Synthesis and Ferromagnetic Spin Alignment in Poly(4-oxyphenyl-1,2-phenyleneethynylene)s

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ABSTRACT: Some non-Kekulé-type organic molecules exhibit a high-spin state based on an intramolecular spin-exchange interaction.   These high-spin molecules can be extended to the corresponding polyradicals with spins that are ferromagnetically aligned.   Poly(4-oxyphenyl-1,2-phenyleneethynylene) was synthesized, and the effect of the head-to-tail connectivity on the ferromagnetic interaction is described.

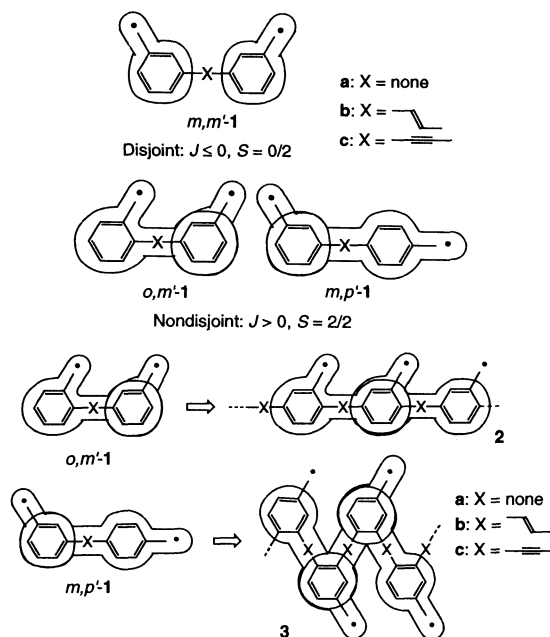KEY WORDS   High-Spin Molecule / Polyradical / Poly(phenyleneethynylene) / Spin-Exchange Interaction /

Theoretical and experimental studies on π-conjugated and alternant, but non Kekulé-type organic molecules bearing multiple radical centers have elucidated a clear correlation between the molecular connectivity or substitution positions of the radical centers on the conjugated skeleton and the spin multiplicity or spin quantum number (S) at the ground state (GS).[1-3]   Some of the non-Kekulé-type molecules exhibit a stabilized high-spin state based on an intramolecular and strong through-bond spin-exchange interaction between the multiple radical centers.   These types of high-spin or ferromagnetic organic radical molecules can be extended to the corresponding non-Kelulé-type polyradical macromolecules.[3]   A very high-spin state or S that is proportional to the degree of polymerization is, at least theoretically, predicted in the polyradical macromolecules, which may correspond to a classical magnetic domain. These non-Kekulé-type polyradicals are expected to be some of new polymers and to display molecular-based magnetism ascribed to the spin-exchange interactions of the p-electrons of C, O, N, etc.   This is different from the magnetism in conventional atom- and d/f-electron-based inorganic materials.

