Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Magnetic Properties of Conjugated Phenoxy Polyradicals

Hiroyuki Nishide[a]; Naoki Yoshioka[a]; Eishun Tsuchida[a]
[a] Department of Polymer, Chemistry Waseda University, Tokyo, Japan

To cite this Article Nishide, Hiroyuki , Yoshioka, Naoki and Tsuchida, Eishun(1990) 'Magnetic Properties of Conjugated Phenoxy Polyradicals', Journal of Macromolecular Science, Part A, 27: 9, 1261 — 1273

To link to this Article: DOI: 10.1080/00222339009349690

URL: http://dx.doi.org/10.1080/00222339009349690

J. MACROMOL. SCI.—CHEM., A27(9–11), pp. 1261–1273 (1990)

MAGNETIC PROPERTIES OF CONJUGATED PHENOXY POLYRADICALS

HIROYUKI NISHIDE, NAOKI YOSHIOKA, and
EISHUN TSUCHIDA*

Department of Polymer Chemistry
Waseda University
Tokyo 169, Japan

ABSTRACT

Formation and magnetic properties of π-conjugated phenoxy radicals bearing a porphyrin macrocycle or a polyacetylenic backbone are described. Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphinatometals (**7-M**) [M = Zn(II), VO(II), and Cu(II)] were oxidized to give the corresponding stable monoradical and biradical. Magnetic properties of the radical species depend on the magnetic orbital of the central metal ion. ESR hfs structure reveals that the biradical for **7-Zn** and **–VO** are in the triplet (S = 1) and quartet state (S = 3/2), respectively. Poly(3,5-di-*t*-butyl-4-hydroxyphenylacetylene) (**8**) and poly(*p*-ethynylphenylhydrogalvinoxyl) (**9**) with molecular weights of $\sim 10^4$ are characterized. ESR spectra with hyperfine structure for **8** indicate that the phenoxy radicals are conjugated with the polyacetylenic main chain over ~ 7 monomer units as a "neutral soliton." Formed polyradicals for **8** and **9** are surprisingly stable, even in the solid state, due to resonance stabilization and/or steric effect of the conjugated main chain. An antiferromagnetic interaction is observed for oxidized **8** with a spin concentration above 10 mol%.

INTRODUCTION

There have been rapidly increasing research activities to determine the organization of ferromagnetic organic radicals and to explore ferromagnetic organic materials in the last few years [1–4]. At present, up to a dozen so-called organic/synthetic ferromagnets have been reported by various laboratories worldwide [5–9], but some of these materials are too complicated to be discussed quantitatively due to the non-uniformity of their chemical structure and the lack of reproducibility of their magnetic behavior.

