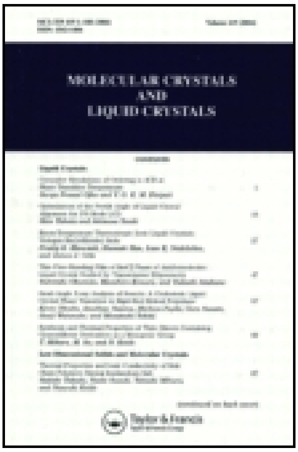


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

π-Conjugated Polyradicals With Poly(Phenylene-Vinylene) Skeleton and Their Through-Bond and Long-Range Interaction

Hiroyuki Nishide [a] , Takashi Kaneko [a] , Shuichi Toriu [a] , Kohya Katoh [a] , Masahiro Takahashi [a] , Eishun Tsuchida [a] & Kizashi Yamaguchi [a] [b]
[a] Department of Polymer Chemistry, Waseda University, Tokyo, 169, Japan
[b] Department of Chemistry, Osaka University, Toyonaka, Osaka, 560, Japan

Version of record first published: 05 Dec 2006.

To cite this article: Hiroyuki Nishide , Takashi Kaneko , Shuichi Toriu , Kohya Katoh , Masahiro Takahashi , Eishun Tsuchida & Kizashi Yamaguchi (1995): π-Conjugated Polyradicals With Poly(Phenylene-Vinylene) Skeleton and Their Through-Bond and Long-Range Interaction, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 272:1, 131-138

To link to this article: http://dx.doi.org/10.1080/10587259508055280

Mol. Cryst. Liq. Cryst., 1995, Vol. 272, pp. 131–138
Reprints available directly from the publisher
Photocopying permitted by license only

π-CONJUGATED POLYRADICALS WITH POLY(PHENYLENE-VINYLENE) SKELETON AND THEIR THROUGH-BOND AND LONG-RANGE INTERACTION

HIROYUKI NISHIDE, TAKASHI KANEKO, SHUICHI TORIU, KOHYA KATOH, MASAHIRO TAKAHASHI, EISHUN TSUCHIDA, AND KIZASHI YAMAGUCHI†
Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan, and
†Department of Chemistry, Osaka University, Toyonaka, Osaka 560, Japan

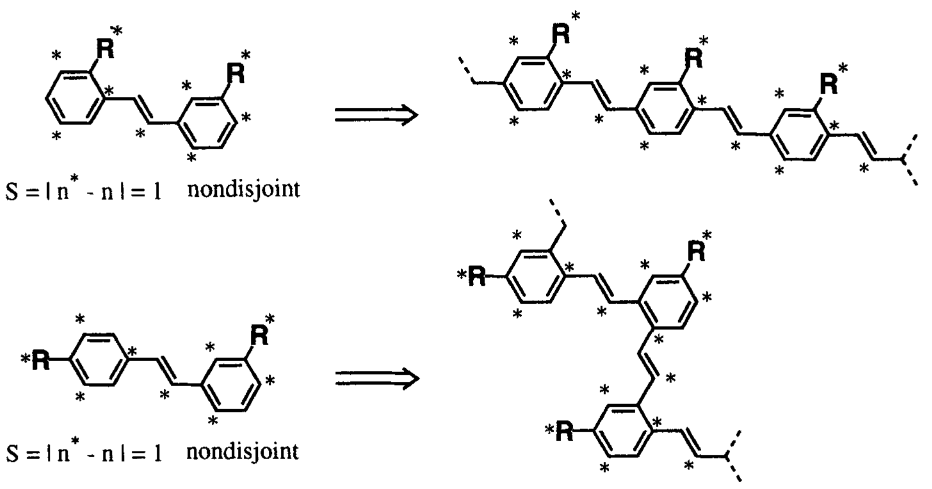
Abstract The poly(phenylenevinylene) skeleton was selected as a magnetic coupler of polyradicals, because of its developed π-conjugation, coplanarity, and solvent-solubility even after substitution on the phenylene ring. By synthesizing poly(1,4- or 1,2-phenylenevinylene)-2- or -4-substituted with a stable phenoxy or nitroxy radical, an intramolecular, through-bond and long-range, but strong, ferromagnetic exchange interaction was realized for the first time. The polyradicals were chemically stable and, even at their spin concentration of *ca.* 0.5, displayed $\bar{S}$ values of 2/2 ~ 4/2.