A qualitative but useful strategy to estimate the S value and the stability of the multiplet or high-spin GS of the non-Kekulé-molecules has been examined by Borden.[4] He proposed a concept of disjoint and nondisjoint connectivity of Hückel nonbonding molecular orbitals (NBMOs) and classified the biradical molecules into two groups depending on whether their NBMOs could be confined to disjoint sets of atoms.   If the two NBMOs are confinable to separate regions of a biradical molecule, the spin-exchange interaction (its magnitude, J) between unpaired electrons in the biradical will be minimized and the triplet (high-spin) and singlet (low-spin) states are almost degenerated.   He called this type of system "disjoint", which is exemplified by using the biradical isomers based on biphenyl **1a**, stilbene **1b**, or tolane **1c** (*p,p'*-, *o,p'*-, and *o,o'*-1 are Kekulé-type and closed-shell molecules, and are ruled out here).   Although three isomers, *o,m'*-, *m,p'*-, and *m,m'*-1, are non-Kekulé-type biradical molecules and have two degenerate NBMOs,
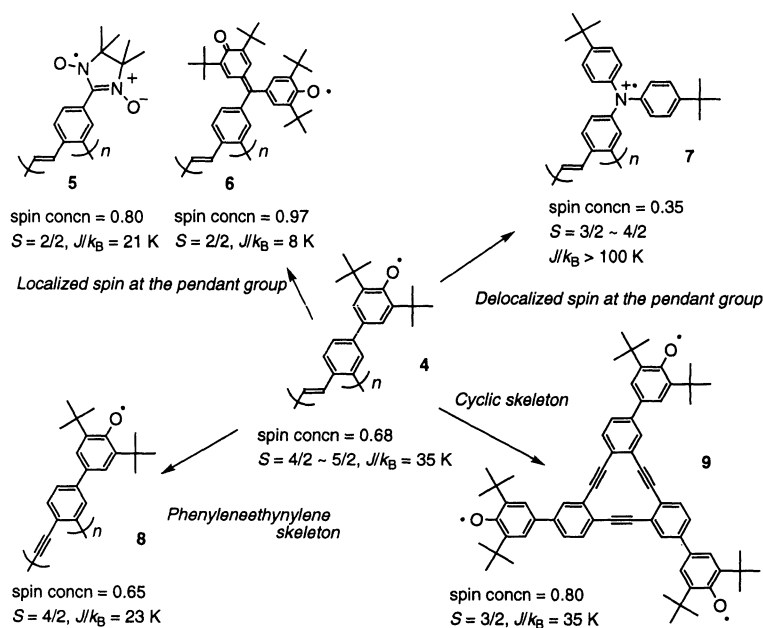
m,m'-**1** is characterized by this disjoint connectivity.   On the other hand, if the NBMOs cannot be localized in the disjoint groups of atoms (*i.e.*, "nondisjoint"), the two NBMOs share the same molecular region (*e.g.*, see *o,m'*- and *m,p'*-1).   The spin-exchange interaction is then ferromagnetic with a positive J value due to a Coulombic repulsion, and the triplet GS is predicted to be sufficiently stabilized.   Experimental results supported these predictions, *e.g.*, for the stilbene biradicals.[5]

o,m'-**1** can be extended to poly(2-radical substituted-1,4-phenylene, -phenylenevinylene, or -phenyleneethynylene), **2a**, **2b**, or **2c**, respectively. m,p'-**1** can also be extended to poly(4-radical substituted-1,2-phenylene, -phenylenevinylene, or -phenyleneethynylene), **3a**, **3b**, or **3c**, respectively.   These polyradicals are classified as nondisjoint molecules, and the effectively overlapped NBMOs on the skeletons (see **2** and **3**) suggest an adequate spin-exchange interaction between the pendant spins.

The poly(1,2-phenylenevinylene)-based polyradicals **4-7** were synthesized by the authors with a molecular weight of *ca.* 10^4.[6-9]   The spin concentration (spin/monomer unit) could be increased up to 0.7 for **4** and to more than 0.8 for **5** and **6**.   These polyradicals were ferromagnetic at low

a: X = none
b: X = 〜
c: X = ══

m,m'-1
Disjoint: $J \leq 0$, $S = 0/2$

o,m'-1 m,p'-1
Nondisjoint: $J > 0$, $S = 2/2$

o,m'-1   ⇒

m,p'-1   ⇒

2

a: X = none
b: X = 〜
c: X = ══

3

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spin concn = 0.80   spin concn = 0.97
$S = 2/2, J/k_B = 21$ K $S = 2/2, J/k_B = 8$ K

