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Through-Bond and Long-Range Ferromagnetic Spin Alignment in a π-Conjugated Polyradical with a Poly(phenylenevinylene) Skeleton

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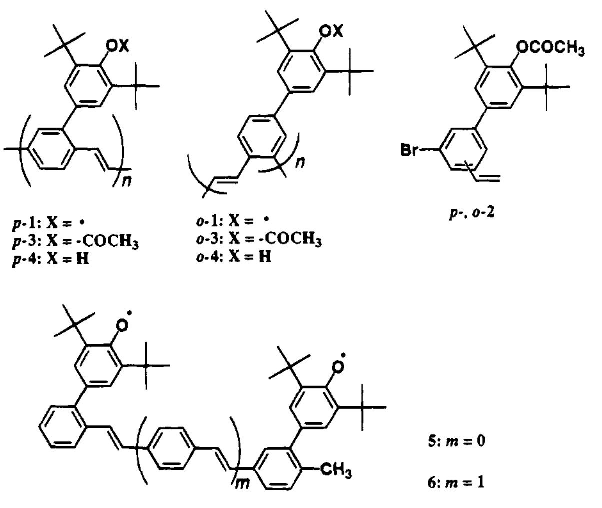
There has recently been a growing interest in the synthesis of organic π-conjugated polyradicals as molecular-based magnetic material.[1] The major synthetic approach is based on cross-conjugated polyradicals or radicals formed in main chains with topologically polarized π-spins.[2−4] Although they displayed a strong through-bond ferromagnetic coupling between two unpaired electrons in the 1,3-connected phenylene radicals at low temperature, however, a small number of defects in the polyradicals significantly prevented an increase in the resulting S because their radicals were formed through cross-conjugated structures. In addition to this drawback, most of these molecules lacked chemical stability at room temperature. We, therefore, focused our synthetic work on π-conjugated linear polymers bearing side-chain or pendant radical groups, which also are π-conjugated with the polymer backbone and have substantial chemical stability.[5] An intramolecular and through-bond interaction between the side-chain spins often has been studied theoretically for this type of polyradical, mainly on polyacetylene-based radicals.[6] However, the expected ferromagnetic interactions have not been observed to date for any poly(phenylacetylene)-based radicals,[5,7] and it was concluded that coplanarity both in the polymer chain itself and in the dihedral angle with a side-chain radical are essential to realize a through-bond exchange interaction leading to intramolecular ferromagnetic behavior.[8]

We have for the first time succeeded in realizing a through-conjugated main-chain bond and long-range, but strong, ferromagnetic exchange interaction between the side-chain unpaired electrons by synthesizing the polyradical with a poly(phenylenevinylene) skeleton. Poly(phenylenevinylene) had been suggested as a potential candidate of the effective backbone for π-conjugated polyradicals, because of its developed conjugation, coplanarity, and solvent solubility (even) after substitution on the phenylene ring.[9] Semiempirical calculations and/or magnetic measurements of the diradicals connected with stilbene (the dimer model of poly(phenylenevinylene)) revealed quantitative spin coupling,[10] which suggests that poly(1,4- or 1,2-phenylenevinylene) 2- or 4-substituted with a built-in radical group will show intramolecular ferromagnetic coupling. This communication describes the poly(1,4- and 1,2-phenylenevinylene) bearing phenoxy radical (*p*- and *o*-**1**), which is π-conjugated with the main chain, has delocalized distribution of spin density, has chemical stability, and produces intramolecular ferromagnetic spin alignment (Chart 1).

