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Poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] and Its Polyradical Derivative

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ABSTRACT: (3,5-Di-*tert*-butyl-4-hydroxyphenyl)acetylene (8) was synthesized and polymerized with WCl_6 and $MoCl_5$, giving a novel and solvent-soluble conjugated polymer, poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] (3). Visible absorption of the polymer indicated a fairly long π-conjugated system along the main chain. The polymer yielded its polyanion 10 and polyradical derivative 4 after the treatment of its solution with an alkali and oxidizing reagent, respectively. The polyradical 4 was surprisingly stable, and spin concentration was increased up to 2.3×10^{23} spins/molar (hydroxyphenyl)acetylene residue. ESR spectra of the polyradical 4 in solution suggested that the formed upaired electrons were delocalized along the polyacetylene main chain. 4 was also very stable even in solid state. Spin-exchange interaction observed in 4 strongly depended on its spin concentration. Antiferromagnetic interaction between the upaired electrons was suggested from the temperature dependency of the ESR signal intensity.

Introduction

Molecular magnetism is one of the most interesting issues in contemporary chemistry.[1-3] Synthesis of polyradical macromolecules[4-7] has been spurred because these polymers are potential candidates of high-spin molecules.[8-11] In contrast to monoradical molecules where the spin-exchange interaction is governed by mutual arrangement in the crystal, spin conduction through chemical bonds is expected for polyradical macromolecules.

Numerous organic polymers bearing stable radical substituents have been synthesized and characterized.[12a] For example, Braun et al.[12b] reported homo- and copolymers of 4-vinyl- and 4-isopropenyl-2,6-di-*tert*-butylphenol and properties of the corresponding polyphenoxy radicals. Although some of these polymers elucidated characteristic behaviors of the polymer-bound radicals[12c] and were applicable as nonfugitive, nonleachable stabilizers and antioxidants,[13] these unpaired spins were magnetically localized and behaved as polymer-bound monoradicals. Recently there have arisen new possibilities for conjugated polymers bearing stable radicals. Delocalization of unpaired electrons and/or magnetic interaction between them are expected for these conjugated polymers. Parallel spin alignment of unpaired electrons by through-bond interaction has been discussed theoretically[8-11] as follows.

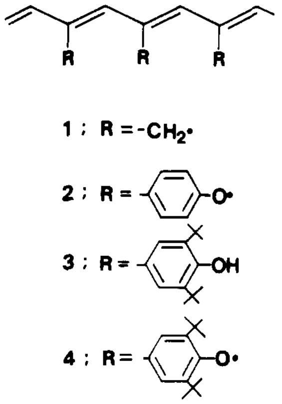
For an alternant π-conjugated molecule, one can star in such a way that no two starred or unstarred spin positions are adjacent. The spin quantum number (S) can be derived from the number of starred π centers (n^*) and unstarred ones (n°) according to eq 1.[10] At $n^* = n^\circ$ the total spin

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

is zero, and the ground state is a singlet. For an alternant π-conjugated macromolecule, if there is a difference between n^* and n°, an increase or decrease of S will be observed depending on bond connectivity of the polymer. The electronic structure of hypothetical polyallyl radical 1 (Chart I; $n^* = 3$, $n^\circ = 2$ per each monomer unit) has been extensively discussed on the basis of molecular orbital theory,[8,9] and of valence-bond theory,[10,11] but this polyradical has not been synthetically realized yet.

Ovchinnikov pointed out that heteroatom substitution would not greatly affect the prediction[14] and proposed a more realizable model composed of poly(phenoxylacetylene) radical 2.[10a] Because the monomer unit of 2 has $n^* = 5$ and $n^\circ = 4$ by his formulation, the polymeric system with an appropriate connectivity (head to tail fashion) would possess a very high-spin ground state and be a one-dimensional ferromagnet. To the best of our knowledge, however, there are no reports on the synthesis and magnetic properties of poly[(4-hydroxyphenyl)acetylene], the prepolymer of Ovchinnikov's model, and its polyradical derivatives other than our preliminary paper on this work.[4] This paper describes the synthesis and characterization of poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] (3) and its polyradical 4.

Chart I



Results and Discussion

Synthesis. The synthetic route of monomer 8 is presented in Scheme I. Although 8 has been previously synthesized[18] as an intermediate for ESR study on radicals, through condensation of 2,6-di-*tert*-butyl-*p*-benzoquinone and lithium acetylide in liquid ammonia and the following reduction of the quinol with $LiAlH_4$, the reported yield of 8 was less than 1% because of the formation of a vinylic byproduct. The acetylenic monomer 7 was obtained via 5 prepared by the Vilsmeier method[16] in a relatively high yield (36%). The acetoxy group was an effective protecting group of the sterically hindered phenolic hydroxy group. Reaction of 7 with $LiAlH_4$[13] under mild conditions gave monomer 8 quantitatively.