Localized spin at the pendant group

5   **6**

spin concn = 0.35
$S = 3/2 \sim 4/2$
$J/k_B > 100$ K

7

Delocalized spin at the pendant group

4

spin concn = 0.68
$S = 4/2 \sim 5/2, J/k_B = 35$ K

Cyclic skeleton

9

Phenyleneethynylene skeleton

8

spin concn = 0.65
$S = 4/2, J/k_B = 23$ K

spin concn = 0.80
$S = 3/2, J/k_B = 35$ K

temperature, but S remained at ca. 2/2 for **5** and **6**.[8] On the other hand, **4** with a spin concn of 0.7 displayed $S = 4/2 \sim 5/2$.[6,7] An ESR study indicated delocalization of an unpaired electron over the polyphenylenevinylene skeleton for **4** and a localized spin distribution within the pendant groups for **5** and **6**. In order to obtain a ferromagnetic exchange interaction through the π-conjugated skeleton, not only the nondisjoint connectivity of the polyradical but the spin density distribution (depending on the pendant radical species) also needs to be considered. However, the spin density delocalization increases the radical reactivity of the sterically unprotected skeleton, which results in the chemical unstabilization of the molecules or in the low spin concn. The spin-exchange interaction and the chemical stability trade off, and the pendant radical species should be carefully designed to synthesize an actual radical polymer.

The spin-exchange interaction or the magnitude of J (J/k_B) to ferromagnetically align the spins was estimated to be 35 K for **4**, which was larger than those of the polyradical bearing localized spins, **5** and **6**. Poly(1,2-phenylenevinylene) bearing the diphenylaminium radical cation at the 4-position (**7**) caused a strong spin-exchange interaction ($J/k_B > 100$ K) and $S = 3/2 \sim 4/2$ even at a spin concn of 0.35.[9] The delocalized spin of the aminium radical cation directly combined with the poly(phenylenevinylene) skeleton in **7**. The S value is affected by the spin concn and the degree of polymerization, i.e., it will increase more in response to the number of pendant spins in the polyradical.

The authors also synthesized poly(1,2-phenyleneethynylene)-based **8**, which exhibited $S = 4/2$.[10] The phenyleneethynylene was useful as a skeleton for the polyradicals because of the sterically compact and hydrogen-free structure of its ethynylene bridge; however, it lacked an alternativity of single-double bonds in the π-conjugation. Cyclic tris(1,2-phenyleneethynylene) or dehydroannulene acted as an effective ferromagnetic skeleton for the pendant spins for **9** in comparison with the corresponding acyclic triradical, because the plural interaction pathways avoided the influence of a spin defect and because the planar skeleton realized a more delocalized
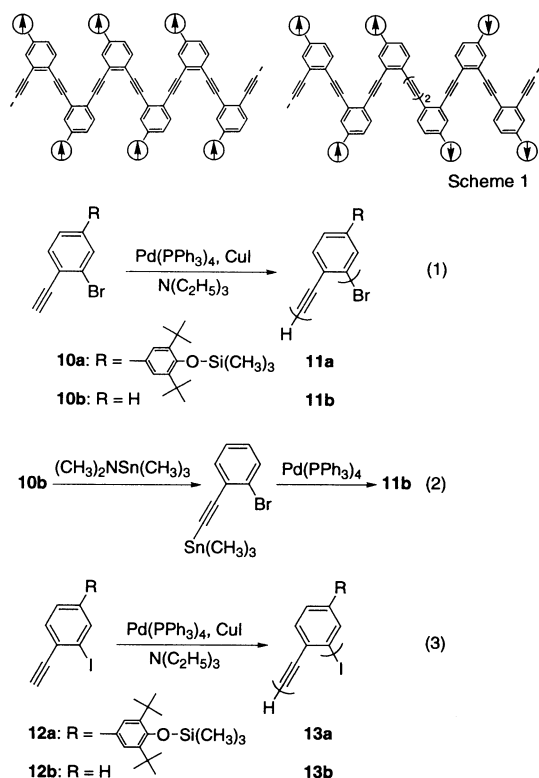
spin distribution of the pendant radicals.[11] This paper described the precise structure needed to synthesize such a high-spin polyradical using the example of poly(4-(3,5-di-*tert*-butyl-4-oxyphenyl)-1,2-phenylene-ethynylene) **8**.

RESULTS AND DISCUSSION

A restricted primary structure is essential for a ferromagnetic spin alignment. A complete head-to-tail linkage of the monomer unit is the first requisite, since a synthetic error in the polymerization cancels out the high-spin alignment (on the right in Scheme 1).