Chart 1



4-Bromo-2-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (*p*-**2**) and 2-bromo-4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)styrene (*o*-**2**) were synthesized[11] as the monomers to be connected through a head-to-tail bond *via* arylation of the olefin with aryl bromide using a Pd catalyst (Heck reaction) to yield poly[2-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)-1,4-phenylenevinylene] (*p*-**3**) and poly[4-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)-1,2-phenylenevinylene] (*o*-**3**) as yellow powders soluble in common solvents.[11] Their head-to-tail and *trans*-stilbene connected structure were confirmed by ^{13}C-NMR signals and fluorescence at 470 (*p*-**3**) and 450 (*o*-**3**) nm, respectively. *p*- and *o*-**3** were deprotected in alkaline solution to give the corresponding hydroxyl polymers *p*- and *o*-**4**, with molecular weights 2.8×10^3, and 2.6×10^3 or 5.1×10^3, respectively. **4** was carefully oxidized with fresh PbO_2 to yield the corresponding polyradicals *p*- and *o*-**1** and isolated as a brownish green powder. **1** was chemically stable at room temperature even in air. GPC elution curves of **1** before and after the radical generation coincided with each other: This is consistent with the assumption that the oxidation does not bring about oxidative degradation or cross-linking of the main chain.

The ESR spectrum of **1**, especially *o*-**1**, at low spin concentration gave a broad hyperfine structure at $g = 2.004_4$ attributed to the five to seven protons of the two phenyl rings and/or

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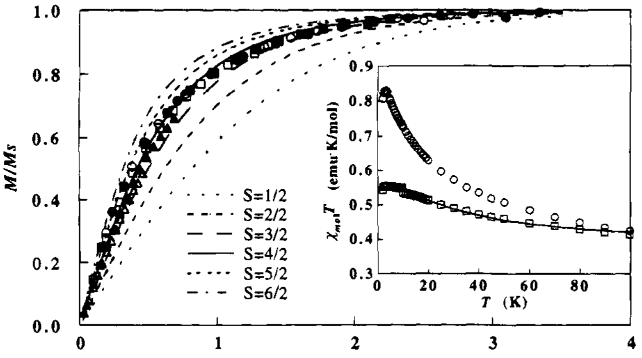

Figure 1. Normalized plots of magnetization (M/M_s) *vs* the ratio of magnetic field and temperature ($H/(T - \theta)$) for *o*-**1** with spin concentration 0.67 spin/monomer unit in 2-methyltetrahydrofuran glass as T = 2 (●), 2.5 (○), 3 (■), 5 (□), 10 (▲), and 15 (△) and the theoretical curves corresponding to the $S = {}^1/_2$, 1, $^3/_2$, 2, $^5/_2$, and 3 Brillouin functions, where θ is a weak antiferromagnetic term and was determined to be −0.1 K from $\chi_{mol}T$ *vs* T plots. Insert: plots of the product of $\chi_{mol}T$ *vs* T plots of *o*-**1** with spin concentration 0.44 (□) and 0.67 (○).

vinylene, which was in contrast to the three-line hyperfine structure of 2,4,6-tri-*tert*-butylphenoxyl or attributed to an unpaired electron localized in the phenoxyl ring. The spin density distribution over the 4-phenyl group in **1** was further supported by the hyperfine structure of the corresponding monomeric radicals.[12] The ESR of *o*-**1** also suggested an effectively delocalized spin distribution into the backbone phenylene probably because of its less hindered steric structure.

Magnetization and static magnetic susceptibility of **1** in frozen solution (2-methyltetrahydrofuran or toluene) to minimize intermolecular magnetic interactions were measured with a SQUID magnetometer as previously described.[8] Figure 1 shows magnetization (M) plots normalized with saturated magnetization (M_s) for *o*-1 with a spin concentration of 0.67 spin/monomer unit.[15] The plots are presented between the Brillouin curves for $S = {}^4/_2$ and $^5/_2$ at 2−5 K, indicating a multiplet ground state of **1**. The average $S \geq {}^4/_2$ of *o*-**1** with a spin concentration of 0.67 means that a defect in the radical generation is not fatal for a partial but ferromagnetic spin alignment between the side-chain unpaired electrons through the π-conjugated poly(phenylenevinylene) backbone.

