Two Modes of Asymmetric Polymerization of Phenylacetylenes Having an L-Amino Alcohol Residue and Two Hydroxy Groups

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ABSTRACT: Four novel chiral phenylacetylenes having an L-amino alcohol residue and two hydroxymethyl groups were synthesized and polymerized by an achiral catalyst ((nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$) or a chiral catalytic system ($[Rh(nbd)Cl]_2$/(*S*)- or (*R*)-phenylethylamine ((*S*)- or (*R*)-PEA)). The two resulting polymers having an L-valinol or L-phenylalaninol residue 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 only for the polymers having an L-valinol residue produced by using (*R*)- and (*S*)-PEA as a cocatalyst, respectively, although the monomer had the same chirality. Even when the achiral catalyst was used, the two resulting polymers having an L-valinol or L-phenylalaninol residue showed Cotton effects despite the long distance between the chiral groups and the main chain. We have found the first example of a new type of chiral monomer, that is, a chiral phenylacetylene monomer having an L-amino alcohol residue and two hydroxy groups that was suitable for both modes of asymmetric polymerization, that is, the helix-sense-selective polymerization (**HSSP**) with the chiral catalytic system and the asymmetric-induced polymerization (**AIP**) with the achiral catalyst. The other two monomers having L-alaninol and L-tyrosinol were found to be unsuitable to neither **HSSP** nor **AIP** because of their polymers' low solubility. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: asymmetric polymerization; catalysts; chiral; conjugated polymers; initiators; L-amino alcohol; polyacetylenes

INTRODUCTION Conjugated polymers like polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical nonlinear susceptibility. Recently, chiral polyacetylenes have received much attention as the chiral structure can enhance the unique properties and add new functions.[1]

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(h)] 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[2(a)] and (+)-*p*-(10-pinanyloxycarbonyl)phenylacetylene[2(g)] obtained with a 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 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 1-, 3-, and/or 5-position of an oligosiloxane chain were polymerized with a Rh complex to produce high-molecular-weight polymers.[2(g)] The polymers with a chiral pinanyl group at the 1-position of an oligosiloxanyl group showed high molar ellipticity in the main-chain region in the CD spectra. On the other hand, the polymers from monomers with a chiral pinanyl group at the 3- or 5-position 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.

In 2003, 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**) by using a chiral catalytic system consisting of a rhodium dimeric complex, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene), as a catalyst, and a chiral amine, (*R*)-1-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.[5(a, b)] On the other hand, 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 which were suitable for both asymmetric polymerizations. Therefore, we reported new monomers suitable to both modes of asymmetric polymerization, that is, **HSSP** and **AIP** for the first time. They were chiral hydrophobic phenylacetylene monomers having an *O*-octylated amino alcohol residue.[5(m)]

In this study, to develop new monomers which can be used for both modes of asymmetric polymerizations, that is, **AIP** and **HSSP**, novel chiral monomers **RDHPA**s (**ADHPA, VDHPA, PDHPA**, and **TDHPA**, Chart 1) were designed and synthesized. Monomers **RDHPA**s contain two hydroxy groups and a chiral group, an L-amino alcohol residue, which was introduced via a relatively long spacer. We previously reported that **VDHPA** was suitable to both **AIP** and **HSSP**.[6] In this article, effects of the kind of amino alcohol residues in **RDHPA**s on the two modes of asymmetric polymerizations will be discussed.

