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Three Mechanisms of Asymmetric Polymerization of Phenylacetylenes Having an L-Amino Ether Residue and Two Hydroxy Groups

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ABSTRACT: Three novel chiral phenylacetylenes having an octyloxyethanolamine residue derived from a L-aminoalcohol and two hydroxymethyl groups were synthesized and polymerized by two achiral catalysts ((nbd)$Rh^{+}[\eta^{6}$-$(C_6H_5)B^{-}(C_6H_5)_3]$ and $[Rh(nbd)Cl]_2$/triethylamine (TEA)) and a chiral catalytic system ($[Rh(nbd)Cl]_2$/(*S*)- or (*R*)-phenylethylamine ((*S*)- or (*R*)-PEA)). All of the resulting polymers showed Cotton effects at wavelengths around 430 nm. This observation indicated that they had an excess of one-handed helical backbones. Positive and negative Cotton effects were observed for the polymers having an L-valinol residue produced by using (*S*)- and (*R*)-PEA as a cocatalyst, respectively, although the monomers had the same chirality. The two polymers having an L-alaninol or L-phenylalaninol residues obtained by using (*S*)- and (*R*)-PEA as a cocatalyst showed CD absorptions with identical signs. Therefore, we found that the chiral monomer having an L-valinol residue was suitable for both modes of asymmetric polymerization, that is, helix-sense-selective polymerization (**HSSP**) with the chiral catalytic system and asymmetric-induced polymerization (**AIP**) with the achiral catalysts. However, the other two monomers having an L-alaninol or L-phenylalaninol residue were not suitable for **HSSP** because the helix sense could not be controlled by the chirality of PEA. To explain the unexpected behaviors in the asymmetric polymerizations of the two chiral monomers having a chiral bidentate ligand, a novel third mechanism of asymmetric polymerization, that is, self-helix-sense-selective polymerization (**SHSSP**), is proposed in this Article. This Article discusses the contribution of the three mechanisms (**AIP**, **HSSP**, and **SHSSP**) in asymmetric polymerizations of the three monomers.

Introduction

Conjugated polymers like polyacetylenes have gained interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical nonlinear susceptibility. Recently, chiral polyacetylenes have received much attention because the chiral structure can enhance the unique properties and add new functions.

In 1993, the authors accidentally found an asymmetric-induced polymerization (**AIP**) that induced a one-handed helical chirality in the main-chain during polymerization of a phenylacetylene having a bulky chiral L-menthoxycarbonyl group.[1] After this finding, the authors synthesized and polymerized many other phenylacetylenes and diphenylacetylenes having a chiral substituent to check whether a main-chain chirality was induced.[2] As a result, many chiral monomers were found to be suitable for the **AIP**. For example, the homopolymers of (−)-*p*-(dimethyl(10-pinanyl)silyl)phenylacetylene[2a] and (+)-*p*-(10-pinanyloxycarbonyl)-phenylacetylene[2g] obtained with an Rh complex showed strong CD absorptions similar to that of *p*-{L-(−)-menthoxycarbonyl}phenylacetylene.[1] Similar results were also reported by other researchers.[3]

To investigate the effects of the position of the chiral groups in the monomers on the induction of chirality in the main chain during polymerization, several oligosiloxanylphenylacetylenes having one or two bulky chiral pinanyl groups at the one-, three-, and five-positions of an oligosiloxane chain were polymerized with a Rh complex to produce high-molecular-weight polymers.[2g] The polymers with a chiral pinanyl group at the one-position of an oligosiloxanyl group showed high molar ellipticity in the main-chain region in the CD spectra. The polymers from monomers with a chiral pinanyl group at the three- or five-positions of an oligosiloxanyl group showed almost no CD absorptions. Therefore, to realize the **AIP**, the chiral group should be substituted at a position close to the polymerizable group in the monomers. In this **AIP**, the sign of the chirality of the formed main-chain was strongly affected by the sign of the chirality of the chiral group. Therefore, only two kinds of chiral polymers, that is, the enantiomers, PD and ML (or PL and MD),[4] could be obtained from the enantiomeric monomers by **AIP**. In other words, it was impossible to synthesize their diastereomers.

The authors have also found a simple and novel synthetic method for obtaining such a chiral polymer from an achiral substituted acetylene monomer by using a chiral catalytic system.[5] In addition, the helical conformation was stable in solution. This is the first example of helix-sense-selective polymerization (**HSSP**) of substituted acetylenes whose chiral helicity is stable in solution without the aid of other chiral substituents or other small molecules. The authors polymerized an achiral phenylacetylene having two hydroxyl groups and a dodecyl group (**DoDHPA**) (Chart 1) by using a chiral catalytic system

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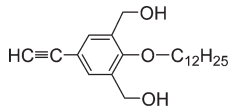
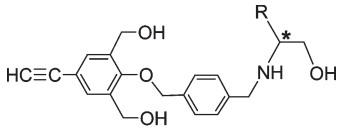
Chart 1. Chemical Structure of DoDHPA in Our Previous Study



DoDHPA

Chart 2. Chemical Structures of the Monomers (RDHPA) in Our Previous Study



-R =
-CH_3 : **ADHPA**
-$CH(CH_3)_2$: **VDHPA**
-$CH_2C_6H_5$: **PDHPA**

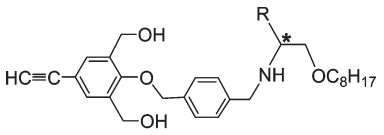
consisting of a rhodium dimeric complex, $[Rh(nbd)Cl]_2$, as a catalyst, and a chiral amine, (*R*)-phenylethylamine ((*R*)-PEA), as a cocatalyst. The polymer showed Cotton effects at wavelengths around 430 and 310 nm, where there are no UV absorptions of **DoDHPA** and (*R*)-PEA.[5a,5b] No **HSSP**s occurred in the case of the corresponding monomers having no hydroxy groups. Therefore, two hydroxy groups were found to be necessary to realize the **HSSP**. In this polymerization, the sense of the main-chain helicity was governed by the sign of the chirality of the cocatalyst used. In this case, also only the pair of the enantiomers (M and P)[4] could be produced.

These monomers described above were suitable only for the **AIP** or the **HSSP**. There had been no monomers that were suitable for both asymmetric polymerizations. We recently reported a novel chiral phenylacetylene having an L-valinol residue and two hydroxymethyl groups (**VDHPA**) (Chart 2).[6] The monomer was suitable for both the **HSSP** with an chiral catalytic system and the **AIP** with an achiral catalyst.[6] This was the first example of such a monomer. Positive and negative Cotton effects were observed for the polymers obtained by using (*R*)-**PEA** and (*S*)-**PEA**, respectively in **HSSP**. The handedness of the main chain was controlled not by the chiral substituent but by the chiral cocatalyst. For all asymmetric polymerizations (**AIP**) of chiral acetylenes reported,[1−3] the chiralities of the main chain and the chiralities of the monomer substituent were not independent. Therefore, only their enantiomers PD and ML (or PL and MD)[4] could be synthesized. We obtained the diastereomers (ML and PL)[4] first from the monomer **VDHPA**, as described in our previous communication.[6] However, the [θ] values and solubilities of the poly(**VDHPA**) were not high.

We also studied the synthesis and polymerization of two other **RDHPA**s (**ADHPA** and **PDHPA**) containing two hydroxy groups and a chiral group, an L-alaninol residue and L-phenylalaninol residue, respectively, as shown in Chart 2.[7] However, because most of the resulting polymers were insoluble or partially soluble in nonpolar solvents such as THF, chloroform, and so on because of their high polarity, it was difficult to obtain a one-handed helical backbone that was maintained by hydrogen bonds in polar solvents, such as methanol, DMF, DMSO, and so on.

Therefore, we needed new monomers that may yield polymers soluble in nonpolar solvents. As such monomers, we designed three new **ORDHPA**s (**OADHPA**, **OVDHPA**, and **OPDHPA**),[8] as shown in Chart 3. To enhance the solubility of the resulting polymers, an octyl group was introduced to the hydroxyl group of the amino alcohol residue in the corresponding RDHPA (Chart 2). Here we discuss which monomer is suitable for both **HSSP** and **AIP**. In addition, we propose a new mechanism of asymmetric polymerization, self-helix-sense-selective polymerization (**SHSSP**), for the first time in this Article. The contribution of the three mechanisms, **AIP**, **HSSP**, and **SHSSP**, to asymmetric polymerizations is discussed.

