Synthesis of one-handed helical cis-cisoidal polyphenylacetylenes by controlled helix-sense-selective polymerization

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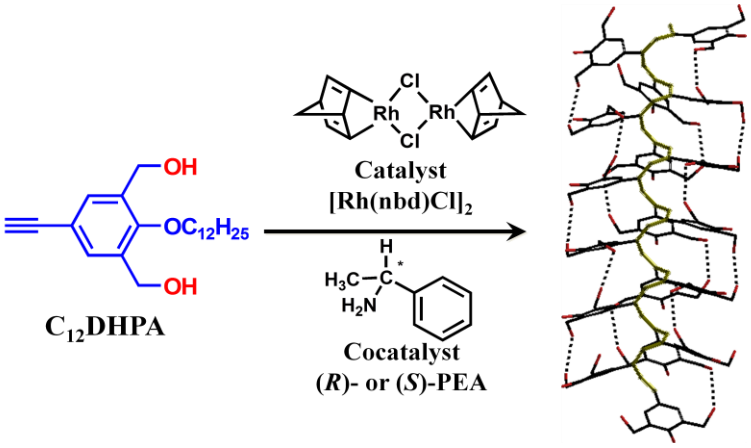
Contents

Abstract

For chirality of one handed helical polyphenylacetylenes prepared by Helix-sense-selective polymerization of achiral phenylacetylenes having two hydroxyl groups reported in our laboratory, there is no any other chiral atoms except the helical main chain. The hydrogen bonds formed among hydroxyl groups attached with the phenyl ring are the key role in the conformation of helical structure.



As the helical main chain shows chirality, the hydroxyl groups attached with helical main chain could be used a chiral source for the helix-sense-selective polymerization of substituted phenylacetylenes having hydroxyl groups. To the best of our knowlege, this is the firs example of polymer catalyst prepared by HSSP of achiral phenylacetylene.

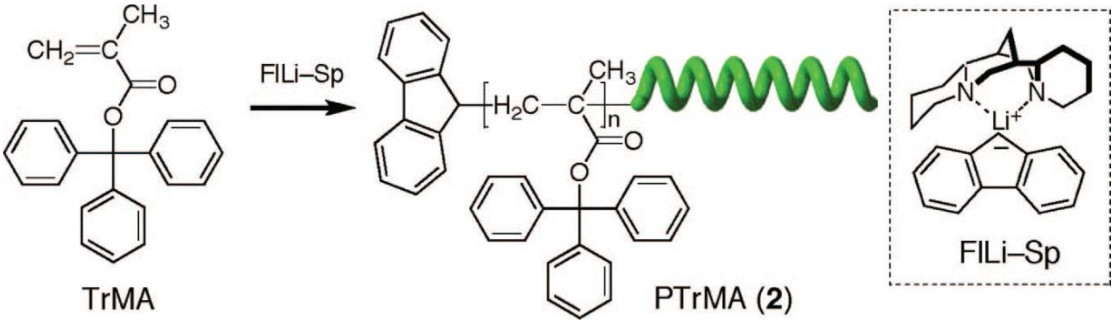
With a novel phenylacetylen having two hydroxyl groups and a chiral pinanyl group and its related phenylacetylenes, chiral amplification phenomenon was observed by using the copolymerization of achiral phenylacetylene having two hydroxyl groups and chiral having chiral pinanyl group. The tight helical cis-cisoidal main chain formed by making intramolecular hydrogen bonds between the hydroxyl groups enhances the efficiency of chiral induction.

General Introduction

I. Helix-sense-selective polymerization (HSSP) of substituted phenylacetylenes

The helix is the most basic and important conformation in biological macromolecules, such as DNA, RNA and enzyme. Importantly, the helical structure is inherently chiral, which is meaningful for generation of life in nature involving molecular recognition, replication, and catalytic activity. Chemist scientists have been engaged to develop artificial helical polymers, supramolecules and so on, aiming at not only the imitation of biological helices and functions but also their potential applications in materials, sensing specific molecules, the seperation of enantiomers, and asymmetric catalysis,

Optically active helical polymers have aroused much attention because of their great interest and importance applications such as optical resolution, chiral sensors, chiral catalysts, microelectronics and chiral magnets[1-7]. Recently, it was reported that a majority of helical polymers have been prepared, including polyisocyanides, polymethacrylates, polyisocyanates, polysilanes, and polyacetylenes[8-12].

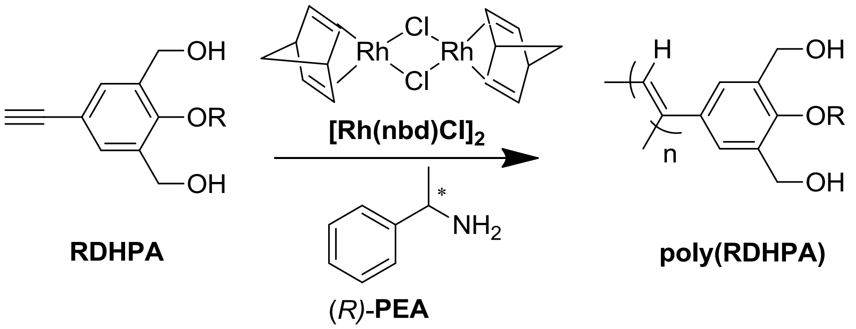


Scheme 1. Helix-sense-selective anionic polymerization of TrMA[23]

Prof. Okamoto and Yuki et al., had reported helical PTrMA for the first time as a vinyl polymer, which was prepared by the helix-sense-selective polymerization (HSSP) of an achiral monomer, triphenylmethyl methacrylate (TrMA) with anionic inititors such as 9-fluorenyllithium complexed with chiral ligands such as (-)-sparteine(Scheme 1) [13].

Many kinds of optical active π-conjugated, dynamic helical polyacetylenes had been prepared by Prof. Ciardelli et al.[14-18] in the past decade, such as the polymerization of optically active phenylacetylenes, propiolic esters, propargyl esters, N-propargylamides, and aliphatic acetylene or the copolymerization with achiral acetylenes.

Helix-sense-selective polymerization, using chiral catalysts or chiral initiators to provide chiral source, is a possible method of preparing various one handed helical polymers since the process demands no chiral moiety in the monomer, giving increased flexibility to monomer design. Previously, the helix-sense-selective polymerization of achiral phenylacetylenes having two hydroxyl groups (RDHPA) by using the chiral catalyst system consisting of $[Rh(nbd)Cl]_2$ (nbd =norbornadiene) as a catalyst and (*R*)-phenylethylamine ((*R*)-PEA) as a cocatalyst was reported by our laboratory[19-22]. It was the first report of obtaining soluble and one-handed helical substituted polyacetylenes having no other chiral moieties.



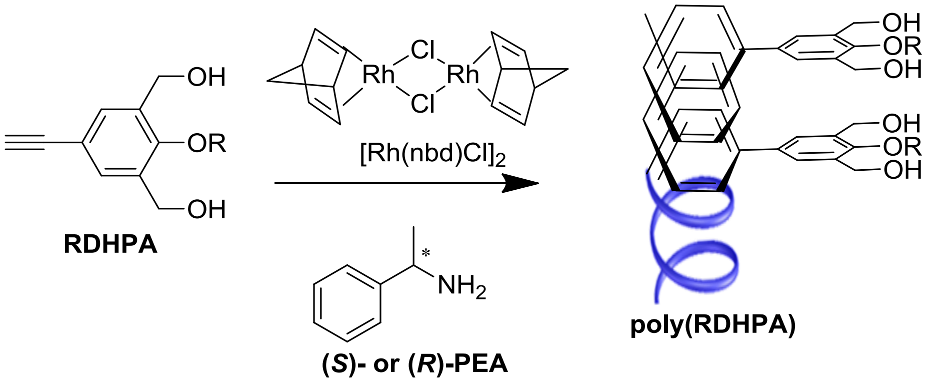
Scheme 2. Helix-sense-selective polymerization of RDHPA

In the study of HSSP of achiral monomers having two hydroxyl groups, like RDHPA, one handed helical conformation could be obtained even by using a catalytic amount of chiral cocatalyst and the helical chirality of resulting polymers were kinetically stabilized by intramolecular hydrogen bonds among hydroxyl groups in the polymers. The chiral structures arised solely from the one-handed helical conformation of the conjugated main chains.

II. Synthesis of polyphenylacetyeles with cis-cisoidal main chains

It is well known that polyacetylene prepared by rhodium catalyst, such as $[Rh(nbd)Cl]_2$ (nbd: norbornadiene), is a typical dynamic helical polymer[23], and its main-chain conformation can be stretched *cis-transoidal* [24-31] or contracted *cis-cisoidal* [19,32-36] depending on the chemical structure of the monomer.

One handed helical polyphenylacetylenes prepared by helix-sense-selective polymerization of achiral phenylacetylenes having two hydroxyl groups using the rhodium catalyst system ($[Rh(nbd)Cl]_2$ and (*R*)- or (*S*)-phenylethylamine) as initiator had been reported in our laboratory. Interestingly, the cis-transoidal regular main chain could be induced to one-handed helicity by chiral source during the polymerization procedure. For the DHPA type polyacetylenes, the structure of main chain tend to be a contracted cis-cisoidal because of intramolecular hydrogen bonds formed in neighbor units.



Scheme 3. Helix-sense-selective polymerization of achiral RDHPA.

III. Purpose of this thesis

In chapter 1, We found that the helix-sense-selective polymerization (HSSP) of achiral phenylacetylenes having two hydroxy groups was realized by using one-handed helical poly(phenylacetylene)s as chiral cocatalysts prepared by HSSP of the same or similar achiral phenylacetylenes having two hydroxy groups. In other words, the chirality caused only by the one-handed helical backbone was found to be able to work as a cocatalyst in the chiral catalytic system. In addition, the efficiency of the chiral induction was high and almost the same as that of the HSSP by using enatiomerically pure phenylethylamine as a cocatalyst.

In chapter 2, A novel phenylacetylene (**1**) having two hydroxyl groups and a chiral pinanyl group together with the other three related phenylacetylenes has been synthesized and (co)polymerized by using an achiral catalytic system. Among the four monomers, only **1** is suitable to the asymmetric-induced polymerization (**AIP**). Chiral amplification phenomenon is only observed in the copolymerization of **1** with an achiral phenylacetylene having two hydroxyl groups (**3**). The tight helical cis-cisoidal main chain formed by making intramolecular hydrogen bonds between the hydroxyl groups in the copoly(**1**/**3**) enhances the efficiency of chiral induction and as a result chiral amplification phenomenon is observed during the copolymerization.

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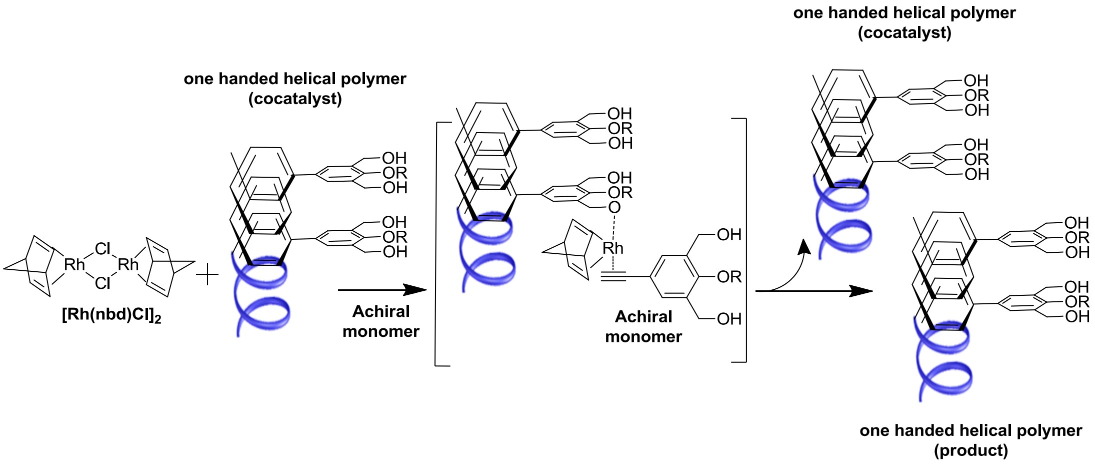
Chapter 1

Helix-sense-selective polymerization of achiral phenylacetylenes by using one-handed helical poly(phenylacetylene)s as chiral cocatalysts prepared by helix-sense-selective polymerization of achiral phenylacetylenes

1.1 Abstract

The helix-sense-selective polymerization (HSSP) of achiral phenylacetylenes having two hydroxy groups was realized by using one-handed helical poly(phenylacetylene)s as chiral cocatalysts prepared by HSSP of the same or similar achiral phenylacetylenes having two hydroxy groups. In other words, the chirality of the one-handed helical backbone was found to be able to work as a cocatalyst in the chiral catalytic system. Also, the efficiency of the chiral induction was high and almost the same as that of the HSSP by using enatiomerically pure phenylethylamine as a cocatalyst.



1.2 Introduction

In our laboratory, the helix-sense-selective polymerization (HSSP) of an achiral monomer (**1**, Scheme 1(B)) with two hydroxyl groups to produce static one-handed helical conjugated polymers by using a chiral catalytic system, [Rh(NBD)Cl]$_2$ (NBD = norborbrnadiene) and (*R*)- or (*S*)-phenylethylamine(PEA, Chart 1).[1] To the best of our knowledge, it has so far been possible to synthesize soluble chiral conjugated polymers directly by polymerization, whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains and that are static and stable alone in solution, only by the HSSP method developed in our laboratory.

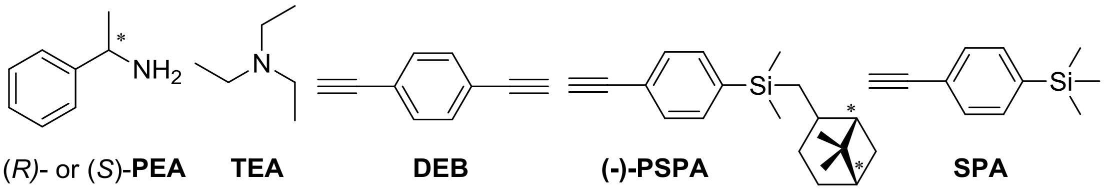


Chart 1. Structures and codes of compounds.