INTRODUCTION

There are limitations of cross-conjugated polyradicals or the radicals formed in 1,3-connected phenylene chains, as molecular-based magnetic, but feasible material, although they display a strong through-bond ferromagnetic coupling between two unpaired electrons in the main chain at low temperature. (i) A small number of defects in the polyradicals significantly prevents an increase in the resulting spin-multiplicity because their radicals are formed through cross-conjugated structures. (ii) Most of these cross-conjugated polyradicals lack chemical stability at room temperature in air.

As another approach to magnetically responsible π-conjugated polyradicals, we synthesized π-conjugated linear polymers bearing pendant radical groups, which are also π-conjugated with the polymer backbone and have substantial chemical stability.[1] An intrachain and through-bond interaction between the chain-side spins has been often theoretically studied for this type of polyradical. A typical example is poly(phenylacetylene)-based radicals.[2,3] However, any of poly(phenylacetylene)-based radicals[1] including all the others synthesized by other groups[4-6] have not displayed the expected ferromagnetic interactions to date. It was concluded that the poly(phenylacetylene) structure does not have a planar polyene backbone and that the phenyl-C=C dihedral angle is significantly twisted. High coplanarity both in the polymer chain itself and the dihedral angle with a chain-side radical are essential to produce an efficient spin distribution through the π-conjugated polymer and to realize a through-bond exchange interaction leading to intrachain ferromagnetism.[7,8]

Poly(phenylenevinylene) (PPV) had been suggested as a potential candidate for the effective backbone for π-conjugated polyradicals, because of its developed conjugation, coplanarity, and solvent-solubility (even) after substitution on the phenylene ring.[9-11] In this paper, we describe the designing of poly(1,4- and 1,2-phenylenevinylene) bearing phenoxy and nitroxy radicals, which are π-conjugated with the main chain and as one of the polyradicals with a PPV skeleton, their π-conjugated structure from UV and UPS, the spin density distribution onto the PPV backbone chain from ESR proton hyperfine structure and from semiempirical calculations, and magnetic properties to reveal the through-conjugated ferromagnetic exchange interaction between the chain-side unpaired electrons.

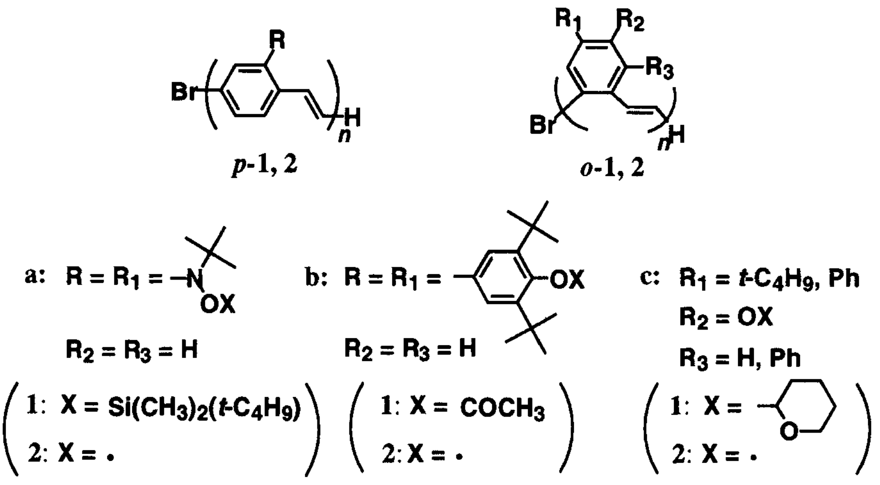


SCHEME 1

MOLECULAR DESIGNING, CHEMICAL STABILITY, AND π-CONJUGATION

Semiempirical calculations and magnetic measurements of the diradicals connected with stilbene (the dimer model of poly(phenylenevinylene)) revealed a quantitative spin coupling,[12] which suggested that poly(1,4- or 1,2-phenylenevinylene)-2- or -4-substituted with a built-in radical group would show intramolecular ferromagnetic coupling (SCHEME 1). It also indicated that the substituted phenylenevinylene is to be connected through a head-to-tail bond.