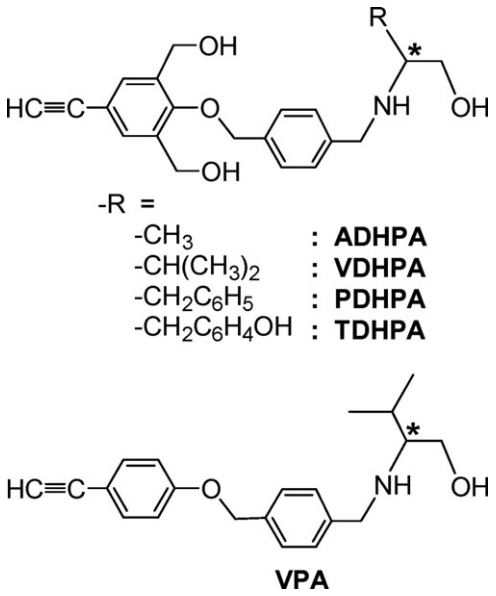


CHART 1 Chemical structures of the chiral monomers (**RDHPA**s and **VPA**).

EXPERIMENTAL

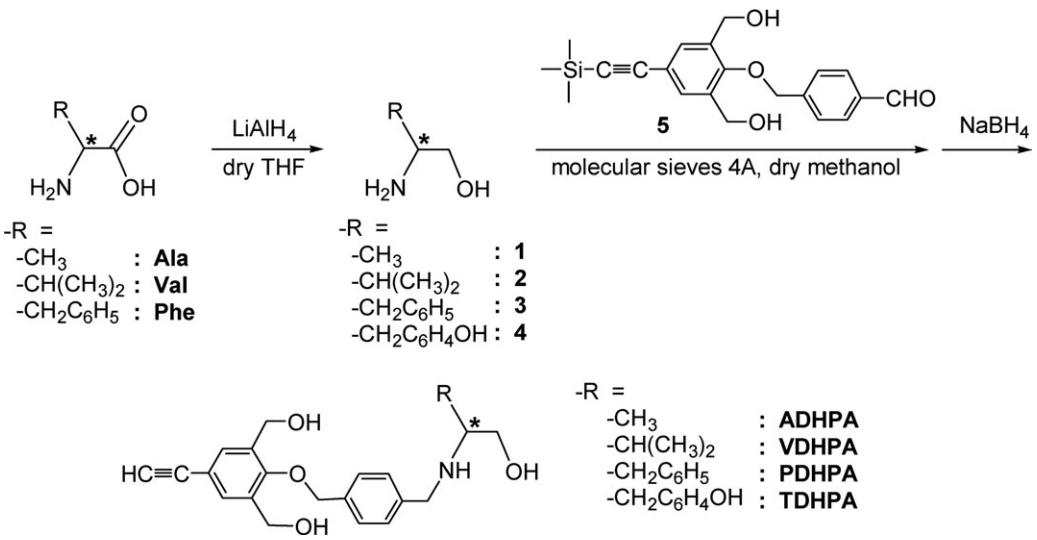
Materials

All 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 Co., was used as received. According to the literature procedures, $(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$ was prepared.[7] L-Alanine (**Ala**, $[\alpha]_D^{20}$: $+14.3^\circ \sim +15.2^\circ$ (*c* 1, 6 molL^{-1} HCl)), L-valine (**Val**, $[\alpha]_D^{20}$: $+27.6^\circ \sim +28.7^\circ$ (*c* 8, 6 molL^{-1} HCl)), L-phenylalanine (**Phe**, $[\alpha]_D^{20}$: $-33.5^\circ \sim -35.0^\circ$ (*c* = 2, H_2O)), and L-tyrosine (**Tyr**, $[\alpha]_D^{20}$: -10.2° (*c* 4, 1 molL^{-1} HCl)) purchased from Junsei Chemical Co., were used as received.

Synthetic Procedures and Characterization of Monomers (ADHPA, VDHPA, PDHPA, TDHPA, and VPA)

All the following reaction procedures were conducted under dry nitrogen (Schemes 1–4).