7 and 8 were polymerized with WCl_6 or $MoCl_5$ as the catalyst (Table I and Scheme II). The polymers were

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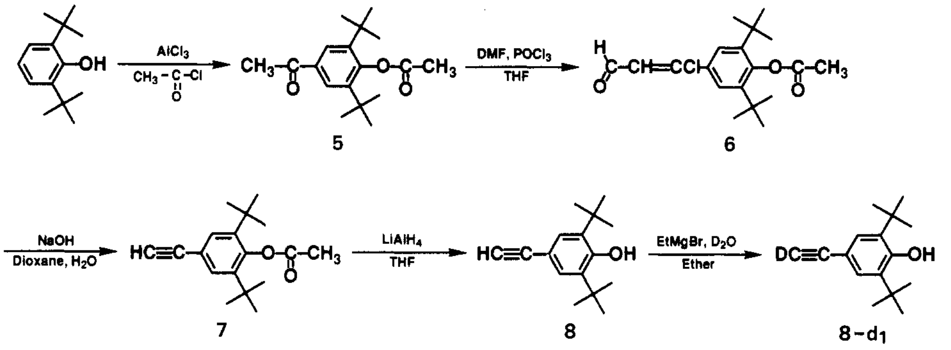
Table I
Polymerization of Monomers 7 and 8

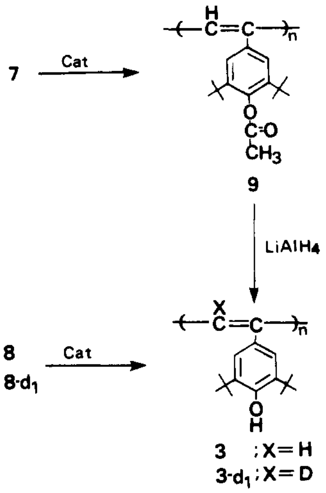
run	polymer	monomer	cat.[a]	solv	temp, °C	yield, %	$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n$
1	3	8	WCl_6	CCl_4	40	3	1.8	2.3
2	3	8	WCl_6–Ph_4Sn[c]	CCl_4	35	3	0.23	1.7
3	3	8	$MoCl_5$	benzene	40	8	1.0	1.7
4	3	8	$MoCl_5$–Ph_4Sn[c]	toluene	35	3	1.4	1.7
5	9	7	WCl_6	toluene	60	52	1.8	2.4
6[b]	3	7					0.79	1.5
7	9	7	WCl_6	CCl_4	60	34	3.1	2.2
8	9	7	$MoCl_5$	CCl_4	70	16	0.62	1.4

[a] $[M]_0$ = 1.0 M, [cat.] = 30 mM, 24 h. [b] After hydrolysis of 3 (run 5). [c] [cocat. (=Ph_4Sn)] = [cat.].

Scheme I



Scheme II



obtained as a dark red powder irrespective of the catalyst. Polymer 3 was soluble in organic solvents, such as $CHCl_3$, benzene, tetrahydrofuran, acetone, and alcohol. It has been reported that, poly(phenylacetylene) (PPA) obtained by the W or Mo catalyst is almost benzene-soluble and methanol-insoluble.[18] Polymer 9 was also insoluble in methanol. Polymer 3 was alcohol-soluble in spite of its high molecular weight, probably due to the presence of a phenolic hydroxy group.

Polymer 3 was also prepared by reductive hydrolysis of polymer 9 by $LiAlH_4$, but a decrease in the molecular weight was observed (run 6, Table I).

While polymer 9 was obtained in a moderate yield, the yield of polymer 3 was low regardless of the polymerization condition, which suggests a poisoning effect of the phenolic hydroxy group against the WCl_6 and $MoCl_5$ catalysts. Tetraphenyltin, which is an effective cocatalyst for the polymerization of phenylacetylene with W or Mo,[17c] also did not accelerate the polymerization (runs 2 and 4, Table I).

Anyway polymer 3 with a molecular weight of 10^4 was obtained as a common solvent-soluble powder via polymerization of monomer 8.

Analysis. IR spectra of polymers 3 and 9 clearly indicated the strong stretching vibration of the C=C bond (1600 cm^{-1}) and the complete disappearance of the stretching vibration of the –C≡C– bond and ≡C—H bond characteristic of monomers 7 and 8. The sharp absorption at 3620 cm^{-1} attributed to the sterically hindered phenolic hydroxy group for polymer 3 and the strong one at 1760 cm^{-1} attributed to the ester carbonyl group for polymer 7 remained after polymerization, respectively.

^1H NMR spectra also supported structures 3 and 9: broad peak at δ 1.4, 5.0, and 6.8 assigned to *tert*-butyl, hydroxy, and phenyl or methine protons, respectively, and no peak around δ 2.7 corresponding to an acetylenic proton in the spectrum of polymer 3; peak at δ 2.1 assigned to the methyl proton of the acetyl group instead of a broad peak at δ 5.0 in that of 9.[19] In ^{13}C NMR, while *tert*-butyl carbons at δ 30 (CH_3) and 34 (>C<) and a broad multiplet around δ 120–155 were observed for polymer 3 and an additional carbonyl carbon at δ 169.3 and an acetoxy methyl at δ 22.1 for polymer 9, two peaks due to the acetylenic carbons of monomer 8 at δ 85.0 and 74.4, and of monomer 7 at δ 84.2 and 76.1, were completely absent in the polymer spectra. IR and ^1H and ^{13}C NMR spectra of 3 obtained by reductive hydrolysis of 9 were identical with those of polymer 3 from direct polymerization of monomer 8.