The plots of the product of molar magnetic susceptibility (χ_{mol}) and T *vs* T (2−100 K) are also shown in Figure 1 using the examples of *o*-1 with spin concentrations of 0.44 and 0.67. $\chi_{mol}T$ increased as low temperature (<50 K) from the theoretical value ($\chi_{mol}T = 0.375$) for $S = {}^1/_2$. The solid line in Figure 1 reproduces the fitting curve for the spin Hamiltonian and the Van Vleck expressions[13] to give the average value[14] of the exchange coupling constant $\overline{2J}$ (Table 1).

Magnetization and $\chi_{mol}T$ *vs* T plots of the diradical model compounds, **5** and **6**, indicated a triplet and a weak triplet ground state, with an exchange coupling constant and a triplet−singlet energy gap ($2J$) of 17 ± 1 and 4 ± 6 cm^{-1}, respectively. A semiempirical calculation is applied to the **5** and **6** analogous compounds, and $2J$ is also evaluated[15] in Table 1. The experimental $2J$ values qualitatively coincide with the semiempirical calculated values; $2J$ is reduced to *ca.* $^1/_5$ (from **5** to **6**) in response to the conjugated but spacing phenylenevinylene unit.

Table 1. Exchange Coupling Constant of the Polyradicals **1** and the Diradicals **5** and **6**

polyradical (DP[a])	spin concn, spin·unit^{-1}	S[b]	$2J$ or $\overline{2J}$,[c] cm^{-1}	MO calcd $2J$, cm^{-1}	
5		$^2/_2$	17 ± 1	40[g]	
6		$^2/_2$	4 ± 6		8[g]
p-**1** (5[d])				53[d,g]	10[d,g,h]
p-**1** (9 6,[e] 7[f])	0.46	$^2/_2$−$^3/_2$	20 ± 2	55[e,g]	11[f,g,h]
o-**1** (8, 6,[e], 7[f])	0.44	$^2/_2$−$^3/_2$	38 ± 3	93[e]	19[f,h]
o-**1** (17)	0.59	$\geq {}^3/_2$	$33 \leq \overline{2J} \leq 69$		

[a] Average degree of polymerization of the precursor polymers **4**. [b] Ground state spin quantum number for **5** and **6** and average spin quantum number for spin state of **1** at 2−5 K. [c] Exchange coupling constant ($2J$) for **5** and **6** and its average value ($\overline{2J}$) for **1**. [d−f] The MO calculation for the polymers with DP = 5,[d] 6,[e] and 7.[f] [g] The MO calculation after the 40° rotation for the phenyl−phenylenevinylene bond, corresponding to steric hindrance between the *o*-phenyl proton and the vinylene proton. [h] They are composed of the radical and the nonradical unit alternatively (spin concentration 0.60,[d] 0.57[f]).

With the degree of polymerization, the calculated $2J$ increases in the order of **5** (DP = 2), *p*-**1** (5), *p*-**1** (6) and of **6** (DP = 3), *p*-**1** (5), *p*-**1** (7) (the latter are composed of the radical and the nonradical unit alternatively), because the spin exchange interaction cooperatively works from both sides along the conjugated main chain. Although the $\overline{2J}$ values of **1** are averaged values, the spin concentration of **1** in Table 1 is almost prepared at *ca.* 0.5. $\overline{2J}$ of the polyradical *p*-**1** (9) is larger than those of the diradical model **5** and **6**: This result is consistent with the polymer effect expected through the calculation. Comparison of *p*-**1** (9) and *o*-**1** (8) reveals a stronger interaction in *o*-**1**, in which the above mentioned ESR result suggested a more effective spin distribution through the chain-side phenoxyl to the backbone conjugation due to its stronger coplanarity in π-conjugation. The calculation also suggests a reduction in $2J$ for the sterically hindered *p*-**1**. The strongest ferromagnetic interaction is observed for the polyradical with the higher molecular weight *o*-**1** (17): the cooperative exchange interaction between the side-chain unpaired electrons through the π-conjugated poly(1,2-phenylenevinylene). The *o*-**1** even with a spin concentration of 0.67 reveals an S value $\geq {}^4/_2$ in Figure 1, which is expected to be much enhanced with the spin concentration.

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