1. L-Alaninol (Scheme 1) (**1**)[6,8]
   A mixture of **Ala** (5.00 g, 56.1 mmol) in dry tetrahydrofuran (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 added slowly. 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). $[\alpha]_D^{20}$: $+8.5^\circ$ (*c* 0.10, THF). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 3.52 and 3.24 (2dd, 2H, C*H*$_2$OH), 3.01 (m, 1H, NH$_2$C*H*), 2.51 (b, 3H, N*H*$_2$ and O*H*), 1.06 (d, 3H, *J* = 6.2 Hz, C*H*$_3$).
2. L-Valinol (**2**) (Scheme 1)[6,8]
   According to the literature procedure, **2** was prepared. Yield: 57.5%. Bp: 42 °C (0.32 mmHg). Appearance: colorless liquid. $[\alpha]_D^{20}$: $+11^\circ$ (*c* = 0.10, THF). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 3.60 and 3.25 (2dd, 2H, C*H*$_2$OH), 2.52 (m, 1H, NH$_2$C*H*), 1.87 (b, 3H, N*H*$_2$ and O*H*), 1.55 (m, 1H, C*H*(CH$_3$)$_2$), 0.87 and 0.90 (2d, 6H, J = 3.4 Hz, CH(C*H*$_3$)$_2$).
3. L-Phenylalaninol (**3**) (Scheme 1)[6,8]
   A similar procedure as described for **1** was used. 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



SCHEME 1 Synthetic route to **RDHPA**s (**ADHPA, VDHPA, PDHPA**, and **TDHPA**).

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, THF). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 7.34–7.17 (m, 5H, phenyl), 3.64 and 3.38 (2dd, 2H, CH_2OH), 3.10 (m, 1H, NH$_2$CH), 2.80 and 2.52 (2dd, 2H, PhCH_2), 2.10 (b, 3H, NH_2 and OH).

Because **Tyr** was insoluble in THF, L-tyrosinol (**4**, Scheme 1) could not be prepared according to a similar procedure as described for **1**. As shown in Scheme 2, **4** was prepared as follows.

4.. L-Tyrosine methyl ester (**6**) (Scheme 2)[9]

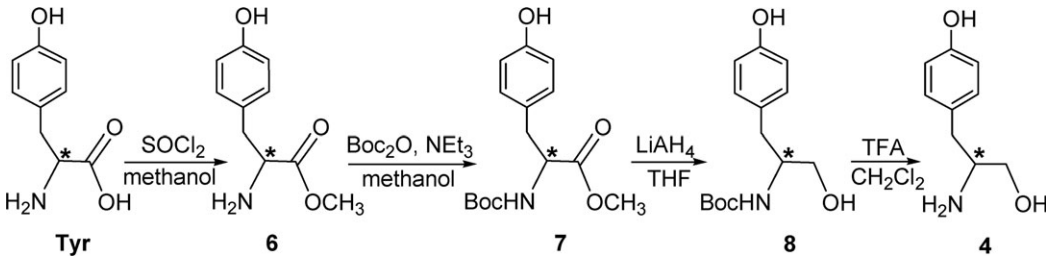
A solution of **Tyr** (1.80 g, 9.94 mmol) in dry methanol (5.0 mL) was added dropwise to a solution of $SOCl_2$ (2.6 mL) in dry methanol (5.0 mL) at −10 °C. The solution was stirred for 48 h at room temperature. After the solution was concentrated, the crude production was purified by crystallization in methanol to give **6** as white solid. Yield: 88.7% (1.72 g). $[\alpha]_D^{20}$: 26° (c = 2.0, methanol). ^{1}H NMR (270 MHz, CD_3OD, δ, ppm): 7.02 (d, 2H, J = 8.6 Hz, HO-C$_6$H$_4$-), 6.73 (d, 2H, J = 8.6 Hz, HO-C$_6$H$_4$-), 4.19 (m, 1H, NH$_2$CH,), 3.77 (s, 3H, OCH_3), 3.10 and 3.00 (2dd, 2H, PhCH_2).

