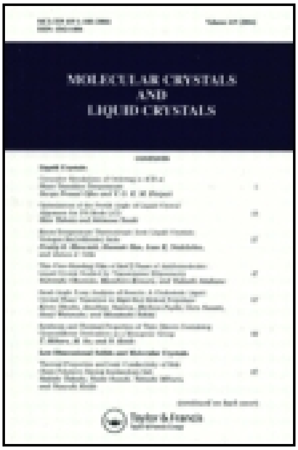

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Magnetic Interaction Observed in the Polyacetylenic Derivatives with High Spin Concentration

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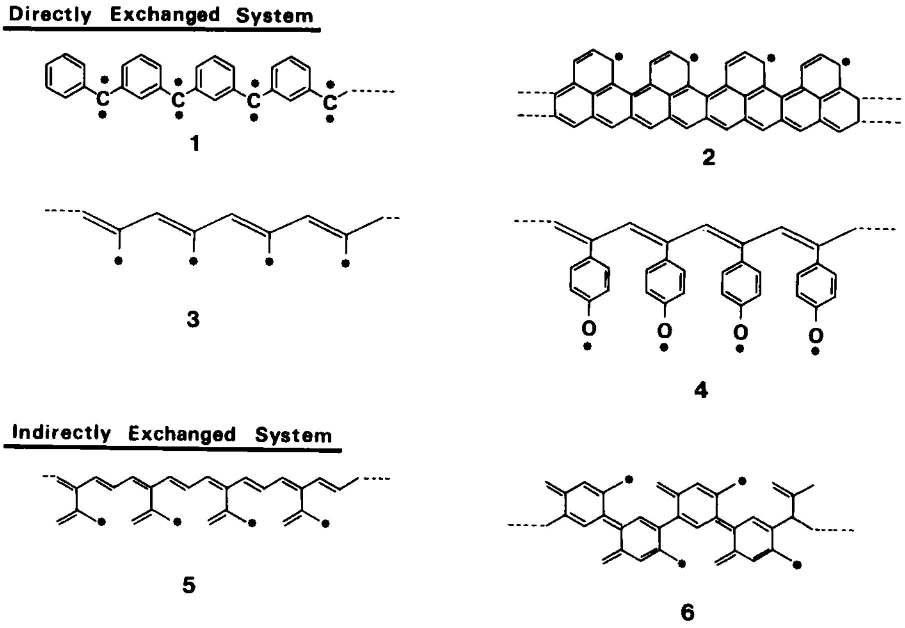
Electronic state and magnetic interaction of π-conjugated phenoxy radicals bearing a polyacetylenic backborn are described. Poly(3,5-di-t-butyl-4-hydroxyphenylacetylene) (**7a**) and poly(p-ethynylphenylhydrogalvinoxyl) (**8a**) with molecular weight ca. 10^4 are characterized. ESR spectra with hyperfine structure for the chemically oxidized **7b** indicate that the phenoxy radical conjugates through the polyacetylenic main chain over ca. 7 monomer units as a "neutral soliton." Polyradicals **7b** and **8b** are surprisingly stable even in the solid state, because of a resonance stabilization and/or a steric effect of the conjugated main chain. An antiferromagnetic interaction is observed for **7b** with spin concentration above 10 mol%. Mechanism of the magnetic interaction is discussed.

INTRODUCTION

Electronic properties of organic polymers are characterized by their diamagnetic ground state due to closed shell structure of constituent atoms. Recently many approaches have been made to realize molecular-based magnets including organic polymers and to the present time several of so-called ferromagnetic polymers have been synthetically attempted by various world laboratories.[1-6] But some of these materials are too complicated to be discussed quantitatively due to non-uniformity of their chemical structure[7] and lack in the reproducibility of their magnetic behavior.[8]