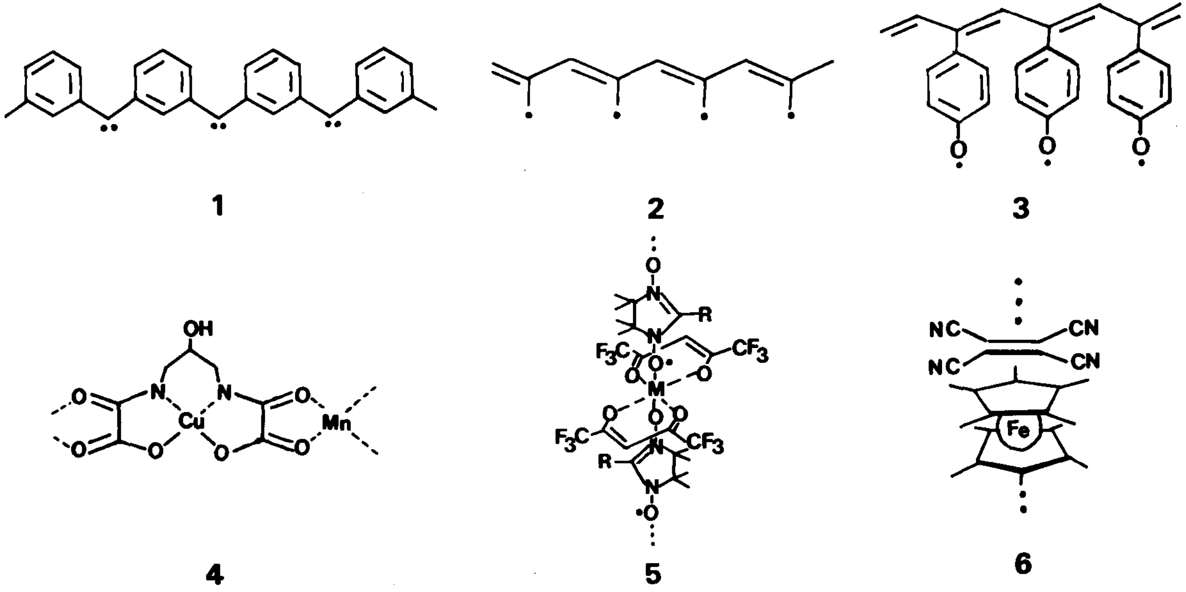
In the theoretical design of ferromagnetic substances, the first requirement is that atoms or molecules of the system are paramagnetic, and second, that the interaction between them is also ferromagnetic. These conditions are fulfilled for transition metal elements which constitute ferromagnets of natural origin. There have been two approaches to achieve organic ferromagnetic materials (Scheme 1). One possible approach is to synthesize molecules with a large spin multiplicity in their ground state. Typical model compounds, which are supported theoretically, are the polyradicals represented in **1–3** [3, 10, 11]. Another approach is to build up coordination polymers in which the ferro- or ferrimagnetic chain is composed of two alternating metal ions with different spin multiplicities **4** [12]. The complex may be bridged through a radical ligand **5** [13] and the charge transfer complex with a nonzero spin **6** [1].

Our approach to the study of electronic interactions between unpaired electrons through a π-conjugated polymeric system deals with model compounds which involve a stable phenoxy radical substituent as the organic radical center, an elucidated chemical structure, and solubility in common solvents to allow spectroscopic measurements.

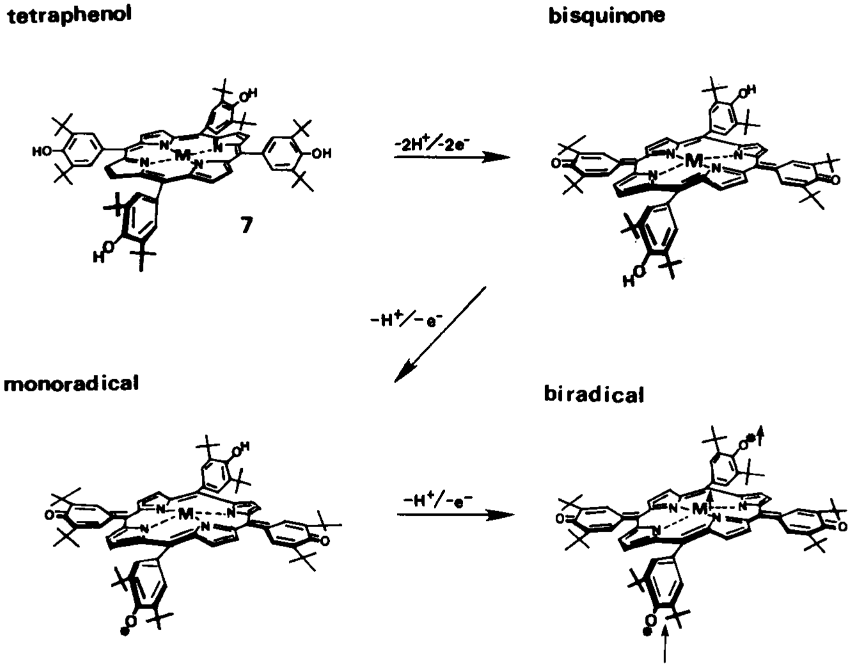
PORPHINATOMETALS WITH STABLE PHENOXY RADICALS

Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphinatometals **(7-M)** [M = Zn(II), VO(II), and Cu(II)] is an interesting compound from the viewpoint of its stable phenoxy radical formation and of an interaction between these radicals and the central metal ion through the π-conjugated porphyrin ring. **7-M** was oxidized to yield a bisquinone, a monoradical, and a biradical derivative (Scheme 2) [14]. These radicals were stable during measurements at room temperature.

