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Poly(phenylenevinylene) Bearing Built-in *tert*-Butylnitroxide. A Polyradical Ferromagnetically Coupled in the Intrachain

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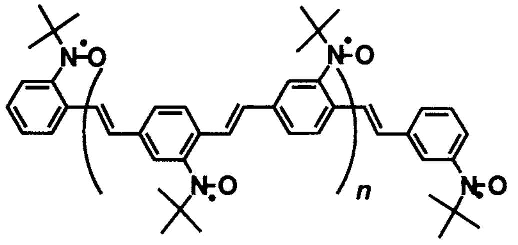
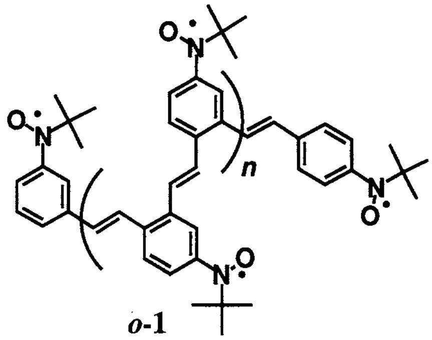
Poly(1,4- or 1,2-phenylenevinylene)s bearing a 2- or 4-substituted nitroxide radical were synthesized by polymerizing [bromo[*N*-*tert*-butyl-*N*-(trialkylsiloxy)-amino]]styrenes with a palladium catalyst. The polyradicals were chemically stable, and their ESR and SQUID measurements indicated an intramolecular and through-bond ferromagnetic coupling.

Magnetic materials consisting of pure organic compounds have been extensively investigated in this decade.1) π-Conjugated macromolecules bearing radical groups have been theoretically and experimentally studied as one of the candidates for magnetically active materials, because the ferromagnetic interaction between the radical groups through the intramacromolecular π-electron system was expected.2-4) However, they were mostly polyacetylene-based polyradicals and their magnetic properties revealed weak antiferromagnetic interactions contrary to the theoretical prediction,4-6) because the highly twisted dihedral angle between the polyene backbone and the chain-sided radical groups reduced the spin density distribution over the polyene chain.7) Recently, we discussed the magnetic interaction between nitroxide radicals through a stilbene frame based on semiempirical calculations and magnetic measurements.8) From the view point of the connectivity of stilbene-di-nitroxides, the *o,m'*- and *m,p'*-isomers were selected as dimer units for constructing the magnetically coupled polyradicals. The extended polymeric structure of the *o,m'*- and *m,p'*-isomers gives poly(1,4-phenylenevinylene) (***p*-1**) and poly(1,2-phenylenevinylene) (***o*-1**) bearing a built-in *tert*-butylnitroxide, respectively. In this paper, we report the synthesis of ***p*-** and ***o*-1** and the ferromagnetic interaction in them.

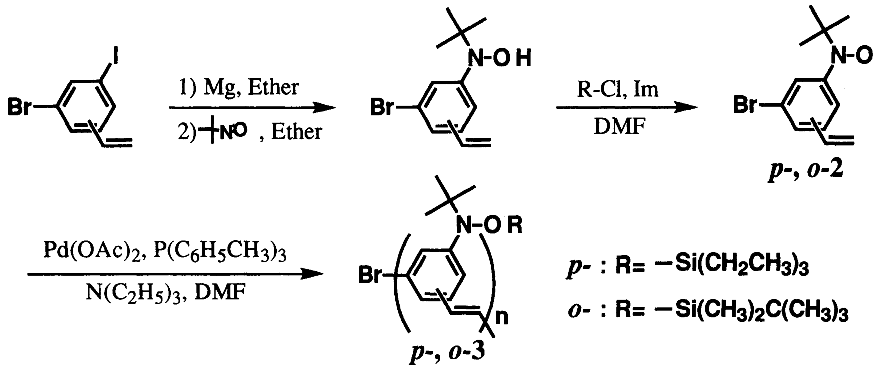


***p*-1**



***o*-1**

The polyradicals of ***p*-** and ***o*-1** have head-to-tail connected structures. The usual precursor method for poly(phenylenevinylene) (PPV) synthesis9) is not applicable because it often resulted in PPV derivatives that lack the head-to-tail connectivity owing to the coupling of the same terminal functional groups. π-Conjugated polymers have been often successfully synthesized through coupling reactions of aryl halogenoids using a palladium catalyst (Heck reaction).10) Polymerization of a benzene derivative with a vinyl and a halogeno group *via* the Heck arylation yields a head-to-tail structure in the PPV synthesis. We prepared 4-bromo-2-[*N*-*tert*-butyl-*N*-(triethylsiloxy)amino]styrene (***p*-2**) and 2-bromo-4-[*N*-*tert*-butyl-*N*-(*tert*-butyldimethylsiloxy)amino]styrene (***o*-2**), and polymerized them to yield the corresponding radical precursor polymers, poly[2-[*N*-*tert*-butyl-*N*-(triethylsiloxy)amino]-1,4-phenylenevinylene] (***p*-3**) and poly[4-[*N*-*tert*-butyl-*N*-(*tert*-butyldimethylsiloxy)amino]-1,2-phenylenevinylene] (***o*-3**), respectively (Scheme 1).



