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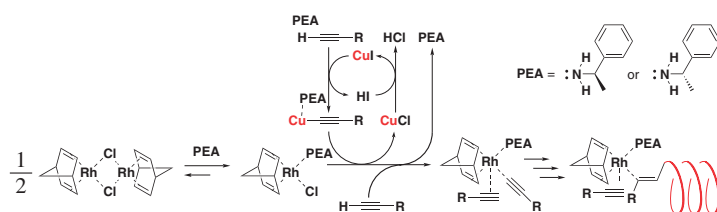
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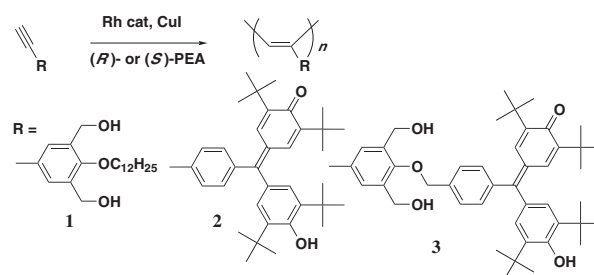
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Achiral phenylacetylene monomers were polymerized using a rhodium (Rh) complex catalyst in the presence of (*S*)-1-phenylethylamine. Addition of copper(I) iodide (CuI) into the catalytic system improved the polymer yield. The monomer, which had two hydroxy groups and a hydrogalvinoxyl unit, gave the corresponding polymer with an optically active helical conformation stabilized by intramolecular hydrogen bonding. The chemical oxidation of the polymer yielded the corresponding optically active helical polyradical with high spin concentration.



Scheme 1.

Substituted polyacetylenes have attracted attention as one of the most interesting π -conjugated functional polymers since it was found that group 5-, 6-, and 9-transition metals effectively catalyzed the polymerization of substituted acetylenes.¹ In particular, some rhodium complex catalysts provide efficient polymerization of monosubstituted acetylenes since these catalysts polymerize bulky monomers such as dendrimers²⁻⁴ and monomers containing functional groups (including stable radicals),⁵ and polymerization proceeds even in aqueous media.⁶ In addition, the polymers obtained often have high degrees of polymerization and stereoregularities, i.e., *cis*-*trans*oidal and helical structures.⁷⁻⁹ Recently, we succeeded in helix-sense-selective polymerization of achiral monomers **1** and **2** using a chiral catalyst system, i.e., polymerization using [Rh(nbd)Cl]₂ catalyst in the presence of (*R*)-1-phenylethylamine ((*R*)-PEA) or (*S*)-1-phenylethylamine ((*S*)-PEA) to give the corresponding poly(phenylacetylene)s poly**1**^{10,11} and poly**2** (Scheme 1).^{12,13} These products exhibited optically active helical conformation in solution, with an excess of one-handed helix kinetically stabilized by intramolecular hydrogen bonds (poly**1**) and the bulkiness of the side groups (poly**2**). In this study, we synthesized the new achiral monomer **3** and found that the helix-sense-selective polymerization of the monomers improved polymer yield by addition of CuI to the catalytic system. Moreover, we succeeded in synthesizing the optically active helical polyradical with high spin concentration via chemical oxidation of the poly**3** with rigid and one-handed helical conformation in THF solution, which is kinetically stabilized by intramolecular hydrogen bonds.

The monomer **3** was polymerized in the presence of several Rh complex catalysts, chiral PEA cocatalyst, and an achiral solvent. The red solid polymer poly**3** was obtained by precipitation from the polymerization mixtures into methanol. The polymerization data for these resultant polymers are summarized in Table 1. Under polymerization conditions without CuI, polymer yields were lower than those in the presence of CuI. Gel permeation chromatography indicated that the polymerization mixture

contained little oligomer; instead it consisted mostly of unreacted monomers. Therefore, GPC results suggest that the low polymer yield resulted from the slow reaction rate of complexation to the polymerization active species. This improvement in polymer yields by addition of CuI also was observed during the polymerization of **1**. In a previously proposed polymerization mechanism,¹⁴⁻¹⁷ the polymerization active species are generated by end-on coordination of acetylide to Rh. The monomers **1** and **3** are relatively bulky and contain hydroxy groups. Thus, it appears that the low polymerization activity was caused by inhibition of acetylide formation due to active protons of the monomer hydroxy groups and by the bulkiness of the monomers. In contrast, addition of CuI to the catalytic system improved polymer yield. Cross-coupling reactions of halogenoaryls with acetylene derivatives using Pd complex catalysts, i.e., Sonogashira coupling,¹⁸ proceeds via end-on coordination of acetylide to Pd, where CuI accelerates acetylide coordination due to formation of copper acetylide. The effect of CuI addition in the polymerization of **1** and **3** is analogous to this coupling reaction, i.e., the transmetalation of copper acetylide to Rh accelerated complexation to polymerization active species as

