}$ and $\nu_{C≡C}$ in the IR spectrum and peaks assignable to the ethynyl group in ¹H and ¹³C NMR spectra of monomer **6** had completely disappeared. Anal. Calcd for (C₃₇H₄₆O₂)ₙ: C, 85.0; H, 8.9. Found: C, 84.6; H, 9.0.

Oxidation. To a 1 mM degassed benzene solution of **5a** was added 3–5 equiv of freshly prepared PbO₂, and the solution was well stirred under inert atmosphere, accompanied by color change from bright orange to reddish brown. After filtration the solution was freeze-dried.

In the dilution experiment, a specific amount of purified polystyrene (average degree of polymerization = 1600–1800) was added to the benzene solution of polyradical **5b** and the resulting mixture was stirred thoroughly more than 30 min. The spin concentration of these diluted samples was unchanged compared with that before the dilution.

Measurement. IR and UV–vis spectra were measured with a JASCO IR-810 and Shimadzu UV-240 spectrophotometer, respectively. The molecular weight of the polymer was estimated by GPC (polystyrene gel column, eluent THF, polystyrene calibration).

The ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with 100-kHz field modulation. The spin concentration of each sample was determined both by careful integration of ESR signal compared with that of TEMPO solution and by iodometric titration.

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