Based on the discovery of the HSSP, we developed unique properties and structures of the one-handed helical polymers such as poly**1** prepared by the HSSP. For example, the polymers were photodegraded to give the corresponding cyclic trimer exclusively (we called it SCAT)[2] because of their tight cis-cisoidal backbone. However, almost no application of the chirality of the one-handed helical polymers has been reported except for optical resolution membranes,[3] although application of the polymers to chiral catalysts has been expected.

Many chiral polymers have been applied to chiral catalysts for enantioselective organic reactions.[4] However, the chiralities of the most of them were derived from chiral substituents containing asymmetric atoms such as asymmetric carbons and there have been only a few reports on enatioselective reactions catalyzed by chiral polymers whose chiral structures arise solely from the one-handed helical conformation.[5] In addition, to the best of our knowledge, no reports on asymmetric polymerizations which were catalyzed by such chiral polymers, although it has been reported that some asymmetric organic reactions were catalyzed by such chiral polymers. [4,5]

In this research, we report the first example of the HSSP catalyzed by chiral polymers having one handed helical main chain prepared by the HSSP. The phenomenon is very interesting and valuable because it is related to self-catalyzed HSSP where the HSSP products produced by the HSSP of a monomer function as chiral cocatalysts *in-situ* during the HSSP of the monomer.

1.3 Experimental

1.3.1 Materials

All the solvents used for synthesis and polymerization of the monomers were distilled as usual. $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene) was purchased from Aldrich Chemical and used as received. The polymerization initiator, Rh complex **A** , was prepared from $[Rh(nbd)Cl]_2$ (nbd = 2,5 norbornadiene) according to the literature procedure [1] . The monomers were reported and synthesized in our previous study.

1.3.2 Measurements

Tosoh liquid chromatography instruments with DP-8020 and UV-8020 and two columns (G2500H) were used for recycling samples. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070 and CD-2095, and two polystyrene gel columns (Shodex KF-807 L). CD spectra were recorded by using a JASCO J-720WI with a Peltier controller (a quartz cell :1.0 mm path length).

1.3.3 Synthesis of the monomers.

The monomers **1**[S1)], **2**[S2)], **3**[S3)], **4**[S3)], (-)-**PSPA**[S4)] and **SPA**[S5)] (Chart 1) were synthesized according to our previous study.

1.3.4 Synthesis of chiral polymer cocatalysts, one-handed helical poly(phenylacetylene)s, by helix-sense-selective polymerization of achiral monomers (1 and 2).[S1-S3)]

1) A solution of $Rh[C(C_6H_5)=C(C_6H_5)_2](nbd)(4-FC_6H_4)_3P$ (46 mg, 60 μmmol) and tris(4-fluorophenyl)-phosphine ($P(Ph-F)_3$, 95 mg, 0.30 mmol) in dry pyridine (1.5 ml) was stirred under nitrogen at room temperature for 1h, and then monomer **1** (104 mg, 0.30 mmol) in pyridine (3.0 ml) was added by syringe to the reaction solution under nitrogen. After it was stirred at room temperature for 1h, polymerization was quenched by addition of a catalytic amount of acetic acid (37% in water, 0.10 ml). The solvent was removed by evaporation to give crude low M_w ($=2.8\times10^4$) racemic poly(**1**) as a viscous liquid, which was further purified by using recycle-GPC (eluent: $CHCl_3$) (Yield: 47%, 49 mg) (Tables 1 and 2, No.1) (Figures S1 and S2(a)).

To a solution of the low M_w ($=2.8\times10^4$) racemic poly(**1**) (49mg) in THF (3ml), (*R)*-PEA (0.5ml) was added by syringe. The solution was stirred under nitrogen for 10h at 40°C. After removing the solvent, recycle-GPC was used to remove the (*R)*-PEA completely. The solvent of the red solution was removed by evaporation to give low M_w ($=2.8\times10^4$) (-)-poly(**1**) (Yield: 71%, 35mg). For the CD, see Figure S1.

2) To a solution of monomer **1** (35 mg, 0.10 mmol) and 1,4-diethynylbenzene (DEB, 1.3 mg, 10 μmol) in toluene (0.50 ml), a solution of $[Rh(nbd)Cl]_2$ (nbd =

norbornadiene) (0.23 mg, 0.50 μmol) and (*R*)-phenylethylamine (PEA, 13 μl, 0.10 mmol) in toluene (0.50 ml) was added by syringe under nitrogen at 28 °C. After stirring for 3h, the polymerization mixture (1.0 ml) was poured into a large amount of methanol(500 ml) and the resulting red solid was collected by filtration. The solid was dried *in vacuo* to give a cross-linked (-)-poly(**1**) (Yield: 95%, 34 mg) (Tables 1 and 2, No.2).

3) To a solution of monomer **2** (20mg, 59 μmmol) in toluene (0.40 ml), (*R*)-phenylethylamine ((*R*)-PEA , 7.6μl, 59 μmmol) was added under nitrogen at 28 °C, and the solution of $[Rh(nbd)Cl]_2$ in toluene(0.20 ml, 0.29 μmol) was added by syringe. After stiring for 3h, the polymerization mixture (0.60 ml) was poured into a large amount of methanol (500 ml). The resulting red solid was collected by filtration and dried in vacuo to give the (-)-poly(**2**) (Yield: 60%,12 mg, red solid) (Tables 1 and 2, No.3). The same procedure was carried out for synthesis of (+)-poly(**2**).

4) The preparation of (-)-poly((-)-**PSPA**) was carried out according to our previous reports[S4] (Tables 1 and 2, No.4) (Figures S5 and S6).

1.3.5 Helix-sense-selective polymerization of achiral phenylacetylenes (1, 3, 4) by using one-handed helical poly(phenylacetylene)s ((+)- or (-)-poly(1), poly(2)) as chiral cocatalysts. [S1-S3)]

1) To a solution of monomer **1** (20 mg, 57 μmmol) and low M_w (-)-poly(**1**) (M_w = 2.8×10^4, 0.17 mg, 0.48 μmol) in toluene (0.40 ml), a solution of $[Rh(nbd)Cl]_2$ in toluene (0.20 ml, 0.29 μmol) was added by syringe under nitrogen at 28 °C. The solution was stirred for 24h, and then was poured into a large amount of methanol (500 ml) to remove low M_w (-)-poly(**1**) used as the cocatalyst. To separate them completely, a recycle GPC was used(eluent: $CHCl_3$) to give a pure product (-)-poly(**1**) (3.0 mg). Yield 15%, M_w = 3.5×10^5, $g = -1.6\times10^{-3}$ (Tables 3 and 4, No.1) (Figures 1 and S2(b)).

2) To a mixture of monomer **1** (20 mg, 57 μmmol) and cross-linked (-)-poly(**1**) (1.0 mg, 2.8 μmol) in toluene (0.40 ml), a solution of $[Rh(nbd)Cl]_2$ in toluene (0.20 ml, 0.29 μmol) was added by syringe under nitrogen at 28 °C. The mixture was stirred for 24h. Then THF (1.0 ml) was added to the polymerization mixture (0.60 ml). The insoluble part, i.e., the cross-linked (-)-poly(**1**) used as a cocatalyst, was easily removed by filtration and the filtrate was poured into a large amount of methanol (500 ml) to give a pure (-)-poly(**1**) as a soluble red solid (1.2 mg). Yield 6.1%, $M_w = 3.3\times10^5$, $g = -1.8\times10^{-3}$ (Tables 3 and 4, No.2) (Figures 1 and S3).

3) To a mixture of monomer **1** (20 mg, 57 μmmol) and (+)-poly(**2**) (0.10 mg, 0.29 μmol) in toluene (0.40 ml), a solution of $[Rh(nbd)Cl]_2$ in toluene (0.20 ml, 0.29 μmol) was added by syringe under nitrogen at 28 °C, and the resulting mixture was stirred for 24h. Then THF (1.0 ml) was added to the polymerization mixture (0.60 ml). The insoluble part, i.e., the (+)-poly(**2**), was easily removed by filtration and the filtrate was poured into a large amount of methanol (500 ml) to give (+)-poly(**1**) as a soluble red solid (2.0 mg). Yield 10%, $M_w = 1.8\times10^5$, $g = 1.9\times10^{-3}$ (Tables 3 and 4, No.3) (Figure 3(A)).

4) To a solution of monomer **1** (20 mg, 0.057 mmol) and (+)-poly((+)-**PSPA**) (1.5 mg, 5.1 μmol) in toluene (0.40 ml), a solution of $[Rh(nbd)Cl]_2$ in toluene (0.20 ml, 0.29 μmol) was added by syringe under nitrogen at 28 °C, and the resulting solution was stirred for 24h. Then the polymerization mixture (0.60 ml) was poured into a large amount of methanol (500 ml) to give a mixture of poly(**1**) and poly(**PSPA**) as a yellow solid (2.1 mg) Yield 9.7%, $M_w = 1.5\times10^6$ (Tables 3 and 4, No.4) (Figures S5 and S7).

5) The polymerization of **1** and **SPA** by using (*R*)-PEA or triethylamine (TEA) as a chiral cocatalys were carried out respectively according to our previous report (Tables 3 and 4, Nos. 5, 6, 11 and 12) (Figures 2 and S4)

6) To a solution of monomer **1** (20 mg, 57 μmmol) in toluene (0.40 ml), a solution of [Rh(nbd)Cl]2 in toluene (0.20 ml, 0.29 μmol) was added by syringe under nitrogen at 28 ˚C, and the resulting solution was stirred for 24h. Then the polymerization solution (0.60 ml) was poured into a large amount of methanol (500 ml) to give poly(**1**) as a red solid (2.2 mg). Yield 11%, Mw = 3.1×105 (Tables 3 and 4, No.7).

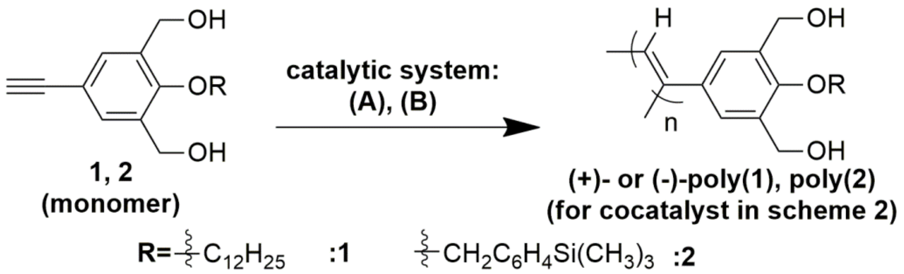
7) Similar procedures as described in 3) was employed to the polymerization of **3** and **4** by using (+)- or (-)-poly(**2**) as a chiral cocatalyst (Tables 3 and 4, Nos. 8-10) (Figure 3(B)).

8) Similar procedures as described in 6) was employed to the polymerization of **SPA** (Tables 3 and 4, No. 13).

1.4 Results and discussion

1.4.1

To detect and confirm such a HSSP, chiral polymers used as chiral cocatalysts should be completely separated with the resulting HSSP products. Therefore, three kinds of chiral polymers, i.e., a low *Mw* (-)-poly(**1**), a cross-linked (-)-poly(**1**), and (-)- or (+)-poly(**2**) having solubilities different from those of the HSSP products of **1** and **2**, were prepared by the HSSP of phenylacetylene monomers (**1** or **2**) with two hydroxyl groups (Scheme 1) [6]. The results are summarized in Table 1. The low *Mw* (-)-poly(1) (*Mw* = 2.8x10^4)(no.1) prepared by using the achiral catalytic system ((A) in Scheme 1) was soluble in toluene, THF, and methanol.[6] The cross-linked (+)-poly(**1**) (no.2), which were synthesized by HSSP of 1 by using the chiral catalytic system (B) in the presence of diethynylbenzene(DEB) as a cross-linking agent, was insoluble in any solvents.[7] (+)-Poly(**2**) (no.3) synthesized by HSSP of **2** by using the chiral catalytic system ((B) in Scheme 1) was insoluble in toluene, THF, and methanol.[8] As a reference, one-handed chiral helical polyphenylacetylene((-)-poly((-)-**PSPA**), see Chart 1) having chiral pendant groups and no polar functional groups like hydroxyl groups was prepared by polymerization of the corresponding chiral monomer((-)-**PSPA**) by using an achiral amine(TEA, see Chart 1) (no.4).[9]



Scheme 1. Preparation of one handed helical poly(**1**, **2**) (cocatalyst) by using the catalytic systems (A): $Rh[C(C_6H_5)=C(C_6H_5)_2](nbd)(4\text{-}FC_6H_4)_3P$ in pyridine and chiral induction[6], and (B): $[Rh(nbd)Cl]_2$ and (*R*)- or (*S*)-PEA in toluene.

Since polymers prepared by the HSSP of achiral monomers with two hydroxyl groups such as **1** and **3** have usually high *Mw'*s (=10^5-10^7) and good solubility in toluene and THF and insolubility in methanol(Table 4), the polymers can be easily and completely separated with the above polymer catalysts by their differences in solubilities. The solubilities are summarized in Table 2.

Table 1. Preparation of one handed helical poly(phenylacetylene) ((+)- or (-)-poly(**1** and **2**)) used as chiral cocatalysts for the helix-sense-selective polymerization (HSSP) of achiral phenylacetylenes(**1**, **3** and **4**)[a]

No.	**Feed**			**Product**				
	Monomer	**Catalytic system**	**Chiral source**	**Polymer**	**Yield /%**	**M_w[b] /10^5**	**M_w/M_n[b]**	**g_{308} /×10^{-3} [c]**
1	**1**	(A)	(*R*)-**PEA**[d]	Low M_w (-)-poly(**1**)	47	0.28	1.4	-8.8
2	**1&DEB**	(B)	(*R*)-**PEA**	Cross-linked (-)-poly(**1**)	95	-[e]	-[e]	-[e]
3	**2**	(B)	(*S*)-**PEA**	(+)-poly(**2**)	60	-[e]	-[e]	-[e]
4	(-)-**PSPA**	(C)[f]	(-)-**PSPA**[g]	(-)-poly((-)-**PSPA**)	94	25	1.9	6.1[h]

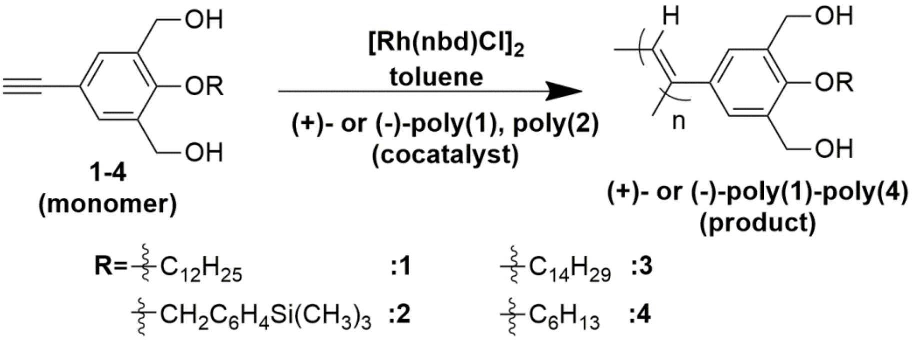
[a] For the codes, see Chart 1 and Scheme 1.[b] By GPC based on PSt standard (eluent: THF). [c] $g_{308} = [\theta]_{308} / (3300\times\varepsilon)$ at 308nm in THF (c = 0.001 mol/L). [d] Not HSSP followed by chiral induction. See Notes 6. [e] Insoluble in THF. [f] $[Rh(nbd)Cl]_2$ and TEA in toluene. [g] Not HSSP. [h] At 308nm.