Visible absorption spectra for the bisquinone species show two broad bands at 460 and 700 nm, while the starting tetraphenol of **7-M** has the


1
2
3
OH
N
N
Cu
O
O
O
O
O
O
Mn
4
O
N
R
N
F3C
O
CF3
O
M
O
O
O
F3C
CF3
N
R
N
O
5
NC
CN
NC
CN
Fe
6

SCHEME 1.



SCHEME 2.

characteristic Soret and Q band of a porphyrin, indicating the formation of a new chromophore, including the quinoid structure, for the bisquinone species. Visible spectra for mono- and biradicals were in agreement with that of the bisquinone, which suggests retention of the local structure around the metal ion through oxidation.

ESR spectra for the mono- and biradical species of **7-Zn** are shown in Fig. 1(a). If an exchange interaction is large compared to a hyperfine interaction ($J >> a$), the observed ESR hyperfine constant (hfs) a^{S} can be written as

$$a^{\mathrm{S}} = a^{\mathrm{d}}/2\mathrm{S} \qquad (1)$$

where a^{d} is coupling constant in the isolated spin (doublet state) [15]. Oxidized **7-Zn** gave a quintet ESR spectrum with a reduced hfs attributed to the biradical triplet state (S = 1), which implies that a rapid electron

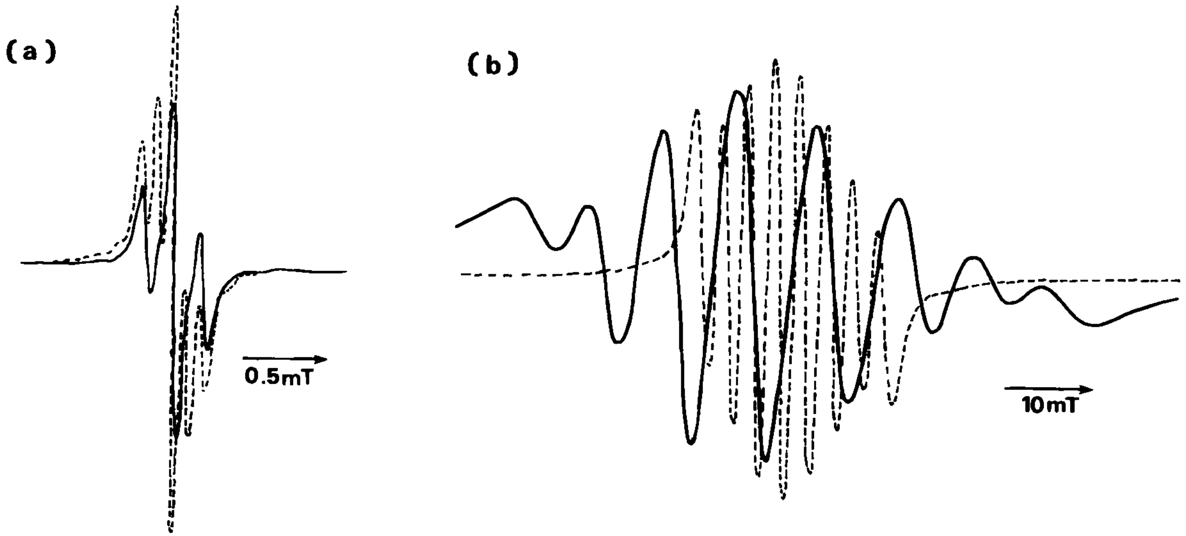


FIG. 1. ESR spectra of the porphinatometals with phenoxy radicals **7-M**. (a) **7-Zn**: monoradical (—) and biradical (- -); (b) **7-VO**: tetraphenol (—) and biradical (- -).

exchange between the two radical sites is established through the conjugated structure.