The usual synthetic route of PPV *via* a soluble precursor[13] is not applicable because of the lack of head-to-tail connectivity. We synthesized the head-to-tail connected and 2- (or 4-) substituted poly(1,4- (or 1,2-) phenylenevinylene) (***p***- and ***o***-**1a,b,c**) *via* reactions of the aryl bromide with the vinyl group of ***p***- (or ***o***-) bromostyrene derivatives using a palladium catalyst (Heck reaction).[14]



SCHEME 2

The polymers were soluble in $CHCl_3$, benzene, and THF. The UV-vis spectrum of ***p*-1** involved an absorption maximum (λ_{max}) at *ca.* 400 nm suggesting a developed π-conjugation as 1,4-PPV. On the other hand, the UV-vis absorption of ***o*-1** extended only to a λ_{max} of *ca.* 300 nm with a shoulder peak at 360nm suggesting a non-developed π-conjugation in comparison with ***o*-1**. This agrees with the values of the ionization threshold (I^{th}) from UPS (ultraviolet photoelectron spectroscopy) spectra; the values of I^{th} for ***o*-1** (5.7-5.9 eV) are larger than those of the corresponding ***p*-1** (5.6-5.7 eV).[15]

Chemical oxidation of ***p***- and ***o*-1a** with fresh PbO_2 in their THF solution including tetrabutylammonium fluoride yielded the corresponding polyradicals ***p***- and ***o*-2a**.[16] After elimination of the protecting group, ***p***- and ***o*-1b** yielded the corresponding polyradicals ***p***- and ***o*-2b** by treatment of the polymer solutions with fresh PbO_2 or alkaline $K_3Fe(CN)_6$. ***o*-2c** was unstable at room temperature due to the less hindered substituent at the inner *o*-position of the oxy group, and its ESR spectrum showed only weak signal at 220 K. Side reactions such as intramolecular oxygen migration probably prevent any increase in spin concentration in ***p*-2a** in which every *tert*-butyl-nitroxide group is neighboring to the vinylene group. ***o*-2a**, ***p*-2b** and ***o*-2b** were chemically stable even at room temperature, and the spin concentration could be increased by the oxidative conditions up to *ca.* 0.8 spin/unit. They could be isolated even as neat powders using a careful freeze-drying procedure.

SPIN DENSITY DISTRIBUTION

The ESR spectrum of ***p*-2a** at a low spin concentration gives a three-line signal (g=2.006, a_N=1.39) assigned to hyperfine coupling with a nitrogen nucleus (Fig. 1a), indicating that the unpaired spins are localized in the chain-side N-O group. This spectrum is similar to that of *o*-stilbene-(*N*-tert-butylnitroxide) (**3**), except for the anti-symmetricity attributed to alignment of the isotropic nitroxide radicals along the PPV main chain. The ESR spectrum of ***o*-2a** shows the three-line hyperfine structure