Table 2. Solubility of the cocatalyst polymers(Tab.1) for the HSSP

No.[a]	**Polymer**[b] **(see Table 1)**	**Solubility**[c]			
		Toluene	**THF**	**Methanol**	**DMF**
1	Low *Mw* (-)-poly(**1**)	+	+	+	+
2	Cross-linked (-)-poly(**1**)	-	-	-	–
3	(+)-poly(**2**)	-	-	-	+
4	(-)-poly((-)-**PSPA**)	+	+	-	+

[a] The numbers correspond to those in Table 1. [b] For the codes, see Scheme 1 and Chart 1. [c] +: soluble, -: insoluble, ±: partly soluble.

By using the three kinds of one-handed helical chiral polymers described above as chiral cocatalysts (Table 1), we tried to carry out the HSSP of three achiral monomers with two hydroxyl groups (**1**, **3**, and **4**) (Scheme 2). The results are shown in Table 3, nos. 1-3 and 8-10. As a reference, polymerization of **1** and SPA by using the chiral amine ((*R*)-PEA), the achiral amine (TEA), and no amines as cocatalysts were carried out (nos. 5-7 and 11-13).



Scheme 2. Helix-sense-selective polymerization(HSSP) of achiral phenyl-acetylenes (**1-4**) by using one-handed helical poly(phenylacetylene)s (poly(**1**) or poly(**2**)) as chiral cocatalysts.

As shown in Figure 1 and Table 3, nos. 1 and 2, because the product poly(**1**)s showed CD peaks, which was originated from the main chain chirality, similar to poly(**1**)s prepared by HSSP of **1** by using (*R*)-PEA(Figure 2 and Table 3, no. 5)[1], it was found that the two kinds of one-handed helical (-)-poly(1)s functioned as the chiral cocatalysts for the HSSP. This is the first example of the HSSP catalyzed by chiral polymers prepared by the HSSP. In addition, since in this case, the HSSP of an achiral monomer **1** was catalyzed by the corresponding chiral polymer of 1 ((-)- poly(**1**)), it is very important and attractive because the phenomenon includes possibility of self-catalyzed HSSP.

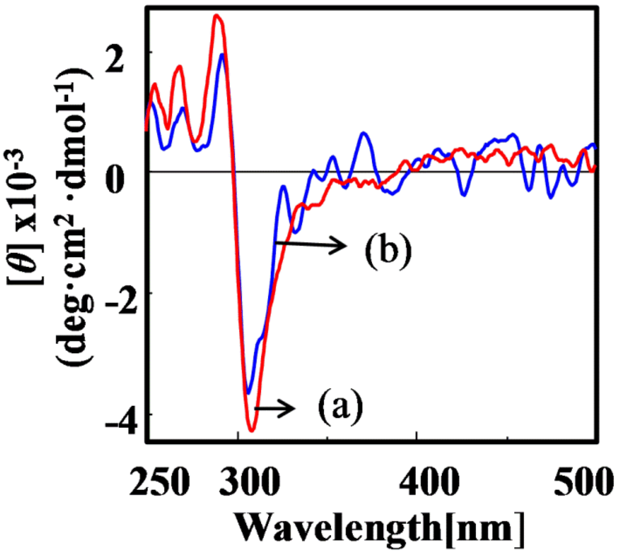


Figure 1. CD spectra of (-)-poly(**1**)s prepared by using (a): low M_w (-)-poly(**1**) and (b): cross-linked (-)-poly(**1**) as chiral cocatalysts.

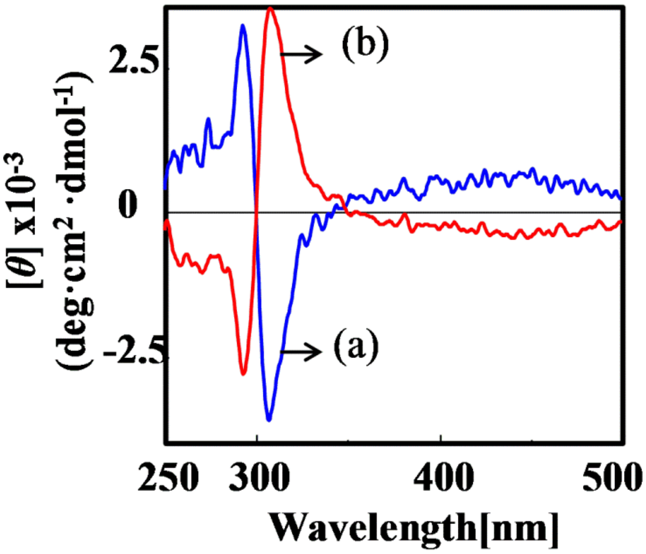


Figure 2. CD spectra of (-)- and (+)-poly(**1**) prepared by using (a): (*R*)-PEA or (b): (*S*)-PEA as chiral cocatalysts, respectively.

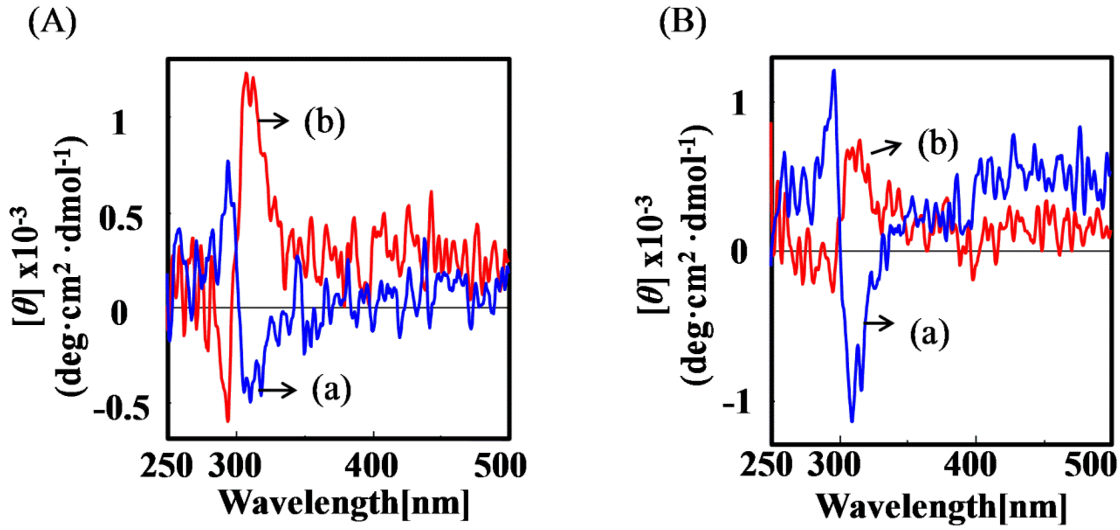


Figure 3. CD spectra of (A) (-)- and (+)-poly(**1**) and (B)(-)- and (+)-poly(**3**) prepared by using (a) (-)- and (b) (+)-poly(**2**) as chiral cocatalysts, respectively.

Similar to the two (-)-poly(**1**)s (Table 3, nos.1 and 2), (+)-poly(**2**) also functioned as a chiral cocatalyst for the HSSP of 1 as shown in Figure 3(a), and Table 3, No.3. In addition, (+)-poly(**2**) could catalyze the HSSP of 3 and 4 also. The sign of the CD of the product polymers of **1**, **3**, and **4** could be controlled by the sign of the cocatalysts as shown in Figure 3(A) and (B), and Table 3, Nos.9 and 10. When a (-)-polymer was used for the cocatalyst of HSSP, a (-)-polymer was obtained and vice versa. It indicates that the helical sense of the catalyst polymers could control the helical sense of the formed polymers.

To estimate their chiral induction efficiency, *g*-values at 308nm of the product (-)-poly(**1**) and the ratio (g / g_{PEA}) of the *g*-values to that (g_{PEA}) in the case of (*R*)-PEA used as a cocatalyst (No.5 in Table 3). The relative *g*-values(g / g_{PEA}) of (-)-poly(**1**) for Nos. 1 and 2 were 80-90% and almost the same as that for No.5 indicating high induction efficiency. Because the enatiomeric excesses(%ee) of the catalyst polymers are thought to be less than 100%ee and the %ee of (*R*)-PEA is about 100%ee, the efficiency is very high. The relative *g*-values (g / g_{PEA}) of the product (+)-poly(**1**) was also high(95%) when (+)-poly(**2**) was used as a cocatalyst (No. 3).

Table 3. Helix-sense-selective polymerization(HSSP) of achiral phenylacetylenes(**1**, **3** and **4**) by using one-handed helical poly(phenylacetylene) ((-)- or (+)-poly(**1**), poly(**2**)) as chiral cocatalysts[a]

No.	**Monomer**[b]	**Cocatalyst**[b]	**[Cocatalyst] [Monomer] /wt%**	**Yield /%**	**M_w**[c] **/10^5**	**M_w/M_n**[c]	**g_{308}**[d] **/×10^{-3}**	**g_{308}/g_{PEA}**[e] **/%**
1	**1**	Low M_w (-)-poly(**1**)	0. 85	35	3.5	2.1	-1.6	80
2		Cross-linked (-)-poly(**1**)	5.0	37	3.3	2.3	-1.8	90
3		(+)-poly(**2**)	0.50	41	1.8	1.7	1.9	95
4		(-)-poly((-)-**PSPA**)	5.0	9.7	15	2.3	0	0
5		(*R*)-**PEA**	0.50	68	16	2.1	-2.0	100(=g_{PEA})
6		**TEA**	0.50	72	69	11	0	0
7		none	-	11	3.1	2.0	0	0
8	**3**	(+)-poly(**2**)	0.50	2.0	7.1	2.1	2.2	46
9	**4**	(-)-poly(**2**)	0.50	7.8	5.3[f]	2.4[f]	-0.46[f]	36[f]
10		(+)-poly(**2**)	0.50	2.0	9.5[f]	2.4[f]	0.39[f]	30[f]
11	**SPA**	(*R*)-**PEA**	0.50	79	1.8	1.6	0	0
12		**TEA**	2.0	88	5.0	1.6	0	0
13		none	-	0	-	-	-	-

[a] [Monomer]= 0.10M, [Monomer]/[$[\text{Rh(nbd)Cl}]_2$]=200, in toluene at 28˚C for 24h. [b] For the codes, see Chart 1 and Scheme 2. [c] By GPC based on PSt standard (eluent: THF). [d] $g_{308} = [\theta]_{308} / (3300 \times \varepsilon)$ at 308 nm in THF (c = 0.0010 mol/L). [e] The relative *g* values to that of No.5. [f] For the soluble part.

Table 4. Solubility product polymers(Table 3) by the HSSP

No.[a]	Polymer (see Table 3)	Solubility[b]			
		Toluene	THF	Methanol	DMF
1-7	Poly(**1**)	+	+	-	-
8	Poly(**3**)	+	+	-	-
9-10	Poly(**4**)	±	±	-	-

[a] The numbers correspond to those in Table 3. [b]+: Soluble, -: insoluble, ±: partly soluble.

In polymerization of substituted acetylenes with a rhodium complex, amines or alcohols should coordinate to the dimeric rhodium complex to form a monomeric complex that acts as an initiator(Scheme S1a)).[10] Therefore, in order that a compound functions as the initiator, the compound should have functional groups which can coordinate the rhodium complex. In addition when *chiral* amines or alcohols are used, the polymerization becomes HSSP (Scheme S1b)) because the corresponding *chiral* complex functions a *chiral* initiator. The mechanism is also supported by the following experimental facts. A monomer **SPA**(Chart 1)(Nos.11-13), which has no chiral groups and no functional groups coordinating to rhodium, could not be polymerized only by the rhodium dimer ($[Rh(NBD)Cl]_2$)(No.13) and could be polymerized when an amine(TEA) (Chart 1) (No.12) was added to the dimer. Even when a chiral amine ((*R*)-PEA) was added (No.11) to the polymerization system of SPA by $[Rh(NBD)Cl]_2$, no HSSP happened because the helical conformation of the resulting poly(**SPA**) was not static nor stable but dynamic and unstable in solution. On the other hand, **1**, which has no chiral groups and functional groups (hydroxyl groups) coordinating to the rhodium, could be polymerized only by the rhodium dimer ($[Rh(NBD)Cl]_2$) (No.7) different from SPA (No.13). It may be caused by the coordination of the hydroxyl groups in the monomer **1** to the rhodium dimer. Therefore, when a chiral amine ((*R*)-PEA), which can coordinate to rhodium, was used, HSSP of **1** occurred because the one-handed helical conformation of the resulting poly(**1**) was static and stable due to the intramolecular hydrogen bonds we reported and concluded before.[1] Therefore, when (-)-poly((-)-**PSPA**) (Chart 1), which has chiral groups and no functional groups coordinating to the rhodium, was added to the polymerization system of **1**, polymerization can start but no HSSP occurred (No.4). Because HSSP was catalyzed by (-)-poly(1) having hydroxyl groups different from (-)-poly((-)-**PSPA**), the mechanism proposed above is supported.

It is known that the one-handed helical polymers such as (-)-poly(**1**), the HSSP products, were stable in nonpolar solvent like toluene at room temperature. Even if chiral compounds such as (*R*)-PEA were added, the chiral structure showed no change as we reported before.[1] Therefore, the chiral additives functioned as a ligand to the rhodium complex.