Although poly(phenyleneethynylene)s with high molecular weights have usually been synthesized via the condensation of diethynylbenzene and dihalogeno-benzene,[12-14] these lack the restricted primary structure of a head-to-tail for the mono-substituted poly(phenylene-ethynylene) formation. The authors attempted and compared in this paper the synthesis of the head-to-tail-linked poly(1,2-phenyleneethynylene)s via the self-condensation of 2-bromoethynylbenzene with the catalyst composed of a palladium-triphenylphosphine complex and cuprous iodide (Sonogashira reaction)[12,14,15] (1), the self-condensation of 2-stanylethynylbenene with the Pd catalyst (Stille reaction)[13,16] (2), and the self-condensation of 2-iodoethynylbenzene with the Pd catalyst (3).
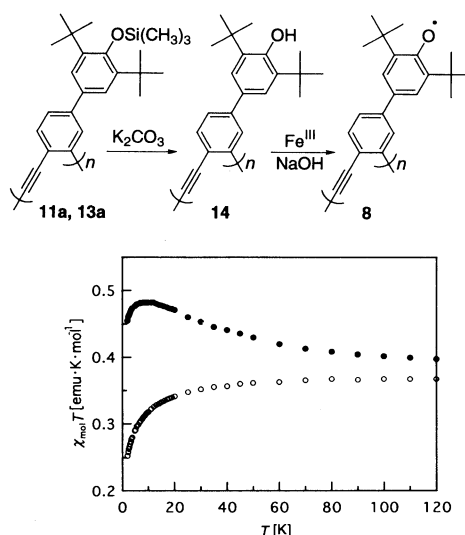
2-Bromoethynylbenzene, as a non-substituted model monomer, was polymerized with the catalyst of a palladium-triphenylphosphine and cuprous iodide in the presence of triethylamine to capture the eliminated hydrogen bromide (Table I, Run 1). The poly(1,2-phenyleneethynylene) **11b** was a slightly tan powder that easily dissolved in common solvents such as benzene, THF, and chloroform. The ^{13}C- and ^{1}H-NMR peaks ascribed to the phenylene ring and the ethynylene bridge supported the phenyleneethynylene structure; however, the ethynyl proton peak of **10b** completely disappeared in **11b** after the polymerization. The terminal bromine content from an elemental analysis was almost twice that calculated using the molecular weight measured by GPC. These indicate that the poly(phenyleneethynylene) obtained under the

1172

Scheme 1

Figure 1. $\chi_{mol}T$ vs T plots (●) of poly(4-(4-oxyphenyl)-1,2-phenyleneethynylene) 8 derived from 13a with spin concn = 0.70 spin/monomer unit, (○) of 8 derived from 11a with spin concn = 0.74 spin/monomer unit in frozen 2-methyltetrahydrofuran.

reaction condition (Run 1) involves one butadiyne bond per polymer (head-to-head linkage via the coupling of the terminal ethynyl groups). Polymerization (1) of 4-(3,5-di-*tert*-butyl-4-trimethylsiloxy-phenyl)ethynylbenzene **10a** also yielded the poly(phenylene-ethynylene) involving one head-to-head linkage (a defect) even in the absence of oxygen.

A cross-coupling reaction of distanylethynylbenzene and dibromobenzene for poly(phenyleneethynylene) formation has been reported.[12-14] This polycondensation was used for the self-condensation of bromo-stanylethylbenzene (2). **10b** was reacted with (dimethylamino)trimethyltin to give 1-bromo-2-tributylstanylethynylbenzene, which was polymerized in the presence of the Pd catalyst (Run 3). However, the obtained polymer again involved one head-to-head linkage, although the molecular weight was increased in comparison with the product via (1).

The bromo substituent of the ethynylbenzene monomer was replaced with iodine to increase the reactivity. 2-Iodoethynylbenzene **12b** was polymerized with the Pd-CuI catalyst: The polymerization proceeded even at room temperature (Run 4 in Table I). The molecular weight measured by GPC agrees well with the terminal iodine content determined from the elemental analysis, which

supports a completely head-to-tail-linked structure. On the other hand, the polymerization of **12b** at 60°C gave the polymer with lower molecular weight and higher iodine content in comparison with the product formed at room temperature (Run 5). That is, the polymerizaiton of the iodoethynylbenzene at low temperature excluded the head-to-head linkage formation.[17] The bromo substituent of **10a** was replaced with iodine to give **12a** in reasonable yield.[11] **12a** was polymerized with the Pd-CuI catalyst at 20°C. The ^{13}C- and ^{1}H-NMR and iodine analysis supported the completely head-to-tail structure of the polymerization product of **12a**.