Chart 3. Chemical Structures of the Monomers Having a Bidentate Ligand (ORDHPA) in This Study[8]



-R =
-CH_3 : **OADHPA**
-$CH(CH_3)_2$: **OVDHPA**
-$CH_2C_6H_5$: **OPDHPA**
-H : **OEDHPA**

Experimental Part

Materials. All of the solvents used for synthesis and polymerizations of the monomers were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene), purchased from Aldrich Chemical was used as received. According to the literature procedures, $(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$[9] and **DoDHPA**[5a] were prepared. L-Alanine (**Ala**, $[\alpha]_D^{20} = +14.3 \sim +15.2°$ (*c* 10 g/dL, 6 mol/L HCl)), L-valine (**Val**, $[\alpha]_D^{20} = +27.6 \sim +28.7°$ (*c* 8 g/dL, 6 mol/L HCl)), L-phenylalanine (**Phe**, $[\alpha]_D^{20} = -33.5 \sim -35.0°$ (*c* 2 g/dL, H_2O)), and 2-aminoethanol (**4**) purchased from Junsei Chemical were used as received. 1-Bromooctane purchased from Tokyo Chemical was used as received.

Synthetic Procedures and Characterization of the Monomers (OADHPA, OVDHPA, OPDHPA, and OEDHPA) (Scheme 1). All of the following reaction procedures were conducted under dry nitrogen.

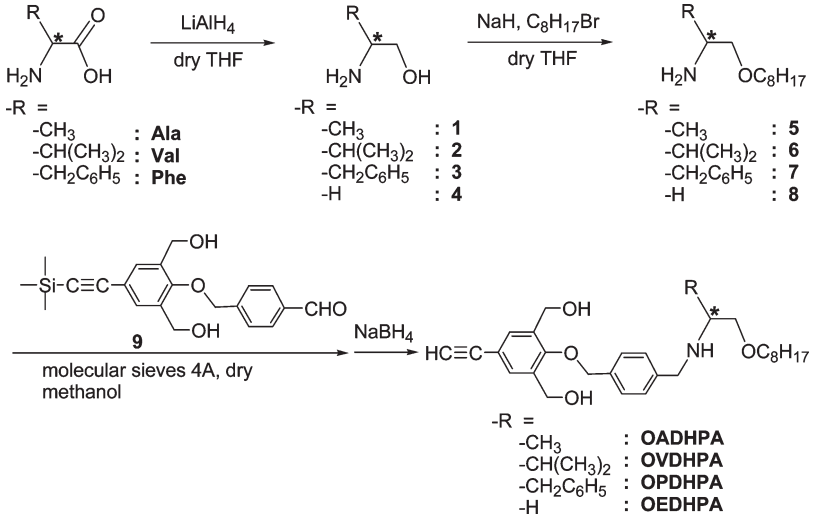
1. L-Alaninol (***1***).[10] A mixture of **Ala** (5.00 g, 56.1 mmol) in dry THF (40 mL) was added slowly to a mixture of lithium aluminum hydride (3.20 g, 84.2 mmol) in dry THF (40 mL) at 0 °C. After the mixture was refluxed for 12 h, water (5 mL) was slowly added. The mixture was filtered, and the solvent was removed. The crude product was purified by vacuum distillation to give **1** as colorless liquid. Yield: 51.1% (2.11 g). bp 55 °C (6.8 mmHg). $[\alpha]_D^{20} = 8.5°$ (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 3.52 and 3.24 (2dd, 2H, CH_2OH), 3.01 (m, 1H, NH_2-C*H*), 2.51 (b, 3H, NH_2 and O*H*), 1.06 (d, 3H, $J = 6.2$ Hz, CH_3).

2. L-Valinol (***2***).[6,10] According to the literature procedure, **2** was prepared. Yield: 57.5%. bp 42 °C (0.32 mmHg). Appearance: colorless liquid $[\alpha]_D^{20} = +11°$ (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 3.60 and 3.25 (2dd, 2H, CH_2OH), 2.52 (m, 1H, NH_2C*H*), 1.87 (b, 3H, NH_2 and O*H*), 1.55 (m, 1H, C*H*(CH_3)$_2$), 0.87 and 0.90 (2d, 6H, $J = 3.4$ Hz, CH(CH_3)$_2$).

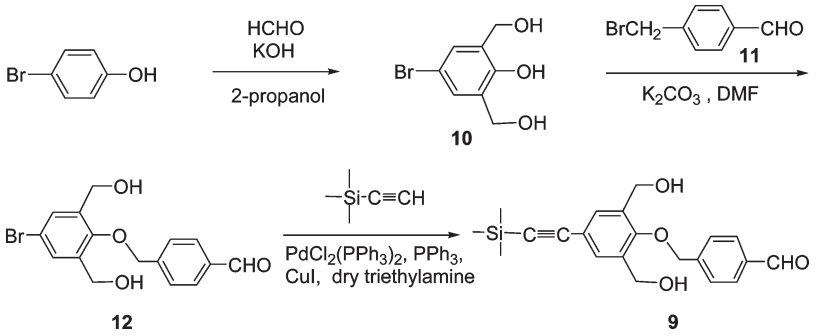
3. L-Phenylalaninol (***3***).[10] A similar procedure as described for **1** was employed. After the reaction, the mixture was filtered, and the solution was concentrated to give a solid residue. The crude product was dissolved in ethyl acetate, and the solution was washed with brine. The water layer was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated to give **3** as yellow solid. Yield: 46.1%. $[\alpha]_D^{20} = -28°$ (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 7.34−7.17 (m, 5H, phenyl), 3.64 and 3.38 (2dd, 2H, CH_2OH), 3.10 (m, 1H, NH_2C*H*), 2.80 and 2.52 (2dd, 2H, PhCH_2), 2.10 (b, 3H, NH_2 and O*H*).

4. (−)-2-Octyloxy-1-methylethylamine (*Octyl Ether of L-Alaninol*) (***5***).[11] A mixture of sodium hydride dispersion in paraffin (1.23 g, 28.1 mmol, content: 55%) in dry THF (25 mL) was added slowly to a solution of **1** (2.11 g, 28.1 mmol) in dry THF (25 mL) at 0 °C. After the mixture was refluxed for 30 min, 1-bromooctane (4.45 mL, 25.6 mmol) was added at room temperature. After the mixture was refluxed for 7 h, water (2 mL) was slowly added. The mixture was filtered, and the solvent was removed. The crude product was purified by silica-gel column chromatography to give **5** as a yellow

Scheme 1. Synthetic Route to ORDHPAs (OADHPA, OVDHPA, OPDHPA, and OEDHPA)



Scheme 2. Synthetic Route to Compound 9



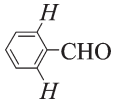
liquid. Yield: 64.2% (3.07 g). R_f = 0.13 (ethyl acetate/methanol 2:1). $[\alpha]_D^{20} = -7.0°$ (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 3.45 and 3.10 (m, 5H, OCH_2CHN, OCH_2CH_2, and NH_2CH), 1.55 (m, 2H, OCH_2CH_2), 1.43 (b, 2H, NH_2), 1.27 (b, 10H, $(CH_2)_5CH_3$), 1.02 (d, 3H, J = 6.2 Hz, NH_2CHCH_3), 0.85 (t, 3H, J = 6.8 Hz, CH_2CH_3).

5. (−)-*2-Octyloxy-1-isopropylethylamine* (*Octyl Ether of* L*-Valinol*) (***6***).[11] A similar procedure as that described for **5** was applied. Yield: 66.0%. Appearance: yellow liquid. R_f = 0.33 (ethyl acetate/methanol 2:1). $[\alpha]_D^{20} = -10°$ (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 3.48 (m, 3H, OCH_aCHNH_2 and OCH_2CH_2), 3.18 (dd, 1H, OCH_bCHNH_2), 2.71 (m, 1H, NH_2CH), 1.56 (m, 3H, $CH(CH_3)_2$ and OCH_2CH_2), 1.26 (b, 10H, $(CH_2)_5CH_3$), 0.90 (m, 9H, $CH(CH_3)_2$ and CH_2CH_3).

