Synthesis of an Optically Active Poly(phenylacetylene) Bearing Galvinoxyl Radicals for Magnetic Materials

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An optically active polyradical was first synthesized by copolymerization of (4-ethynylphenyl)hydrogalvinoxyl and chiral acetylene monomer using Rh-catalyst. The circular dichroism spectrum of the polyradical showed a Cotton effect indicating the exess of one-handed helix backbone and the induced chirality of side-chain galvinoxyl units. Intermoleculer antiferromagnetic interaction observed for the polyradical was larger than that of the corresponding polyradical without excess of one-handed helix.

Recently, polyradicals indicating organic ferromagnetism have been investigated with much attention as one of undeveloped electronic properties of organic polymers.[1,2] The possibility of high-spin states in π-conjugated organic radicals has been previously discussed,[3,4] and the through-bond or intra-chain high spin alignment through the π-conjugation of the polyradicals has been realized during the last decade[2,5] although the spin quantum number S was ten at most.[6] However, interchain ferromagnetic interaction has not been controlled for any polyradicals yet.

Optically active helical polymers, one of stereoregular polymers, have become of great importance from a viewpoint of the polymer function due to the specific chiral structure which plays an important role in molecular arrangement and assembly.[7] However, there has been no report on the magnetic property of optically active polyradicals to date. On the other hand, poly(phenylacetylene)s have been well investigated as a backbone structure of the polyradical for magnetic materials.[8] It has recently been reported that some rhodium complexes catalyzed the polymerization of phenylacetylenes to yield the corresponding poly(phenylacetylene)s with stereoregularities, i.e., cis-transoidal and helical structures,[9] and that the polymerization of some chiral phenylacetylene monomers yielded the corresponding polymers with excess of one-handed helical structure showing optical activity,[10-12] but achiral phenylacetylenes yielded the achiral or the racemic helical poly(phenylacetylene)s. The aforementioned poly(phenylacetylene)-based polyradicals also should not have one-handed helical structures, and they yielded only para- or weak antiferromagnetic interaction. In this study, we first synthesized stereoregular one-handed helical polyradical with the induced chirality of achiral side-chain, i.e., an optically active poly(phenylacetylene) bearing galvinoxyl units, which are known as a stable radical, was synthesized by copolymerization of (4-ethynylphenyl)hydrogalvinoxyl (**1a**)[13] and a chiral acetylene monomer, 4-(dimethyl(10-(1S)-pinanyl)silyl)phenylacetylene (**2**),[14] using rhodium catalyst. The optical activity and magnetic interaction of the polyradical were discussed in terms of the circular dichroism (CD) spectra and SQUID measurements, respectively.

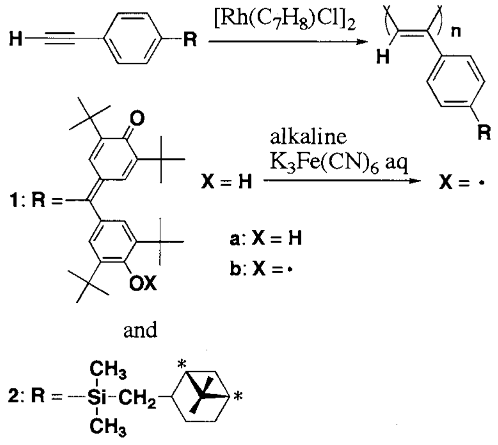

Table 1. Copolymerization[a] of **1a** with **2** and Characterization of the Copolymers

No.	Feed[b] /mol%	Polym[c] /mol%	Yield /%	$\overline{M}_n$[d] /x 10^5	$\overline{M}_w/\overline{M}_n$[d]	Precip[e]	λ_{abs}[f] /nm	λ_{CD}[g] /nm
1	10	10	90	3.1	1.4	Meth	540	–
2	30	27	96	4.3	2.2	Meth	553	540
3	50	49	81	1.2	1.6	Hex	577	560
4	70	67	41	0.9	2.0	Hex	591	590
5	80	82	72	1.7	2.1	Hex	611	600
6	90	88	85	3.6	2.5	Hex	616	610

[a] Polymerization conditions: chloroform, $[M]_0$=0.1 mol/dm^3; $[Rh(C_7H_8)Cl]_2$-triethylamine (1:10), $[cat.]_0/[M]_0$ = 1/100; 25 °C, 0.5 h. [b] Feed composition of **1a**. [c] Copolymer composition of **1a** determined from ^{1}H NMR (0.1 ppm for $-CH_2Si(CH_3)_2-$ and 6.0 ~ 8.0 ppm for ArH) or visible absorption (420 nm). [d] Measured by GPC calibrated with polystyrene standard. [e] Precipitant. Meth: methanol, Hex: hexane. [f] Wavelength of the absorption edge (ε < 10 dm^{3}mol^{-1}cm^{-1}). [g] Wavelength of the positive CD signal edge ($[\theta] < 100$ deg·cm^{2}dmol^{-1}) in the absorption region of the backbone chromophore.

1a was copolymerized with **2** using (bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst, $[Rh(C_7H_8)Cl]_2$, in chloroform, and the polymerization solutions were poured into hexane or methanol to yield the corresponding poly(**1a**-co-**2**) as shown in Table 1. All the copolymers were obtained in good yield with high molecular weight ($\overline{M}_n \approx 10^5$), and the compositions of the copolymers were almost the same as the feed compositions of monomers. The formation of copolymers was confirmed by the unimodal molecular weight distribution and the CD spectra of the polymers formed. Those spectra were different from that of the blend polymers, and the CD spectrum of the homopolymer blends was the same as that of poly(**2**).[14] A bathochromic shift of the absorption edge was observed in the UV/visible absorption spectra with increasing composition of **1a**. In all the CD spectra of the copolymers, positive Cotton effects were observed in the absorption region (450 - 550 nm) of the backbone chromophore, and the peaks also shifted to longer wavelength with the bathochromic shift of the absorption edge, indicating excess of one-handed helical polyacetylene backbone.[11,12] With increasing composition of **1a**, split-type induced CD signal appeared and increased its intensity in the absorption region (420 nm) of the hydrogalvinoxyl chromophore. This result indicates not only excess of one-handed helix but also an induced chirality of side-chain galvinoxyl units.