5. L-*N*-*t*-butyloxycarbonyltyrosine methyl ester (**7**) (Scheme 2)[9]

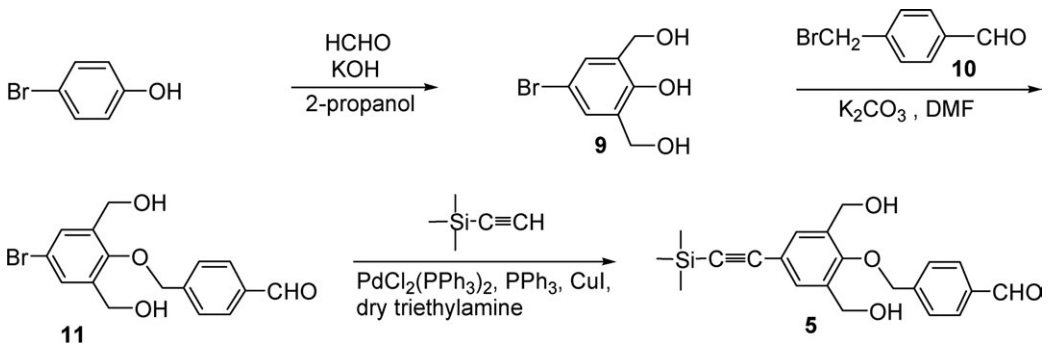
A solution of **6** (1.72 g, 8.81 mmol), di(*t*-butyl)dicarbonate (Boc_2O, 2.12 g, 9.69 mmol), and triethylamine (2.5 mL) in methanol (10 mL) was stirred for 17 h at room temperature. After the solution was concentrated, the crude product was purified by silica-gel column chromatography to give **7** as white solid. Yield: 77.3% (2.00 g). R_f: 0.36 (chloroform:methanol:acetic acid = 97:2:1). $[\alpha]_D^{20}$: 18° (c = 2.0, methanol). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 6.96 (d, 2H, J = 8.6 Hz, HO-C$_6$H$_4$-), 6.72 (d, 2H, J = 8.6 Hz, HO-C$_6$H$_4$-), 4.97 (b, 1H, PhOH), 4.50 (m, 1H, NHCH), 3.70 (s, 3H, OCH_3), 3.00 and 2.98 (2dd, 2H, PhCH_2), 1.40 (s, 9H, C(CH_3)$_3$).

6.. L-*N*-*t*-butyloxycarbonyltyrosinol (**8**) (Scheme 2)[6,8]

A similar procedure as described for **1** was applied. 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 **8** as white solid. Yield: 69.6%. $[\alpha]_D^{20}$: −16° (c = 2.0, methanol). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 7.03 (d, 2H, J = 8.3 Hz, HO-C$_6$H$_4$-),



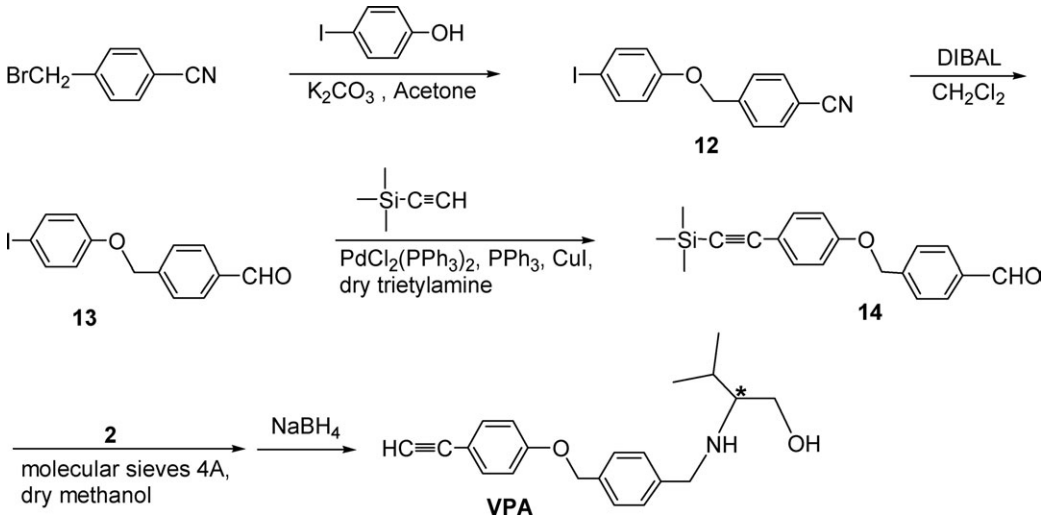
SCHEME 2 Synthetic route to L-tyrosinol (**4**).



