Synthesis and Magnetic Properties of Conjugated Stable Polyradicals

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SYNTHESIS AND MAGNETIC PROPERTIES OF CONJUGATED STABLE POLYRADICALS

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ABSTRACT

Synthesis and magnetic properties of π-conjugated stable polyradicals bearing a polyacetylene backbone are described. 2,6-Di-*tert*-butyl-4-ethynylphenol (**8**) and 4-ethynylphenylhydrogalvinoxyl (**9**) are polymerized with W, Mo chloride or Rh complex to yield their polyacetylene derivatives with molecular weight of ca. 10^4, while 2-ethynylphenalenone (**10**) gives only its oligomer. The polymers are soluble in common solvents and converted to the corresponding conjugated polyradicals via heterogeneous chemical oxidation using PbO_2 or alkaline $K_3Fe(CN)_6$. The polyradicals with extremely high spin concentration (up to 4.8×10^{23} spins/monomer mol) are obtained by regulating the oxidative conditions. The polyradicals are quite stable in solution and even in the solid state because of resonance stabilization and/or a steric effect of the substituents. Magnetic interactions between the unpaired spins in the conjugated stable polyradicals are discussed.

INTRODUCTION

Synthesis of organic and molecular-based ferromagnets and their characterization have been of great interest in recent years. In 1986, Korshak and Ovchinnikov reported unusual ferromagnetic properties of

black polymeric products formed by thermal, photochemical, and glow discharge treatment of their organic diradical **1** (Scheme 1) [1], which drew much attention to possible ferromagnetic behavior of their organic polymers. Reports on polymers with (unusual) ferromagnetic characteristics have continued: E.g., thermally treated product of **2** [2], poly(*s*-triaminobenzene) polymerized with iodine oxidation **3** [3], and theromosetting resin composed of triarylmethane structure (COPNA) **4** prepared under a magnetic field [4] also exhibit ferromagnetic characteristics. While these reports suggest a certain possibility of organic ferromagnetism using polymeric materials, ill-defined chemical structure, low yields, and poor reproducibility in the magnetic results of these polymers [5, 6] prevent us from elucidating their magnetic characteristics or discussing the mechanism of their magnetism. Under these circumstances, syntheses of polyradicals with well-defined chemical structures are very important because inspection of the magnetic interaction mechanism in purely organic system will become feasible by using these model polymers.

In contrast to monoradicals where magnetic interaction is governed by the mutually spatial position in their crystals, spin conduction through


1   **2**

3   **4**
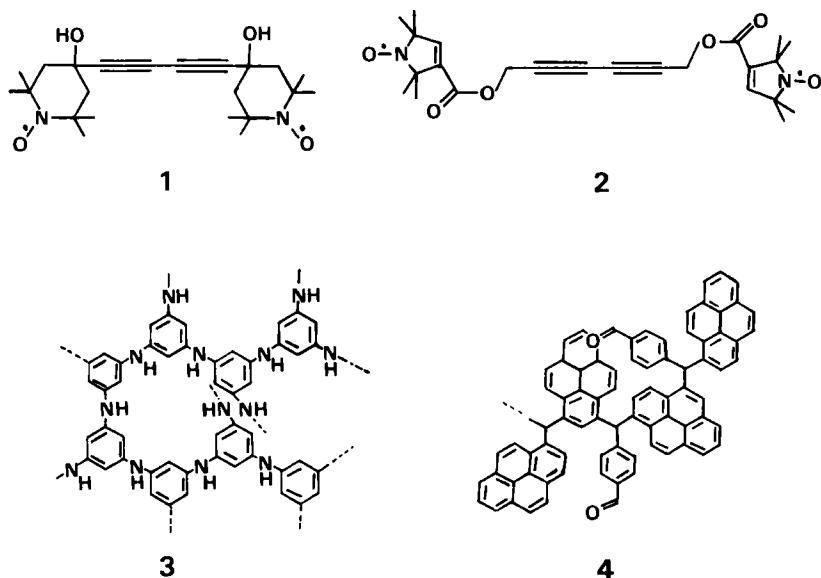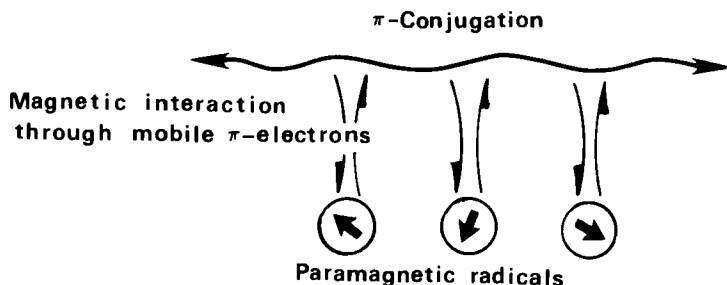
SCHEME 1.