Polymer 3 should have the regular head to tail structure because the head to head structure seems difficult to form as evidence by CPK models. The microstructure of the main chain of polymer 3 was estimated by the IR spectrum. Simionescu and Percec reported the characteristic bands for trans and cis isomers of PPA.[20] The bands at 740, 895, and 1380 cm^{-1} are specific for the cis isomer, and the bands at 922, 970, and 1265 cm^{-1} are specific for the trans isomer. 8 polymerized with $MoCl_5$ shows IR absorption at 740 cm^{-1} with a medium intensity and 860 cm^{-1} with a very weak one, and these bands were decreased and increased, respectively, in their intensity for polymer 3 obtained with WCl_6. In the IR spectrum of polymer 3-d_1 obtained from monomer 8-d_1 with WCl_6, a shoulder peak at 860 cm^{-1} was absent and absorption at 640 cm^{-1} was newly present, which indicates that the peak at 860 cm^{-1} is assigned to an out-of-plane bending mode of the trans =C—H bond of the

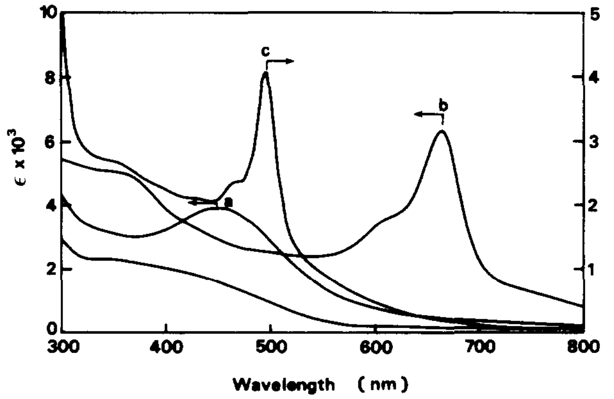
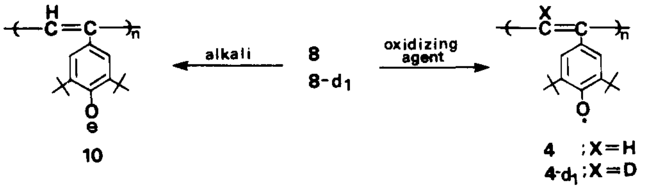


Figure 1. Visible spectra of the polymers: (a) polymer **3** in benzene; (b) polyanion **10** in methanol; (c) polyradical **4** in benzene.

Scheme III



main chain. Therefore, polymers **3** obtained with $MoCl_5$ and WCl_6 were assigned to cis- and trans-rich polyacetylene derivatives, respectively.

The visible spectrum of polymer **3** (Figure 1) had a broad absorption maximum at 450 nm (molar absorption coefficient log ϵ = 3.6; a unit of ϵ is a L/(cm mol) monomer unit) which is a much longer wavelength than that of PPA ($\lambda_{max} < 300$ nm), suggesting some π conjugation in polymer **3** (Figure 1). π conjugation along the polyacetylene main chain is also supported by the ionization threshold energy (I^{th}) measured by ultraviolet photoelectron spectroscopy: the I^{th} of polymer **3** was 5.5 eV, which is lower than that of PPA (5.7 eV) and poly(3,5-di-*tert*-butyl-4-hydroxystyrene) (6.3 eV).[6] Substitution of the polyacetylene chain with an alkyl group usually reduces the effective conjugation length of the chain because the polyene chain is twisted at the single bonds due to steric hinderance of the side-chain substituent, as reported for poly(methylacetylene)[21] or poly(*tert*-butylacetylene).[22] On the contrary, a bathochromic shift has been reported for some ortho-substituted PPAs,[23] e.g., λ_{max} = 440, 458, and 542 nm for *o*-methyl-,[23a] *o*-trifluoromethyl-,[23b] and *o*-trimethylsilyl-substituted[23c] PPA, respectively. There has been no report on the meta-substitution effect on the electronic state of the polyene chain. But the extended overlap of the π orbitals in polymer **3** in comparison with PPA is caused by reduction of the main chain–substituent mixing which is results from the restricted bond rotation between the main chain and the phenyl ring and/or crowded packing of the chain-sided substituent.

Polyanion and Polyradical Formation. Polymer **3** is converted to the corresponding polyanion **10** and polyradical **4** when it is treated with an alkali and an oxidizing agent, respectively (Scheme III). Treatment of a methanolic solution of polymer **3** with excess KOH yielded the dark green polyanion **10** (λ_{max} = 655 nm, log ϵ = 3.9).

Careful oxidation of polymer **3** with fresh PbO_2 or alkaline $K_3Fe(CN)_6$ in benzene under oxygen-free atmosphere gave a deep brownish solution. The absorption at 495 nm is increased (log ϵ = 4.6) with enhancement of the ESR signal intensity. The spin concentration of polyradical **4** can be controlled by oxidative conditions, e.g., up to 2.3×10^{23} spins/molar monomer unit (38 mol %). Other oxidizing reagents such as active MnO_2, Fetizon reagents[24] also could be used, but spin concentration of polyradical **4** was less than 5 mol %. The spectral pattern consisting of three maxima agreed with that characteristic for phenoxy radicals.[25] The IR spectrum of polyradical **4** (KBr pellet) showed strong absorptions at 1660 and 1610 cm^{-1} attributed to a quinoid structure,[26] accompanied by the complete disappearance of the absorption at 3620 cm^{-1} attributed to the hydroxy group.