1.5 Conclusions

In conclusion, we found and confirmed the HSSP cocatalyzed by the chiral polymers, whose chirality was caused by solely by the conformational chirality, prepared by the HSSP cocatalysed by chiral amines. This is the first example of the HSSP catalyzed by chiral polymers. Because the phenomenon includes possibility of self-catalyzed HSSP, further investigation will be carried out.

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[6] Only about the low ***Mw*** (-)-poly(**1**), the one-handed helicity was induced by heating the racemic poly(**1**), produced by the achiral catalytic system(A), in a polar solvent in the presence of (*R*)-PEA, because the chiral catalytic system(B) could not produce low ***Mw*** (-)-poly(**1**)(See Supporting information for the detail procedure and this new method will be discussed elsewhere.)

[7] Because HSSP of **1** by (*R*)-PEA gave (-)-poly(**1**), it was named as cross-linked (-)-poly(**1**) in spite of no CD data due to its insolubility.

[8] Because HSSP of **1** by (*S*)-PEA gave (+)-poly(**1**), it was named as (+)-poly(**2**), although the CD could not be measured due to its insolubility.

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[10] M.Tabata, W. Yang, K. Yokota, *Polym. J*, **1990**, *22*, 1105.

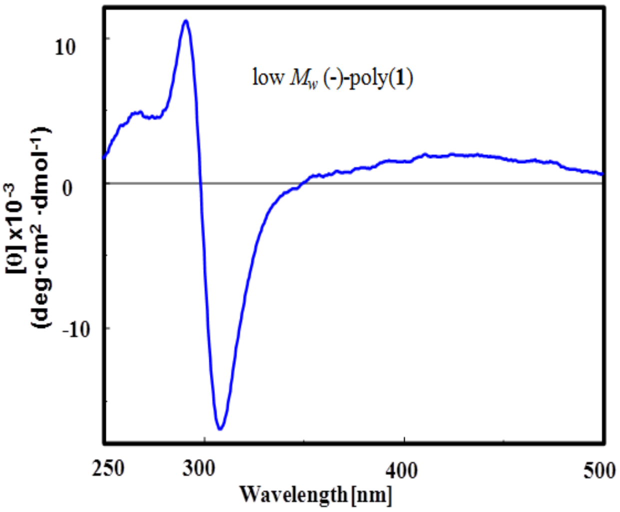


Figure S1. CD spectrum of low M_w (-)-poly(**1**) (Table 1, No.1).

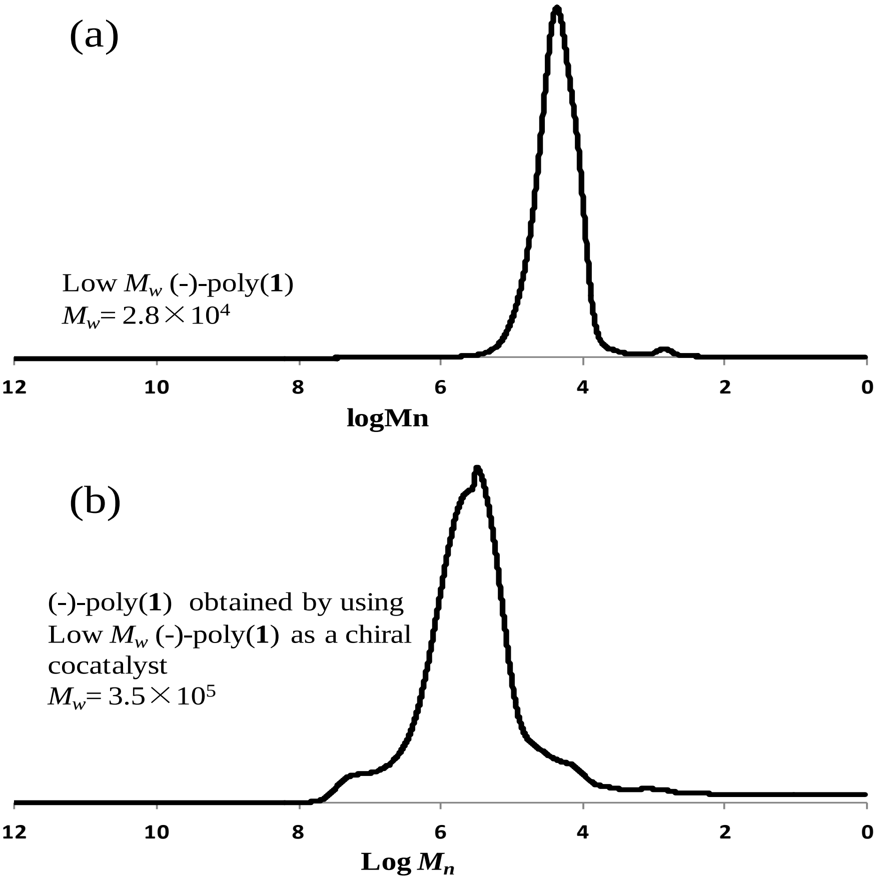


Figure S2. GPC of (a): low M_w (-)-poly(**1**) (Table 1, No.1) and (b): (-)-poly(**1**) obtained by using Low M_w (-)-poly(**1**) as a chiral cocatalyst (Table 3, No.1).

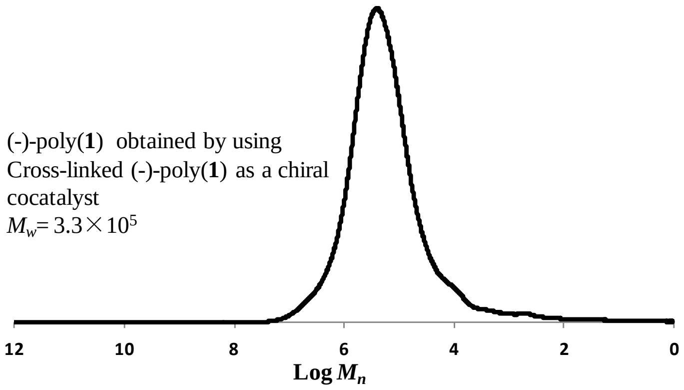


Figure S3. GPC of (-)-poly(**1**) obtained by using cross-linked (-)-poly(**1**) as a chiral cocatalyst (Table 3, No.2)

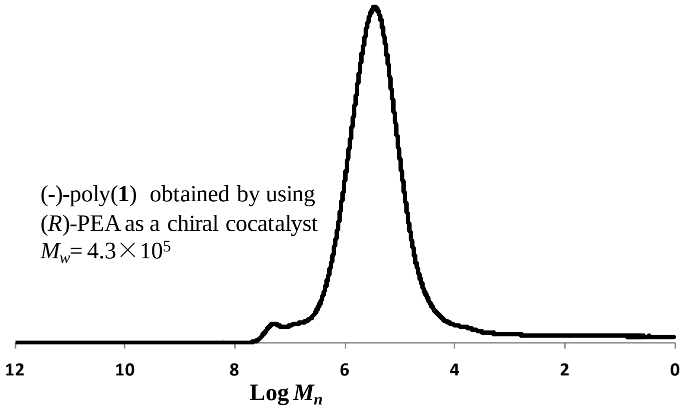


Figure S4. GPC of (-)-poly(**1**) obtained by using (*R*)-PEA as a chiral cocatalyst (Table 3, No.5).

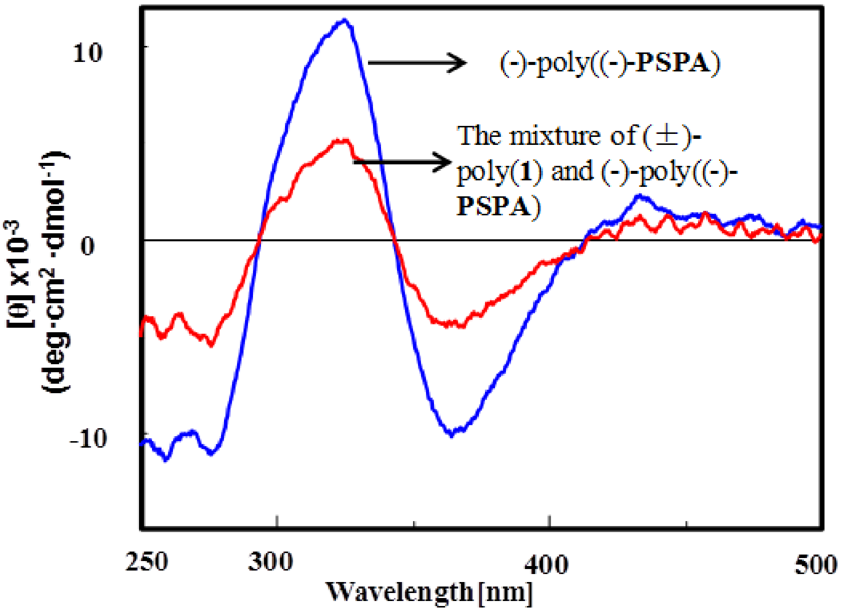


Figure S5. CD spectra of (-)-poly((-)-**PSPA**) (Table 1, No.5), and the mixture of (±)- poly(**1**) (product) and (-)-poly((-)-**PSPA**) (cocatalyst) (Table 1, No.4 and Table 3, No.4).

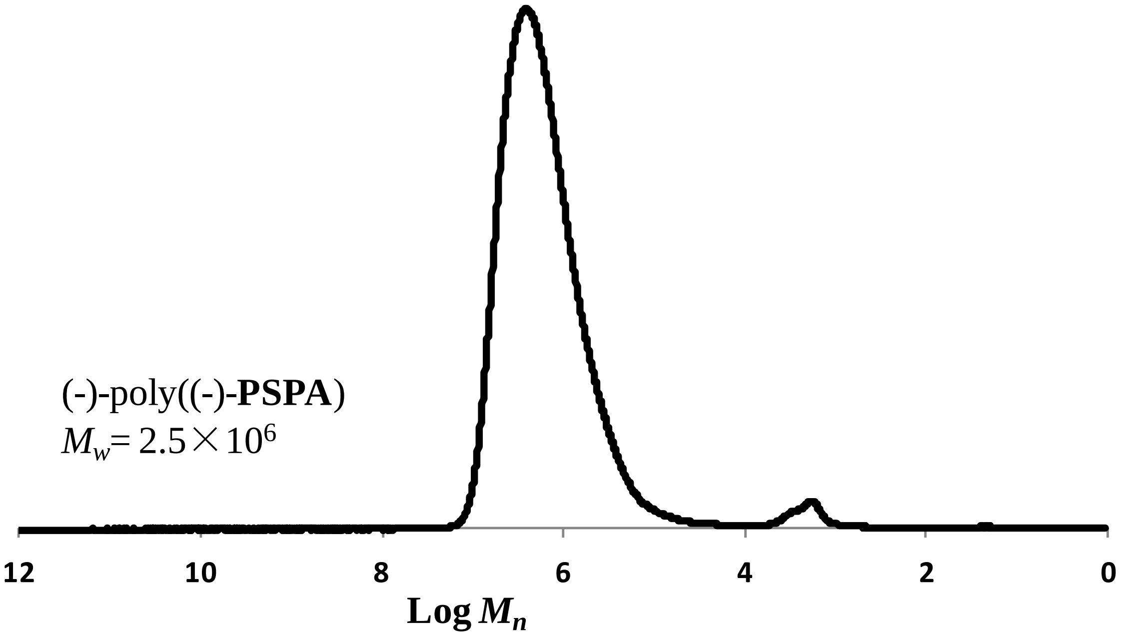


Figure S6. GPC of (-)-poly((-)-**PSPA**) (Table 1, No.4).

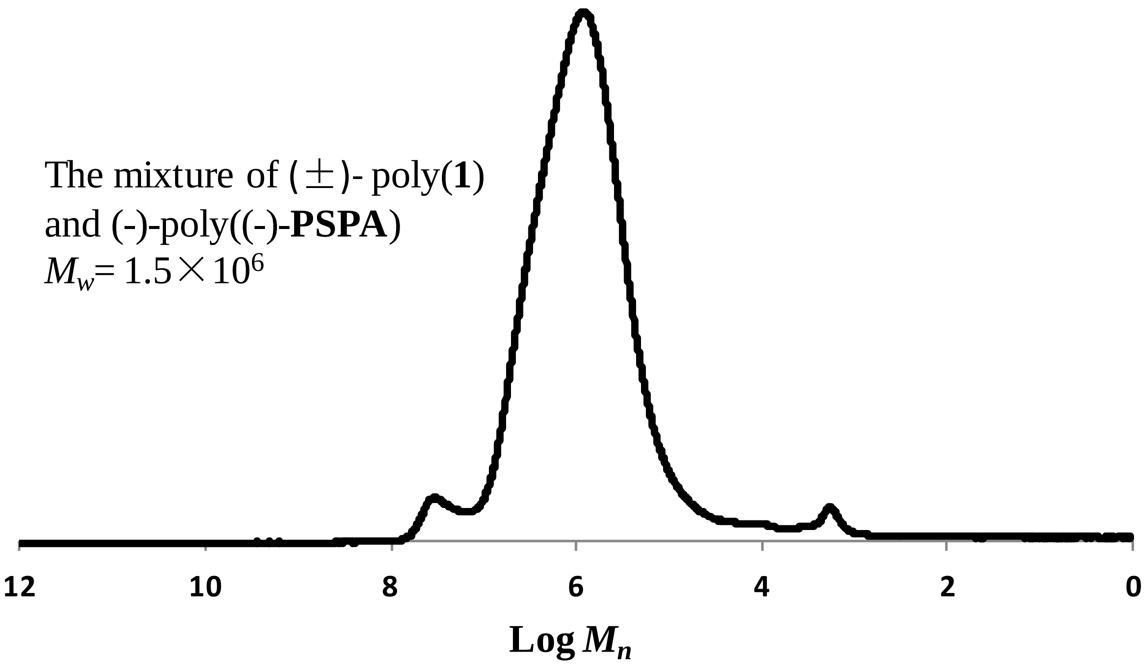
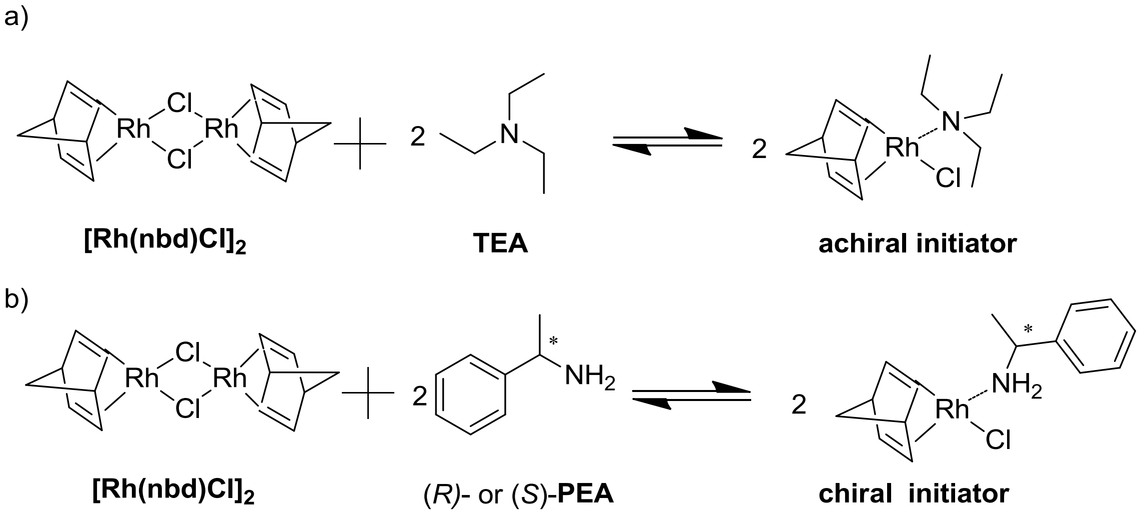


Figure S7. GPC of the mixture of (±)- poly(**1**) and (-)-poly((-)-**PSPA**) (less than 5.0wt%) (Table 3, No.4).