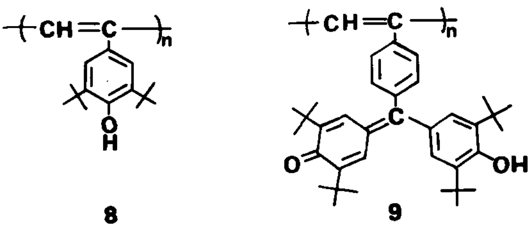
The oxidized **7-VO** showed an 8-line spectrum attributed to ^{51}V ($I = 7/2$) with a splitting constant reduced to $\sim$1/3 of that before the oxidation (Fig. 1b). This indicates the existence of a $S = 3/2$ spin state for a ferromagnetically coupled three spin system. A g-value shift from 1.993 for the tetraphenol to 2.000 for the biradical also supports the notion that a strong interaction exists between the central VO ion and the phenoxy radicals.

On the other hand, the ESR spectrum for the oxidized **7-Cu** consists of a weakened copper signal, which implies an antiferromagnetic interaction between the central copper ion and the two phenoxy radical sites. The opposite magnetism between these two oxidized **7-Ms** is explained by the electronic character of the central metal ion. The VO(II) ion has one unpaired electron on the d_{xy} orbital, which induces a π-character for bonding between V and the coordinating N atoms, and contributes to parallel spin alignment based on accidental degeneracies of the d_{xy} orbital and the porphyrin π-system. This alignment provides a pathway for ferromagnetic electron exchange between the two phenoxy radicals (all-up spin as schematically represented in Scheme 2).

POLYACETYLENES WITH STABLE PHENOXY RADICALS

To extend the magnetically coupled spin system to a purely organic polymer, polyacetylenic derivatives **8** and **9** with stable phenoxy radicals in their side chains were synthesized (Scheme 3) [16, 17].

A large organic macromolecule with conjugated bonds such as poly(4-



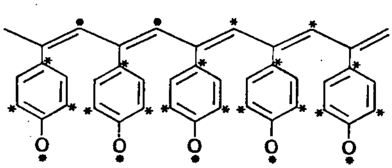
SCHEME 3.

hydroxyphenylacetylene) (**3**) is one of the most realizable compounds for a high spin polymer [5]. It is well known that in alternant hydrocarbons the atoms can be divided into two groups, denoted by starred atoms and unstarred atoms. **3** corresponds to the class in which the number of starred atoms (N*) and that of unstarred (N) is unequal. The ground state of these molecules has high spin multiplicity; the total spin S is proportional to the degree of polymerization (Scheme 4).

Poly[(3,5-di-*t*-butyl-4-hydroxyphenyl) acetylene] **8** [16] is thought to be a promising model compound of **3**. However, **8** had not been synthesized due to the difficulty in synthesizing [18] and polymerizing the corresponding monomer. Poly(*p*-ethynylhydrogalvinoxyl) (**9**) also belongs to this polymer class, based on small spin distribution over the central phenyl ring [19]. **8** and **9** were polymerized with W, Mo, or Rh catalyst according to the polymerization procedure for substituted acetylenes [20]. The polymers were obtained as dark red and brown powders for **8** and **9**, respectively, and were soluble in $CHCl_3$, benzene, tetrahydrofuran, and alcohol. The structures represented in **8** and **9** were confirmed by elemental analysis and spectroscopic analysis. The molecular weights of **8** and **9** were 0.5–3 × 10^4 and 0.9–7.0 × 10^4, respectively [16, 17].

8 and **9** are extended π-conjugated systems. For example, the UV-visible spectrum of **8** showed a broad absorption with maximum at $\sim$450 nm, extending out to 600 nm; this indicates a fairly long π-conjugated system in the polyacetylenic main chain. Treatment of the polymer solutions with excess alkali yielded dark green- and blue-colored phenolate anions of **8** and **9**, respectively. Their moderate oxidation with fresh PbO_2 or $K_3Fe(CN)_6$ in an oxygen-free atmosphere gave deep brownish solutions. A strong absorption band appeared at 495 nm for both oxidized **8** and **9**.

These polyradicals remained stable upon standing at room temperature over a few days, implying that the radical species are very stable.



n = Degree of polymerization
N = Number of starred atom
N* = Number of unstarred atom

$$S = \frac{|N^* - N|}{2} = \frac{5-4}{2} \cdot n = \frac{n}{2}$$

SCHEME 4.