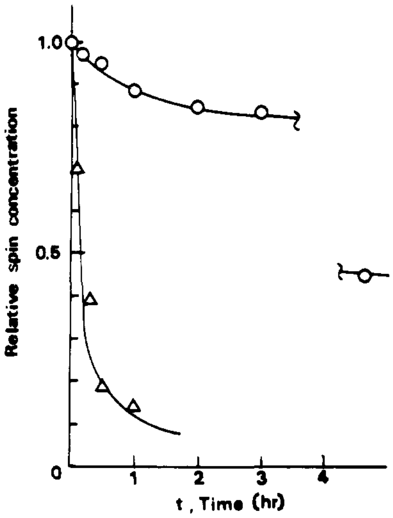


Figure 2. Time dependence of the spin concentration under atmospheric conditions: (○) **4** (the right plot of ○ indicates the data after 5 days); (△) 2,4,6-tri-*tert*-butylphenoxy radical.

It has been reported that 2,6-di-*tert*-butyl-4-R-phenoxy radicals (R = methyl, ethyl, *tert*-butyl, and styryl) show a characteristic broad absorption at ca. 400 nm irrespective of the substituted R group[25,27] and that 2,6-di-*tert*-butyl-4-arylphenoxy radicals have their absorption maxima at ca. 500 nm.[28,29] This suggests that the phenoxy radical substituent in polyradical **4** interacts electronically with the conjugated polyacetylene chain.

The electrical conductivity of **4** is below 10^{-8} $S \cdot cm^{-1}$, which is comparable to those of polymer **3** and PPA.

Chemical Stability of the Polyradical. The visible absorption intensity of polyradical **4** in benzene solution under atmospheric conditions stayed constant over 1 day and then gradually decreased. The decay of the spin concentration was monitored by the ESR signal area as shown in Figure 2. The radical concentration of polyradical **4** decreased gradually, with a half-life of ca. 5 days, which was in contrast to the 2,4,6-tri-*tert*-butylphenoxy radical whose spin concentration steeply decreased due to the formation of peroxides.[30] Under oxygen-free atmosphere polyradical **4** in solution was still alive after 1 month. Polyradical **4** was ESR active even in the solid state, and the spin concentration of polyradical **4** was kept constant under atmospheric conditions for 1 month. This remarkably stable radical formation is in contrast to the corresponding low molecular weight phenols. E.g., 3,5-di-*tert*-butyl-4-hydroxycinnamate[31] and 2,6-di-*tert*-butyl-4-(β-styryl)phenol[27] were oxidized to give the equilibrium mixture between the corresponding bisquinone methide and phenoxy radical in solution, and both of them gave diamagnetic bisquinone methides in the solid state. The GPC curve, i.e., the molecular weight and its distribution, of polyradical **4** was almost the same as that of polymer **3**. This is consistent with the assumption that the oxidation does not bring about oxidative degradation or cross-linking of the main chain.

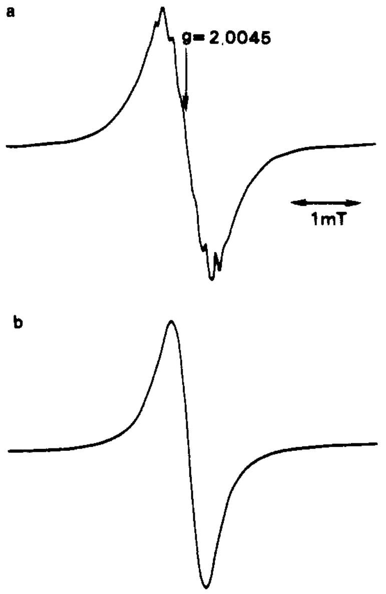
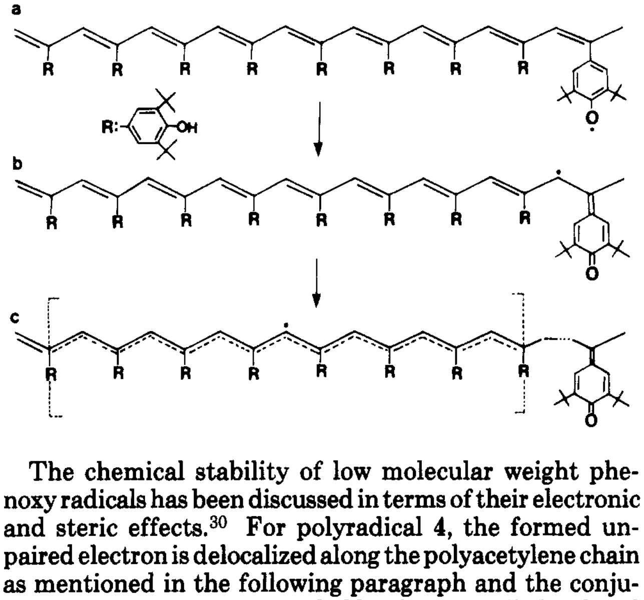


Figure 3. ESR spectra of polyradicals in benzene: (a) 4; (b) 4-d_1.

Scheme IV



The chemical stability of low molecular weight phenoxy radicals has been discussed in terms of their electronic and steric effects.[30] For polyradical 4, the formed unpaired electron is delocalized along the polyacetylene chain as mentioned in the following paragraph and the conjugated main chain is surrounded by the sterically hindered substituents. These factors satisfy both electronic and steric requirements for the chemical stability of polyradical 4 to suppress peroxide formation and intermolecular bond formation between unpaired electrons.