Table 1. Polymerization^a of **3** in toluene using Rh complexes in the presence of (*S*)-(-)-phenylethylamine

No.	Rh ^b complex	Temp /°C	[CuI] / [Rh]	Yield ^c /%	M_w^d /10 ⁵	M_w/M_n^d
1	Rh I	25	0	5	27	30
2	Rh I	25	1	15	8.3	14
3	Rh I	0	2	9	7.8	8.7
4	Rh II	0	0	27	4.2	4.7
5	Rh II	0	1	72	3.5	3.6

^a[M]₀ = 0.05 M; [M]₀/[Rh]₀ = 20; [PEA]₀/[Rh]₀ = 100; 1 h (No. 1–3), 4 h (No. 4), and 2 h (No. 5); PEA: phenylethylamine.

^bRh I: [Rh(nbd)Cl]₂; Rh II: Rh⁺(nbd)[(η⁶-C₆H₅)B⁻(C₆H₅)₃].

^cMethanol insoluble fraction. ^dMeasured by GPC calibrated with polystyrene standard.

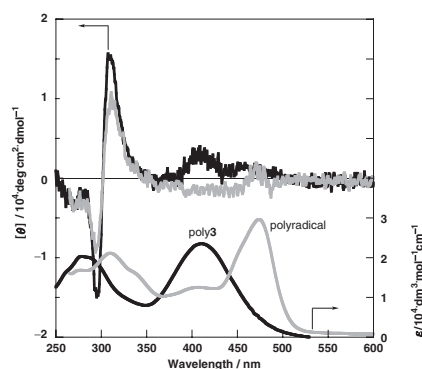


Figure 1. CD (top) and UV-vis (bottom) absorption spectra of poly $\mathbf{3}$ (No. 5 in Table 1) and its polyradical with spin concentration of 0.8 spin/unit in THF (0.5 mmol/dm^3).

shown in the Graphical Abstract. Moreover, replacement of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ by $\text{Rh}^+(\text{nbd})[(\eta^6\text{-C}_6\text{H}_5)\text{B}^-(\text{C}_6\text{H}_5)_3]^{19}$ in the polymerization catalytic system appeared to enhance the reactivity remarkably, probably because elimination of tetraphenyl borate anion proceeded more readily compared to chloride anion.²⁰

Of all polymers obtained, poly $\mathbf{3}$ possessed optical activity, and split-type induced CD signals were observed for the THF solution of $\mathbf{3}$ at 300 nm as shown in Figure 1, indicating an excess of one-handed helical polyacetylene backbone.²¹ It is clear that the helix-sense-selective polymerization occurred in the presence of chiral PEA because monomer $\mathbf{3}$ has no chiral moieties and the CD signal at 300 nm was similar to that of previously reported poly $\mathbf{1}$. The polymer obtained by polymerization at low temperature (0°C) showed a larger Cotton effect compared to the polymers obtained by polymerization at room temperature. These results indicate improvement of the helix-sense-selectivity for the polymerization. The CD intensity of poly $\mathbf{3}$ was nearly constant, even when the solution was heated to 60°C , because the rigid and one-handed helical conformation was stabilized by intramolecular hydrogen bonds. This behavior is in contrast to previous results reported for poly $\mathbf{2}$, whose CD signal intensity was dependent on temperature over the experimental range and decreased reversibly with increasing temperature for the CD spectra of poly $\mathbf{2}$ in solution used immediately after preparation.¹³

The hydrogalvinoxyl units of poly $\mathbf{3}$ were converted to the corresponding galvinoxyl radicals after treatment with fresh PbO_2 under an oxygen-free atmosphere, and the color of the THF solution turned from orange to brown. 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 ESR spectrum of the polyradical showed a broad signal at $g = 2.0047$, indicating formation of the phenoxy radical. The spin concentration of the polyradical was determined by doubly integrating the ESR signal in comparison with that of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) solution as a standard. Spin concentration of the polyradical reached ca. 0.6–0.8 spin/unit by adjusting oxidative conditions. The polyradical was stable enough to maintain initial spin concentration under ESR and CD measurement conditions. In the CD spectra of the polyradical, the Cotton effect was still observed at 300 nm, as shown in Figure 1. This indicates that maintenance of the excess of the one-handed helix

was achieved even after the oxidation reaction, and successful synthesis of an optically active polyradical with high spin concentration occurred, i.e., with high radical contents compared to previously reported optically active helical copolymer-polyradical.²² The magnetic and magneto-optical properties of the optically active helical polyradicals will be discussed in greater detail in a subsequent paper.

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