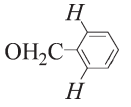
6. (−)-*2-Octyloxy-1-benzylethylamine* (*Octyl Ether of* L*-Phenylalaninol*) (***7***).[11] A similar procedure as that described for **5** was applied. Yield: 64.0%. Appearance: yellow liquid. R_f = 0.12 (ethyl acetate/hexane 2:1). $[\alpha]_D^{20} = -20°$ (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 7.32−7.18 (m, 5H, phenyl), 3.45 and 3.23 (m, 5H, OCH_2CHN, OCH_2CH_2, and NH_2CH), 2.78 and 2.54 (2dd, 2H, $PhCH_2$), 1.55 (m, 4H, OCH_2CH_2 and NH_2), 1.27 (b, 10H, $(CH_2)_5CH_3$), 0.88 (t, 3H, J = 6.8 Hz, CH_3).

7. *2-Octyloxyethylamine* (***8***).[11] A similar procedure as that described for **5** was applied. Yield: 48.2%. Appearance: yellow liquid. R_f = 0.10 (ethyl acetate/ methanol 7:3). ^{1}H NMR ($CDCl_3$, TMS, δ): 3.42 and 3.37 (2t, 4H, OCH_2CH_2N and $OCH_2CH_2CH_2$), 2.81 (t, 2H, J = 5.1 Hz, $NH_2CH_2CH_2$), 1.54 (m, 4H, $OCH_2CH_2CH_2$ and NH_2), 1.22 (b, 10H, $(CH_2)_5CH_3$), 0.83 (t, 3H, J = 6.8 Hz, CH_3).

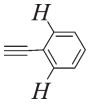
8. *4-{4-Trimethylsilylethynyl-2,6-(bishydroxymethyl)-1-phenoxymethyl}benzaldehyde* (***9***) (*Scheme 2*).[5,6] According to the method we reported before, **9** was prepared. Total yield (based on *p*-bromophenol): 25.0%. Appearance: yellow liquid. R_f = 0.69 (ethyl acetate: hexane = 2:1). ^{1}H NMR ($CDCl_3$, TMS, δ): 10.04 (s, 1H, CHO), 7.92 (d, 2H, J = 8.3 Hz,



), 7.61 (d, 2H, J = 8.3 Hz,



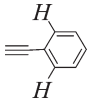
), 7.51 (s, 2H,



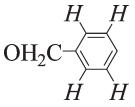
), 5.07 (s, 2H, $PhOCH_2Ph$), 4.67 (d, 4H, J = 5.9 Hz, $Ph(CH_2OH)_2$), 1.88 (t, 2H, J = 5.9 Hz, $Ph(CH_2OH)_2$), 0.24 (s, 9H, $Si(CH_3)_3$).

9. (+)-*4-[4-{(2-Octyloxy-1-methyl)ethylaminomethyl}benzyloxy]-3,5-bis(hydroxymethyl)-phenylacetylene* (***OADHPA***)[6,12,13] A solution of **5** (254 mg, 1.36 mmol) and **9** (500 mg, 1.36 mmol) in dry methanol (10 mL) was stirred in the presence of molecular sieves 4 Å (2.0 g) for 24 h at room temperature. Sodium tetrahydroborate (51.6 mg, 1.36 mmol) was added to the solution, which was stirred for 36 h again. After the solution was filtered, the solvent was

removed. The crude product was purified by silica-gel column chromatography to give **OADHPA** as a yellow liquid. Yield: 75.0% (476 mg). Appearance: yellow liquid. R_f = 0.35 (ethyl acetate/methanol 8:1). $[\alpha]_D^{20}$ = 5.0° (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 7.51 (s, 2H,

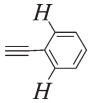


), 7.35 (b, 4H,

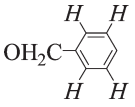


), 4.91 (s, 2H, PhOCH_2Ph), 4.61 (s, 4H, Ph(CH_2OH)$_2$), 3.89 (2d, 2H, J = 13 Hz, PhCH_2NH), 3.40 and 3.29 (m, 4H, OCH_2CHN and OCH_2CH$_2$), 3.04 (s, 1H, *H*C≡C), 2.92 (m, 1H, NHC*H*), 2.12 (b, 3H, (O*H*)$_2$ and N*H*), 1.56 (m, 2H, OCH$_2$CH_2), 1.26 (b, 10H, (CH_2)$_5$CH$_3$), 1.06 (d, 3H, J = 6.2 Hz, CHCH_3), 0.86 (t, 3H, J = 6.8 Hz, CH$_2$CH_3). IR (cm^{-1}, KBr): 3279, 2925, 2858, 1595, 1459, 1368, 1203, 1117, 974, and 891. Anal. Calcd for $C_{29}H_{41}NO_4$: C, 74.48; H, 8.84; N, 3.00. Found: C, 74.38; H, 9.04; N, 2.87.

10. (−)-*4*-[*4*-{(*2-Octyloxy-1-isopropyl*)*ethylaminomethyl*}*benzyloxy*]-*3,5-bis*(*hydroxymethyl*)-*phenylacetylene* (***OVDHPA***)[6,12,13] A similar procedure as that described for **OADHPA** was applied. Yield: 80.1%. Appearance: yellow liquid. R_f = 0.60 (ethyl acetate/methanol 4:1). $[\alpha]_D^{20}$ = −27° (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 7.50 (s, 2H,



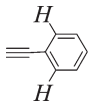
), 7.35 (b, 4H,



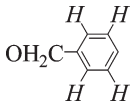
), 4.94 (s, 2H, PhOCH_2Ph), 4.64 (s, 4H, Ph(CH_2OH)$_2$), 3.82 (s, 2H, PhCH_2NH), 3.48 and 3.34 (m, 4H, OCH_2CHN, OCH_2CH$_2$), 3.05 (s, 1H, *H*C≡C), 2.57 (m, 1H, NHC*H*), 1.90 (b, 3H, (O*H*)$_2$ and N*H*), 1.57 (m, 3H, OCH$_2$CH_2CH$_2$ and C*H*(CH$_3$)$_2$), 1.26 (b, 10H, (CH_2)$_5$CH$_3$), 0.90 (m, 9H, CH(CH_3)$_2$ and CH$_2$CH_3). IR (cm^{-1}, KBr): 3305, 2927, 2862, 1603, 1460, 1367, 1203, 1110, and 1076. Anal. Calcd for $C_{31}H_{45}NO_4$: C, 75.11; H, 9.15; N, 2.83. Found: C, 74.93; H, 9.34; N, 2.80.

11. (−)-*4*-[*4*-{(*2-Octyloxy-1- benzyl*)*ethylaminomethyl*}*benzyloxy*]-*3,5-bis*(*hydroxymethyl*)-*phenylacetylene* (***OPDHPA***)[6,11,12] A similar procedure as that described for **OADHPA** was applied. Yield: 79.0%. Appearance: yellow liquid. R_f = 0.35 (chloroform/methanol 4:1). $[\alpha]_D^{20}$ = −38° (*c* 0.10 g/dL, THF). ^{1}H NMR ($CDCl_3$, TMS, δ): 7.50−7.14 (m, 11H, phenyl), 4.95 (s, 2H, PhOCH_2Ph), 4.64 (s, 4H, Ph(CH_2OH)$_2$), 3.85 (s, 2H, PhCH_2NH), 3.46−3.32 (m, 4H, OCH_2CHN and OCH_2CH$_2$), 3.02 (m, 2H, *H*C≡C and NHC*H*), 2.84 and 2.75 (2dd, 2H, PhCH_2CH), 2.09 (b, 3H, (O*H*)$_2$ and N*H*), 1.52 (m, 2H, OCH$_2$CH_2), 1.23 (b, 10H, (CH_2)$_5$CH$_3$), 0.84 (t, 3H, J = 6.8 Hz, CH_3). IR (cm^{-1}, KBr): 3269, 3029, 2925, 2858, 1454, 1368, 1245, 1200, 1127, 1069, 1029, and 992. Anal. Calcd for $C_{35}H_{45}NO_4$: C, 77.31; H, 8.34; N, 2.58. Found: C, 77.35; H, 8.32; N, 2.56.