ESR Spectra of the Polyradical. The ESR spectrum for polyradical 4 with 5 mol % oxidation is shown in Figure 3a. The g value of the spectrum is 2.0044 ± 0.0002,[32] which indicates the formation of an oxygen-centered radical. However, if the formed unpaired electron is isolated in the phenoxy side chain, this polyradical should give a three-line pattern with relative intensities of 1:2:1 similar to the 2,4,6-tri-*tert*-butylphenoxy radical.[33] To assign the hyperfine structure (hfs) in Figure 3a, ENDOR measurement was tried for the toluene solution of 4 in the temperature region 170–300 K, but the ENDOR transition could not be observed (no saturation in ESR spectra up to 200 mW in irradiation power).

To discuss this puzzling delocalization profile of the unpaired electron in polyradical 4, hfs, which is caused by magnetic interaction between an unpaired electron and two kinds of magnetically nonequivalent protons, is analyzed by the ESR spectrum of the selectively deuterated polymer 4-d_1 (Figure 3b). The absorption became narrower and the hfs disappeared, which indicates that hfs in Figure 3a is caused by the interaction between an unpaired electron and protons belonging to the main chain.

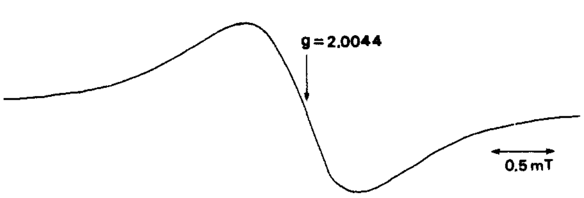


Figure 4. ESR spectrum of 4 in the solid state at 120 K.

The delocalization of unpaired electrons is explained by the following assumption (Scheme IV). The first step of the oxidation reaction takes place in the phenol side chain (Scheme IVa). The possibility of direct backbone hydrogen abstraction was disproved by the fact that no change of spin concentration was observed in the chemical oxidation of PPA with active PbO_2 or $K_3Fe(CN)_6$. The unpaired electron migrates to the main chain as in the tautomeric structure (Scheme IVb), and the phenoxy side chain is converted to quinone methide which acts as a break in the polyene structure. The migrating unpaired electron is delocalized along the conjugated system (Scheme IVc). A similar delocalization of the unpaired electron is also reported in PPA.[34-36] PPA shows hfs only at high temperature (>390 K) and a single broad absorption at room temperature. That is, polyradical 4 gives sharp ESR spectra with hfs even at room temperature due to its high solubility in organic solvents and its higher spin concentration than those of PPA.

The powder ESR spectrum of polyradical 4 in the Δm_s ± 1 region showed a single signal with Gaussian shape, whose g value was 2.0044 ± 0.0002 (Figure 4). ΔH_{pp} was slightly increased with a lowering of the temperature: from 0.98 mT at 300 K to 1.13 mT at 110 K for polyradical 4 with a spin concentration of 16 mol %.

Magnetic Property of the Polyradical. The spin concentration of polyradical 4 in the solid state in the temperature range 110–470 K is shown in Figure 5, with those of polymer 3 and PPA. The spin concentration of PPA irreversibly increased up to 470 K when the polymer was annealed above 350 K. This behavior has been reported by Percec[35] and Tabata[36] and was explained by cis–trans isomerization accompanied with conformational defect formation. The spin concentration of polymer **3** increases reversibly from 110 to 350 K, and above 350 K the spin concentration (0.02 mol %) decreases irreversibly. The inherent spin concentration of polymer **3** is higher than that of poly(phenylacetylene) probably due to the development of the conjugation length along the main chain stabilizing the unpaired spin. The reported higher spin concentrations of poly[[*o*-(trifluoromethyl)phenyl]acetylene][23b] (6.1×10^{17} spins/g = 0.01 mol %) and poly[[*o*-(trimethylsilyl)phenyl]acetylene][23c] (7.3×10^{17} spins/g = 0.02 mol %) also support the above notion. The g value (=2.0037) for polymer **3** (before oxidation) indicates the formed defect is a carbon-center radical. The spin concentration of polyradical 4 is 10^3 times higher than that of the parent polymer **3**.

The ESR signal area (S_{ESR}) is proportional to the static magnetic susceptibility (χ) which usually obeys the Curie–Weiss law for organic radicals (eq 2). Because χ is