Chemical stability of oxidized **9** was superior to that of oxidized **8**. The stable radical formation for **8** is in contrast to the radical formation of the corresponding low molecular weight phenols, e.g., 3,5-di-*t*-butyl-4-hydroxycinnamate; the latter had been reported to give bisquinone methides rapidly and irreversibly. The sterically crowded structure of the polymer and the resonance stabilization of unpaired electrons through the conjugated main chain probably suppresses intermolecular bond formation between unpaired electrons. GPC curves of oxidized **8** and **9** after the oxidation were the same as those before oxidation; this is consistent with the assumption that oxidation does not bring about oxidative degradation or crosslinking of the main chain.

ESR spectrum with a hyperfine structure for 5 mol% oxidized **8** is shown in Fig. 2 [21]. The *g*-value 2.004 indicates the formation of an oxygen-centered radical. The spectrum is in contrast to the ESR spectra for polyacetylenes, where ESR absorption is a structureless symmetric sharp signal due to a carbon-center radical with a *g*-value of 2.002. If the 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-*t*-butylphenoxy radical. The ESR spectrum of the deuterated polymer **8-d$_1$** showed a narrower absorption (Fig. 2c) where the hyperfine structure has disappeared. This is crucial evidence that the hyperfine structure in Fig. 3(a) is caused by the interaction with the polyacetylenic protons and that the unpaired electrons formed are delocalized in the main chain. The spectrum is well simulated (Fig. 3b) on the assumption [22] that the unpaired electron formed behaves as a magnetic defect or a neutral soliton in polyene which is delocalized over seven monomer units (Scheme 5). The wave function ($\psi(n)$) and hfs constant ($a_H(n)$) for the unpaired spin in the soliton at the *n*th carbon atom away from the center of soliton can be written as

$$\psi(\mathbf{n}) = (1/\sqrt{N})\ \mathrm{sech}\ (n/N)\ \cos\ [(\pi/2\mathrm{l})n\mathrm{l}] \tag{2}$$

where l = C—C spacing along the main chain
$2N$ = length of the delocalization

$$a_H(n) = a_0|\psi(n)|^2 \tag{3}$$

where a_0 = hfs constant for an unpaired spin localized to single C—H units.

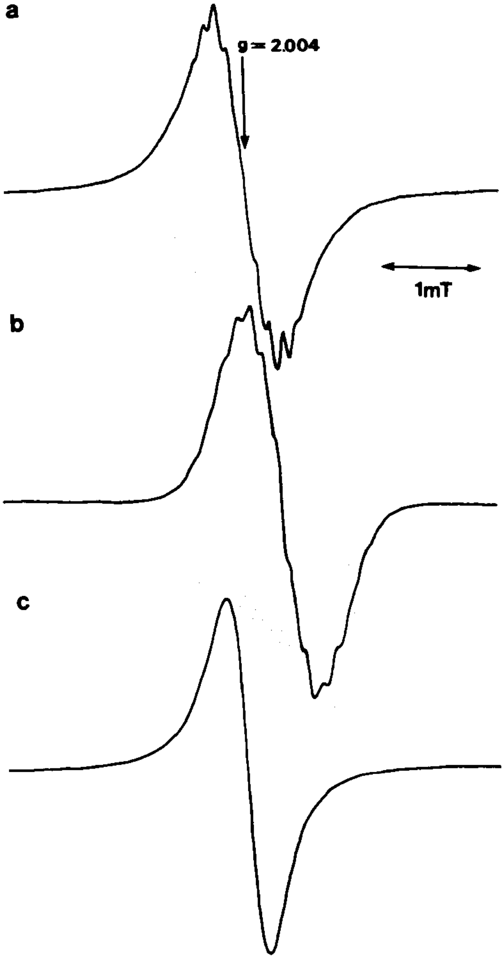


FIG. 2. ESR spectra of the polyradicals. (a) Polyradical of **8** (spin concentration 5 mol%); (b) simulated spectrum; (c) polyradical of **8-d$_1$**.