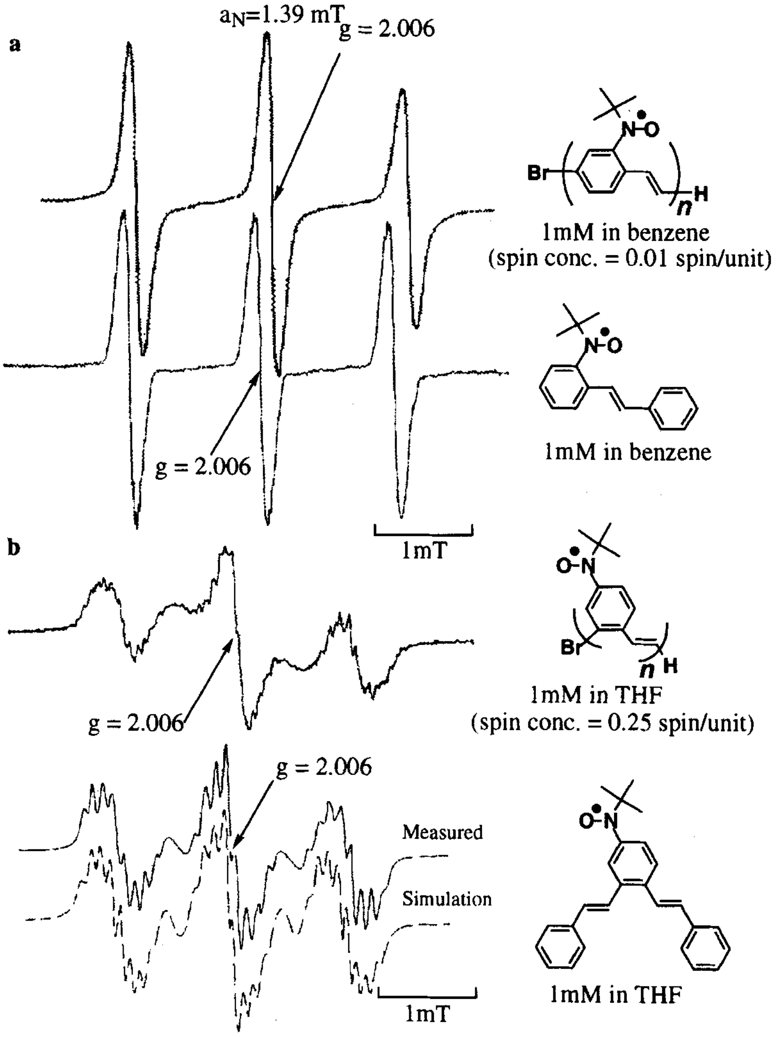
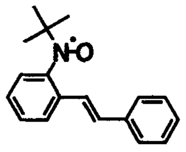


FIGURE 1 ESR spectra of the polyradicals (***p*-2a** and ***o*-2a**) and the corresponding monoradicals in THF solution at room temperature.

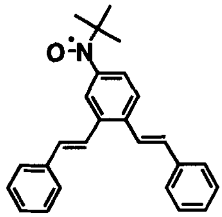
ascribed to the nitrogen nucleus at g=2.006 accompanying the multiplet caused by the *o*-PPV backbone protons (Fig. 1b), suggesting that the spin density is distributed onto the main chain. This is supported by the spectrum of distyrylphenyl *tert*-butylnitroxide (**4**), which almost agrees with that of ***o*-3a**. These spectra have two small signals between the three split lines, which probably implies a partial exchange interaction between intermolecular radicals caused by overlapping of the π-conjugated and coplanar distyrylbenzene structure. These ESR spectra including those of the monoradicals **5** and **6** were simulated (TABLE I) in order to discuss the spin density distribution over the molecules.

TABLE I The ESR hyperfine coupling constans (mT) estimated by the spectra simulation

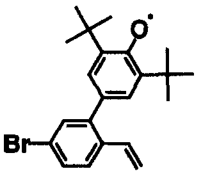
compounds	phenyl ring substituted with the radical			vinyl or vinylene	radical	
	o- a_H	*m*- a_H	*p*- a_H	a_H	a_N	a_H
3	-	-	-	-	1.42	
4	0.19	0.09		0.12, 0.02	1.15	
5	0.11	0.06	0.11	0.03		0.17
6	0.17	0.10		0.09		0.18