$$S_{ESR} \propto \chi = \frac{N_s g \mu_B^2 S(S+1)}{3k(T-\Theta)} \qquad (2)$$

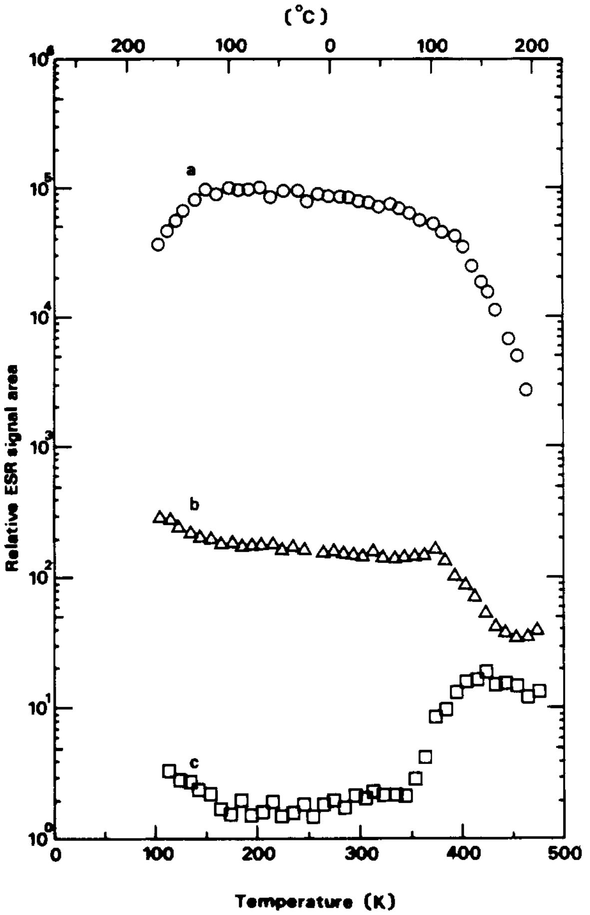


Figure 5. Relative ESR signal area in the solid state: (a) 4; (b) 3; (c) PPA.

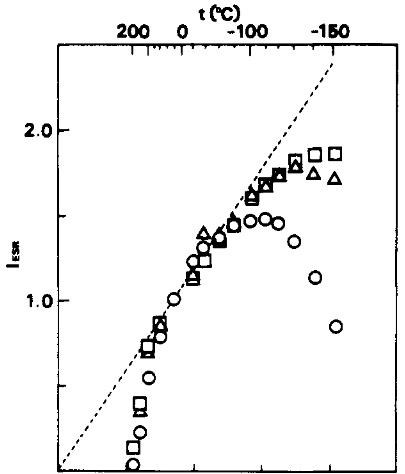
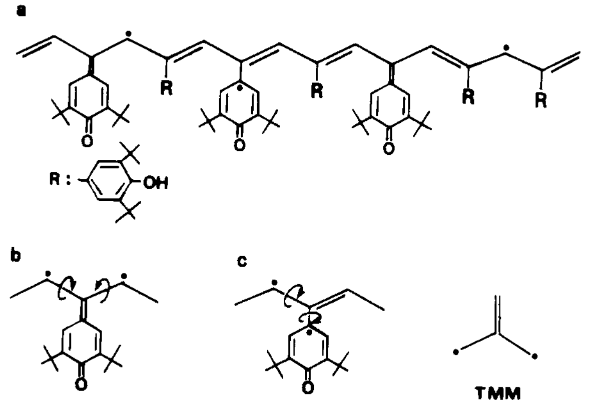


Figure 6. Temperature dependence of the ESR signal intensity I_{ESR} of 4 in the solid state at 20 °C with the spin concentrations (mol %) (○) 16, (△) 10, and (□) 3.

proportional to the number of unpaired spins (N_s), the spin quantum number (S) and the reciprocal of the absolute temperature (T), magnetic interaction between unpaired electrons can be discussed from the temperature dependency of S_{ESR}.[37] In our study, S_{ESR} at T (K), normalized by the value of S_{ESR} at 293 K, is used as the relative ESR area (I_{ESR}) at T (K) for the ESR analysis of polyradicals with different spin concentrations.[38]

The I_{ESR} of polyradical 4 in the solid state is plotted against $1/T$ in Figure 6. If there is no magnetic interaction between unpaired electrons, a plot of I_{ESR} vs $1/T$ gives a straight line (dashed line in Figure 6). While the I_{ESR} of polyradical 4 follows this line between 350 and 190 K, deviations at both higher and lower temperature regions are observed. The deviations above 350 K are irreversible, corresponding to a decrease in N_s due to thermal decomposition of radical sites in polyradical 4. On the other hand, the deviation at the lower temperature region is reversible and its profile depends on the spin concentration: the higher the spin concentration in polyradical 4, the higher the temperature at which the deviation begins. If S at room temperature is assumed to be $^1/_2$, these deviations are attributed to the decrease in N_s. These data suggest the presence of an antiferromagnetic interaction in polyradical 4 at the relatively low spin concentration of 3 mol % and even at the relatively high temperature of 170 K.

Chart II



The absence of a rapid decrease or increase in the ESR line width of polyradical 4 disproved a long-range magnetic interaction and suggested a spin-exchange interaction among small numbers of unpaired spins. Analysis of the solution ESR spectra of polyradical 4 in Figure 3 indicates that polyradical 4 has at least two kinds of unpaired electrons: one delocalized along the polyacetylenic main chain and the other localized in the side chain. Migration of the unpaired spin from the side chain to the main chain gives a local planar structure of the substituent to the main chain accompanied with serious deformation in the polymer structure, while localization of unpaired electrons within the side-chain phenoxy group gives less structural change. At low spin concentration unpaired electrons migrate to the main chain with permissible deformation. As the oxidation proceeds some unpaired electrons should localize in the side chain, because all the structural deformation will not be allowed due to steric repulsion between the bulky di-*tert*-butylbenzoquinone methide units.