Electronic properties of polyacetylene as a one-dimensional conjugated polymer have long been the subject of intense experimental and theoretical studies. Unfortunately, both undoped and doped polyacetylene are insoluble and their unpaired electrons may be associated with either *cis*-

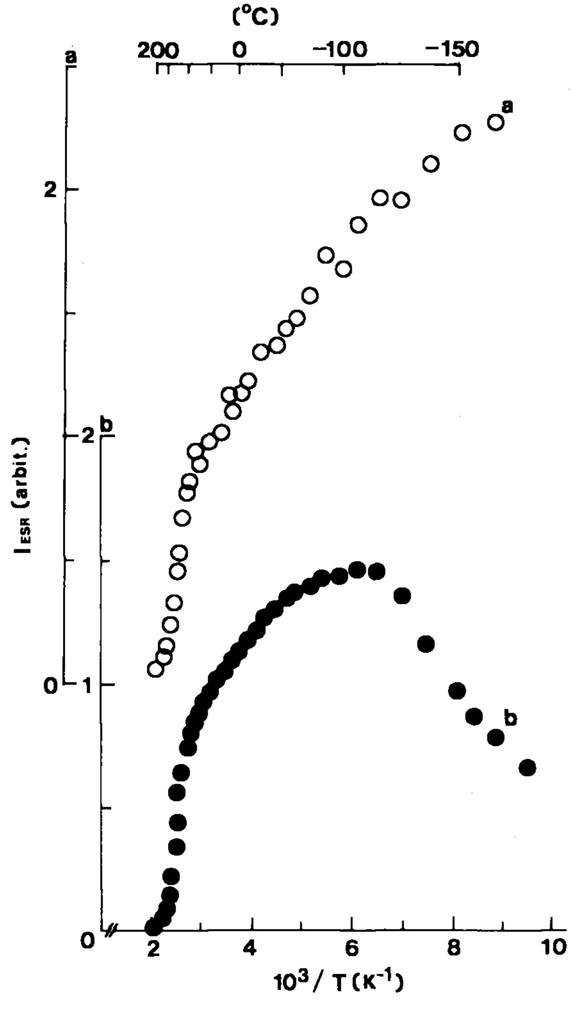
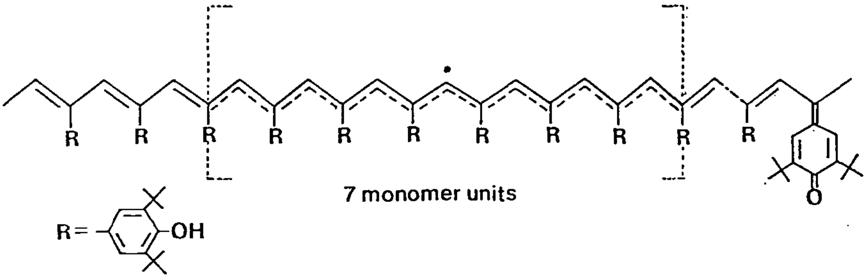


FIG. 3. Temperature dependence of the ESR signal intensity of the oxidized **8** in the solid state. (a) spin concentration 4 mol% at 20°C; (b) 14 mol%.

trans isomerization and/or crosslinking species. The previously mentioned result is the first example demonstrating the soliton-like delocalization of an unpaired electron; this was accomplished by using a structurally well-characterized, solvent soluble, and π-conjugated polymer at room temperature.



SCHEME 5.

The ESR spectrum for oxidized **9** consists of a broad quintet hfs signal with a relative intensity of 1 : 4 : 6 : 4 : 1, indicating that the unpaired electron interacts with the four equivalent ring protons of the galvinoxyl residue [17]. The relatively broad signal is explained by a dipole interaction between the unpaired electrons.

Spin concentration in the oxidized **8** varied with the oxidative reaction condition up to 9.0 × 10^{22} spins per molar monomer unit. Both **8** and **9** were ESR active even in the solid state [21]. At a spin concentration below 3.6 × 10^{22} spins/mol, the ESR signal intensity for **8** obeyed Curie's law in a manner similar to undoped polyacetylene. On the other hand, at relatively high spin concentration $>6.0 \times 10^{22}$ spins/mol, the spin susceptibility below −130°C decreased with lowering temperature, suggesting the presence of an antiferromagnetic interaction between the unpaired electrons.