12. *4*-{*4*-(*2- Octyloxyethylaminomethyl*)*benzyloxy*}-*3,5-bis*-(*hydroxymethyl*)*phenylacetylene* (***OEDHPA***)[6,11,12] A similar procedure as that described for **OADHPA** was applied. Yield: 50.0%. Appearance: yellow liquid. R_f = 0.31 (ethyl acetate/methanol 4:1). ^{1}H NMR ($CDCl_3$, TMS, δ): 7.51 (s, 2H,



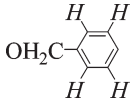
), 7.35 (b, 4H,



), 4.92 (s, 2H, PhOCH_2Ph), 4.62 (s, 4H, Ph(CH_2OH)$_2$), 3.82 (s, 2H, PhCH_2NH), 3.56 (t, 2H, OCH_2CH$_2$N), 3.43 (t, 2H, OCH_2-CH$_2$CH$_2$), 3.05 (s, 1H, *H*C≡C), 2.80 (t, 2H, NHCH_2CH$_2$), 2.14 (b, 3H, (O*H*)$_2$ and N*H*), 1.57 (m, 2H, OCH$_2$CH_2CH$_2$), 1.27 (b, 10H, (CH_2)$_5$CH$_3$), 0.87 (t, 3H, J = 6.8 Hz, CH_3). IR (cm^{-1}, KBr): 3301, 2927, 2860, 1738, 1603, 1458, 1367, 1207, and 1122. Anal. Calcd for $C_{28}H_{39}NO_4$: C, 74.14; H, 8.67; N, 3.09. Found: C, 73.90; H, 8.95; N, 3.08.

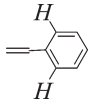
Polymerizations[5,6] Asymmetric polymerizations were carried out by two achiral catalysts, (nbd)Rh$^+$[η^6-(C$_6$H$_5$)B$^-$(C$_6$H$_5$)$_3$] and [Rh(nbd)Cl]$_2$/triethylamine (TEA), and a chiral catalytic system, [Rh(nbd)Cl]$_2$/(*R*)- or (*S*)-PEA, respectively.

1. Polymerization of ***OADHPA***. A typical polymerization procedure was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.490 mg, 1.07 μmol) and (*R*)-PEA (68.0 μL, 535 μmol) in THF (0.53 mL) was added to a solution of monomer **OADHPA** (50.0 mg, 107 μmol) in THF (0.54 mL). The reaction solution was stirred at room temperature for 4 h. The formed polymer was purified by precipitation of the THF solution in a large amount of ethyl acetate/hexane 2:1 and dried in vacuum to give a red poly-(**OADHPA**). Yield: 11.2% (5.60 mg). M_w = 85 000. M_w/M_n = 2.4 (Table 1, no. 4). ^{1}H NMR (THF-d_8/DMSO-d_6 9:1 (V/V), TMS, δ): 7.28 (b, 4.30H,



and

), 6.95 (b, 2H,



), 5.97 (b, 0.70H,

), 4.71 (b, 2H, PhOCH_2Ph), 4.41 (b, 4H, Ph(CH_2OH)$_2$), 3.76 (b, PhCH_2NH), 3.38 and 3.29 (2b, 4H, OCH_2CHN and OCH_2CH$_2$), 2.82 (b, NHC*H*, (O*H*)$_2$ and N*H*), 1.53 (b, 2H, OCH$_2$CH_2), 1.28 (b, 10H, (CH_2)$_5$CH$_3$), 1.02 (b, 3H, CHCH_3), 0.88 (b, 3H, CH$_2$CH_3). cis % = 70%. The other polymerizations were also conducted similarly.

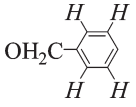
2. Polymerization of ***OVDHPA***. Similar procedures as those described for polymerizations of **OADHPA** were applied. The formed polymer was purified by precipitation of the THF solution into a large amount of methanol and dried in vacuum

Table 1. Polymerizations of ORDHPAs by Using Achiral or Chiral Catalytic Systems Based On [Rh(nbd)Cl]$_2$[a]

			[cocatalyst]					
no.	monomer	cocatalyst	mol/L	vol %	yield (%)	M_w ($\times 10^4$)[b]	M_w/M_n[b]	$[\theta]_{430}$ ($\times 10^3$)[c]
1[d]	**OADHPA**	none	(0.1)[e]	0.0	55.2	13.5	2.2	5.1
2		TEA	0.5	6.7	56.2	14.8	2.5	4.3
3		TEA	2.4	33.3	34.8	2.8	1.8	1.9
4		(*R*)-PEA	0.5	5.9	11.2	8.5	2.4	9.6
5		(*S*)-PEA	0.5	5.9	5.2	6.9	1.5	1.2
6		(*S*)-PEA	2.5	33.3	12.5	3.9	2.1	−2.8
7[d]	**OVDHPA**	none	(0.1)[e]	0.0	36.1	10.1	3.8	−1.9
8		TEA	0.5	6.7	43.1	6.5	4.1	−1.5
9		TEA	2.4	33.3	42.1	2.5	2.0	−2.8
10		(*R*)-PEA	0.5	5.9	14.1	9.2	2.9	2.0
11		(*S*)-PEA	0.5	5.9	14.1	10.5	2.8	−2.3
12[d]	**OPDHPA**	none	(0.1)[e]	0.0	85.1	25.7	7.7	−5.4
13		TEA	0.5	6.7	42.6	17.8	5.4	2.7
14		TEA	2.4	33.3	44.5	2.5	1.7	3.2
15		(*R*)-PEA	0.5	5.9	25.4	11.5	2.3	−2.8
16		(*S*)-PEA	0.5	5.9	12.4	6.7	2.7	−3.3
17		(*S*)-PEA	2.5	33.3	20.7	1.9	1.7	−2.7
18[d]	**OEDHPA**	none	(0.1)[e]	0.0	29.2	1.2	1.1	0.0
19		TEA	0.5	6.7	23.1	1.1	1.1	0.0
20		(*R*)-PEA	0.5	5.9	14.2	3.2	1.2	0.4
21		(*S*)-PEA	0.5	5.9	8.8	1.2	1.1	−0.3

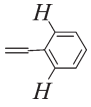
[a] At room temperature in THF, [monomer] = 0.1 mol/L, [catalyst] = 1×10^{-3} mol/L, [monomer]/[catalyst] = 100. [b] Determined by GPC correlating polystyrene standard with THF eluent. [c] In deg·cm^2/dmol, 1.0 mmol/L, in THF. [d] By using (nbd)Rh$^+$[η^6-(C_6H_5)B$^-$(C_6H_5)$_3$] as a catalyst. [e] Concentration of the monomer working as a cocatalyst also.

to give a red poly(**OVDHPA**). Yield: 14.1%. M_w = 92 000. M_w/M_n = 2.9 (Table 1, no. 10). ^{1}H NMR (THF-d_8/DMSO-d_6 9:1 v/v, TMS, δ): 7.30 (b, 4.24H,



and

), 6.98 (b, 2H,



), 5.98 (b, 0.76H,

), 4.95−4.43 (b, 6H, PhOCH_2Ph and Ph(CH_2OH)$_2$), 3.80 (b, PhCH_2NH), 3.39 (b, 4H, OCH_2CHN and OCH_2CH$_2$), 2.86 (b, (O*H*)$_2$ and N*H*), 2.50 (b, NHC*H*), 1.87 (b, C*H*(CH$_3$)$_2$), 1.54 (b, 2H, OCH$_2$CH_2CH$_2$), 1.28 (b, 10H, (CH_2)$_5$CH$_3$), 0.91 (b, 9H, CH(CH_3)$_2$ and CH$_2$CH_3). cis % = 76%.