While the plural unpaired electrons can exist in the same polymeric chain of polyradical 4 with a few percent of spin concentration, through-bond spin-exchange interaction between delocalized unpaired electrons along the same polyene unit should be interfered by quinone methide formation (Chart IIa). The nearest approach of two unpaired spins across a quinone methide unit is shown in Chart IIb. Another situation between delocalized unpaired electrons along the main chain and localized electrons in the side chain is schematized as Chart IIc. The structures b and c in Chart II have a trimethylenemethane (TMM) skeleton which as the triplet ground state in a planar structure.[39] The lowest singlet state of TMM has one methylene group twisted out of conjugation. The latter may correspond to the twisted structure b or c. These distorted conformations contribute to the observed antiferromagnetic interaction in polyradical 4. This structural speculation is recently supported by Lahti using a molecular mechanics computation for model oligomers of hypothetical polyradical 2.[8a]

The difference between theoretical expectation and experimental observation in this paper is attributed to this conformational deconjugation and/or nonplanar geometry in polyradical 4.

Conclusion

A conjugated and solvent-soluble polymer, poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene], is synthesized from polymerization of the corresponding monomer. The polymer yields through careful chemical oxidation a conjugated polyradical, which is remarkably stable and possesses a high spin concentration. Solution ESR spectra of the polyradical and its selectively deuterated derivative indicate delocalization of unpaired electrons formed in the phenolic side chain along the conjugated main chain. Spin-exchange interaction observed in 4 in the solid state is antiferromagnetic. Deconjugation accompanied by the migration of unpaired electrons and nonpolar conformation are the main reasons for the unexpected result. While the present experimental data are negative for constructing high spin molecules, a possibility of spin conduction through a chemical bond even at low spin concentration encourages us to further explore conjugated polymers bearing various paramagnetic centers.

Experimental Section

Monomer Synthesis. β-Chloro-3,5-di-*tert*-butyl-4-acetoxycinnamaldehyde (6). $POCl_3$ (23 mL) was added to DMF (28 mL) with stirring and cooling in an ice bath. Then the mixture was allowed to come to room temperature, and a solution of 4-acetyl-2,6-di-*tert*-butylphenyl acetate 5[15] (29.0 g, 0.10 mol) in THF (55 mL) was added to the mixture slowly. After stirring overnight at room temperature, ether (250 mL) was added and mixed thoroughly. The lower layer was added to a stirred solution of 19.5 g of sodium acetate in water (3 L). Yellow precipitate was collected, dried in vacuo, and recrystallized from acetonitrile, affording 17.2 g of β-chloro-3,5-di-*tert*-butyl-4-acetoxycinnamaldehyde (6) as a pale yellow crystal (yield 51%); mp 127–128 °C; ^{1}H NMR ($CDCl_3$, Me_4Si standard) δ 10.2 (2 H, s, aldehyde), 7.7 (2 H, s, phenyl), 6.6 (1 H, d, methine), 2.3 (3 H, s, acetoxy), 1.4 (18 H, s, *t*-Bu); IR (KBr pellet, cm^{-1}) 1760 ($\nu_{C=O}$ acetoxy), 1670 ($\nu_{C=O}$ aldehyde), 1600 ($\nu_{C=C}$). Anal. Calcd for $C_{19}H_{25}O_3Cl$: C, 67.7; H, 7.5; Cl, 10.5. Found: C, 67.5; H, 7.4; Cl, 10.6.

(3,5-Di-*tert*-butyl-4-acetoxyphenyl)acetylene (7). A total of 16.8 g (0.05 mol) of 6 in dioxane–water was refluxed for 4 h with 5 N aqueous NaOH (200 mL) according to the literature.[16] After cooling, the mixture was poured into dilute hydrochloric acid containing crushed ice and then extracted with ether. After evaporation, the crude tar product was distilled under reduced pressure (1 mmHg, 125 °C) affording 10.0 g of 7 as a viscous liquid which was easily solidified to white crystal upon standing (yield 70%); mp 59 °C; ^{1}H NMR ($CDCl_3$, Me_4Si standard) δ 7.4 (2 H, s, phenyl), 3.0 (1 H, s, $\equiv$CH), 2.3 (3 H, s, acetoxy), 1.3 (18 H, s, *t*-Bu); ^{13}C NMR ($CDCl_3$, Me_4Si standard) δ 170.4, 148.8, 143.0, 130.3, 119.5, 84.2, 76.1, 35.4, 31.4, 22.5; IR (KBr pellet, cm^{-1}) 3300 ($\nu_{\equiv C-H}$), 2100 ($\nu_{C\equiv C}$), 1760 ($\nu_{C=O}$ acetoxy). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.4; H, 8.9. Found: C, 79.3; H, 8.7.