chemical bonds is expected for polyradicals. Polynitroxides **5–7** (Scheme 2) have been synthesized by the direct polymerization of corresponding monomeric radicals. While a high spin concentration (2.4×10^{21} spins/g) was realized in **5**, each chain-sided nitroxide behaved as a monoradical without appreciable magnetic interaction [7]: only slight through bond interactions via amide bridge were discussed in **6** and **7** [8]. While these polynitroxides possess a high spin concentration and high stability, magnetic interaction through bonds leading to a magnetically ordered state is scarcely expected because the unpaired electron in nitroxides strongly localizes over the N—O bond and electronic interactions between them are prevented by σ-bonds. It is believed that a conjugated electronic structure in polyradicals is one requirement needed to establish a through bond interaction or a long-range magnetic ordering among spins. From these standpoints we designed the molecular structure of the polyradicals as model compounds to study magnetic interaction between unpaired electrons and we synthesized the conjugated polyradicals.

MOLECULAR DESIGN OF THE CONJUGATED POLYRADICALS

An intramolecular magnetic interaction between unpaired spins is expected for a multiradical having a conjugated electronic structure derived from delocalization of unpaired spins through a π-conjugation system and/or from spin polarization accompanied by spin-alignment transmission (Scheme 3), based on the following prediction. Ovchinnikov described a convenient theorem [9], converted from valence bond theory and recently supported by computational examination [10], which esti-

**5**   **6**   **7**

SCHEME 2.

π-Conjugation
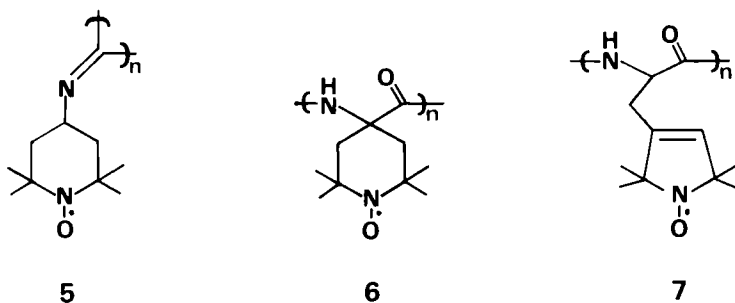
SCHEME 3.

mates the ground state spin quantum number S for an alternant conjugated π-system with N^* α (up)-spin centers and N β (down)-spin centers:

$$S = (N^* - N)/2 \tag{1}$$

Extension of this theorem to the electronic state of a conjugated polymer yields a very large S that is proportional to its molecular size [9–12]. Such a polyradical is often called a "high spin polymer," and it is to correspond to one "magnetic domain" that makes up inorganic ferromagnetic compounds. Synthesis of polyradicals with high spin multiplicities is one of the most promising approaches to realizing an organic ferromagnet.

If one can introduce chemically stable radical moieties with a conjugated electronic structure into a conjugated polyene chain at high concentration, delocalization of the unpaired electrons and/or spin polarization along the polyene chain will be expected; i.e., magnetic interaction among spins is created. But experimental investigations on these conjugated polymers have been limited due to the difficulty of synthesis and the instability of the polyradical derivatives formed.

Our approach to the study of electronic interactions between unpaired electrons through a π-conjugated polymeric system deals with a π-conjugated radical bearing a conjugated polyacetylene backbone (Scheme 4) Polyradical **8** shows a fully conjugated electronic structure due to direct spin delocalization of the unpaired electrons formed and is the most promising model polymer of poly(4-ethynylphenoxyl) pointed out by Ovchinnikov as a "high spin polymer" [9]. On the other hand, indirect magnetic interaction [11] appears in polyradical **9**; the unpaired electron is mainly localized at the phenylgalvinoxyl side chain. The spin density is distributed mainly over the galvinoxyl substituent, but it is also over the