3. Polymerization of ***OPDHPA***. Similar procedures as those described for polymerizations of **OADHPA** were applied. The formed polymer was purified by precipitation of the THF solution into a large amount of methanol and dried in vacuum to give a red poly(**OPDHPA**). Yield: 85.1%. M_w = 257 000. M_w/M_n = 7.7 (Table 1, no. 12). ^{1}H NMR (THF-d_8/DMSO-d_6 9:1 (v/v), TMS, δ): 7.69−7.20 (3b, 11.23H, phenyl and

), 5.97 (b, 0.77H,

), 4.73 and 4.45 (2b, 6H, PhOCH_2Ph and Ph(CH_2OH)$_2$), 3.76 (b, PhCH_2NH), 3.32 and 3.28 (2b, 4H, OCH_2CHN and OCH_2CH$_2$), 2.84 (b, NHC*H*, (O*H*)$_2$ and N*H*) 1.51 (b, 2H, OCH$_2$CH_2), 1.26 (b, 10H, (CH_2)$_5$CH$_3$), 0.86 (b, 3H, CH_3). cis % = 77%.

4. Polymerization of ***OEDHPA***. Similar procedures as those described for polymerizations and purifications of **OADHPA** were applied. Yield: 14.2%. M_w = 32 000. M_w/M_n = 1.2 (Table 1, no. 20). ^{1}H NMR (THF-d_8/DMSO-d_6 9: 1 (v/v), TMS, δ): 7.29 (b, 6.28H, phenyl and

), 5.97 (b, 0.72H,

), 4.89−4.41 (b, 6H, PhOCH_2Ph and Ph(CH_2OH)$_2$), 3.79 (b, PhCH_2NH), 3.47 (b, 2H, OCH_2CH$_2$N), 3.39 (b, 2H, OCH_2CH$_2$CH$_2$), 2.82 (b, NHC*H*, (O*H*)$_2$ and N*H*), 1.53 (b, 2H, OCH$_2$CH_2CH$_2$), 1.28 (b, 10H, (CH_2)$_5$CH$_3$), 0.88 (b, 3H, CH_3). cis % = 72%.

For the other data such as M_w and CD, see Tables 1 and 2, Figures 1−7, and Figures S1−S4 (Supporting Information).

Measurements. ^{1}H NMR (270 MHz) spectra were recorded on a JEOL LEOLEX-270 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatograph instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20 °C (a quartz cell of 1 mm path length; sample concentration: 0.10 to 2.0 mM based on the monomer unit). The specific rotations were recorded with

Table 2. Solubility of Poly(ORDHPA)s and Poly(RDHPA)s[a]

polymer	$CHCl_3$	THF	methanol	DMF	DMSO
poly(**OADHPA**)	++	++	+	+	+
poly(**OVDHPA**)	++	++	−	−	−
poly(**OPDHPA**)	++	++	−	−	−
poly(**OEDHPA**)	++	++	+	+	+
poly(**ADHPA**)[b]	−	−	++	++	++
poly(**VDHPA**)[b]	−	+	+	+	+
poly(**PDHPA**)[b]	−	−	++	++	++

[a] ++: soluble, +: partially soluble, −: insoluble. [b] From ref 6.

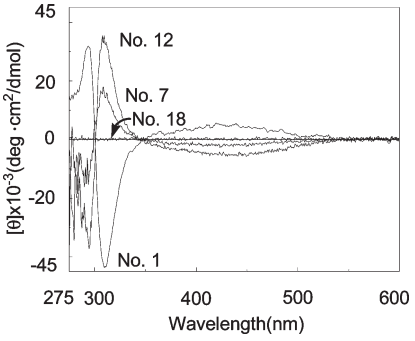


Figure 1. CD spectra of poly(**ORDHPA**)s in THF prepared by using (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ (Table 1, nos. 1, 7, 12, and 18).

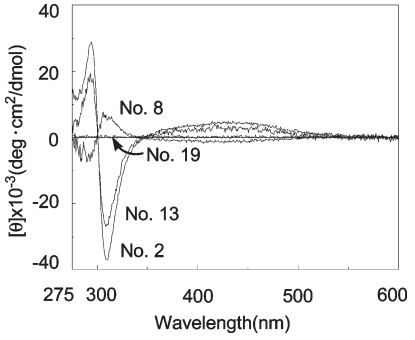


Figure 2. CD spectra of poly(**ORDHPA**)s in THF prepared by using $[Rh(nbd)Cl]_2$/TEA (Table 1, nos. 2, 8, 13, and 19).

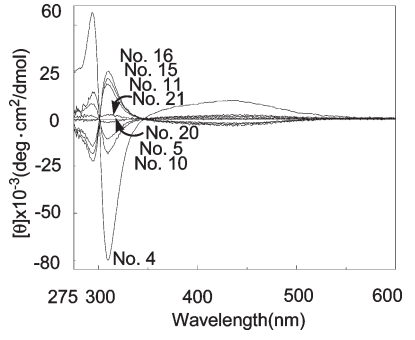


Figure 3. CD spectra of poly(**ORDHPA**)s in THF prepared by using $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA (Table 1, nos. 4, 5, 10, 11, 15, 16, 20, and 21).

Polarimeter SEPA-200 (Horiba). The infrared spectra were recorded on FT/IR-4200 (JASCO).

Results and Discussion

Asymmetric Polymerization and Solubility of the Formed Polymers. The results of polymerizations are shown in Table 1. Except for the two polymers of an achiral **OEDHPA**

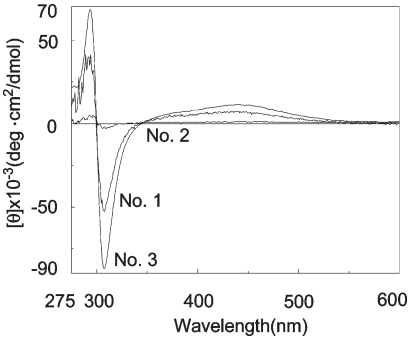


Figure 4. CD spectra of poly(**DoDHPA**)s in THF prepared by using octyl ethers of L-amino alcohols as a chiral cocatalyst (Table 3, nos. 1−3).

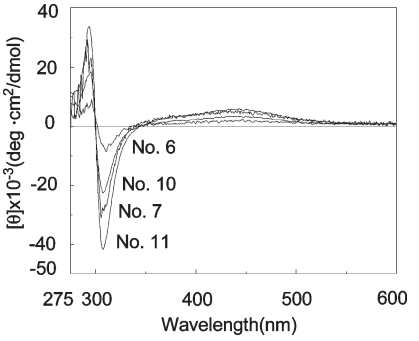


Figure 5. CD spectra of poly(**DoDHPA**)s in THF prepared by using a 1:1 (v/v) mixture of (*R*)- or (*S*)-PEA and octyl ether of L-alaninol or octyl ether of L-phenylalaninol as cocatalysts (Table 3, nos. 6, 7, 10, and 11).

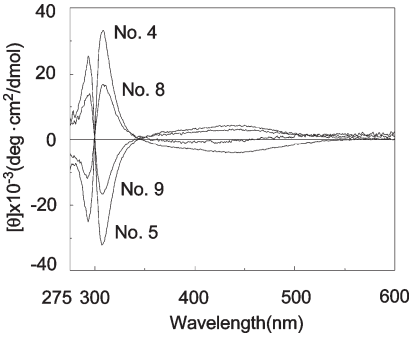


Figure 6. CD spectra of poly(**DoDHPA**)s in THF prepared by using a 1:1 (v/v) mixture of (*R*)- or (*S*)-PEA and octyl ether of L-valinol as cocatalysts (Table 3, nos. 8 and 9), and by using (*R*)- or (*S*)-PEA as cocatalysts (Table 3, nos. 4 and 5).

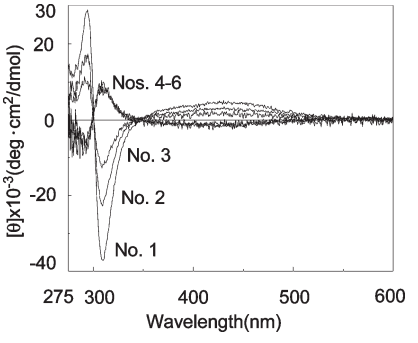


Figure 7. Effect of monomer concentration on CD of poly(**ORDHPA**)s by using an achiral catalytic system (Table 4, nos. 1−6).