(3,5-Di-*tert*-butyl-4-hydroxyphenyl)acetylene (8). To 5.7 g (0.02 mol) of 7 in dry THF (500 mL) $LiAlH_4$ (1.35 g) was added under a nitrogen atmosphere. The mixture was warmed at 40 °C for 24 h. After cooling, unreacted $LiAlH_4$ was decomposed with 14 mL of water in 300 mL of THF, and the solution was acidified by dilute hydrochloric acid. After extraction with ether, the ether layer was washed with water thoroughly and dried over Na_2SO_4. Recrystallization from hexane gave (3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (8) as a white crystal (4.5 g, yield 98%); mp 107 °C (lit.[18] mp 106–107 °C); ^{1}H NMR ($CDCl_3$, Me_4Si standard) δ 7.2 (2 H, s, phenyl), 5.2 (1 H, s, hydroxy), 2.7 (1 H, s, CH), 1.4 (18 H, s, *t*-Bu); ^{13}C NMR ($CDCl_3$, Me_4Si standard) δ 154.8, 136.4, 129.1, 113.5, 85.0, 74.4, 34.5, 31.0; IR (KBr pellet, cm^{-1}) 3620 (ν_{O-H}), 3270 ($\nu_{\equiv C-H}$), 2100 ($\nu_{C\equiv C}$); MS *m/z* 230.1 (M^+). Anal. Calcd for $C_{16}H_{22}O$: C, 79.4; H, 8.9. Found: C, 79.3; H, 8.7.

(3,5-Di-*tert*-butyl-4-hydroxyphenyl)acetylene-d_1 (8-d_1). To 2.3 g (0.01 mol) of 8 in absolute ether (50 mL) was added at room temperature under a nitrogen atmosphere ethylmagnesium bromide in THF (1.0 M). After stirring overnight, the ether solution was evaporated, and 20 mL of deuterium oxide was added. After neutralizing with deuterium chloride (4.6 mL) in deuterium oxide (13.8 mL), the solution was extracted with ether and dried over Na_2SO_4 (yield 93%): mp 107 °C; ^{1}H NMR ($CDCl_3$, Me_4Si standard) δ 7.2 (2 H, s, phenyl), 5.2 (1 H, s, hydroxy), 1.4 (18 H, s, *t*-Bu); IR (KBr pellet, cm^{-1}) 3620 (ν_{O-H}), 2600 ($\nu_{\equiv C-D}$), 2100 ($\nu_{C\equiv C}$); MS *m/z* 231.1 (M^+).

Polymerization. Polymerization was carried out basically as described by the literature.[17a] To a monomer solution containing 7 or 8 (13 mmol) and solvent (50 mL) was added under a nitrogen atmosphere a solution of WCl_6 or $MoCl_5$. Polymerization conditions are listed in Table I. After 24 h, the reaction was terminated by adding a small amount of methanol. The solution was concentrated and poured in hexane, and the precipitated powder was washed with hexane and dried in vacuo. The polymer was purified by reprecipitation twice from the benzene solution in hexane and furthermore by gel permeation chromatography (GPC: polystyrene gel column, eluent THF).

Polymer 3 (polymerization of monomer 8). Anal. Calcd for $(C_{16}H_{22}O)_n$: C, 83.5; H, 9.6. Found: C, 83.2; H, 9.4. Polymer 9 (polymerization of monomer 7). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.4; H, 8.9. Found: C, 79.3; H, 9.0. The content of W or Mo in the polymer after the above purification was less than 1 ppm by ICP analysis.

Reductive hydrolysis of polymer 9 protected with an acetoxy group was carried out in a manner similar to the preparation of monomer 8 to afford polymer 3.

Poly(phenylacetylene) (PPA) as a control material was prepared using WCl_6 as in the literature.[17b]

Oxidation. Chemical oxidation of polymer 3 was carried out as follows. Oxidation using PbO_2: A total of 0.23 g (1 mmol) of 3 was stirred in benzene with PbO_2 (2.4 g, 10 mmol) under an oxygen-free atmosphere for 30 min. After removal of PbO_2 by filtration, the benzene solution was evaporated. Oxidation using $K_3Fe(CN)_6$: To a solution of 0.023 g (0.1 mmol) of 3 in benzene (200 mL) were added under an inert atmosphere 4.4 g of $K_3Fe(CN)_6$ and 2.7 g of NaOH in water (60 mL). After stirring for 1 h, the mixture was transferred to a separatory funnel. The organic layer was washed with water thoroughly, dried over Na_2SO_4, and evaporated.

Oxidized polymer 4 was purified by a method similar to that of the parent polymer 3.

Polyradical 4 (oxidation using PbO_2). Anal. Calcd for $(C_{16}H_{21}O)_n$: C, 83.8; H, 9.2. Found: C, 82.5; H, 9.3.

Measurements. IR, UV/vis, and ^{13}C and ^{1}H NMR mass spectra were measured with Jasco IR-810. Shimadu UV-240, JEOL FX-90Q, and JEOL JMS-DX300 spectrometers, respectively. ICP analysis was carried out with Nippon Tarrell-Ash ICAP-575Mk.II. 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 the sample was determined by comparison of the ESR signal area of the benzene solution of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) with the known spin concentration (98%, Aldrich). The ENDOR measurement was performed by a JEOL JES-2XG ESR spectrometer equipped with a JEOL ES-EDX4 ENDOR spectrometer.

The electrical conductivity was measured by a two-probe technique for pressed samples at room temperature.

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Registry No. **3**, 116233-36-4; **5**, 30392-04-2; **6**, 137593-94-3; **7**, 126739-17-1; **8**, 36384-85-7; **8**-d_1, 137569-97-2; **8**-d_1 (homopolymer), 137569-99-4; **9**, 137569-98-3; WCl_6, 13283-01-7; Ph_4Sn, 595-90-4; $MoCl_5$, 10241-05-1; CCl_4, 56-23-5; benzene, 71-43-2; toluene, 108-88-3.