To realize ferromagnetic parallel spin alignment in polymeric system, several ideas to expect high spin ground state are proposed theoretically[9-16] (Scheme 1). These systems can be classified into two categories, i.e. directly exchanged system and indirectly exchanged one. The polyradicals represented in **1–4** show electronic structure with alternating signs of the spin densities at the atoms. Their spin multiplicity is to be proportional to their degree of polymerization, if their radicals are fully delocalized and direct exchange between the radical sites through the main chain is positive. Such a unique structure attributes to degenerated non-bonding molecular orbitals (NBMOs) with one and the same spin.[9-15] Another type of conjugated system such as **5,6** where NBMOs are localized within each monomeric

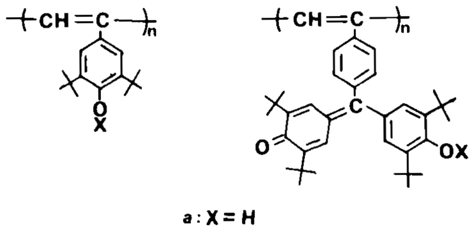


SCHEME 1

unit and where direct exchange interaction between the uncoupled NBMO electrons is negligibly small.[16] Still, an indirect exchange mediated by the delocalized π-electron system may exist and this model is similar to the superexchange of some lanthanide magnets where magnetic exchange interaction between the localized f orbitals occurs due to the delocalized s-electron system.

Experimental investigations for these conjugated polymers have been limited due to difficulties in monomer preparation and in polymerization. Itoh[17] and Iwamura[18] have synthesized the oligodiphenylcarbenes as a model of **1** and showed the high spin state as were expected theoretically. While those oligocarbenes showed high spin ground state, they were highly chemical reactive and were stable only below 150 K, and their magnetic properties were reported only for the doped state.

To the best of our knowledge there are no reports on the preparation and magnetic property of conjugated polymer with high spin concentration other than our preliminary communication of this work.[19] Our approach to study electronic interactions between unpaired electrons through a π-conjugated polymeric system deals with model compounds poly[(3,5-di-t-butyl-4-oxyphenyl) acetylene] **7b**, poly(p-ethynylphenylgalvinoxyl) **8b** (Scheme 2), which involve a stable phenoxy radical substituent as the organic radical center, elucidated chemical structure, and solubility in common solvents to allow spectroscopic measurements. **7b** is one of the most promising model compound of **4**,[19,20] and **8b**[21] belongs to indirectly exchanged system. In this paper, magnetic interaction observed in these conjugated polyradicals with high spin concentration is discussed in connection with its mechanism and their electronic state.



a : X = H
b : X = •

7 **8**

SCHEME 2

RESULTS AND DISCUSSION

Electronic state Prepolymers **7a** and **8a** were polymerized with W, Mo catalysts according to the polymerization procedure for substituted acetylenes.[19,20] The polymers were obtained as dark red or orange powder, and were soluble in $CHCl_3$, benzene, tetrahydrofuran and alcohol. The structures represented in **7a** and **8a** were confirmed by elemental analysis and spectroscopies. The molecular weights of **7a** and **8a** were $0.5-3 \times 10^4$ and $0.9-7.0 \times 10^4$, respectively.

7a has π-conjugated system; i.e. UV-vis spectrum of **7a** showed a broad absorption with maximum at ca. 450 nm extended to 600 nm, which indicates a fairly long π-conjugated system in the polyacetylenic main chain. Treatment of the polymer solutions with excess alkali yielded dark green-colored phenolate anion of **7a**. Their moderate oxidation with fresh PbO_2 or $K_3Fe(CN)_6$ under an oxygen-free