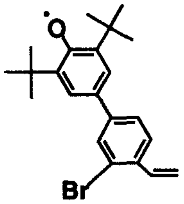
3



4



5



6

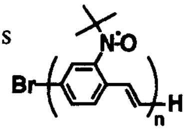
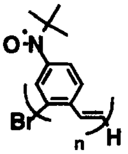
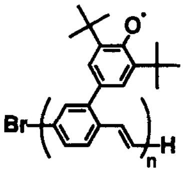
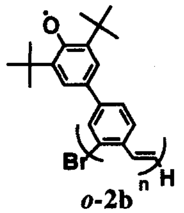
The proton hyperfine structure of **3** was hardly observed, indicating localization of the spin density on the N-O bond probably because of twisting of the N-O bond toward the phenyl ring. On the other hand, the hyperfine coupling constants attributed to 5-7 protons of the two phenyl rings and/or the vinylene for **5** sterically suggest less hindrance of the phenoxy group in comparison with the *tert*-butylnitroxide group, which was in contrast to the simple three line hyperfine structure of 2,4,6-tri-*tert*-butylphenoxyl attributed to an unpaired electron localized in the phenoxyl ring. The spin density (ρ) of ***o*-2a** was also estimated using the INDO calculation as ρ_N = 0.237, ρ_O = 0.737, ρ_C = 0.10 (*o*- and *p*-), -0.08 (*m*-), -0.09 (*p*-α- and *m*-β-vinylene) and 0.09 (*p*-β- and *m*-α-vinylene). These also suggest a distributed spin density onto the PPV main chain. For **4** and **6**, the radical moieties do not suffer the steric hindrance of the *m*- and *p*- substituents on the phenyl ring, and yield the larger proton hyperfine coupling constants ascribed to the phenyl and the vinylene or vinyl as compared to those for **3** and **5**, respectively. This comparison suggests that an effectively delocalized spin distribution into the backbone phenylene for ***o*-2a** and ***o*-2b** because of their less hindered steric structures. The ESR spectrum of ***o*-2a** showed a broad signal with spin concentration and $\Delta m_S=\pm 2$ transition ascribed to the triplet species that clearly appeared at $g = 4$ in 2-MeTHF glass.

FERROMAGNETIC INTERACTION

Magnetization (0 - 7 T) and static magnetic susceptibility (2 - 300 K at 0.5 T) of the polyradicals were measured using with a SQUID magnetometer. The spin concentration was determined from the Curie constant or the saturated magnetization at 2K to be 0.4-0.6 spin/monomer unit. The magnetic interaction was analyzed from the $\chi_{mol}T$ -T correlation (χ_{mol}: molar paramagnetic susceptibility). No ferromagnetic aspect was observed for ***p*-2a** due to both its low spin concentration (0.10 spin/unit) and the spin localization in the N-O bond as previously described. For the magnetic susceptibility of the powder sample of ***p*-2b** and ***o*-2a,b**, $\chi_{mol}T$ deviated upward from the theoretical value ($\chi_{mol}T = 0.375$) for $S = 1/2$ with a decrease in temperature at 20-300K, however, it was reduced below *ca.* 20 K. This behavior indicates a relatively strong through-bond and intrachain ferromagnetic interaction, and a weak through-space and interchain antiferromagnetic interaction. The magnetization and magnetic susceptibility in frozen solution (2MeTHF or toluene) could minimize the interchain magnetic interaction resulting in cancellation of the decrease in $\chi_{mol}T$ below 20 K for the powder sample.

The average spin coupling constant $2J$ (positive for ferromagnetic) and the average spin quantum number $\overline{S}$ were estimated by curve fitting of the $\chi_{mol}T$ -T data and the magnetization data in frozen solution, respectively (TABLE II). The curve fitting of the $\chi_{mol}T$ -T data was performed using a linear triradical system including diradical and monoradical contamination, because the average spin quantum number remained as $\overline{S} \leq 3/2$ at the spin concentration of *ca.* 0.5 in this experiment. The average spin quantum number reply to the degree of polymerization and the spin concentration, *i.e.*, is in response to the number of spins along the polyradical chain. The $\overline{2J}$ values of ***o*-2a,b** are larger than that of ***p*-2b**, which is explained by contribution of the spin density distribution onto the phenylenevinylene backbone as previously discussed. The *o*-**2b** even with a spin conc. of 0.67 spin/unit reveals an $\bar{S}$ value ≥ 3/2. The π-conjugated and planarized poly(phenylenevinylene)-based polyradicals possess a spin density distribution onto the backbone, and displayed a through-conjugated main chain bond and a long-range, but strong, ferromagnetic exchange interaction between the chain-side unpaired electrons. The ferromagnetic interaction is expected to be enhanced with the spin concentration, the degree of polymerization, and the spin density distribution onto the main chain.