Scheme 1.

***p*-and *o*-2** were polymerized by modifying the previously reported procedure;10b) *e.g.*, Pd(OAc)$_2$ (2.5 mmol), tri-*o*-tolylphosphine (5 mmol) and triethylamine (125 mmol) were added to a 0.3M DMF solution of ***p*- and *o*-2** (83 ml). The solution was then heated at 100 ^{o}C for 24 h. The mixture was purified by gel permeation chromatography and by reprecipitation from THF in methanol. ***p*- and *o*-3** were obtained as yellow powders in the yield of 59 and 60%, respectively, and were soluble in CHCl$_3$, benzene and tetrahydrofuran, but insoluble in alcohols and aliphatic hydrocarbons. The $\overline{Mw}$ of ***p*- and *o*-3** was 2.8-3.5x10^3 and 2.1-6.8x10^3 (GPC, polystyrene standard), respectively, depending on the polymerization conditions. The IR spectra of ***p*- and *o*-3** indicated an out-of-plane bending mode of the *trans*-vinylene bond hydrogen at 960-970 cm^{-1} and disappearance of the stretching vibration of the C=C bond of vinyl group at 1630 cm^{-1}. The ^{1}H-NMR spectra of ***p*- and *o*-3** showed a multiplet peak of 5 protons at δ 6.9-8.1 ppm attributed to the vinylene and phenyl ring protons. The ^{13}C-NMR spectrum of ***o*-3** gave 8 lines ascribed to carbons of the vinylene and phenyl ring. This supports the head-to-tail connected structure in the *o*-PPV chain of ***o*-3**.

The UV-vis spectrum of ***p*-3** involved an absorption maximum (λ_{max}) at 410 nm in CHCl$_3$, suggesting a developed π-conjugation as *p*-PPV (λ_{max} 417-472 nm11)). The fluorescence at 485 and 510 nm (λ_{ex} 420 nm) of ***p*-3** was ascribed to the *trans*-stilbene structure (475 nm for ***o*-3**). On the other hand, the UV-vis absorption of ***o*-3** extended only to λ_{max} 309 nm with a shoulder peak at 360 nm, suggesting a non-developed π-conjugation in ***o*-3**.

After elimination of the protecting silyl group, ***p*- and *o*-3** yielded the corresponding polyradical ***p*- and *o*-1** by treatment of the polymer solution with fresh PbO$_2$. The ESR spectrum of ***p*-1** at a low spin concentration gave a three-line signal (g=2.006, a_N=1.39) ascribed to the hyperfine coupling with a nitrogen nucleus (Fig. 1a). That of ***o*-1** shows not only the hyperfine structure attributed to the nitrogen nucleus but also a multiplet attributed to the *o*-PPV backbone protons (Fig. 1b). A similar a_N and a_H were reported for *tert*-butylnitroxide substituted stilbenes.8) A delocalized spin distribution into the phenyl ring of the PPV backbone is suggested in ***o*-1**, because the *tert*-butylnitroxide group is not twisted to the phenyl ring in comparison with ***p*-1** which suffers steric hindrance at the *o*-substitution. The ESR spectrum of ***o*-1** shows a broad signal with increasing spin concentration (Fig. 1c). The $\Delta m_S = \pm 2$ transition ascribed to the triplet species was observed at g = 4 in 2-methyltetrahydrofuran glass (Fig. 1d). We could not prepare the ***p*-1** sample with a high spin concentration. In ***p*-1**, every *tert*-butyl-nitroxide group is neighboring to the vinylene group, and side reactions such as intramolecular oxygen migration probably prevent any increase in spin concentration.