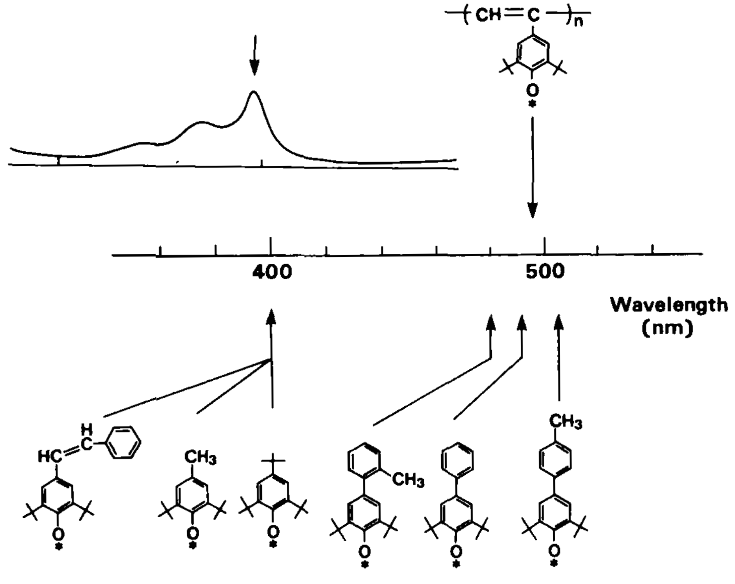


FIGURE 1 Peak position of various 2,6-di-tert-butylphenoxy radical and polyradical **7b** in the visible region.

atmosphere gave deep brownish solutions. A strong absorption band appeared at 495 nm for the polyradical **7b** with increase in the ESR signal intensity.

It has been reported that 2,6-di-tert-butyl-4-R-phenoxy radicals (R = methyl, ethyl, t-butyl, and styryl) show characteristic broad absorption at ca. 400 nm irrespective of the substituted R group,[22,23] and that 2,6-di-tert-butyl-4-aryl-phenoxy radicals have their absorption maxima at around 500 nm[24,25] (Figure 1). This indicates electronic effect of phenoxy radical substituent in **7b** on the polyacetylenic main chain.

ESR spectrum with a hyperfine structure for the 5 mol% oxidized **7b** is shown in Figure 2(a). The g-value 2.004 indicates the formation of an oxygen-center radical. The spectrum is in contrast to the ESR spectra for polyacetylenes, where ESR absorption is a structureless symmetric sharp signal due to carbon-center radical with g-value of 2.002. If the formed unpaired electron localizes in the phenoxy side chain, the radical should give a three-line spectrum with relative intensities of 1:2:1 similar to 2,4,6-tri-tert-butylphenoxy radical. ESR spectrum of the deuterated polymer **7b-d**$_1$ showed a narrower absorption (Figure 2(b)) where the hyperfine structure is disappeared. This is a crucial evidence that the hyperfine structure in (a) is caused by the interaction with the polyacetylenic protons and