The polymers poly(**1a**-co-**2**) were converted to the corresponding polyradicals poly(**1b**-co-**2**) after the treatment with aqueous alkaline $K_3Fe(CN)_6$ solution, and gave a deep brownish solution. The absorption maximum at 420 nm due to the hydrogalvinoxyl chromophore decreased and a new absorption peak due to the galvinoxyl radical chromophore appeared at 470 nm. The polyradical was stable enough to maintain the initial spin concentration under ESR, CD and SQUID measurement conditions. In the CD spectra of the polyradical containing more than 20 mol% of **2**, Cotton effect was observed in the absorption region (470 nm) of the galvinoxyl radical chromophore and in that (450 - 550 nm) of the backbone chromophore, as shown in Figure 1. This fact indicates the maintenance of the excess of one-handed helix even after the oxidation reaction, and successful synthesis of an optically active polyradical. In the ESR spectrum for the solution of the polyradical with 67 mol% galvinoxyl unit, a single broad signal was observed at g=2.0047. The spin concentration of polyradical determined from doubly integrating the ESR signal reached ca. 0.6 ~ 0.8 spin/unit.

Static magnetic susceptibility of the polyradical in a powder sample with 67 mol% galvinoxyl unit was measured with a SQUID magnetometer at 2 - 250 K. The reciprocal of magnetic susceptibility, $1/\chi_g$, was linear against T as required by the Curie-Weiss law ($\chi_g = C/(T-\theta)$). The Curie constant (C) and Weiss temperature (θ) were estimated by linear fitting to $1/\chi_g$ *vs* T plots, giving 4.5 x 10^{-4} emu·K/g and -2.2 K, respectively.[15] The spin concentration estimated from the Curie constant was 0.79 spin/unit which agreed with that from integration of the ESR signal. The negative Weiss temperature indicates antiferromagnetic interaction between unpaired electrons, but this negative θ value was larger than the previously reported value of θ = -0.7 K[16] for the poly(**1b**) without excess of one-handed helical structure. This result suggests that the excess of one-handed helix facilitated well-packing between the polymer chains to give a more extensive and stronger antiferromagnetic through-space interaction between the radical units, although the effect of comonomer can not be ruled out. Although the observed magnetic interaction of the polyradical showed intermolecular antiferromagnetic interaction, the larger negative Weiss temperature in comparison with that of the poly(**1b**) without excess of one-handed helical structure supports that stereoregular polyradical is one of the significant prerequisites to control magnetic interaction between polyradicals.

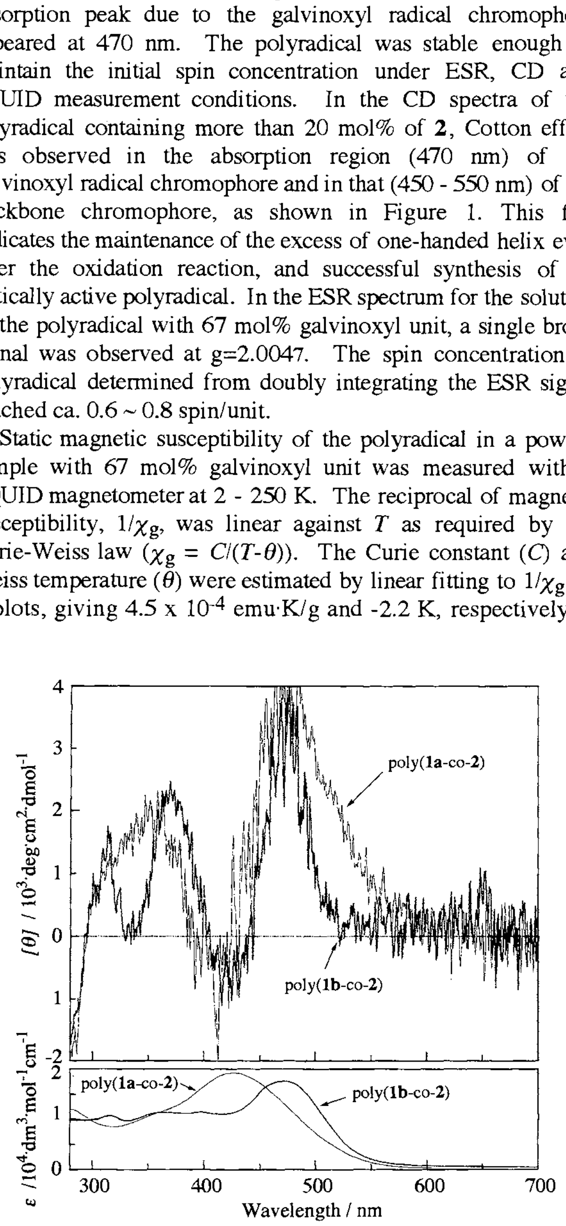

Figure 1. (Top) CD and (bottom) UV/visible absorption spectra of poly(**1a**-co-**2**) and poly(**1b**-co-**2**) with 67 mol% galvinoxyl unit and spin concentration of 0.7 spin/unit in chloroform (1.3 mmol/dm^3).

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