(Chart 3) prepared by using two achiral catalysts (Table 1, nos. 18 and 19), all of the new resulting polymers (**ORDHPA** in Chart 3) showed CD absorptions assigned to their main chains (Figures 1−3).[5] The absorption band at 430 nm is assigned to the conjugated main chain, and the peaks at 310 nm may arise from a chiral position between adjacent pendant groups. They indicated that the polymers had a one-handed helical structure in their main chains.

As shown in Table 2, all of the polymers having octyl groups (**ORDHPA** in Chart 3) in this study were soluble in chloroform and THF and insoluble or partially soluble in polar solvents such as methanol, DMF, and DMSO. By introducing an octyl group to the corresponding **RDHPA**s (Chart 2) in our previous study,[6] the resulting polymers changed from being insoluble in chloroform and THF and soluble in polar solvents to being soluble in chloroform and THF, in which the hydrogen bonds in the resulting polymers were maintained. This is a very important point because intramolecular hydrogen bonds are needed to maintain the one-handed helicity.[5]

Effect of the Catalytic Systems on the Asymmetric Polymerizations. *Asymmetric-Induced Polymerization Using the Achiral Catalysts ((nbd)Rh$^+$[η^6-(C_6H_5)B^-(C_6H_5)$_3$] or [Rh(nbd)Cl]$_2$/TEA).* As shown in Figures 1 and 2, chiral **ORDHPA**s (**OADHPA**, **OVDHPA**, and **OPDHPA**) were polymerized by the achiral catalysts (nbd)Rh$^+$[η^6-(C_6H_5)B^-(C_6H_5)$_3$] or [Rh(nbd)Cl]$_2$/TEA to give chiral polymers showing CD absorptions assignable to the main chains (Table 1, nos. 1, 7, 8, 12, and 13). Despite the long distance between the chiral group and the polymerizable group, one-handed helicity was induced. Therefore, the three chiral monomers having an L-amino ether residue seemed to be suitable for **AIP**, where the chiral source is the L-amino ether residue.

In general, monomers having a bulkier chiral substituent tend to give polymers showing larger CD absorption at the main-chain region. However, in these polymerizations (**AIP**) mentioned above, some unexpected results were observed. The absolute [θ] values of poly(**OADHPA**) and poly(**OPDHPA**) were similar (Table 1, nos. 1, 2, 12, and 13), and the sign of the [θ] value for poly(**OPDHPA**) prepared by using (nbd)Rh$^+$[η^6-(C_6H_5)B^-(C_6H_5)$_3$] was opposite to that prepared by using [Rh(nbd)Cl]$_2$/TEA (Table 1, nos. 12 and 13). To explain these unexpected phenomena, we propose the existence of a third mechanism for the asymmetric polymerization of **ORDHPA**s other than **AIP** and **HSSP**. In the case of polymerization of chiral **ORDHPA**s (**OADHPA**, **OVDHPA**, and **OPDHPA**) having a chiral bidentate ligand, their chiral ligand can coordinate to the rhodium catalyst, and the formed complex can work as a chiral catalytic system in **HSSP**. We call it **SHSSP**.

We suppose that the decreasing order of coordination ability to the rhodium of the L-amino ether residues in **ORDHPA** is **OADHPA** > TEA > **OPDHPA**, judging from the following experimental results. Because both poly(**OADHPA**)s prepared by two kinds of achiral catalysts showed similar [θ] values (Table 1, nos. 1 and 2), the effect of TEA added as a cocatalyst was thought to be small. Because both poly(**OPDHPA**)s prepared by two kinds of achiral catalysts showed completely different [θ] values (Table 1, nos. 12 and 13), in the case of polymerization of **OPDHPA** by using [Rh(nbd)Cl]$_2$/TEA, TEA may preferentially coordinate to rhodium compared with the bidentate ligand in **OPDHPA**; therefore, **SHSSP** was thought to be suppressed. In other words, when TEA was used, mainly **AIP** occurred, and when TEA was not used, mainly **SHSSP** occurred. A detailed discussion of this point will be presented in a later section.

Helix-Sense-Selective Polymerization Using [Rh(nbd)Cl]$_2$/(R)- or (S)-PEA. The results of polymerization of **ORDHPA**s by using a chiral catalytic system, [Rh(nbd)Cl]$_2$/(*R*)- or (*S*)-PEA, are shown in Table 1 and Figure 3. Poly(**OVDHPA**)s (Table 1, nos. 10 and 11) and poly(**OEDHPA**)s (Table 1, nos. 20 and 21) prepared by using this catalyst showed CD absorptions having opposite signs for (*R*)- and (*S*)-PEA. Poly(**OADHPA**)s (Table 1, nos. 4 and 5) and poly(**OPDHPA**)s (Table 1, nos. 15 and 16) showed CD absorptions having the same signs when (*R*)- or (*S*)-PEA was used (Figure 3). The sense of the helicity of the main chains of poly(**OVDHPA**) and poly(**OEDHPA**) can be controlled by the chirality of the cocatalysts, but the helical sense of poly(**OADHPA**) and poly(**OPDHPA**) cannot be controlled in this way. Therefore, we concluded that **OVDHPA** and **OEDHPA** were suitable for **HSSP**, whereas **OADHPA** and **OPDHPA** were not.

However, in the case of **OEDHPA**, the [θ] values were much smaller (Table 1, nos. 20 and 21, and Figure 3) than those in the case of **DoDHPA** (Chart 1) (Table 3, nos. 4 and 5, and Figure 6) . This may also be because the achiral amino ether residues in **OEDHPA** coordinated to the rhodium preferentially compared with chiral PEAs. As a result, the amino ether ligands suppressed **HSSP** by chiral PEAs. A detailed discussion appears in the following section.

Self-Helix-Sense-Selective Polymerization. Why is it that only in the case of **OVDHPA** the helical sense of the polymer was controlled by the chirality of PEA as a cocatalyst? Why is it that a similar degree of control to **OVDHPA** was not possible for **OADHPA** and **OPDHPA**? Furthermore, why were the [θ] values of poly(**OEDHPA**)s prepared by **HSSP** so small? To explain these unexpected behaviors in asymmetric polymerizations (**AIP** and **HSSP**) of **ORDHPA**s, we present here details of the third mechanism briefly mentioned above, **SHSSP**.

We have already reported that (*R*)- or (*S*)-PEA coordinated to the rhodium catalyst acted as a cocatalyst and controlled the helix sense in the **HSSP** of the achiral monomer, **DoDHPA** (Chart 1).[5] In this study, the chiral amino ether residues in the monomer and the resulting polymer were thought to work as a ligand and cocatalyst of **HSSP** instead of (*R*)- and (*S*)-PEA.[14]

To obtain supporting evidence of the possibility of the existence of the new **SHSSP** mechanism, a model **HSSP** experiment was carried out as follows: an achiral monomer **DoDHPA** (Chart 1) was polymerized by using octyl ethers of L-alaninol, L-valinol, or L-phenylalaninol as cocatalysts. The results are listed in Table 3. It shows that these L-amino ethers also are effective for **HSSP** (Table 3, nos. 1−3, and Figure 4). Judging from the [θ] values of the formed polymers, the abilities for asymmetric induction of octyl ethers of L-alaninol (Table 3, no. 1) and L-phenylalaninol (Table 3, no. 3) are similar to each other, and much better than that of octyl ether of L-valinol (Table 3, no. 2). These findings were consistent with the results that **OADHPA** and **OPDHPA** produced unexpected behavior in polymerization and **OVDHPA** did not. Therefore, they support some contribution of **SHSSP** to the asymmetric polymerization of **OADHPA** and **OPDHPA** having octyl ethers of L-alaninol and L-phenylalaninol, respectively.