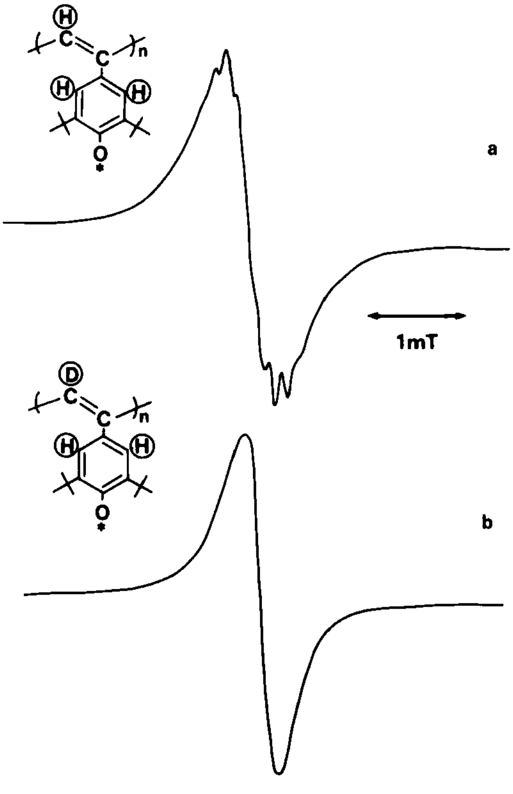


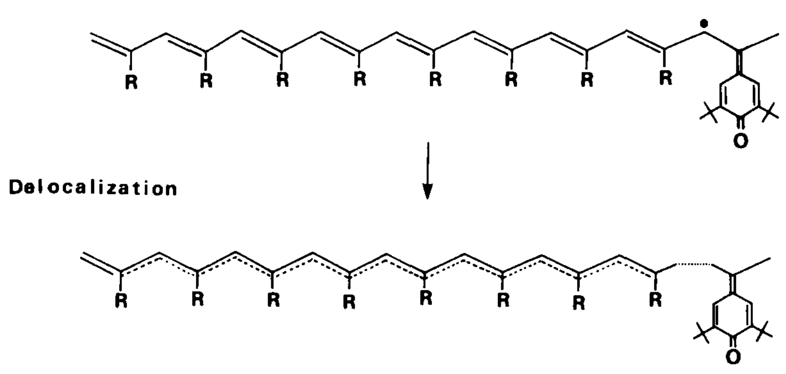
FIGURE 2 ESR spectra of the polyradicals: a: polyradical of **7b** (spin conc. 5 mol%); b: polyradical of **7b-d**$_1$.

that the formed unpaired electrons are delocalized in the main chain. The spectrum is well simulated on the assumption[26] that the formed unpaired electron behaves as a magnetic defect or a neutral soliton in polyene which is delocalized over seven monomer units (Scheme 3).

The ESR spectrum of polyradical **8b** at low spin concentration showed broadened hfs with relative signal intensity of 1:4:6:4:1 due to the magnetic interaction of an unpaired electron with four equivalent protons. This supported the delocalization of unpaired spin within galvinoxyl substituent.

The ESR signal intensity of these polyradicals at room temperature stayed constant over a few days, meaning that the formed radical species are very stable. The stable radical formation of **7b** is in contrast to the radical formation of the corresponding low molecular phenols, e.g. 3,5-di-tert-butyl-4-hydroxycinnamate[27]; the latter had been reported to give bisquinone methides rapidly and irreversibly. A sterically crowded structure of the polymer and a resonance stabilization of unpaired electrons through the conjugated main chain probably suppresses intermolecular bond formation between unpaired electrons. GPC curves of the oxidized **7b** and **8b** were the almost same as those of before the oxidation: This is consistent with the assumption that the oxidation does not bring about oxidative degradation or cross-linking of the main chain.

Magnetic interaction Magnetic properties of **7b** and **8b** are summarized in Table I, with the reference data for other polyacetylenes. Spin concentration of chemically oxidized **7b** and **8b** can be controlled by oxidative condition up to 3.9 × 10^{20} spins/g (15 mol%) and 6.9 × 10^{20} spins/g (60 mol%), respectively. These values are



SCHEME 3

TABLE I

Spin concentration and ESR g-value of Polyacetylenes

Polymer	g-value	Spin conc. (spins/g)	Spin conc. [M]/[S][a]	Ref.
7b	2.0044	3.9×10^{20}	6.7	19, 20)
8b	2.0045	6.9×10^{20}	1.7	21)
PA[b] (cis)	2.0030	$>5.8 \times 10^{17}$	<40000	28)
PA (trans)	2.0030	$0.4\text{–}1.2 \times 10^{19}$	2000–6000	28)
PCNA[c]	2.0030	2.5×10^{18}	4600	28)
PDCNA[d]	2.0030	1.2×10^{18}	6300	28)
PPA[e]	2.0027	$0.8\text{–}5.1 \times 10^{17}$	11000–75000[f]	29)

[a]the number of monomer unit per one unpaired spin,
[b]polyacetylene, [c]polycyanoacetylene
[d]polydicyanoacetylene, [e]polyphenylacetylene,
[f]calculated from reported value

extraordinarily high in comparison with those of other polyacetylenes in which magnetic defects with g-value 2.0027–2.0030 are formed mainly by cis-trans isomerization.

ESR signal intensity of **7b** in the solid state is plotted against the reciprocal of absolute temperature in Figure 3. At spin concentration below 3.6×10^{22} spins per molar monomer unit, ESR signal intensity reversibly increases in proportional to the reciprocal of temperature in the region of $-160 \sim 80$°C. This indicates that the paramagnetic susceptibility of the polyradical **7b** obeys the Curie's law. On the other hand, at relative high concentration $> 6.0 \times 10^{22}$ spins/mol the spin susceptibility below -130°C decreases with lowering temperature, suggesting the presence of an antiferromagnetic interaction in the solid state.