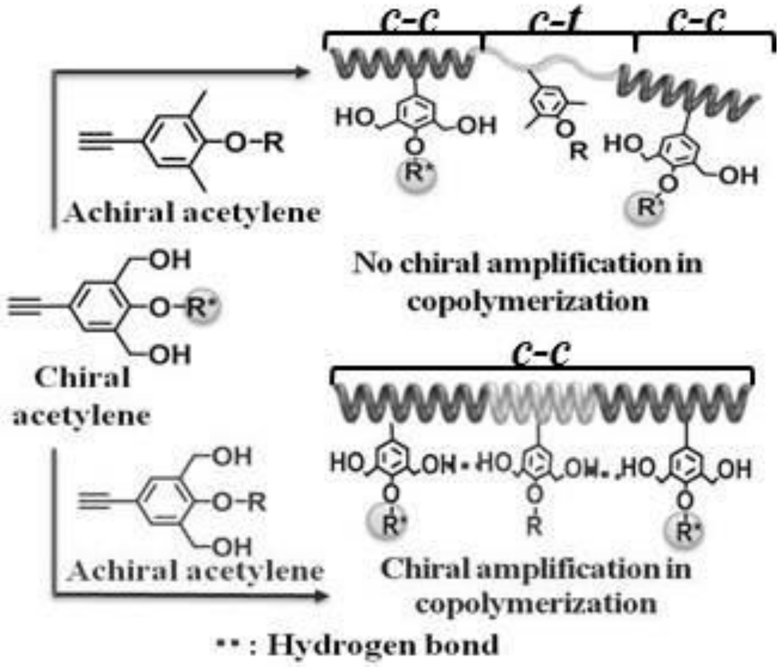
Scheme S1. Formation of rhodium complexes coordinated by a) triethylamine (TEA) and b) (*R*)- or (*S*)-phenylethylamine(PEA)

Chapter 2

Chiral amplification during asymmetric-induced copolymerization of phenylacetylenes with tight cis - cisoidal main chains

2.1 Abstract

A novel phenylacetylene (**1**) having two hydroxyl groups and a chiral pinanyl group together with the other three related phenylacetylenes has been synthesized and (co)polymerized by using an achiral catalytic system. Among the four monomers, only **1** is suitable to the asymmetric-induced polymerization (**AIP**). Chiral amplification phenomenon is only observed in the copolymerization of **1** with an achiral phenylacetylene having two hydroxyl groups (**3**). The tight helical cis-cisoidal main chain formed by making intramolecular hydrogen bonds between the hydroxyl groups in the copoly(**1**/**3**) enhances the efficiency of chiral induction and as a result chiral amplification phenomenon is observed during the copolymerization.

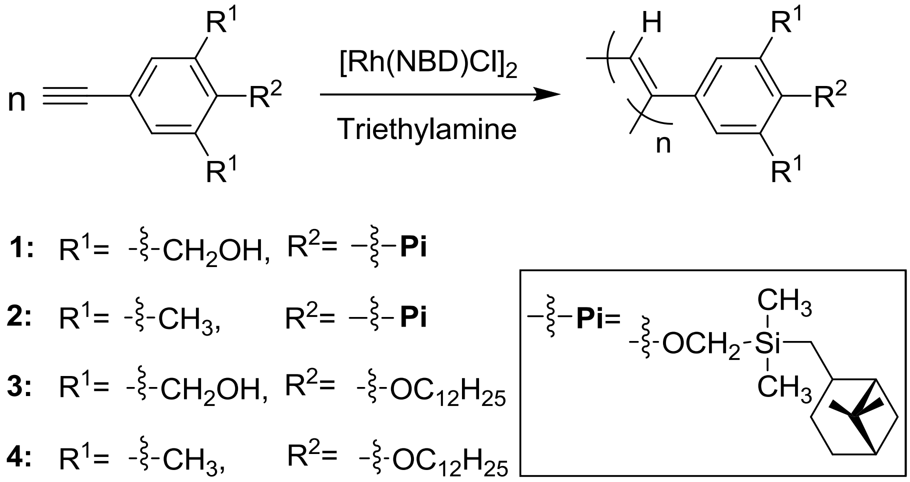


2.2 Introduction

To produce optically active compounds effectively, the chiral amplification could be an unique and important interesting phenomenon and is useful for the development of one of the ideal methods.[1] Previously, chiral amplification had been reported in several fields such as dynamic chiral helical polymers,[2] supramolecular chirality,[3] optical resolution,[4] asymmetric catalysis and liquid crystalline.[5,6] Dynamic helical conformations of the polymers such as polyisocyanates, polysilanes, polyacetylenes, and some foldamer-based helical polymers had an extremely high sensitivity to a chiral environment.[7] One-handed helical senses induced through covalent or noncovalent bonding with chiral biases have been reported in a variety of artificial helical polymers.[7,8,9] The chiral amplification following "sergeants and soldiers" and "majority rule" effects have also been observed in a variety of helical polymers, such as polysilanes and polyacetylenes.[6,7,8,10]

For a typical dynamic helical polymer,[7]Polyacetylene, prepared by rhodium catalyst, such as $[Rh(nbd)Cl]_2$(nbd: norbornadiene), its main-chain conformation can be cis-transoidal [14-21] or cis-cisoidal [22-27] depending on the chemical structure of the monomer. Our laboratory have developed two synthetic routes for one-handed helical poly(substituted acetylene)s. One is asymmetric-induced polymerization(**AIP**) in which chiral substituted acetylenes are used as a monomer to afford dynamic helical cis-transoidal polyacetylenes.[11-13] The other is helix-sense-selective polymerization(**HSSP**) in which achiral acetylene monomers having two hydroxyl groups and a chiral initiator are used to afford static helical cis-cisoidal polyacetylenes.[26-31] Chiral amplification phenomena has been widely studied and observed in a variety of dynamic helical cis-transoidal polyacetylenes.[7] However, there were no reports regarding chiral amplification during asymmetric polymerization(**AIP**) to yield static one-handed helical cis-cisoidal polyacetylenes and the effect of main-chain conformation on the chiral amplification.

In this work, we designed and synthesized a phenylacetylene (**1**, Scheme 1) having two hydroxyl groups and a chiral pinanyl group together with the three other related phenylacetylenes (**2-4**, Scheme 1). The phenylacetylenes were homo- and copolymerized. We measured the CD and UV-vis spectra of the resulted polymers in solutions.



Scheme 1. Monomer structures and their polymerization by the rhodium catalytic system.

Here, we report chiral amplification during asymmetric polymerization to yield static helical cis-cisoidal polyacetylenes and discuss effect of the tight helical backbone on chiral amplification in **AIP** of phenylacetylenes.

2.3 Experimental

2.3.1 Materials

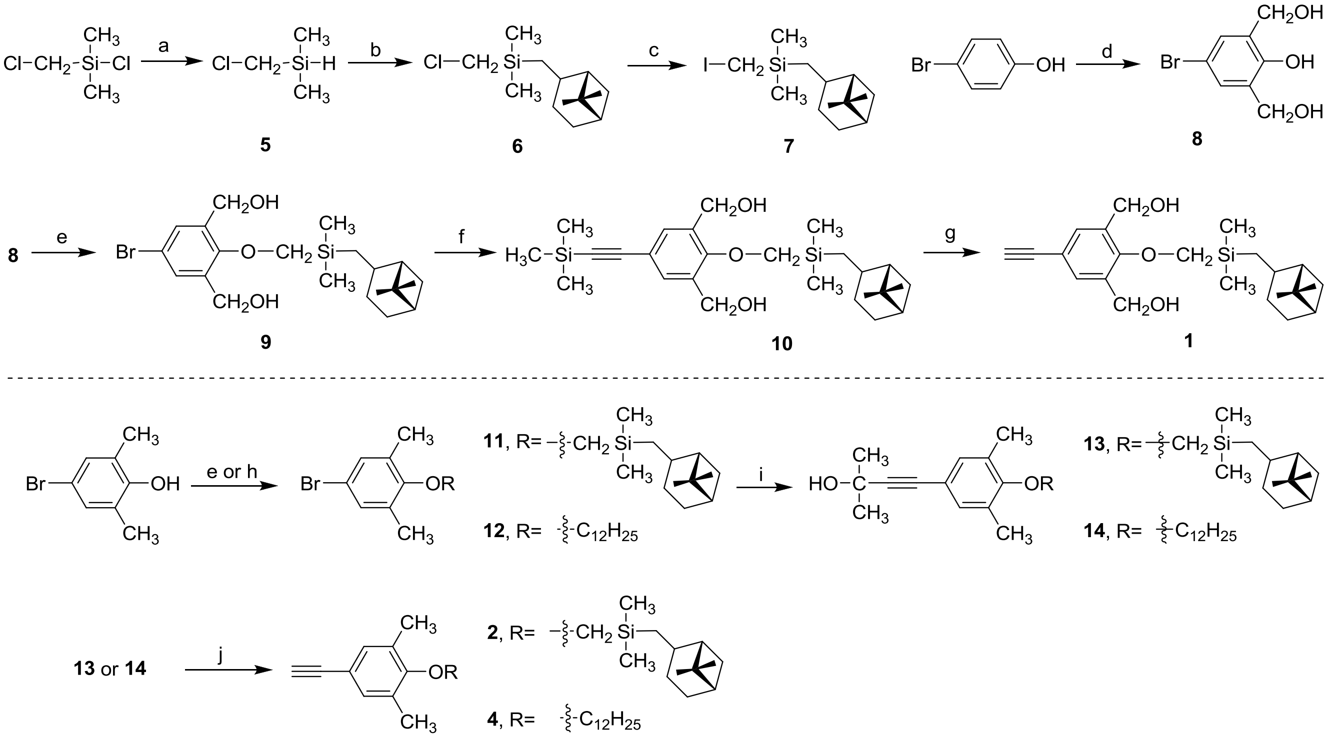
All the solvents including triethylamine (TEA) used for monomer synthesis and polymerization were distilled as usual. (-)-*β*-Pinene [97% enantiomeric excess (%ee)] and chloromethyldimethylchlorosilane, used as starting materials, were purchased from Aldrich Chemical Co., Inc. The polymerization initiator,

$[Rh(NBD)Cl]_2$ (NBD=2,5-norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received.

2.3.2 Measurements

Average molecular weights (*Mn* and *Mw*) were estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD 2095, and two polystyrene gel columns (Shodex KF 807L). NMR spectra were recorded on a JEOL GSX 270 at 270 MHz for ^{1}H. IR spectra were recorded on a JASCO FTIR 4200 spectrometer. CD spectra were measured with a JASCO J 720 spectropolarimeter.

2.3.3 Synthetic procedures of all the monomers



Scheme 2. Synthesis of monomers **1**, **2**, and **4**.

a: $LiAlH_4$ and dimethyl ether; b: (-)-*β*-Pinene, $H_2PtCl_6\cdot 6H_2O$, and toluene; c: NaI and acetone; d: CH_2O, KOH, and 2-propanol; e: **7**, K_2CO_3, and acetone; f: PPh_3, CuI, $PdCl_2(PPh_3)_2$, trimethylsiliylacetylene, and Et_3N; g: K_2CO_3 and methanol; h: 1-bromododecane, K_2CO_3, and acetone; i: PPh_3, CuI, $PdCl_2(PPh_3)_2$, 3-hydroxy-3-methyl-1-butyne, and Et_3N; j: NaH and toluene.

Monomers **1**, **2**, and **4** were synthesized according to the synthetic route shown in Scheme S1. Monomer **3** was synthesized according to a method we reported previously.[26] All the following reaction procedures were conducted under dry nitrogen.

Chloromethyldimethylsilane (**5**)

To a mixture of diethyl ether (150 mL) and lithium aluminum hydride (8.65g, 228 mmol), chloromethyldimethylchlorosilane (100mL, 760mmol) was added dropwise at 0 ℃. The mixture was stirred for 1h at room temperature. To the mixture, deionized water (50 mL) was added dropwise. After the mixture was filtered, diethyl ether was removed by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by distillation at 80 ℃ (ambient pressure) to give **5** as a clear liquid. Yield: 50.1% (41.4g). ^1H NMR (270MHz, $CDCl_3$, TMS,): 4.05 (sept, 1H, $(CH_3)_2Si\textit{H}$), 2.87(d, 2H, $ClC\textit{H}_2Si(CH_3)_2$), 0.210 (d, 6H, $HSi(C\textit{H}_3)_2$).