The precursor trimethylsiloxy polymer **13** was converted to the corresponding hydroxy polymer **14** after complete elimination of the protecting trimethylsiloxy group in alkaline solution. The hydroxy polymer **14** was heterogeneously oxidized with aqueous ferricyanide solution to yield the polyradical **8**. The brownish green **8** was also soluble in common solvents.

The molar magnetic susceptibility (χ_{mol}) was measured with a SQUID magnetometer for the 2-methyltetrahydrofuran solutions of two **8** samples derived from **11a** and from **13a**. The plots of the product of χ_{mol} and temperature (T) vs T are shown in Figure 1. $\chi_{mol}T$ for sample **8** derived from **13a** increases at low temperature from the theoretical value for $S = 1/2$ ($\chi_{mol}T = 0.375$ (emu·K/mol)): The upward deviation means a ferromagnetic interaction in the polyradical. A slight decrease is

Table I. Polymerization of 2-halogenoethynylbenzene derivatives with a palladium catalyst

Run	Monomer[a]	Reaction	Catalyst[b]	Solvent	Temp/°C	Time/hr	Yield/%	$M_w/10^3$	M_w/M_n	Br or I/%[c]
1	10b	(1)	Pd(PPh₃)₄ + CuI	Tol	110	24	50	1.1	1.2	16.₂ (8.8)
2	10a	(1)	Pd(PPh₃)₄ + CuI	Tol	110	24	56	2.0	1.1	10.₇ (4.5)
3	10b	(2)	Pd(PPh₃)₄	Tol	110	24	62	2.7	1.7	10.₀ (5.1)
4	12b	(3)	Pd(PPh₃)₄ + CuI	THF	20	40	40	3.2	1.4	4.0 (5.6)
5	12b	(3)	Pd(PPh₃)₄ + CuI	THF	60	16	44	1.1	1.2	20.₄ (14.₀)
6	12a	(3)	Pd(PPh₃)₄ + CuI	THF	20	40	69	2.9	1.2	5.1 (5.3)

[a] $[M]_0 = 0.2$ mol l⁻¹, [b] $[Pd]/[M]_0 = 1/50$, [c] found(calcd).

Polym. J., Vol. 31, No. 11-2, 1999

1173

observed at < 5K, suggesting a through-space antiferromagnetic interaction even after the dilution with a diamagnetic 2-methyltetrahydrofuran medium. On the other hand, the $\chi_{mol}T$ curve for **8** derived from **11a** significantly deviated downward from the value of $S = 1/2$ even at relatively high temperature, indicating a low-spin ($S = 0/2$) GS or an antiferromagnetic interaction in the polyradical. The poly(4-oxyphenyl-1,2-phenylene-ethynylene) **8** derived through the deprotection and the following oxidation of **11a** involves one head-to-head structure (structural defect) per polymer; the head-to-head linkage part is characterized by disjoint connectivity as illustrated in the bottom of Scheme 1. These $\chi_{mol}T$ results not only agree with the prediction mentioned in the Introduction but do support the validity of the precise synthesis of the head-to-tail-linked polymer.

These findings suggest a strategy using precision polymers and their three-dimensional extensions to realize very high-spin organic molecules.

EXPERIMENTAL
Synthetic Procedures

2-Bromo- and -iodo-ethynylbenzenes, **10b** and **12b**, and 2-bromo- and -iodo-4-(3,5-di-tert-butyl-4-trimethylsiloxy-phenyl)ethynylbenzenes, **10a** and **12a**, were prepared based on the previous papers.[10,11]

10b (5.5 mmol) was reacted with the equivalent of (dimethylamino)trimethyltin without solvent at room temperature overnight under dry nitrogen. The crude product was extracted with diethylether and washed with water. The organic layer was concentrated to give a red viscous oil of (2-bromophenyl)trimethyltin, which was used for the following polymerization.