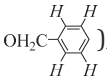
SCHEME 3 Synthetic route to Compound **5**.

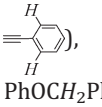
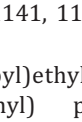
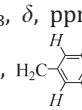
6.73 (d, 2H, J = 8.3 Hz, HO-C$_6$H$_2$-H), 4.71 (b, 1H, PhO*H*), 3.80 (m, 1H, NHC*H*), 3.64 and 3.50 (2dd, 2H, CH_2OH), 2.72 (d, 2H, J = 7.2 Hz, PhCH_2), 1.40 (s, 9H, C(CH_3)$_3$).

7. L-Tyrosinol (**4**) (Scheme 2)[9]
   A solution of **8** (1.18 g, 4.45 mmol) and trifluoroacetic acid (10 mL) in CH_2Cl_2 (10 mL) was stirred for 20 h at room temperature. After $NaHCO_3$ aqueous (1 molL^{-1}, 50 mL) was added, the mixture was extracted with brine and CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated. Then, the crude product was purified by recrystallization in ethyl acetate to give **4** as yellow solid. Yield: 79.0% (0.587 g). $[\alpha]_D^{20}$: −13° (c = 2.0, methanol). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 7.06 (d, 2H, J = 8.6 Hz, HO-C$_6$H$_2$-H), 6.77 (d, 2H, J = 8.6 Hz, HO-C$_6$H$_2$-H), 6.56 (b, 1H, PhO*H*), 4.16 (m, 1H, NH_2CH), 3.70 and 3.66 (2dd, 2H, CH_2OH), 2.86 (d, 2H, J = 7.2 Hz, PhCH_2).
8. 4-{4-Trimethylsilylethynyl-2,6-(bishydroxymethyl)-1-phenoxymethyl}benzaldehyde (**5**) (Scheme 3)[5(a, b),6]
   According to the method we reported before, **5** 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 (270 MHz, $CDCl_3$, δ, ppm): 10.04 (s, 1H, C*H*O), 7.92 (d, 2H, J = 8.3 Hz, CHO-C$_6$H$_2$-H), 7.61 (d, 2H, J = 8.3 Hz, OH$_2$C-C$_6$H$_2$-H), 7.51 (s, 2H, ≡-C$_6$H$_2$-H), 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$_2$O*H*)$_2$), 0.24 (s, 9H, Si(CH_3)$_3$).
9. (+)-4-[4-{(2-Hydroxy-1-methyl)ethylaminomethyl}benzyloxy]-3,5-bis(hydroxymethyl) phenylacetylene (**ADHPA**) (Scheme 1)[6,10,11]
   A solution of **5** (1.22 g, 3.32 mmol), **1** (0.248 g, 3.32 mmol) in dry methanol (30 mL) was stirred in the presence of molecular sieves 4 Å (3.0 g) for 24 h at room temperature. Sodium tetrahydroborate (0.126 g, 3.32 mmol) was added, 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 **ADHPA** as white solid. Yield: 50.0% (0.580 g). R_f: 0.10 (chloroform:methanol = 4:1). $[\alpha]_D^{20}$: 12° (c = 0.10, THF). ^{1}H NMR (270 MHz,



SCHEME 4 Synthetic route to **VPA**.