8,9 R':X =H   R:X= •
10   R':X =C·O   R:X= CH•
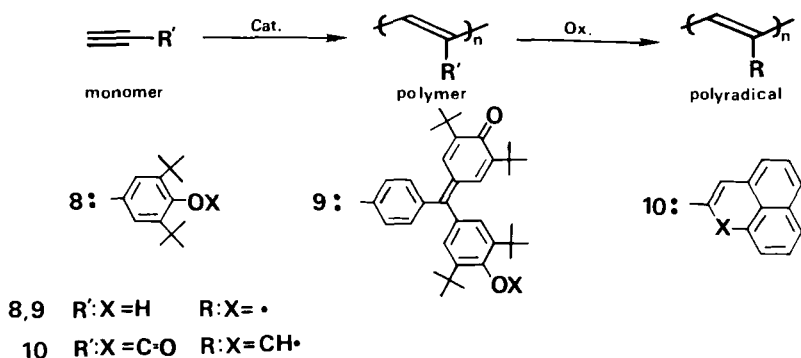
SCHEME 4.

phenyl ring to some extent due to a spin polarization mechanism. In the polyradical **10**, an intermediate electronic state between the polyradical **8** and **9** is realized because symmetrical spin distribution over the phenalenyl ring leads to effective spin polarization over the polyacetylene main chain.

SYNTHESIS OF THE CONJUGATED POLYRADICALS

Monomer **8** was obtained after hydrolysis of 3,5-di-*tert*-butyl-4-acetoxyphenylacetylene, which is prepared via the Vilsmeiyer reaction of 4-acetoxy-2,6-di-*tert*-butyl-phenyl acetate [11]. Monomer **9** was synthesized via organometallic synthesis as follows: methyl 4-[(trimethylsilyl)-ethynyl]benzoate was treated with (2,6-di-*tert*-butyl-4-lithiophenoxy)-trimethylsilane, followed by deprotection of three trimethylsilyl groups with methanolic KOH [12]. Monomer **10** was obtained by a coupling reaction between 2-bromophenalenone and trimethylsilylacetylene in the presence of Pd catalyst followed by hydrolysis with alkali.

These monomers were polymerized with W, Mo, or Rh catalyst according to the polymerization procedure for substituted acetylenes [13, 14]. The polymerization of these monomers is summarized in Table 1. The polymerization rates of our substituted acetylenes were ca. 1/10–100 times smaller than that of the unsubstituted phenylacetylene due to sterically crowded substituents at the meta- or para-position. Monomer **10** gave only a oligomeric fraction, probably because the electron-

TABLE 1. Polymerization of the Acetylene Monomers **8-10**

Monomer	Catalyst[a]	Solvent	Yield, %	$M_n \times 10^{4}$ [b]	M_w/M_n
8	WCl_6	CCl_4	3	2.2	2.0
	$MoCl_5$	Bz	8	1.0	1.7
	Rh^c	EtOH	3	0.3	2.0
9	WCl_6-Ph_4Sn	Bz	0.2	0.4	2.2
	Rh^d	THF	1	1.2	3.7
10	$MoCl_5$	THF	1	1.0	1.3
	Rh^d	THF	2	1.1	1.2

[a]$[M]_0 = 0.1$-$1.0\,M$, [catalyst] $= 0.4$-$30\,mM$.
[b]Determined by GPC.
[c]$[Rh(C_8H_{12})(P(C_6H_5)_3)_2]PF_6$.
[d]$[RhCl(C_8H_{12})]_2$.

donating carbonyl oxygen atom poisons the catalyst. Monomers **8** and **9** gave high polymers with molecular weight of 10^4 in spite of their bearing phenolic hydroxy groups. These groups are assumed to be effectively protected by the neighboring and sterically hindered *tert*-butyl substituents during polymerization.

These polymers were obtained as dark red or orange powders, and they were soluble in $CHCl_3$, benzene, tetrahydrofuran, and alcohols, which allowed spectroscopic measurements [15-19]. The structures represented in Polymers **8-10** were confirmed by various spectroscopies [15, 16]. Polymer **8** has a fairly long π-conjugation along the polyacetylene main chain; i.e., the UV-vis spectrum of Polymer **8** showed broad absorption with a maximum at ca. 450 nm which extended to 600 nm. This is in contrast to that of unsubstituted poly(phenylacetylene) (PPA) whose absorption maxima is below 300 nm. This agrees with the lower ionization threshold energy of Polymer **8** (5.5 eV) compared to that of PPA (5.7 eV) [19].

