Helix-sense-selective Polymerization of a Phenylacetylene Bearing an Achiral and Bulky Galvinoxyl Moiety

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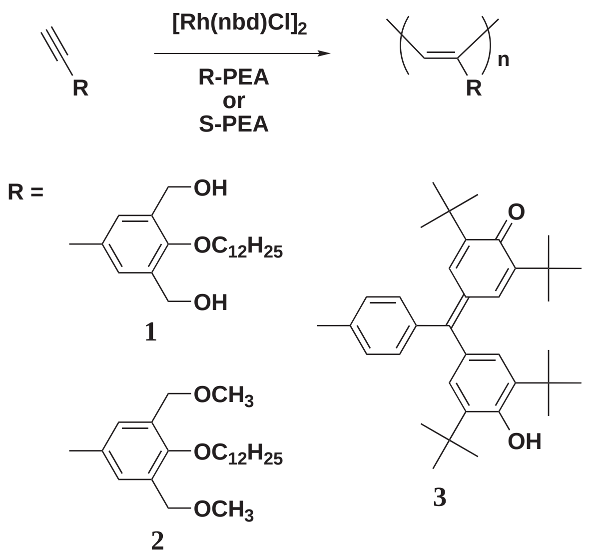
An achiral and bulky phenylacetylene monomer, (4-ethynylphenyl)hydrogalvinoxyl), was polymerized using $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene) catalyst in chiral phenylethylamine. The circular dichroism (CD) spectra of the obtained polymers indicated that an excess of one-handed helical polyacetylene backbone was induced by helix-sense-selective polymerization despite the achiral monomer.

There has been growing interest in the synthesis of optically active helical polymers due to their unique properties, which are based on their optically active helical structure.[1] We have already synthesized various optically active helical polyacetylenes by polymerization of the corresponding monomers with chiral side groups, and reported enantioselective permeability as their membrane properties.[2–9] Recently, we have newly developed helix-sense-selective polymerization of achiral monomers using a chiral catalyst system, i.e. polymerization using the catalyst $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene) in the presence of (*R*)-1-phenylethylamine ((*R*)-PEA) or (*S*)-1-phenylethylamine ((*S*)-PEA).[10,11] In this chiral catalyst system, the monomer **1**, which have two hydroxymethyl groups, polymerized to give the corresponding optically active helical polymers which showed clear Cotton effects in the CD spectrum, while the monomer **2**, whose hydroxyl groups are protected by methyl groups compared to **1**, yielded the optically inactive polymer. This result shows that rigid and one-handed helical conformation in solution is kinetically stabilized by intramolecular hydrogen bonds among hydroxyl groups in poly(**1**). On the other hand, polyacetylenes are one of the backbone structures that are able to induce the novel electronic properties due to the π-conjugated and one-handed helical structure.[12–15] In particular, poly(phenylacetylene)s have been well investigated as a backbone structure of the polyradical for magnetic materials,[16–19] and we previously reported that an optically active helical poly(phenylacetylene) was synthesized by copolymerization of (4-ethynylphenyl)-hydrogalvinoxyl (**3**) and a chiral acetylene monomer using $[Rh(nbd)Cl]_2$, and its polyradical showed the larger intermolecuer antiferromagnetic interaction than the corresponding polyradical without excess of one-handed helix.[13] In this study, we report helix-sense-selective polymerization of the achiral and bulky monomer **3** using our chiral catalyst system described above, and the first successful example yielding the corresponding optically active helical polymer without the intramolecular hydrogen bonds.



Scheme 1.

Table 1. Polymerization[a] of **3** using $[Rh(nbd)Cl]_2$ in (*R*)- or (*S*)-1-phenylethylamine

No.	Solvent	Yield[c] /%	M_n[d] /× 10^4	M_w/M_n[d]	$[\theta]$[e] /10^3 deg·cm^2·dmol^{-1} at 400 nm	$[\theta]$[e] /10^3 deg·cm^2·dmol^{-1} at 530 nm
1	(*R*)-PEA[b]	10	2.0	1.6	4.8	2.5
2	(*S*)-PEA[b]	22	1.8	1.7	−4.8	−2.7
3	DL-PEA[b]	7	0.78	1.5	0	0
4	NEt_3	15	0.80	1.8	0	0

[a] $[M]_0 = 0.1$ M, $[M]_0/[Cat.]_0 = 50$, 25–30 °C, 0.5 h. [b] PEA: 1-phenylethylamine. [c] Hexane insoluble fraction. [d] Measured by GPC calibrated with polystyrene standard. [e] Molar ellipticity at 20 °C in chloroform.