Paramagnetism observed for the polyradical **7b** at low spin concentration is probably explained as shown in Scheme 4. The unpaired electron formed in the phenoxy side chain migrates to the main chain, and delocalize along the conjugated polyacetylenic chain. The spin concentration is so dilute, that magnetic interaction between the unpaired electrons is suppressed because the quinoid structure acts as an edge of the π-conjugated system, and the distance between the quinoid structure is represented as a "Domain Wall of Soliton." But even at this state **7b** shows quite high spin concentration compared with pristine polyacetylene, e.g. cis- and trans-polyacetylene have one unpaired spin per 40000 and 2000 carbons, respectively. Through bond magnetic interaction is scarcely expected for the polyacetylenes because the polyacetylene is consist of, for example, only 800 carbons for it with molecular weight 10000.

On the other hand, at relative high concentration above 6.0×10^{22} spins/mol (10 mol%) the presence of antiferromagnetic interaction in the solid state was suggested. The shortest allowed distance between the quinoid structures is expected to be 7 monomer units, because soliton can delocalize over 7 monomer units. If the further oxidation takes place just in the "Domain wall of Soliton," the formed new "Domain Wall of Soliton" contains two unpaired spins. These two spins can

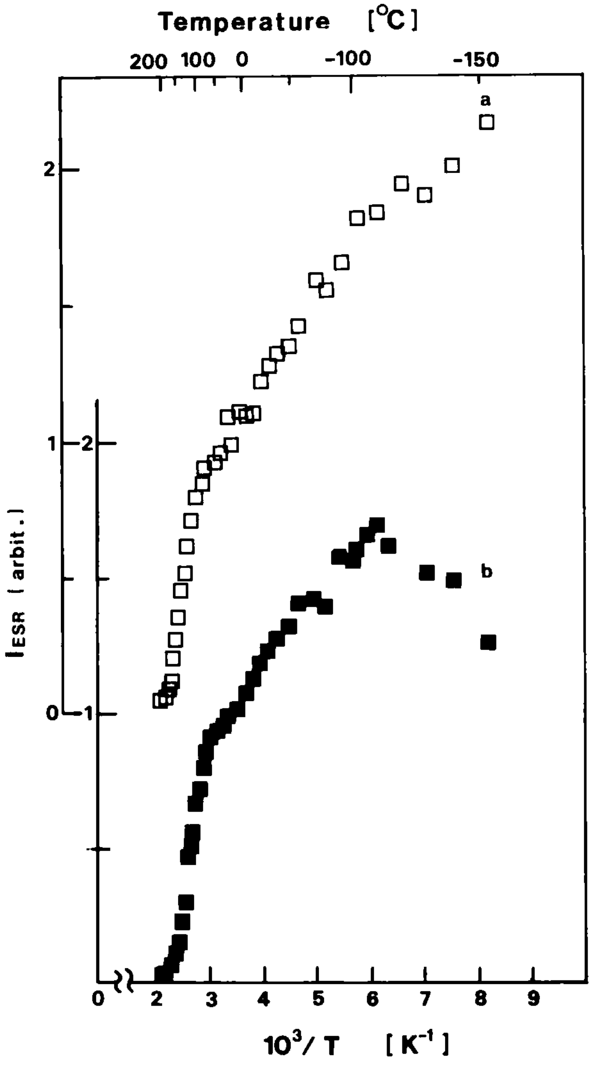
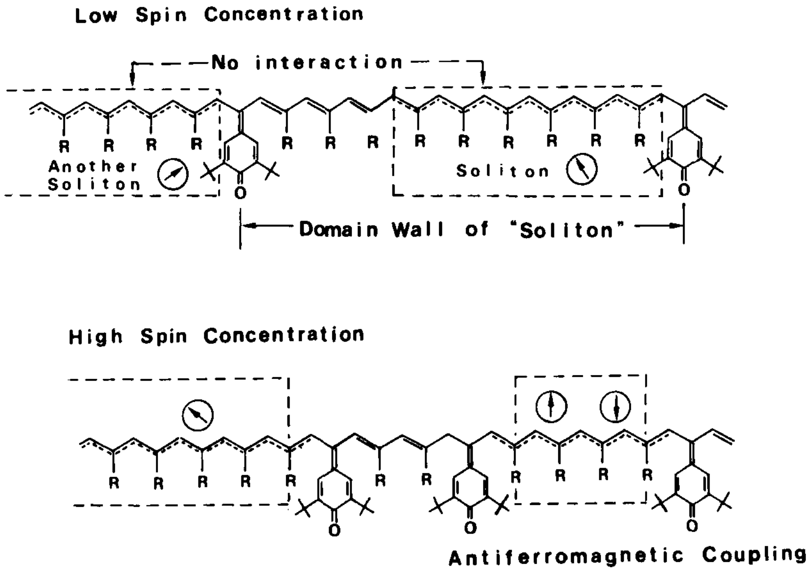