DMSO-d_6, δ, ppm): 7.47 (s, 2H, ),7.38 (b, 4H, ), 5.20 (b, 3H, Ph(CH_2OH)$_2$ and $CHCH_2OH$), 4.82 (s, 2H, PhOCH_2Ph), 4.52 (s, 4H, Ph(CH_2OH)$_2$), 4.08 (b, 1H, N*H*), 3.75 (2d, 2H, J = 13 Hz, PhCH_2NH), 3.27 (m, 2H, $CHCH_2$OH), 3.16 (s, 1H, *H*C≡C), 2.62 (m, 1H, NHC*H*), 0.94 (d, 3H, J = 6.2 Hz, $CHCH_3$). IR (cm^{-1}, KBr): 3263, 2967, 2926, 2855, 1728, 1630, 1599, 1516, 1456, 1420, 1362, 1346, 1293, 1269, 1209, 1141, 1106, 1067, 1050, 1029.

10. (−)-4-[4-{(2-Hydroxy-1-isopropyl)ethylaminomethyl}-benzyloxy]-3,5-bis(hydroxymethyl) phenylacetylene (**VDHPA**) (Scheme 1).[6,10,11]
    According to the method we reported before, **VDHPA** was prepared. Yield: 64.0%. Appearance: white solid. R_f: 0.29 (chloroform:methanol = 4:1). $[\alpha]_D^{20}$: −71° (c = 0.50, THF). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 7.49 (s, 2H, ), 7.34 (b, 4H, ), 4.95 (s, 2H, PhOCH_2Ph), 4.57 (s, 4H, Ph(CH_2OH)$_2$), 3.79 (2d, J = 13 Hz, 2H, PhCH_2NH), 3.58 and 3.33 (2dd, 2H, $CHCH_2$OH), 3.03 (s, 1H, *H*C≡C), 2.44 (m, 1H, NHC*H*), 1.86 (m, 5H, Ph(CH_2OH)$_2$, $CHCH_2OH$, N*H* and $CH(CH_3)_2$), 0.97 and 0.90 (2d, 6H, J = 6.8 Hz, $CH(CH_3)_2$). IR (cm^{-1}, KBr): 3246, 2954, 2874, 2104, 1608, 1459, 1364, 1291, 1205, 1135, and 1063.
11.. (−)-4-[4-{(2-Hydroxy-1-benzyl)ethylaminomethyl}benzyloxy]-3,5-bis(hydroxymethyl) phenylacetylene (**PDHPA**) (Scheme 1)[6,10,11]
    A similar procedure as described for **ADHPA** was applied. Yield: 67.0%. Appearance: white solid. R_f: 0.20 (chloroform:methanol = 4:1). $[\alpha]_D^{20}$: −13° (c = 0.10, THF). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 7.49 (s, 2H, ), 7.40–7.14 (m, 9H, Phenyl), 4.93 (s, 2H, PhOCH_2Ph), 4.59 (s, 4H, Ph(CH_2OH)$_2$), 3.74 (2d, 2H, J = 13 Hz, PhCH_2NH), 3.57 and 3.29 (2dd, 2H, $CHCH_2$OH), 3.02 (s, 1H, *H*C≡C), 2.90 (m, 1H, NHC*H*), 2.77 (dd, 2H, PhCH_2CH), 2.00 (b, 4H, Ph(CH_2OH)$_2$, $CHCH_2OH$ and N*H*). IR (cm^{-1}, KBr): 3289, 3025, 2925, 2828, 2107, 1633, 1602, 1514, 1495, 1454, 1419, 1357, 1203, 1134, 1115, 1067, and 1036.
12. (−)-4-[4-{2-Hydroxy-1-(4-hydroxybenzyl)ethylaminomethyl} benzyloxy]-3,5-bis(hydroxymethyl) phenylacetylene (**TDHPA**) (Scheme 1)[6,10,11]
    A similar procedure as described for **ADHPA** was applied. Yield: 71.0%. Appearance: white solid. R_f: 0.24 (chloroform:methanol = 2:1). $[\alpha]_D^{20}$: −11° (c 0.1, THF). ^{1}H NMR (270 MHz, DMSO-d_6, δ, ppm): 7.48 (s, 2H, ), 7.44–7.18 (m, 8H, Phenyl), 5.25 (b, 4H, Ph(CH_2OH)$_2$, $CHCH_2OH$ and PhO*H*), 4.83 (s, 2H, PhOCH_2Ph), 4.55 (s, 4H, Ph(CH_2OH)$_2$), 4.10 (m, 1H, N*H*), 3.77 (2d, 2H, J = 13 Hz, PhCH_2NH), 3.37 (m, 2H, $CHCH_2$OH), 3.17 (s, 1H, *H*C≡C), 2.68 (m, 2H, PhCH_2CH), 1.91 (m, 1H, NHC*H*). IR (cm^{-1}, KBr): 3285, 2928, 2881, 2360, 1790, 1700, 1631, 1600, 1516, 1477, 1423, 1405, 1367, 1310, 1285, 1227, 1146, 1111, and 947.
13. (−)-4-[4-{(2-hydroxy-1-isopropyl)ethylaminomethyl}benzyloxy]phenylacetylene (**VPA**) (Scheme 4)[6,10,11]
    According to the method we reported before, **VPA** was prepared. Yield: 79.1%. Appearance: white solid. R_f: 0.30 (chloroform:methanol = 8:1). $[\alpha]_D^{20}$: −13° (c = 0.10, THF). ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 7.42 (d, 2H, J = 8.7 Hz, ), 7.38 (b, 4H, ), 6.89 (d, 2H, J = 8.7 Hz, ), 5.03 (s, 2H, PhOCH_2Ph), 3.80 (2d, 2H, J = 13 Hz, PhCH_2NH), 3.63 and 3.38 (2dd, 2H, CH_2OH), 2.98 (s, 1H, *H*C≡C), 2.48(m, 1H, NHC*H*), 2.15 (b, 2H, O*H* and N*H*), 1.87 (m, 1H, $CH(CH_3)_2$), 0.96 and 0.90 (2d, 6H, J = 6.8 Hz, $CH(CH_3)_2$). IR (cm^{-1}, KBr): 3277, 3156, 2958, 2927, 2871, 2097, 1604, 158, 1506, and 1468.