Chloromethyldimethyl(10-pinanyl)silane (**6**)

According to a similar manner we reported previously **6** was synthesized.[3f] The crude product of **6** was purified by vacuum distillation at 116 ℃ (4.0 mmHg) to give **6** as a clear liquid. Yield: 74.8% (69.8g). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 2.77 (s, 2H, $ClCH_2Si(CH_3)_2$), 1.21 (s, 3H, *gem*-CH_3), 0.819(s, 3H, *gem*-CH_3), 2.15~0.550(m, 11H, C*H* and CH_2 in pinane), 0.0750(s, 6H, $ClCH_2Si(CH_3)_2$).

Iodomethyldimethyl(10-pinanyl)silane (**7**)

To an acetone solution (150mL) of sodium iodide (47.0g, 314mmol), **6** (69.8g, 285mmol) was added dropwise at room temperature. The mixture was stirred for 5h at room temperature. After filtration and concentration, the crude product was purified by distillation at 125 ℃ (4.0mmHg) to give **7** as a clear liquid. Yield: 97.1% (93.1g). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 2.01 (s, 2H, $ICH_2Si(CH_3)_2$), 1.18 (s, 3H, *gem*-CH_3), 0.819(s, 3H, *gem*-CH_3), 2.08~0.624(m, 11H, C*H* and CH_2 in pinane), 0.141(s, 6H, $ICH_2Si(CH_3)_2$).

4-Bromo-2, 6-bis (hydroxymethyl)-1-phenol (**8**) [26]

According to the literature procedure **8** was prepared. Yield: 52.3% (106g). ^{1}H-NMR (270MHz, DMSO-d_6,): 8.76 (s, 1H, PhO*H*), 7.29 (s, 2H, Ph*H*), 5.31 (t, 2H, CH_2OH), 4.51 (d, 4H, CH_2OH).

4-Bromo-2,6-bis(hydroxymethyl)-1-{dimethyl(10-pinanyl)silylmethoxy}benzene (**9**)

To a mixture of **8** (15.0g, 64.4mmol), potassium carbonate (44.5g, 322mmol), and 7 (25.3mL, 96.6mmol), acetone (200mL) was added with a syringe. The mixture was stirred and refluxed for 50 h at 60℃. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **9** as a white solid. Yield: 58.1% (16.5g). Rf = 0.31 (ethyl acetate / hexane = 1/4). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.48 (s, 2H, $(CH_3)_2SiCH_2OPh\text{-}H$), 4.68 (s, 4H, $Ph(CH_2OH)_2$), 3.58(s, 2H, $PhOCH_2Si(CH_3)_2$), 1.19 (s, 3H, *gem*-CH_3), 0.830(s, 3H, *gem*-CH_3), 2.20~0.697(m, 11H, C*H* and CH_2 in pinane), 0.194(s, 6H, $OCH_2Si(CH_3)_2$).

4-(Trimethylsilylethynyl)-2,6-bis(hydroxymethyl)-1-{dimethyl(10-pianyl)silylmethoxy}benzene (**10**)

A mixture of **9** (16.5g, 37.4mmol), triphenylphosphine (294mg, 1.12mmol), copper (I) iodide (213mg, 1.12mmol), bis(triphenylphosphine)palladium(II) dichloride (394mg, 0.561mmol) and trimethylsilylacetylene (7.78mL, 56.2mmol) in triethylamine (150mL) was refluxed for 24 h. After the mixture was filtered, the solvent was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **10** as a brown liquid. Yield: 85.0% (14.6g). Rf = 0.35 (ethyl acetate/hexane = 1/4). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.46 (s, 2H, $(CH_3)_2SiCH_2OPh\text{-}H$), 4.67 (s, 4H, $Ph(CH_2OH)_2$), 3.61(s, 2H, $PhOCH_2Si(CH_3)_2$), 1.19 (s, 3H, *gem*-CH_3), 0.829(s, 3H, *gem*-CH_3), 2.16~0.690(m, 11H, C*H* and CH_2 in pinane), 0.237(s, 9H, $C{\equiv}CSi(CH_3)_3$), 0.193(s, 6H, $OCH_2Si(CH_3)_2$).

4-Bromo-2,6-dimethyl-1-{dimethyl(10-pinanyl)silylmethoxy}benzene (**11**)

A reaction and purification similar to those for **9** were run with 4-bromo-2,6-dimethyl-1-phenol instead of **8** to give **11** as a clear liquid. Yield: 50.3% (10.2g). Rf = 0.3 (hexane). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.12 (s, 2H, $(CH_3)_2SiCH_2OPh$-*H*), 3.43(s, 2H, $PhOC\mathit{H}_2Si(CH_3)_2$), 2.16 (s, 6H, $Ph(C\mathit{H}_3)_2$), 1.19 (s, 3H, *gem*-$C\mathit{H}_3$), 0.828(s, 3H, *gem*-$C\mathit{H}_3$), 2.19~0.691(m, 11H, C*H* and $C\mathit{H}_2$ in pinane), 0.174(s, 6H, $OCH_2Si(C\mathit{H}_3)_2$).

4-Bromo-2,6-dimethyl-1-dodecyloxybenzene (**12**)

A reaction and purification similar to those for **11** were run with bromododecane instead of **7** to give **12** as a clear liquid. Yield: 92.9% (17.1g). Rf = 0.40 (ethyl acetate: hexane = 1/20). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.13 (s, 2H, $C_{12}H_{25}OPh$-*H*), 3.71(t, 2H, $PhOC\mathit{H}_2C_{11}H_{23}$), 2.24 (s, 6H, $Ph(C\mathit{H}_3)_2$), 1.76 (tt, 2H, $PhOCH_2C\mathit{H}_2CH_2$), 1.26~1.51 (m, 18H, $(C\mathit{H}_2)_9CH_3$), 0.856 (t, 3H, $CH_2C\mathit{H}_3$).

4-(3-Hydroxy-3-methyl-1-butynyl)-2,6-dimethyl-1-{dimethyl(10-pinanyl)silylmethoxy}benzene (**13**)

According to a method similar to our reported method, **13** was synthesized.[5a] The crude product was purified by silica-gel column chromatography to give **13** as a orange liquid. Yield: 72.8% (7.51g). Rf = 0.28 (ethyl acetate / hexane = 1/9). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.08 (s, 2H, $(CH_3)_2SiCH_2OPh$-*H*), 3.45(s, 2H, $PhOC\mathit{H}_2Si(CH_3)_2$), 2.21 (s, 6H, $Ph(C\mathit{H}_3)_2$), 1.97(S, 1H, $C(CH_3)_2O\mathit{H}$), 1.60(s, 6H, $HOC(C\mathit{H}_3)_2$), 1.19 (s, 3H, *gem*-$C\mathit{H}_3$), 0.825(s, 3H, *gem*-$C\mathit{H}_3$), 2.19~0.682(m, 11H, C*H* and $C\mathit{H}_2$ in pinane), 0.174(s, 6H, $OCH_2Si(C\mathit{H}_3)_2$).

4-(3-Hydroxy-3-methyl-1-butynyl) -2,6-dimethyl -1-dodecyloxybenzene (**14**)

A reaction and purification similar to those for **13** were run with **12** instead of **11** to give **14** as a yellow solid. Yield: 84.1% (14.5g). Rf = 0.21 (ethyl acetate: hexane = 1/9). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.09 (s, 2H, $C_{12}H_{25}OPh\text{-}\mathit{H}$), 3.73(t, 2H, $PhOC\mathit{H}_2C_{11}H_{23}$), 2.23(s, 6H, $Ph(C\mathit{H}_3)_2$), 1.97(S, 1H, $C(CH_3)_2O\mathit{H}$), 1.76 (tt, 2H, $PhOCH_2C\mathit{H}_2CH_2$), 1.56(s, 6H, $HOC(C\mathit{H}_3)_2$),1.26~1.51 (m, 18H, $(C\mathit{H}_2)_9CH_3$), 0.856 (t, 3H, $CH_2C\mathit{H}_3$).

4-{Dimethyl(10-pinanyl)silylmethoxy}-3,5-bis(hydroxylmethyl)phenylacetylene (**1**)

A mixture of **10** (14.6g, 31.8mmol), potassium carbonate (440mg, 3.18mmol), and methanol (150mL) was stirred for 15h at room temperature. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **1** as a white solid. Yield: 52.8% (6.49g). Rf = 0.25 (ethyl acetate/ hexane = 1/4). $[\alpha]^{20}_{365}$: –4.42 deg dm^{-1} g^{-1} cm^{3}. ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.48 (s, 2H, $(CH_3)_2SiCH_2OPh\text{-}H$), 4.67 (s, 4H, $Ph(CH_2OH)_2$), 3.61(s, 2H, $PhOCH_2Si(CH_3)_2$), 3.03(s, 1H, $C{\equiv}CH$), 1.19 (s, 3H, gem-CH_3), 0.828(s, 3H, gem-CH_3), 2.16~0.691(m, 11H, CH and CH_2 in pinane), 0.197(s, 6H, $OCH_2Si(CH_3)_2$). ^{13}C-NMR (270MHz, $CDCl_3$, TMS,): 158, 133, 132, 118, 83.1, 76.8, 69.9, 60.5, 49.4, 40.7, 39.6, 31.1, 27.0, 26.7, 25.6, 24.8, 23.1, 20.1, –3.51, –3.75. Anal. Calcd for $C_{23}H_{34}O_3Si$: C 71.46, H 8.86; Found: C 71.33, H 8.91.

4-{Dimethyl(10-pinanyl)silylmethoxy}-3,5-dimethylphenylacetylene (**2**)

To a mixture of sodium hydride (730mg, 18.2mmol) and toluene (20mL), a toluene solution (50mL) of **13** (7.51g, 18.2mmol) was added by syringe. The mixture was reflux for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **2** as a clear liquid. Yield: 89.9% (5.78g). Rf = 0.70 (ethyl acetate/ hexane = 1/9). $[\alpha]^{20}_{365}$: –3.78 deg dm^{-1} g^{-1} cm^{3}. ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.15 (s, 2H, $(CH_3)_2SiCH_2OPh$-H), 3.46(s, 2H, $PhOCH_2Si(CH_3)_2$), 2.21 (s, 4H, $Ph(CH_3)_2$), 2.97(s, 1H, C≡CH), 1.19 (s, 3H, gem-CH_3), 0.828(s, 3H, gem-CH_3), 2.16~0.691(m, 11H, CH and CH_2 in pinane), 0.197(s, 6H, $OCH_2Si(CH_3)_2$). ^{13}C-NMR (270MHz, $CDCl_3$, TMS,): 159, 132, 130, 117, 83.8, 75.7, 69.9, 66.4, 49.4, 40.7, 39.6, 31.1, 27.0, 26.7, 25.6, 24.8, 23.1, 21.9, –3.40, –3.61. Anal. calcd for $C_{23}H_{34}O_3Si$: C 77.90, H 9.66; Found: C 77.36, H 8.76.

4-Dodecyloxy-3,5-dimethylphenylacetylene (**4**)

A reaction and purification similar to those for **2** were run with **14** instead of **13** to give **4** as a yellow liquid. Yield: 97.7% (12.0g). Rf = 0.68 (ethyl acetate/ hexane = 1/20). ^{1}H-NMR (270MHz, $CDCl_3$, TMS,): 7.16 (s, 2H, $C_{12}H_{25}OPh$-H), 3.74(t, 2H, $PhOCH_2C_{11}H_{23}$), 2.98(s, 1H, C≡CH), 2.23(s, 6H, $Ph(CH_3)_2$), 1.79 (tt, 2H, $PhOCH_2CH_2CH_2$), 1.26~1.51 (m, 18H, $(CH_2)_9CH_3$), 0.856 (t, 3H, CH_2CH_3). ^{13}C-NMR (270 MHz, $CDCl_3$, TMS,): 156, 133, 131, 117, 83.8, 75.8, 72.5, 32.0, 30.5, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 16.2, 14.2. Anal. calcd for $C_{23}H_{34}O_3Si$: C 84.02, H 10.90; Found: C 83.76, H 10.72.

2.3.4 (Co)polymerization of the monomers.

A typical procedure was as follows. A solution of $[Rh(NBD)Cl]_2$ (1.32mg, 2.80μmol) and triethylamine (TEA) (80.0μl, 0.56mmol) in toluene (10.0mL) was added to a toluene (4.00mL) solution of **1** (540mg, 1.4mmol). The reaction solution was stirred at room temperature for 4h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and dried *in vacuo* to give a red solid.

Other (co)polymerizations were carried out similarly (Scheme 1).

Poly(**1**): ^{1}H-NMR (DMSO d_6/CCl_4=2/5): δ=6.47(br, 2H, Ph-*H*), 5.83(br, cis proton in the main chain), 4.68(br, 4H, CH_2OH), 3.60(br, 2H, $PhOCH_2Si$), 2.18~0.61(br, proton in pinanyl group), 0.13(br, 6H, $Si(CH_3)_2$);

Poly(**2**): ^{1}H-NMR ($CDCl_3$): δ=6.32 (br, 2H, Ph-*H*), 5.75(br, cis proton in the main chain), 3.24(br, 2H, $PhOCH_2Si$), 2.00 (br, 6H, $Ph(CH_3)_2$), 2.16~0.64(br, proton in pinanyl group), 0.13(s, 6H, $Si(CH_3)_2$);

Poly(**4**): ^{1}H-NMR ($CDCl_3$): δ=6.36 (br, 2H, Ph-*H*), 5.73(br, cis proton in the main chain), 3.45(br, 2H, $PhOCH_2$), 2.00 (br, 6H, $Ph(CH_3)_2$), 1.82~1.21 (br, 20H, $OCH_2(CH_2)_{10}CH_3$), 0.89 (br, 3H, $OCH_2(CH_2)_{10}CH_3$);

Copoly(**1**/**3**): ^{1}H-NMR (DMSO d_6/CCl_4=2/5): δ=6.47(br, Ph-*H*), 5.83(br, cis proton in the main chain), 4.63(br, CH_2OH), 3.63-3.32 (br, $PhOCH_2$), 2.10~0.79 (br, proton in dodecyl group and pinanyl group), 0.14(br, $Si(CH_3)_2$);

Copoly(**1**/**4**): ^{1}H-NMR (DMSO d_6/CCl_4=1/5): δ=6.47-6.34(br, Ph-*H*), 5.83(br, cis proton in the main chain), 4.63(br, CH_2OH), 3.65-3.32 (br, $PhOCH_2$), 1.98 (br, Ph(CH_3)$_2$), 2.10~0.81 (br, proton in dodecyl group and pinanyl group), 0.13(br, Si(CH_3)$_2$);

Copoly(**2**/**3**): ^{1}H-NMR (DMSO d$_6$/CCl$_4$=1/5): δ=6.49-6.33(br, Ph-*H*), 5.79(br, cis proton in the main chain), 4.68(br, CH_2OH), 3.6-3.3(br, PhOCH_2), 1.98 (br, Ph(CH_3)$_2$), 2.10~0.79 (br, proton in dodecyl group and pinanyl group), 0.12 (br, Si(CH_3)$_2$);

Copoly(**2**/**4**): ^{1}H-NMR (CDCl$_3$): δ=6.34 (br, Ph-*H*), 5.74(br, cis proton in the main chain), 3.42-3.29(br, PhOCH_2), 2.00 (br, Ph(CH_3)$_2$), 2.2~0.8 (br, proton in dodecyl group and pinanyl group), 0.13 (br, Si(CH_3)$_2$);

For Mw, UV, and CD see Table 1 and Figure 1.