The monomer **3** was polymerized in the presence of the $[Rh(nbd)Cl]_2$ catalyst, and chiral or achiral amines. A red solid polymer poly(**3**) was obtained by precipitation from the polymerization mixtures into hexane. The polymerization data for these resultant polymers are summarized in Table 1, and CD spectra of the polymers are shown in Figure 1. There, the positive and negative Cotton effects are observed for the polymers obtained by polymerization using (*R*)-PEA and (*S*)-PEA as solvent (Table 1, No. 1 and 2; abbreviated as poly(3_R) and poly(3_S), respectively) in the absorption region (450–600 nm) of the backbone chromophore, respectively, indicating an excess of one-handed helical polyacetylene backbone. Split-type induced

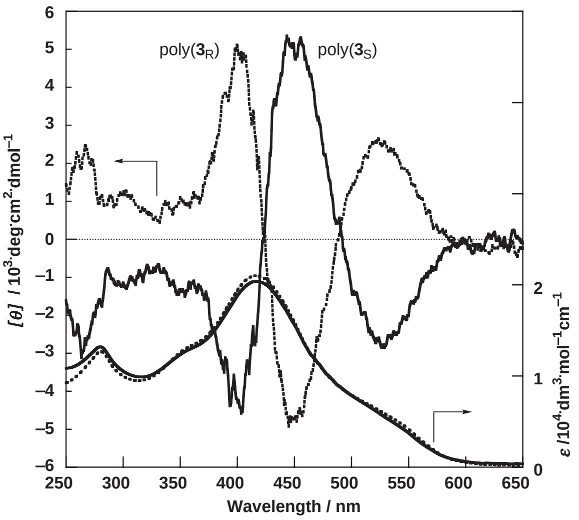


Figure 1. CD and UV–vis absorption spectra of poly($\mathbf{3}_{\mathrm{R}}$) and poly($\mathbf{3}_{\mathrm{S}}$) at 20 °C in chloroform (1.0 mM).

CD signals, which are mirror images of each other, also appear in the absorption region (420 nm) of the hydrogalvinoxyl chromophore.[20] On the other hand, no Cotton effects were observed for the polymers obtained by polymerization using racemic 1-phenylethylamine and triethylamine as solvent (Table 1, No. 3 and 4). These results indicate that the achiral or racemic polymer were obtained under the optically inactive polymerization conditions. It is clear that the helix-sense-selective polymerization occurred in the presence of the chiral PEA because no Cotton effects were observed for the achiral or racemic polymer solution, even when excess amounts of (*R*)-PEA were added to the solution. Additionally, when excess amounts of (*R*)-PEA (or (*S*)-PEA) were added to the poly($\mathbf{3}_{\mathrm{S}}$) (or poly($\mathbf{3}_{\mathrm{R}}$)) solution, or even if the poly($\mathbf{3}_{\mathrm{S}}$) (or poly($\mathbf{3}_{\mathrm{R}}$)) were dissolved in (*R*)-PEA (or (*S*)-PEA) then precipitated into hexane, the CD signal intensity of poly($\mathbf{3}_{\mathrm{S}}$) (or poly($\mathbf{3}_{\mathrm{R}}$)) did not change in chloroform. These behavior was summarized in Graphical Abstract. The CD signals of poly($\mathbf{3}_{\mathrm{R}}$) and poly($\mathbf{3}_{\mathrm{S}}$) remained for a long time in chloroform solution, but the half-life of the CD signal intensity was more than three days at room temperature in the chloroform solution. This behavior is in contrast to the previous result of poly(**1**), whose half-life of the CD signal intensity was more than five months at room temperature in the chloroform solution.[10] It seems that the steric hindrance of the bulky galvinoxyl moiety is not more effective to kinetically stabilize the one-handed helical conformation for poly($\mathbf{3}_{\mathrm{R}}$) and poly($\mathbf{3}_{\mathrm{S}}$) than the intramolecular hydrogen bonds among hydroxyl groups in poly(**1**). However, we have succeeded in obtaining the novel poly(phenylacetylene) with an excess of one-handed helix kinetically stabilized by the achiral side group's own bulkiness to observe its Cotton effect in the CD spectrum. The formation of polyradical for optically active poly(**3**), and its magnetic property will be discussed in more detail in a subsequent paper.

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