In addition, **DoDHPA** was polymerized by using 1:1 molar ratio mixtures of octyl ethers of L-alaninol, L-valinol, or L-phenylalaninol and (*R*)- or (*S*)-PEA as cocatalysts (Table 3, nos. 6−11). In the case of mixtures containing octyl ether of L-alaninol or octyl ether of L-phenylalaninol, the signs of the [θ] values of the formed polymers were the same irrespective of the chirality of PEA used (Table 3, nos. 6, 7, 10, and 11 and

Table 3. Polymerizations (HSSP) of DoDHPA by Using $[Rh(nbd)Cl]_2$ As a Catalyst and Octyl Ethers of L-Amino Alcohols (5−7) As Cocatalysts[a,b]

no.	cocatalyst	yield (%)	M_w ($\times 10^6$)[c]	M_w/M_n[c]	$[\theta]_{430}$ ($\times 10^3$)[d]
1	octyl ether of L-alaninol (**5**)	58.3	1.6	3.1	6.9
2	octyl ether of L-valinol (**6**)	55.6	3.5	2.7	0.8
3	octyl ether of L-phenylalaninol (**7**)	37.2	1.2	2.3	11.0
4	(*R*)-PEA	5.36	3.2	2.3	−4.0
5	(*S*)-PEA	68.2	3.5	1.7	4.1
6[e]	(*R*)-PEA/octyl ether of L-alaninol (**5**)	81.6	1.9	3.2	1.9
7[e]	(*S*)-PEA/octyl ether of L-alaninol (**5**)	78.5	2.3	3.8	4.9
8[e]	(*R*)-PEA/octyl ether of L-valinol (**6**)	79.2	1.3	2.8	−3.1
9[e]	(*S*)-PEA/octyl ether of L-valinol (**6**)	79.5	1.5	3.1	3.0
10[e]	(*R*)-PEA/octyl ether of L-phenylalaninol (**7**)	42.3	1.1	2.3	3.0
11[e]	(*S*)-PEA/octyl ether of L-phenylalaninol (**7**)	75.2	1.1	2.4	5.5

[a] See Scheme 1. [b] At room temperature in toluene, [monomer] = 0.1 mol/L, [monomer]/[catalyst] = 100, [cocatalyst]/[catalyst] = 100. [c] Determined by GPC correlating polystyrene standard with THF eluent. [d] In deg·cm^2/dmol, 1.0 mmol/L, in THF. [e] Molar ratio is 1: 1.

Figure 5). In the case of the mixtures containing octyl ether of L-valinol, the signs of the $[\theta]$ values of the formed polymers were opposite (Table 3, nos. 8 and 9, and Figure 6), like the case of **HSSP** of **DoDHPA** by (*R*)- or (*S*)-PEA, where the absolute values of $[\theta]$ of the resulting polymers were the same and the signs were opposite[5] (Table 3, nos. 4 and 5, and Figure 6). Therefore, abilities of octyl ethers of L-alaninol and L-phenylalaninol for asymmetric induction were higher than those of octyl ether of L-valinol and (*R*)- or (*S*)-PEA, and that of octyl ether of L-valinol was lower than that of PEA. These findings can also explain the unexpected phenomena observed in the asymmetric polymerization of **OADHPA** and **OPDHPA** described above.

We supposed that the observed differences in asymmetric induction ability were mainly caused by the coordinating ability of the ligands to rhodium. We expect the order of coordinating ability to decrease as follows: **OADHPA** > **OPDHPA** > (*R*)- or (*S*)-PEA > **OVDHPA**. In other words, we concluded that in the case of asymmetric polymerization of **OADHPA** and **OPDHPA**, the preferred mechanism was a combination of **SHSSP** and **AIP**. In the case of asymmetric polymerization of **OVDHPA**, the preferential mechanism was **HSSP**. In the case of **OADHPA** and **OPDHPA**, the resulting one-handed helicity was caused by their L-amino alcohol residues. Therefore, the sign of the $[\theta]$ values of the formed polymers were the same (Table 1, nos. 4, 5, 15, and 16); therefore, they were not suitable for **HSSP**. Only the main chain helicity of poly(**OVDHPA**) could be controlled by PEA; therefore, **OVDHPA** was suitable for **HSSP** in addition to **AIP**. The extent of contribution of the three mechanisms will be discussed in the last section.

Asymmetric Polymerization Behavior of ORDHPA. *Asymmetric Polymerization Behavior of OADHPA*. When **OADHPA** was polymerized by using two achiral catalysts, $(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$ and $[Rh(nbd)Cl]_2$/TEA, and a chiral catalytic system, $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA, the signs of the $[\theta]$ values of all the resulting polymers were unexpectedly the same except for no. 6 (Table 1, nos. 1−5 and Figure S1 of the Supporting Information). Therefore, **SHSSP** was thought to be the preferential mechanism in the asymmetric polymerizations of this monomer by any catalytic systems by using cocatalysts because the order of the coordinating ability to the rhodium was thought to be **OADHPA** > TEA > PEA.

However, when the concentration of (*S*)-PEA was high (no. 6 in Table 1), the sign of the $[\theta]$ values was opposite to that of the others. Therefore, the one-handed helicities (nos. 4−6) may be caused not only by the L-amino ether residues but also by (*R*)- or (*S*)-PEA. The main mechanism of the asymmetric polymerization was **SHSSP**, but **HSSP** also contributed to the asymmetric induction in the polymerization. The contribution of **AIP** may be small because of the small size of the methyl group at the chiral center of the L-amino ether residues.

Asymmetric Polymerization Behavior of OVDHPA. Poly(**OVDHPA**)s prepared by using the chiral catalytic system, $[Rh(nbd)Cl]_2$/(*R*)- and (*S*)-PEA, showed CD absorptions having opposite signs; therefore, they had one-handed helixes whose senses were opposite (Figure S2 of the Supporting Information and Table 1, nos. 10 and 11). In addition, poly(**OVDHPA**)s prepared by using the two achiral catalytic systems showed CD absorptions (Figure S2 of the Supporting Information and Table 1, nos. 7−9); therefore, they also had one-handed helicities. These findings indicated that **OVDHPA** was suitable for both **HSSP** and **AIP**. In this case, the ability of PEA for asymmetric induction was thought to be higher than that of L-valinol residue in **OVDHPA** because the coordination ability of PEA was higher than that of **OVDHPA**. In other words, the degree of contribution of **HSSP** was higher than that of **SHSSP**. The contribution of **AIP** was thought to be small but present.

*Asymmetric Polymerization Behavior of **OPDHPA***. The two poly(**OPDHPA**)s prepared by using (*R*)- or (*S*)-PEA showed CD absorptions having the same signs; therefore, the senses of the helix were found to be the same (Figure S3 of the Supporting Information and Table 1, nos. 15 and 16). This unexpected finding indicated that **OPDHPA** was not suitable for **HSSP**, and the coordination ability of a L-phenylalaninol residue in **OPDHPA** was thought to be larger than that of (*R*)- or (*S*)-PEA. In the polymerization of **OPDHPA**, the main mechanism was some combination of **SHSSP** and **AIP**.

The sign of $[\theta]$ for poly(**OPDHPA**) prepared by using $(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$ was opposite to that by using $[Rh(nbd)Cl]_2$/TEA (Table 1 and Figure S3 of the Supporting Information). The coordination ability of TEA is likely to be higher than that of L-phenylalaninol residue in **OPDHPA**. Therefore, in the case of polymerization of **OPDHPA** by using $[Rh(nbd)Cl]_2$/TEA, **SHSSP** was suppressed and **AIP** dominated. Therefore, **AIP** had a relatively large contribution in this polymerization. In summary, the coordination ability decreases as TEA > **OPDHPA** > (*R*)- or (*S*)-PEA. Both **AIP** and **SHSSP** have larger contribution than **HSSP** by PEA in the polymerization of **OPDHPA**.