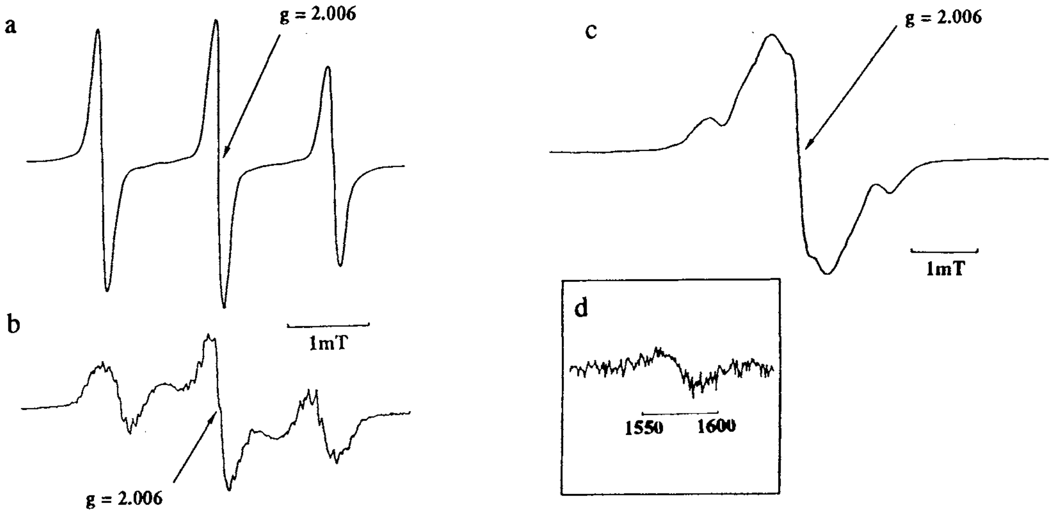
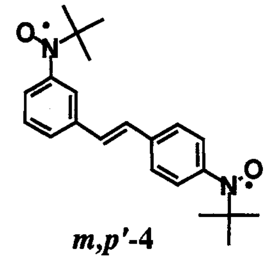
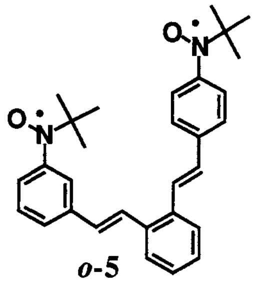


Fig. 1. ESR spectra of the polyradicals ***p*-**, ***o*-1**. (a) ***p*-1** in benzene: polymer conc. 1 unit mM (spin conc. 0.01 spin/unit), (b) ***o*-1** in THF: polymer conc. 1 unit mM (spin conc. 0.25 spin/unit), (c) ***o*-1** in THF: polymer conc. 1 unit mM (spin conc. 0.48 spin/unit), (d) ***o*-1** in 2-MeTHF (spin conc. 0.38 spin/unit) at 77 K.

Magnetization and static magnetic susceptibility of ***o*-1** were measured in 2-methyltetrahydrofuran glass using a SQUID magnetometer (Quantum Design MPMS; 0.5-7 T, 1.8-300 K). The spin concentration was estimated from the Curie constant to be 0.5-0.6 spin/monomer unit. The magnetic interaction was analyzed from $\chi_{mol}T$ -T correlation (χ_{mol}: molar paramagnetic susceptibility). The average spin coupling constant $\overline{2J}$ (positive for ferromagnetic) was estimated by the curve fitting of a modified Bleaney-Bowers relationship[12] because the spin concentration was not very high and the average spin quantum number remained within $1/2<\overline{S}<2/2$, which is summarized in Table 1. This shows that the $\overline{2J}$ value of ***o*-1** almost coincides with the triplet-singlet energy gap of *m,p'*-stilbene-bis(*tert*-butylnitroxide) (***m,p'*-4**) $2J$ = 41cm^{-1} (117 cal/mol)[8] and that the spins of polyradical ***o*-1** are partially but ferromagnetically coupled through the π-conjugated PPV backbone.



***m,p'*-4**



***o*-5**

Table 1. Average spin coupling constant $\overline{2J}$ in the polyradical ***o*-1** and the triplet-singlet energy gap $2J$ in the diradicals ***m,p'*-4** and ***o*-5**

	Spin conc. spin/unit	$\overline{2J}$ or $2J$ cm^{-1}	$\overline{S}$[a] or S
***o*-1**	0.50 - 0.59	$28 < \overline{2J} < 40$	$1/2 < \overline{S} < 2/2$
***m,p'*-4**	-	41 ± 1	2/2
***o*-5**	-	3 ± 2	2/2

a) average spin quantum number.

As model compounds for the polyradical obtained through incomplete spin generation, we also synthesized di-styrylbenzenes in which two nitroxides are connected with the non-radical phenylenevinylene spacing unit, 1-[3-(*N*-*tert*-butyl-*N*-oxyamino)styryl]-4-[4-(*N*-*tert*-butyl-*N*-oxyamino)styryl]benzene (***p*-5**) and 1-[3-(*N*-*tert*-butyl-*N*-oxyamino)styryl]-2-[4-(*N*-*tert*-butyl-*N*-oxyamino)styryl]benzene (***o*-5**). The ESR spectra of both ***p*-** and ***o*-5** showed a five-line hyperfine structure attributed to the two nitrogen nuclei with a sufficient interelectronic exchange $J > a_N$. However, a quantitative ferromagnetic interaction was observed only for ***o*-5** in the magnetization measurement and its triplet-singlet energy gap ($2J = 3\pm2\ \mathrm{cm}^{-1}$) was much smaller than that of ***m,p'*-4**. It is concluded that a partial, but strong, ferromagnetic interaction is established through the conjugated PPV backbone, even in the presence of a spin defect for polyradical ***o*-1**. The *o*-PPV derivative is considered to be one of the most synthetically accessible polyradicals with ferromagnetic interaction.

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