FIGURE 3 Temperature dependence of the ESR signal intensity of the polyradical **7b** in the solid state: a: spin conc. 5 mol%; b: 10 mol% at 20°C.

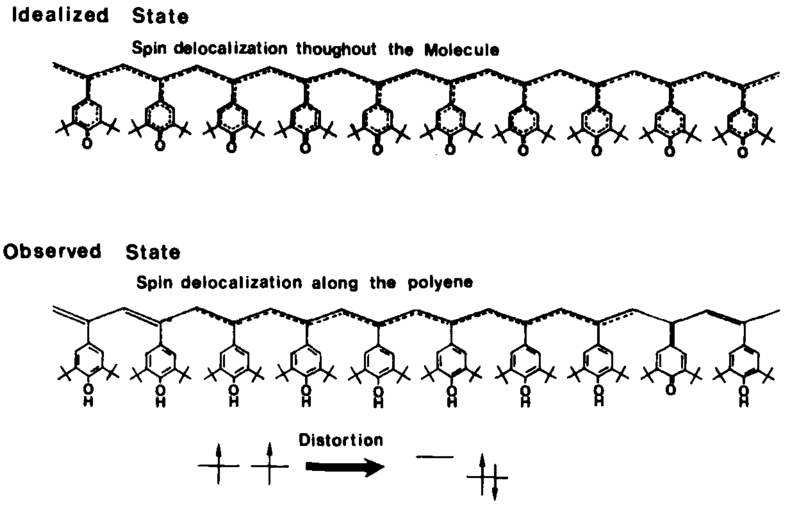
interact antiferromagnetically because they delocalize in the same conjugated system.

The magnetic coupling expected for the polyradical **7b** is, however, to be ferromagnetic, if it is in accordance with the Ovchinnikov's prediction.[10] Magnetic interaction in the oxidized **7b** is considered to occur mainly along the polyacetylenic main chain, which is supported by the IR and ESR spectroscopies. The gap between the observed magnetism and the theoretical prediction is probably attributed to the delocalization range of unpaired electrons (Scheme 5). That is, an antiferromagnetic interaction is predominant if the unpaired electron delocalizes



SCHEME 4

along the polyacetylenic main chain because polyene chain cannot stabilize the triplet state, while a ferromagnetic coupling may be expected when an interaction between unpaired electrons takes place in the whole molecule including side chain group. Temperature dependence of the spin susceptibility for the **8b** obeyed Curie's law but antiferromagnetic interaction was not observed even at high spin concentration. This suggests that the distribution of unpaired electron in the side chain group prevents the antiferromagnetic interaction of unpaired electrons.



SCHEME 5

CONCLUSION

Conjugated and solvent-soluble polymers, poly[(3,5-di-tert-butyl-4-hydroxy-phenyl)acetylene] and poly(p-ethynylphenylhydrogalvinoxyl), are synthesized from polymerization of the corresponding monomers with the WCl_6 or $MoCl_5$ catalyst. The polymers yield through chemical oxidation π-conjugated polyradicals, which are very stable and possess high spin concentration. Magnetic interaction between unpaired electrons is observed for polyradicals with high spin concentration. These polyradicals are expected to be a potential candidate as a magnetically condensed organic material.

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