The magnetic coupling expected for the polyradical **8** is ferromagnetic if it is in accordance with Ovchinnikov's prediction [10]. The magnetic interaction in oxidized **8** is considered to occur mainly along the polyacetylenic main chain which is supported by IR and ESR spectroscopy. The difference between the observed magnetism and the theoretical prediction is probably attributed to the delocalization range of unpaired electrons. That is, an antiferromagnetic interaction is predominant if the unpaired electron delocalizes along the polyacetylenic main chain, while a ferromagnetic coupling may be expected when an interaction between unpaired electrons takes place in the whole molecule, including the side-chain group. Temperature dependence of the spin susceptibility for oxidized **9** with 6.0 × 10^{22} spins/mol obeyed Curie's law, but antiferromagnetic interaction was not observed. This suggests that the distribution of unpaired electrons in the side-chain group prevents the antiferromagnetic interaction of unpaired electrons.

The magnetic properties of these polyradicals are expected to find applications as a magnetically condensed material.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research on the Priority Area of Macromolecular Complexes from the Ministry of Education, Science and Culture, Japan.

REFERENCES

[1] J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev., 88*, 201 (1988).

[2] P. Delhaes and M. Drillon, *Organic and Inorganic Low-Dimensional Crystalline Materials*, Plenum, New York, 1987.

[3] H. Iwamura, *Pure Appl. Chem., 58*, 187 (1986).

[4] R. D. Willett, D. Gatteschi, and O. Karn, *Magneto-Structural Correlations in Exchange Coupled Systems*, Reidel, Dortdrecht, 1985.

[5[Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, and V. N. Spector, *Nature, 326*, 370 (1987).

[6] Y. Cao, P. Wang, Z. Hu, S. Li, L. Zhang, and J. Zhao, *Synth. Met., 27*, B625 (1988).

[7] K. Kamachi, X. S. Cheng, H. Aota, W. Mori, and M. Kishita, *Chem. Lett.*, p. 2331 (1987).

[8] J. B. Torrance, S. Oostra, and A. Nazzal, *Synth Met., 19*, 709 (1987).

[9] G. Chouteau and C. V. Jeandey, *J. Phys., 42*, 1441 (1981).

[10] A. A. Ovchinnikov and V. O. Cheranovskii, *Sov. Phys. Solid State, 29*, 1779 (1987); A. A. Ovchinnikov, *Theoret. Chim. Acta, 47*, 297 (1978).

[11] D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Masten, *J. Chem. Phys., 77*, 3101 (1982).

[12] O. Kahn, in Ref. 2, p. 93.

[13] C. Benelli, A. Ganeschi, D. Gatteschi, and P. Rey, in Ref. 2, p. 109.

[14] H. Nishide, N. Yoshioka, K. Akaike, and E. Tsuchida, Unpublished Results.

[15] B. Kirste, M. Grimm, and H. Kurreck, *J. Am. Chem. Soc., 111*, 108 (1989).

[16] H. Nishide, N. Yoshioka, K. Inagaki, and E. Tsuchida, *Macromolecules, 21*, 3119 (1988).

[17] H. Nishide, N. Yoshioka, K. Kaneko, and E. Tsuchida, *Ibid., 23*, 4487 (1990).

[18] S. Hauff, P. Krauss, and A. Rieker, *Chem. Ber., 105*, 1446 (1972).
[19] K. Mukai, T. Kamata, T. Tamaki, and K. Ishizu, *Bull. Chem. Soc. Jpn., 49*, 3376 (1976).
[20] T. Masuda and T. Higashimura, *Adv. Polym. Sci., 81*, 121 (1987).
[21] H. Nishide, N. Yoshioka, T. Kaku, K. Inagaki, E. Tsuchida, and O. N. Ohya, Unpublished Results.
[22] B. R. Weinberger, E. Ehrenfreund, A. Pron, A. J. Heeger, and A. G. MacDiarmid, *J. Chem. Phys., 72*, 4749 (1980).