The polymers were moderately oxidized by treating their solutions heterogeneously with freshly prepared PbO_2 or alkaline $K_3Fe(CN)_6$ to afford a deep brownish solution upon increasing the ESR signal intensity. These polyradicals remained stable at room temperature for a few days. The sterically crowded structures of the polymers and/or resonance stabilization of unpaired electrons through the conjugated main

chain probably suppresses intermolecular bond formation between the unpaired electrons. Stable radical formation could not be observed for Oligomer **10** due to inter- or intrachain bond formation.

The solution ESR spectrum of Polyradical **8** with a hyperfine structure at a g value of 2.0045 is attributed to the formation of an oxygencenter radical. The hyperfine structure completely disappeared after selective deuteration of the polyenic protons (Fig. 1) [17, 18]. The spectrum of Polyradical **9** at a low spin concentration (< 10 mol%) gave a hyperfine structure at a g value of 2.0045, with its relative signal intensity of 1:4:6:4:1 attributed to the magnetic interaction of an unpaired electron with four equivalent protons, similar to that of the corresponding lowmolecular weight phenylgalvinoxyl (Fig. 2). The spectrum became broader and coalesced into a single broad line with an increase in the spin concentration per chain, thereby supporting a high local spin concentration within the macromolecular domain even in dilute solution. This broadening is explained by an intrachain dipole–dipole interaction accompanied by a reduction in distance between the chain-sided radical moieties.

GPC curves of Polyradicals **8** and **9** were consistent with those made before oxidation. This means that oxidation does not bring about oxidative degradation or crosslinking of the main chain.
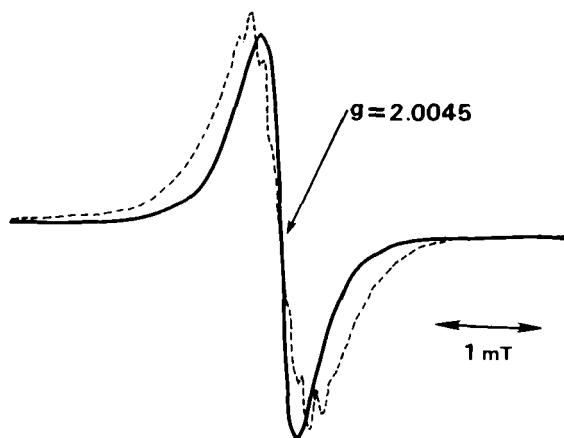

FIG. 1. Solution ESR spectra of Polyradical **8** in benzene at room temperature (spin concentration 5 mol%) (---); **8** with selectively deuterated main chain (——).
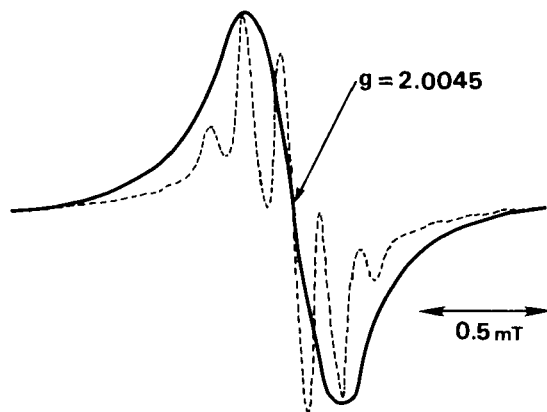
FIG. 2. Solution ESR spectra of Polyradical 9 in benzene at room temperature immediately after oxidation (---); 8 with high spin concentration (70 mol%, 3.6 × 10^{-4} mol/L) (——).

MAGNETIC PROPERTY OF THE CONJUGATED POLYRADICALS

The spin concentrations of Polyradicals 8 and 9 can be enhanced by oxidative conditions up to 3.9 × 10^{20} spins/g (15 mol%) and 9.3 × 10^{20} spins/g (80 mol%), respectively [17, 18]. These values are extraordinarily high in comparison with those of other polyacetylenes in which magnetic defects are formed mainly by *cis-trans* isomerization (10^{16}–10^{17} spins/g) and g values of 2.0030–2.0027 (Fig. 3).