TABLE II Magnetic exchange coupling and spin multiplicity of the polyradicals

polyradicals	 *p*-**2a**	 *o*-**2a**	 *p*-**2b**	 *o*-**2b**	
deg. polymn.	9	7	9	8	17
spin conc. (spin/unit)	0.10	0.50 ~ 0.59	0.46	0.44	0.59
$\bar{S}$		1/2 ~ 2/2	≤ 3/2	≤ 3/2	≥ 3/2
$\overline{2J}$ (cm^{-1})		28 ~ 40	20 ± 2	38 ± 3	-

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No.228/04242104 and /04242101) and for Scientific Research (No.040852) from the Ministry of Education, Science and Culture, Japan. We thank Prof. T. Enoki (Tokyo Institute of Technology) and Dr. M. Mitsuya (Advanced Research Laboratory, Hitachi Ltd.) for the use of their SQUID magnetometers. We appreciate the productive comments of Prof. P. M. Lahti (University of Massachusetts).

REFERENCES

1. (a) H. Nishide, N. Yoshioka, K. Inagaki, and E. Tsuchida, *Macromolecules* **21**, 3119 (1988). (b) H. Nishide, N. Yoshioka, T. Kaneko, and E. Tsuchida, *Macromolecules* **23**, 4487 (1990). (c) H. Nishide, N. Yoshioka, K. Inagaki, T. Kaku, and E. Tsuchida, *Macromolecules* **25**, 569 (1992). (d) N. Yoshioka, H. Nishide, T. Kaneko, H. Yoshiki, and E. Tsuchida, *Macromolecules* **25**, 3838

(1992). (e) H. Nishide, T. Kaneko, N. Yoshioka, H. Akiyama, M. Igarashi, and E. Tsuchida, *Macromolecules* **26**, 4567 (1993).

2. A. A. Ovchinnikov, *Theoret. Chem. Acta.* **47**, 297 (1978).
3. D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Masten, *J. Chem. Phys.* **77**, 3101 (1982).
4. A. Fujii, T. Ishida, N. Koga, and H. Iwamura, *Macromolecules* **24**, 1077 (1991).
5. Y. Miura, K. Inui, F. Yamaguchi, M. Inoue, Y. Teki, T. Yakui, and K. Itoh, *J. Polym. Sci. Polym. Chem. Ed.* **30**, 959 (1992).
6. L. Dulog and S. Lutz, *Makromol. Chem. Rapid Commun.* **14**, 147 (1993).
7. H. Nishide, T. Kaneko, R. Gotoh, and E. Tsuchida, *Mol. Cryst. Liq. Cryst.* **233**, 89 (1993).
8. H. Nishide, T. Kaneko, M. Igarashi, E. Tsuchida, N. Yoshioka, and P. M. Lahti, *Macromolecules* **27**, 3082 (1994).
9. H. Nishide, T. Kaneko, Y. Kuzumaki, N. Yoshioka, and E. Tsuchida, *Mol. Cryst. Liq. Cryst.* **232**, 143 (1993).
10. K. Yamaguchi, Y. Toyoda, and T. Fueno, *Synth. Met.* **19**, 81 (1987).
11. P. M. Lahti and A. Ichimura, *J. Org. Chem.* **56**, 3030 (1991).
12. N. Yoshioka, P. M. Lahti, T. Kaneko, Y. Kuzumaki, E. Tsuchida, and H. Nishide, *J. Org. Chem.* **59**, 4272 (1994).
13. (a) D. R. Gagnon, J. D. Capistran, F. E. Karasz, and R. W. Lenz, *Polym. Bull.* **12**, 293 (1984). (b) I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.*, **25**, 327 (1984).
14. H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, and K. Yamaguchi, *J. Am. Chem. Soc.* **116**, submitted (1994).
15. T. Kaneko, E. Ito, K. Seki, E. Tsuchida, and H. Nishide, *Macromolecules* **27**, submitted (1994).
16. T. Kaneko, S. Toriu, Y. Kuzumaki, H. Nishide, and E. Tsuchida, *Chem. Lett.* , submitted (1994).