2.4 Results and discussion

2.4.1 Effects of the chemical structures of the monomers (1-4) on the conformation of the main chain of the resulting homopolymers

To discuss the effect of the main-chain conformation on efficiency of chiral induction during **AIP** of the phenylacetylenes, phenylacetylene **1** together with the three other related phenylacetylenes **2**, **3** and **4** having a 3,4,5-trisubstituted phenyl ring (Scheme 1) were synthesized and (co)polymerized (Scheme S1). (The results of homopolymerizations of each monomer are summarized in Table S1.)

As shown in Figure 1 and Table S1, in the four kinds of homopolymers, only poly(**1**) having two hydroxyl groups and a chiral substituent in the monomer unit showed CD signals. This finding indicates that only the homopolymer of **1** took a predominant one-handed helical conformation in the main-chain. The CD active structure of poly(**1**) may be caused by a stable regular conformation supported by their intramolecular hydrogen bonds. Similar to our previous study,[26-31] the UV-vis spectra of poly(**1**) and poly(**3**) having hydroxyl groups showed stronger absorptions around 307nm, and weaker absorptions around 430nm than those of poly(**2**) and poly(**4**) having no hydroxyl groups (Figure 1). These findings indicate that poly(**1**) and poly(**3**) took tight helical cis-cisoidal conformation, poly(**2**) and poly(**4**) took loose helical cis-transoidal conformation, and the spatial distance between the pendant phenyl groups were shorter in poly(**1**) and poly(**3**) than in poly(**2**) and poly(**4**). These were supported by our previous results that the HSSP of **3** having two hydroxyl groups yielded a very rigid polymer having a one-handed helical cis-cisoidal main-chain maintained by intramolecular hydrogen bonds.[26,27]

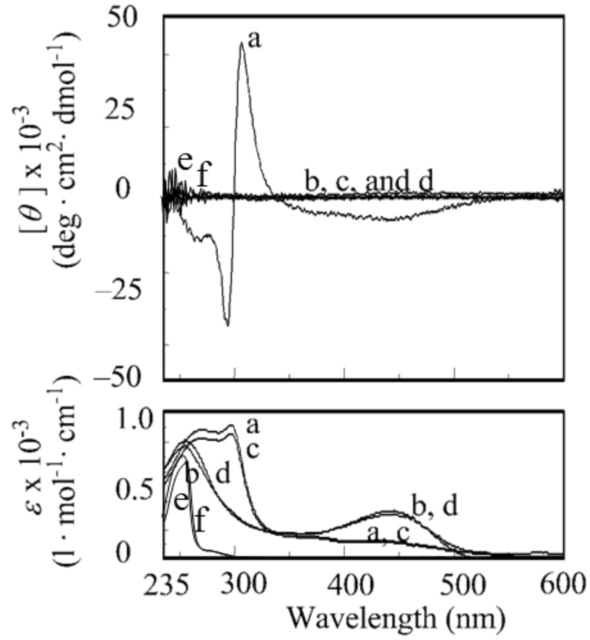


Figure 1. CD and UV-vis spectra in chloroform at 20 ℃ of a:poly(**1**), b:poly(**2**), c:poly(**3**)， d:poly(**4**)，e: monomer **1** and f: monomer **2** at room temperature.

Poly(**2**) was CD inactive unlike poly(**1**), although the corresponding monomers (**1** and **2**) had the same spacer and a chiral pinanyl group. Only the difference between the two monomers was that **1** has two hydroxyl groups and **2** does not have. Therefore, the two hydroxyl groups in the monomer unit were important for making one-handed helical conformation. It may be because the intramolecular hydrogen bonds between the hydroxyl groups in poly(**1**) made the main-chain more rigid and tight and then stabilized the conformation. Since poly(**1**) by the AIP showed CD and UV absorptions similar to the poly(**3**) prepared by the HSSP in our previous study[26-31], one-handed helical conformation of the main chain of poly(**1**) was also thought to be kept by intramolecular hydrogen bonds. This was supported by the fact that the CD signals disappeared and the UV absorption shifted to longer wavelength when a polar solvent was added. The more rigid and tight helical cis-cisoidal main chain of poly(**1**) means that the helical pitch and the spatial distance between the chiral pendant groups in poly(**1**) was shorter than that in poly(**2**). The close spatial position between the chiral pendant groups could control the helical sense of the poly(**1**) more easily.

Since **2** does not have any hydroxyl groups, poly(**2**) had a looser helical cis-transoidal main-chain conformation and a less tight spatial positions between the chiral pendant groups. In addition, the steric effect of the two methyl groups may make spatial position of the chiral pendant groups irregular. It was difficult for the main chain to keep chiral structures because of the loose helical main chain and the irregular spatial position of the pendant groups.

In summary, formation of the one-handed helical main chain of poly(**1**) was realized only by coexistence of the chiral pinanyl groups and the hydroxyl groups in the polymer. The tight helical cis-cisoidal conformation of the main-chain and closer spatial positions of the chiral pendant groups caused by intramolecular hydrogen bonds acted key roles for keeping the one-handed helical structure of the polymer.

2.4.2 Chiral amplification: non-linear effects between the composition and the main chain chirality of the resulting copolymers in copolymerization of

the chiral monomer (1) with the achiral monomer (3) having two hydroxyl groups

The results of four copolymerizations of the chiral monomer **1** with the achiral monomer **3** or **4**, and the chiral monomer **2** with the achiral monomer **3** or **4** are shown in Table 1 and S2~S4. Figure 2 shows plots of $[\theta]_{307}$ values (Figure 2A) or $|[\alpha]_D^{20}|$ values (Figure 2B) of the four copolymers versus the contents of the chiral units (**1**or **2**) in the copolymers. Figure S1 shows CD and UV spectra of these copolymers.

As shown in Figure 2, when the content of the chiral **1** units in copoly(1/3) was only 40mol%, the $|[\alpha]_D^{20}|$ value and $[\theta]_{307}$ value of copoly(**1**/**3**) (623 °and 3.02×10^4) reached 88.7% and 71.2 % of the values of homopoly(**1**) (702 °and 4.24×10^4), respectively (Table 1, No.4 and 8).

Table 1. Copolymerization of chiral monomer **1** with achiral monomer **3**.

No.	**1 in feed** [a] **(mol %)**	**Copolymer**				
		1 Units in polymer [b] **(mol %)**	**Yield (%)**	***Mw*** [c] **($\times10^5$)**	**$[\alpha]_D^{20}$** [d] **(deg)**	**$[\theta]_{307}/10^3$** [e] **(deg· cm^2· dmol^{-1})**
1	0	0	30.7	19.2	0	0
2	10.0	9.80	42.9	6.89	-396	13.4
3	20.0	20.7	45.5	6.18	-541	21.8
4	40.0	40.4	45.0	6.33	-623	30.2
5	50.0	49.7	46.7	7.55	-644	34.4
6	70.0	70.1	45.1	5.30	-673	39.1
7	90.0	90.1	49.9	5.37	-693	41.5
8	100	100	47.9	4.49	-702	42.4

[a] By $[Rh(nbd)Cl]_2$/TEA as a catalytic system in toluene at room temperature for 4 h. [Monomer]=0.1 mol L^{-1}, [monomer]/$[[Rh(nbd)Cl]_2]$=500, [triethylamine]/$[[Rh(nbd)Cl]_2]$=200. [b] Determined by ^{1}H NMR. [c] Determined by GPC correlating polystyrene standard; eluent: THF. [d] In chloroform, *c*=0.035-0.044 g dL^{-1}. [e] In chloroform.

Therefore, the relationship of the values for the CD signals or specific rotation of copoly(**1**/**3**)s with the composition was unusual and non-linear, i.e., chiral amplification was observed in the copolymerization of **1** with **3**. On the other hand, the plots of the CD signals or the specific rotation of copoly(**1**/**4**)s versus the content of the chiral **1** units in the copolymer showed a usual linear relationship. Copoly(**2**/**3**)s and copoly(**2**/**4**)s did not show any CD signals at absorption wavelengths assigned to the main chain because the chiral monomer **2** was not suitable to **AIP**. Just a small increase only in the specific rotation was observed with increasing the content of the chiral **2** units in the copolymers due to their chiral groups which the monomer originally had (Figure 2B and Table S4).

In addition, all the copoly(**1**/**3**)s showed the similar UV spectra to homopoly(**1**). (Figure 1 and Figure S1 A). In the case of UV spectra of copoly(**1**/**4**), with increasing content of **4** units having no hydroxyl groups, the absorption around 307nm decreased and the absorption around 430nm increased (Figure S1 B). These findings indicate that copoly(**1**/**3**)s had tight cis-cisoidal conformations, and with increasing content of **4** units in copoly(**1**/**4**), the ratio of tight cis-cisoidal sequence in the main chain decreased and the ratio of loose cis-transoidal sequence increased.

The non-linear relationship of the values of $[\theta]_{307}$ assigned to the main-chain with the content of the chiral **1** units in copoly(**1**/**3**)s indicates that not only sequences of the chiral units from **1** but also the sequences of the achiral units from **3** contributed to the CD signals of copoly(**1**/**3**)s. In other words, copoly(**1**/**3**)s have a predominant one-handed helicity in the main-chain of the sequences of both **1** units and **3** units. Since the comonomer **3** is achiral, the chirality of the main-chains of the sequences of **3** units should be induced from the one-handed helical main-chains and the chiral spatial positions of the chiral pendant groups in the sequences consisting of **1** units. According to CD and UV spectra of copoly(**1**/**3**)s, the intramolecular hydrogen bonds by the hydroxyl groups of **1** units and **3** units could make the main-chain more rigid and tight to form a helical cis-cisoidal conformation, and therefore the chiral information could transfer more effectively from the one-handed helical sequences of the chiral 1 units to the sequences of the achiral **3** units. Therefore, the **AIP** copolymerization of **1** with **3** was followed by the rule of "sergeant and soldiers".

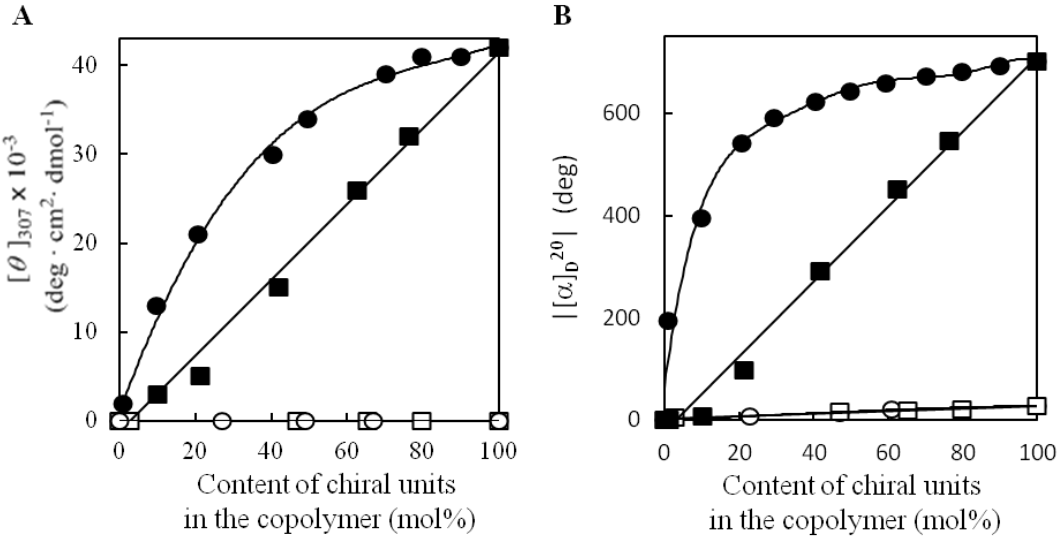


Figure 2. Plots of **A**:$[\theta]_{307}$x10^{-3} values, and **B**:$|[\alpha]_D^{20}|$ values in chloroform versus the contents of chiral units in the copolymers. (●)copoly(**1**/**3**), (■)copoly(**1**/**4**), (○)copoly(**2**/**3**), and (□)copoly(**2**/**4**).

The usual linear relationship of the values of $[\theta]_{307}$ or $[\alpha]_D^{20}$ with the content of the chiral **1** units in copoly(**1**/**4**)s (Figure 2) indicates that only the sequences of the chiral **1** units took a predominant one-handed helicity and contributed to the CD signals and the specific rotations of copoly(**1**/**4**)s. Therefore, no chiral amplification was observed. Only the difference in the chemical structure between **3** and **4** was that **3** has two hydroxyl groups and **4** does not have. Therefore, the sequences of **4** should be cis-transoidal and the sequences of **1** should be cis-cisoidal. Since the main chains and the spatial positions between the pendant groups in the sequences of **4** units must be looser and less tight than those in **1**, it was difficult for the sequences of **4** units to accept the chiral information effectively from the adjacent one-handed helical sequences of the chiral **1** units. The copolymerization of **1** with **4** could not follow the rule of “sergeant and soldiers”.

Since the chiral monomer **2** does not have any hydroxyl groups, the sequences of **2** units in copoly(**2**/**3**)s and copoly(**2**/**4**)s had main-chains with looser cis-transoidal conformation. This was supported by their UV spectra (Figure S1 C and D). It made the main chain difficult to accept the chiral information from the chiral pendant groups. Therefore, the copolymers of **2** did not show CD signals similar to the homopolymer as described above.