Order of the Coordinating Ability to the Rhodium and the Extent of Contribution of SHSSP. We have discussed above the order of the coordinating ability of the cocatalysts and ligand moieties in the monomers judging from the results of asymmetric polymerizations of the four new monomers by using four catalytic systems. Finally, we will discuss the order again this time based on the chemical structures of the cocatalysts and ligand moieties in the monomers. Because

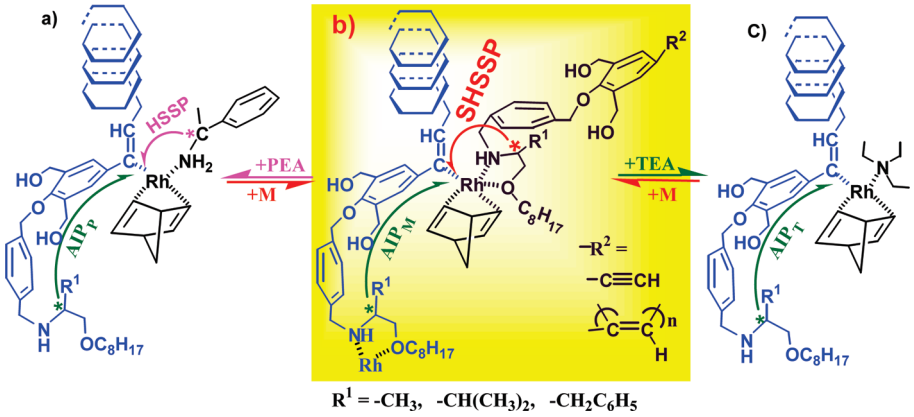


Figure 8. Three mechanisms (**HSSP**, **SHSSP**, and **AIP**) of asymmetric polymerizations of **ORDHPA**s having a chiral bidentate ligand by using achiral and chiral catalytic systems. (a) **HSSP** by using (*R*)-PEA. (b) **SHSSP** by using no cocatalysts. (c) **AIP** by using TEA.

Table 4. Effect of the Monomer Concentration on Polymerizations of ORDHPAs by Using an Achiral Catalytic System, [Rh(nbd)Cl]$_2$/TEA[a]

no.	monomer	[monomer] (mol/L)	yield (%)	M_w ($\times 10^4$)[b]	M_w/M_n[b]	$[\theta]_{430}$ ($\times 10^3$)[c]
1	**OADHPA**	0.1	56.2	14.8	2.5	4.3
2		0.04	47.5	1.8	1.1	2.8
3		0.02	37.5	1.8	1.2	2.0
4	**OVDHPA**	0.1	43.1	6.5	4.1	−1.5
5		0.04	32.8	1.9	1.3	−1.6
6		0.02	32.5	1.9	1.2	−1.4

[a] At room temperature in THF, [catalyst]/[TEA(cocatalyst)] = 500, [monomer]/[catalyst] = 100. [b] Determined by GPC correlating polystyrene standard with THF eluent. [c] In deg·cm^2/dmol, 1.0 mmol/L, in THF.

TEA, **ORDHPA**s, and PEA are tertiary, secondary, and primary amines, respectively, the decreasing order of the basicity is TEA > **ORDHPA** > PEA. The order of the coordinating ability is probably the same. Because the α-carbon of the asymmetric carbons of **OADHPA**, **OPDHPA**, and **OVDHPA** are primary, secondary, and tertiary, respectively, the increasing order of the bulkiness should be **OADHPA** < **OPDHPA** < **OVDHPA**. Therefore, the decreasing order of the coordinating ability may be **OEDHPA** > **OADHPA** > **OPDHPA** > **OVDHPA.**

Judging from the above discussion and the facts that **ORDHPA**s contain a bidentate ligand and TEA and PEA are monodentate ligands, we expect the coordination ability to decrease in the order **OEDHPA** > **OADHPA** > TEA > **OPDHPA** > PEA > **OVDHPA**. This order reasonably explains the relative contributions of the three mechanisms of the asymmetric polymerizations discussed above.

Extent and Control of Contribution of the Three Mechanisms by Changing the Concentrations of TEA, the Monomers, and PEA (Figure 8). As described above in the case of asymmetric polymerizations of the chiral monomers by achiral catalysts, two mechanisms, that is, **AIP** and **SHSSP**, were thought to operate. However, the extent of both contributions was not clear. To obtain information on the extent, we planned to eliminate **SHSSP**. For this purpose, we planned to suppress coordination of the chiral ligands in the monomers to the rhodium by increasing [TEA] or decreasing [monomer]. When [TEA] is higher or [monomer] is lower, some of the ligands in the monomers coordinating to the rhodium may be exchanged with TEA. As a result, the extent of the contribution of **SHSSP** must be lowered (Figure 8b,c).

In the case of asymmetric polymerization of **OADHPA** by achiral catalysts, when [TEA] increased or [**OADHPA**] decreased, the [θ] values decreased (Table 1, nos. 2 and 3, or Figure S4 of the Supporting Information and Table 4, nos. 1−3, and Figure 7). This fact indicated that the asymmetric polymerization proceeded by both **AIP** and **SHSSP** and the extent of the contribution of **SHSSP** could be controlled by the concentration of TEA and **OADHPA**. In addition, the sign of [θ] could be changed by enhancing [(*S*)-PEA], that is, **HSSP** was realized (Table 1, no.6). Therefore, in the case of polymerization of **OADHPA**, **SHSSP** had large contribution and **AIP** had only small contribution. In summary, in asymmetric polymerization of **OADHPA**, the contribution of three mechanisms could be controlled by changing [TEA], [**OADHPA**], and [(*S*)-PEA] because of the small contribution of **AIP** (Figure 8a−c)).

In the case of asymmetric polymerization of **OVDHPA** by achiral catalysts, when [TEA] increased (Table 1, nos. 8 and 9, and Figure S4 of the Supporting Information) or [**OADHPA**] decreased (Table 4, nos. 4−6, and Figure 7), the [θ] values did not decrease. This observation may indicate that the contribution of **SHSSP** was originally small. As described above, **OVDHPA** was suitable to HSSP (Table 1, nos. 10 and 11). In summary, in asymmetric polymerization of **OVDHPA**, the contribution of **AIP** and **HSSP** could be controlled because of the small contribution of **SHSSP** (Figure 8a,c)).

In the case of asymmetric polymerization of **OPDHPA** by achiral catalysts, the sign of [θ] could be changed by adding [TEA] (Table 1, nos. 12 to 13, and Figure S3 of the Supporting Information). This fact may indicate that the transformation of **SHSSP** to **AIP** occurred. However, the signs of [θ] could not be changed by enhancing [(*S*)-PEA] (Table 1, nos. 16 to 17). Therefore, **HSSP** could not be realized because the contribution of **AIP** was too large. In summary, in asymmetric polymerizations of **OPDHPA**, the contribution of **AIP** and **SHSSP** could be controlled (Figure 8b,c).

Conclusions

Three mechanisms for the asymmetric polymerizations of four new monomers were discussed, **HSSP**, **AIP**, and **SHSSP**, the latter being proposed for the first time in this Article. To illuminate the contribution of the three mechanisms to each

asymmetric polymerization, the order of coordination ability was investigated. The following order was postulated: **OEDHPA** > **OADHPA** > TEA > **OPDHPA** > PEA > **OVDHPA**. As a result of the differing coordination abilities, the contributions to the three mechanisms were different in each polymerization. In the case of polymerization of **OADHPA**, **SHSSP** was the preferential mechanism. In the case of polymerization of **OVDHPA**, **HSSP** was the preferential mechanism with some contribution from **AIP**, whereas the contribution of **SHSSP** was small. In the case of polymerization of **OPDHPA**, **AIP** was thought to be the main mechanism, but the contribution of **SHSSP** was significant. Therefore, only **OVDHPA** was suitable for both **HSSP** and **AIP**. **VDHPA** (Chart 2) was also suitable for both **HSSP** and **AIP**, as previously reported. In addition, by changing the concentrations of the cocatalysts and the monomers, the extent of the contribution of the three mechanisms could be controlled to some extent.

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Supporting Information Available: CD spectra for the polymers prepared and a CD spectrum for the chiral catalytic system. The material is available free of charge via the Internet at http://pubs.acs.org.

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(8) In ORDHPA, DH and PA mean dihydroxy groups and phenylacetylene, respectively. In OADHPA, OVDHPA, and OPDHPA, OA, OV, and OP mean the residue of the octyl ether of L-alaninol, L-valinol, and L-phenylalaninol, respectively.

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