At a spin concentration of Polyradical 8 below 3.6 × 10^{22} spins per molar monomer unit, the ESR signal intensity in the solid state increases in proportion to the reciprocal of the temperature in the temperature range from −160 to 80°C, which indicates that the spin susceptibility obeys Curie's law. On the other hand, at relative high concentrations (>6.0 × 10^{22} spins/mol), the spin susceptibility below −130°C decreased with lowering temperature, implying an antiferromagnetic interaction among the unpaired spins.

Ovchinnikov predicted, however, that the magnetic coupling for Polyradical 8 is expected to be ferromagnetic [9]. The spectroscopies of Polyradical 8 suggests that a magnetic interaction occurs along the conjugated polyene chain, not in the whole molecule. The gap between the observed magnetism and the theoretical prediction is attributed to the
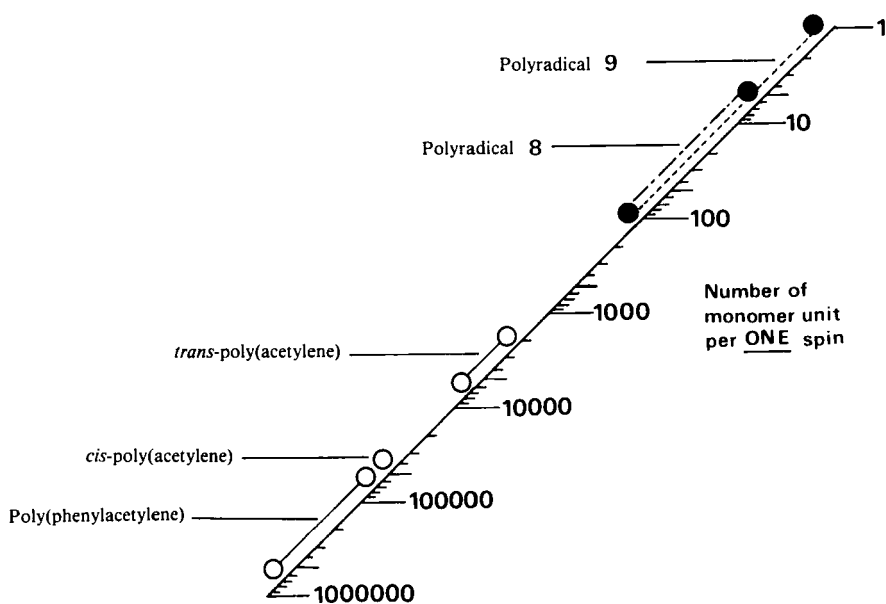
FIG. 3. Schematic diagram of spin concentration of chemically oxidized polyradicals.

delocalization range of unpaired electrons. That is, if the unpaired electron delocalizes along the polyacetylenic main chain, an antiferromagnetic interaction predominates because a polyene chain cannot stabilize the triplet state, while a ferromagnetic coupling is expected when an interaction between unpaired electrons takes place in the whole molecule, including the side-chain groups.

For Polyradical **9**, the temperature dependency of the spin susceptibility obeyed Curie's law and an antiferromagnetic interaction was not observed even at high spin concentration (56 mol%) [16]. At an extremely high spin concentration (4.8 × 10^{23} spins/monomer mol), the spin susceptibility increased below − 50°C, deviating from the extrapolation line of Curie's law. This suggests that the localization of unpaired electrons in the chain-sided galvinoxyl group prevents antiferromagnetic interaction of unpaired electrons. The line width of the ESR signal in the solid state was 0.25 mT at room temperature, but it rapidly increased below − 100°C and reached 1.70 mT at − 150°C, which suggests a short-range ordering among the unpaired spins.

CONCLUSION

We obtained polyradicals with a polyene backbone, and the spin concentration of these polymers almost reached Avogadro's number. While bulk magnetism has not yet been realized, a profile of magnetic interactions can be described by using polyradicals with chemically elucidated structures. Polyradicals 8 and 9 are thought to have two limiting electronic states: Polyradical 8 is a spin delocalized model and Polyradical 9 has a spin localized structure. We presume that mixing both types of spin in one polymer chain will lead to a cooperative magnetic phenomenon because ferromagnetic elements in nature, such as iron, have both delocalized free electrons and localized spin on the metal orbitals, and the former transmits its spin alignment effectively. Therefore, these two polyradicals are expected to be key compounds in constructing ferromagnetic polymers.

ACKNOWLEDGMENT

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