Polymerization

All polymerizations were carried out in a dry nitrogen atmosphere by modifying the conditions described in the previous papers.[12-14] Tertakis(triphenylphosphine)-palladium, cuprous iodide, and triethylamine were added to the monomer solution, and the mixture was heated (The polymerization conditions are listed in Table I). The polymerization mixture was filtered off and extracted for three times with chloroform. The organic layer was washed with brine and concentrated. The chloroform solution was poured into methanol, and the crude polymer was purified by reprecipitation from chloroform to methanol to yield polymers as yellow powders. The molecular weight of the polymer was measured by a GPC (polystyrene-gel column, eluent THF, polystyrene calibration).

11b (Run 1): IR (KBr pellet, cm^{-1}) 3057 (v_{C-H}), 2209 ($v_{C\equiv C}$); ^{1}H-NMR (500 MHz, CDCl$_3$, ppm) δ 7.85-6.24 (m, 4H, Ar); ^{13}C-NMR (125 MHz, CDCl$_3$, ppm) δ 136-122, 92.5; Anal for H-(C$_8$H$_4$)$_n$-Br (n = 8.4): Calcd C, 87.5; H, 3.6; Br, 8.8, Found C, 80.4; H, 3.2; Br, 16.2.

11a (Run 2): IR (KBr pellet, cm^{-1}) 1255 (v_{Si-C}), 927 (v_{Si-O}); ^{1}H-NMR (500 MHz, CDCl$_3$, ppm) δ 7.80-7.20 (m, 5H, Ar), 1.43 (s, 18H, -C(CH$_3$)$_3$), 0.44 (s, 9H, Si-CH$_3$); ^{13}C-NMR (125 MHz, CDCl$_3$, ppm) δ 158-129, 93.3, 89.5, 82.0, 74.4; Anal for H-(C$_{25}$H$_{32}$OSi)$_n$-Br (n = 4.6): Calcd C, 76.2; H, 8.1; Br, 4.5, Found C, 70.4; H, 7.7; Br, 10.7.

13b (Run 4): IR (KBr pellet, cm^{-1}) 3056 (v_{C-H}), 2208 ($v_{C\equiv C}$); ^{1}H-NMR (500 MHz, CDCl$_3$, ppm) δ 7.78-6.24 (m, 4H, Ar);

^{13}C-NMR (125 MHz, CDCl$_3$, ppm) δ 135-125, 92.5; Anal for H-(C$_8$H$_4$)$_n$-I (n = 21.6): Calcd C, 90.6; H, 3.8; I, 5.6, Found C, 89.8; H, 4.2; I, 4.0.

13a (Run 6): IR (KBr pellet, cm^{-1}) 1256 (v_{Si-C}), 928 (v_{Si-O}); ^{1}H-NMR (500 MHz, CDCl$_3$, ppm) δ 7.75-7.21 (m, 5H, Ar), 1.42 (s, 18H, C(CH$_3$)$_3$), 0.41 (s, 9H, Si(CH$_3$)$_3$); ^{13}C-NMR (125 MHz, CDCl$_3$, ppm) δ 158-126, 93.2, 89.4; Anal for H-(C$_{25}$H$_{32}$OSi)$_n$-I (n = 6.1): Calcd C, 75.5; H, 8.1; I, 5.3, Found C, 73.9; H, 7.7; I, 5.1.

Deprotection and Oxidation

The trimethylsiloxy precursors were hydrolyzed in sodium hydroxide alkaline solution. The product was extracted with chloroform and reprecipitated in methanol to yield the corresponding hydroxy polymers. The hydroxy precursors were carefully oxidized with phase-separated aqueous alkaline K$_3$[Fe(CN)$_6$] in a nitrogen atmosphere.

Magnetic Measurement

The 2-methyltetrahydrofuran solution of polyradicals immediately after oxidation was used for the magnetic measurement. Static magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS-7) in a 500 gauss magnetic field at 1.8–200 K.

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1174

Polym. J., Vol. 31, No. 11-2, 1999