In conclusion, the two hydroxyl groups in monomer units which can make intramolecular hydrogen bonds made the conformation of the main-chains of the corresponding sequences in the copolymer more rigid and tight cis-cisoidal strcture. As a result, the spatial distances of the pendant groups became shorter. The tight cis-cisoidal conformation and the closer spatial position between the pendant groups acted key roles for the chiral amplification from the sequences of the chiral units to the sequences of the achiral units in **AIP** copolymerization of **1** with **3**. In the other words, the tight cis-cisoidal conformation of the main chain enhanced the efficiency of chiral induction and resulted in the chiral amplification phenomenon in the **AIP** of phenylacetylenes. To the best of our knowledge this is the first example of chiral amplification during **AIP** of phenylacetylenes.

2.5 Conclusions

A novel phenylacetylene having two hydroxyl groups and a chiral pinanyl group (**1**) and the other three related chiral and achiral phenylacetylenes were synthesized and (co)polymerized by using an achiral catalytic system. Only the chiral phenylacetylene **1** was suitable to the **AIP**. Amplification in chiral induction to the main-chain was observed only in the copolymerization of **1** with

3 having two hydroxyl groups. The tight helical *cis-cisoidal* main-chain maintained by intramolecular hydrogen bonds made the spatial position of chiral pendant groups in the polymers more tight. These enhanced efficiency of chiral induction in the **AIP** of the phenylacetylenes, and therefore, the chirality of the chiral pedant groups could be transferred to the main chain and the adjacent sequences more effectively.

References and Notes

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Supporting Information

Table S1. Homopolymerization of the phenylacetylene monomers (**1**~**4**)

	Monomer		Polymer					
No.	**Code**	**$[\alpha]_D^{20}$ b) (deg)**	**Yield (%)**	***Mw* c) ($\times 10^5$)**	***Mw/Mn* c)**	**Cis% d)**	**$[\alpha]_D^{20}$ b) (deg)**	**$[\theta]_{307}/10^3$ e) (deg· cm^2· $dmol^{-1}$)**
1 a)	**1**	-4.42	47.9	4.49	2.23	98.1	-702	42.0
2 a)	**2**	-3.78	81.0	4.22	2.30	95.2	-27.4	0
3 a)	**3**	0	30.7	19.2	5.38	100	0	0
4 a)	**4**	0	80.3	4.56	2.38	100	0	0
5 f)	**3**	0	59.6	76.7	3.84	97.6	-340	31.1

a) By $[Rh(nbd)Cl]_2$/TEA as a catalytic system in toluene at room temperature for 4 h. [Monomer] = 0.1 $molL^{-1}$, [monomer]/$[[Rh(nbd)Cl]_2]$ = 500, [triethylamine]/$[[Rh(nbd)Cl]_2]$ = 200. b) In chloroform, c = 0.035-0.218 g dL^{-1}. c) Determined by GPC correlating polystyrene standard; eluent: THF. d) *Cis*-proton content (%) determined by ^{1}H-NMR. e) In chloroform. f) Poly(**3**) prepared by **HSSP**. [26]

Table S2. Copolymerization of chiral monomer **1**with achiral monomer **4**

No.	1 in feed [a] (mol %)	Copolymer					
		1 Units in polymer [b] (mol %)	**Yield (%)**	***Mw*** [c] **($\times 10^5$)**	***Mw*/*Mn*** [c]	**$[\alpha]_D^{20}$** [d] **(deg)**	**$[\theta]_{307}/10^3$** [e] **(deg· cm^2· $dmol^{-1}$)**
1	0	0	80.3	4.56	2.38	0	0
2	1.00	0.500	73.5	4.43	2.88	0	0
3	10.0	1.30	54.0	5.89	3.12	0	0
4	20.0	10.4	68.9	5.18	3.17	-8.30	3.10
5	30.0	21.3	55.6	4.57	3.48	-97.2	4.90
6	50.0	41.9	45.3	5.52	2.51	-291	15.1
7	70.0	62.6	50.2	4.89	3.35	-451	26.2
8	90.0	76.4	45.2	4.52	3.01	-547	32..3
9	100	100	47.9	4.49	2.23	-702	42.4

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a) By $[Rh(nbd)Cl]_2$/TEA as a catalytic system in toluene at room temperature for 4 h. [Monomer] = 0.1molL^{-1}, [monomer]/$[[Rh(nbd)Cl]_2]$ = 500, [triethylamine]/$[[Rh(nbd)Cl]_2]$ = 200. b) Determined by IR. c) Determined by GPC correlating polystyrene standard; eluent: THF. d) In chloroform, c = 0.035-0.044 g dL^{-1}. e) In chloroform.

Table S3. Copolymerization of chiral monomer **2** with achiral monomer **3**

No.	**2 in feed** a) **(mol %)**	**Copolymer**					
		2 Units in polymer b) **(mol %)**	**Yield (%)**	***Mw*** c) **($\times 10^5$)**	***Mw/Mn*** c)	**$[\alpha]_D^{20}$** d) **(deg)**	**$[\theta]_{307}/10^3$** e) **(deg· cm^2· dmol^{-1})**
1	0	0	30.7	19.2	5.38	0	0
2	1.00	2.80	35.2	14.5	5.48	-5.00	0
3	30.0	46.9	46.9	7.88	3.56	-16.3	0
4	50.0	65.3	45.3	7.52	2.56	-18.5	0
5	60.0	79.8	69.3	5.61	2.49	-22.1	0
6	100	100	81.0	4.22	2.30	-27.4	0

a) By [Rh(nbd)Cl]$_2$/TEA as a catalytic system in toluene at room temperature for 4 h. [Monomer] = 0.1 mol L^{-1}, [monomer]/[[Rh(nbd)Cl]$_2$] = 500, [triethylamine]/[[Rh(nbd)Cl]$_2$] = 200. b) Determined by IR. c) Determined by GPC correlating polystyrene standard; eluent: THF. d) In chloroform, c = 0.035-0.044 g dL^{-1}. e) In chloroform.

Table S4. Copolymerization of chiral monomer **2** with achiral monomer **4**

No.	**2 in feed** a) **(mol %)**	**Copolymer**					
		2 Units in polymer b) **(mol %)**	**Yield (%)**	***Mw*** c) **($\times 10^5$)**	***Mw/Mn*** c)	**$[\alpha]_D^{20}$** d) **(deg)**	**$[\theta]_{307}/10^3$** e) **(deg· cm^2· dmol^{-1})**
1	0	0	80.3	4.56	2.38	0	0
2	27.0	23.0	85.3	4.57	2.48	-8.02	0
3	49.0	47.0	81.6	4.52	2.50	-14.1	0
4	67.0	61.0	81.0	4.44	2.44	-20.4	0
5	100	100	81.0	4.22	2.30	-27.4	0

a) By [Rh(nbd)Cl]$_2$/TEA as a catalytic system in toluene at room temperature for 4 h. [Monomer] = 0.1 mol L^{-1}, [monomer]/[[Rh(nbd)Cl]$_2$] = 500, [triethylamine]/[[Rh(nbd)Cl]$_2$] = 200. b) Determined by IR. c) Determined by GPC correlating polystyrene standard; eluent: THF. d) In chloroform, c = 0.035-0.044 g dL^{-1}. e) In chloroform.

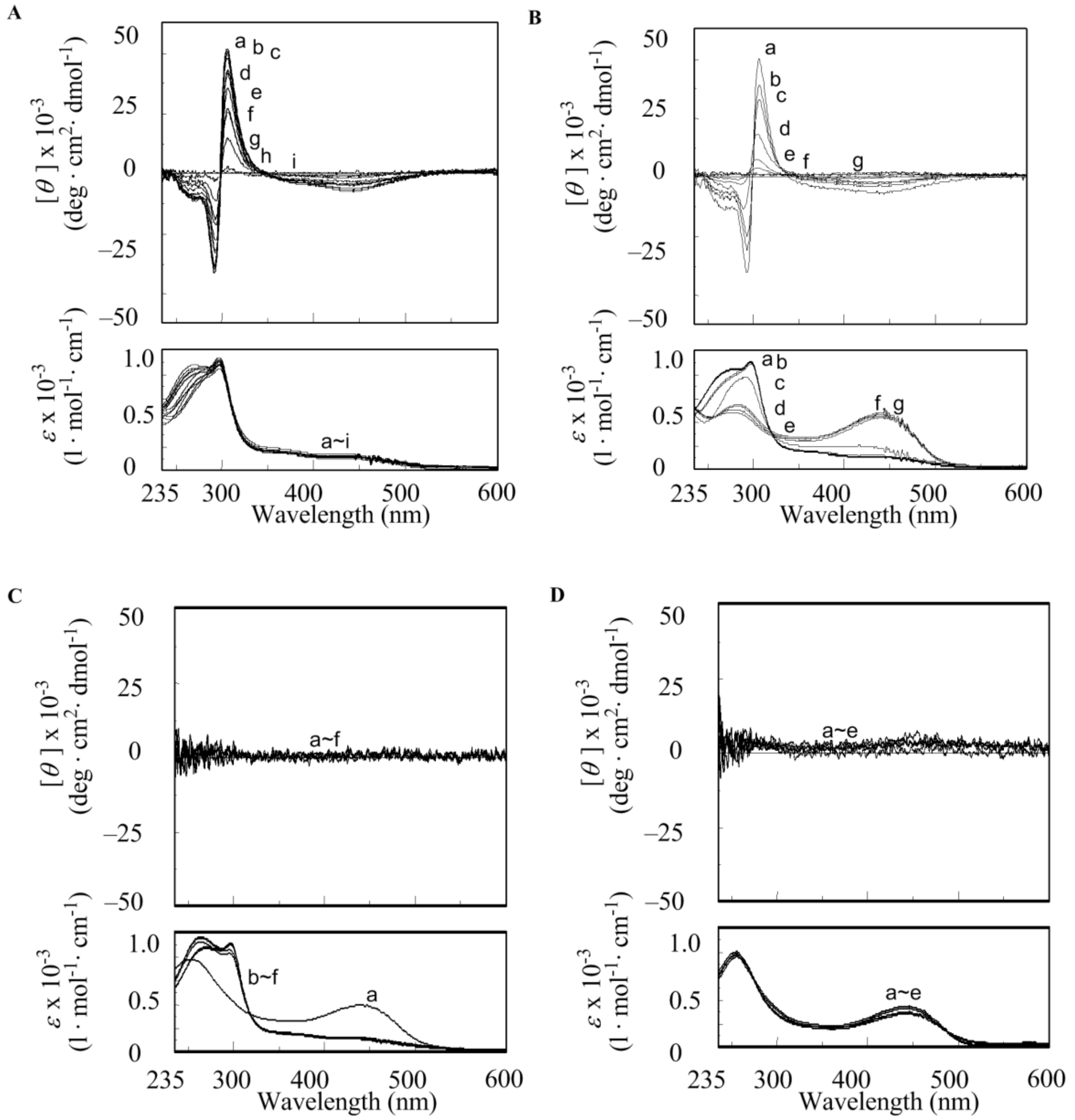

Figure S1. CD and UV-vis spectra in chloroform at 20 ℃ of **A**: copoly(**1/3**) (the content of **1** uints in the copolymer (mol%): a: 100, b: 90.1, c: 79.8, d: 70.1, e: 40.4, f: 20.7, g: 9.80, h: 1.00, i: 0), **B**: copoly(**1/4**) (the content of **1** uints in the copolymer (mol%): a: 100, b: 76.4, c: 62.6, d: 41.9, e: 21.3, f: 10.4, g: 0), **C**: copoly(**2/3**) (the content of **2** units in the copolymer (mol%): a: 100, b: 79.8, c: 65.3, d: 46.9, e: 2.80, f: 0), and **D**: copoly(**2/4**) (the content of **2** units in the copolymer (mol%): a: 100, b: 61.0, c: 47.0, d: 23.0, e: 0).

General conclusions

Based on the above data, we found some new and intersting application of one handed helical polyphenylacetylenes prepared by using HSSP of achiral monomers having two hydroxyl groups, such as the polymer cocatalyst, which was showing higher cocatalytic efficience.

It is well known that the hydroxyl groups are active reagent to complex with Rhodium atom. As the helical main chain shows chirality, the hydroxyl groups attached with helical main chain could be used a chiral source for the helix-sense-selective polymerization of substituted phenylacetylenes having hydroxyl groups. To the best of our knowlege, this is the firs example of polymer catalyst prepared by HSSP of achiral phenylacetylene.

With the hydrogen bonds among the pendants, chiral amplication effect was also researched. During the copolymerization of chiral and achiral phenylacetylenes having two hydroxyl groups, the chirality of chiral pendants could be transmit to the achiral pendant, in the way of which helical sense was induced and enhanced compared with homopolymeriation of chiral monomers.

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Geng Zhang

February 2015

List of Publications and Presentations

Papers

1. Geng Zhang, Lijia Liu, Toshiki Aoki, Masahiro Teraguchi, and Takashi Kaneko, Helix-sense-selective polymerization of achiral phenylacetylenes

by using one-handed helical poly(phenylacetylene)s as chiral cocatalysts

prepared by helix-sense-selective polymerization of achiral phenylacetylenes, *Chem.Lett.* **2015**, *44*, 318. (Chapter 1)

2. Lijia Liu, Kazuomi Mottate, Geng Zhang, Toshiki Aoki, Takashi Kaneko, Masahiro Teraguchi, Chiral Amplification during Asymmetric-Induced Copolymerization of Phenylacetylenes having Tight Cis-Cisoidal Main Chain，*Macromol. Rapid Commun.* **2013**,*34*,1140. (Chapter 2)

International Conference

1. Geng Zhang, Sawa Taguchi, Masahiro Teraguchi, Takashi Kaneko and Toshiki Aoki, Unusual Phenomenon in Helix-Sense-Selective Polymerization --Control of the Helical Sense of Polyphenylacetylenes by Changing an Achiral Condition, 13th Pacific Polymer Conference, **2013**, S1-094.

Domestic Conference

1. Geng Zhang, Sawa Taguchi, Masahiro Teraguchi, Takashi Kaneko, Toshiki Aoki, *Polym. Prep., Jpn.,* **2013**,*62*(2), 2591-2592.

2. Sawa Taguchi, Geng Zhang, Masahiro Teraguchi, Takashi Kaneko, and Toshiki Aoki. Control of the helix sense of chiral polyacetylenes prepared by helix-sense-selective polymerization without using any chiral source, *Polym. Prep., Jpn.,* **2014**,*63*(1), 737.