Polymerizations

The **AIP** and the **HSSP** were performed by an achiral catalyst, (nbd)Rh$^+$[η^6-(C_6H_5)B$^-$(C_6H_5)$_3$] and a chiral catalytic system, [Rh(nbd)Cl]$_2$ (nbd = 2,5-norbornadiene)/(*R*)- or (*S*)-PEA, respectively.[5,6]

1. Polymerizations of **VDHPA**[5,6]
   A solution of [Rh(nbd)Cl]$_2$ (0.24 mg, 0.52 μmol) and an amine such as (*R*)-phenylethylamine (35 μL, 0.26 mmol) in THF (0.65 mL) was added to a solution of monomer **VDHPA** (50 mg, 0.13 mmol) in THF (0.65 mL). The reaction solution was stirred at room temperature for 4 h. The formed polymer was purified by precipitation of the polymerization solution into a large amount of acetone and dried in vacuum to give a red polymer. The other polymerizations of **VDHPA** were also conducted similarly by using (nbd)Rh$^+$[η^6-(C_6H_5)B$^-$(C_6H_5)$_3$]. For the other data such as yield, M_w, and CD, see Table 1 and Figure 1.
2. Polymerizations of **ADHPA**[5,6]
   A similar procedure as described for polymerization of **VDHPA** was applied. The formed polymer was purified by precipitation of the polymerization solution into a large amount of acetone and dried in vacuum to give a red polymer. For the other data such as yields, M_w, and CD, see Table 1.
3. Polymerizations of **PDHPA**[5,6]
   A similar procedure as described for polymerization of **VDHPA** was applied. The formed polymer was purified by precipitation of the polymerization solution into a large amount of acetone and dried in vacuum to give a red polymer. The other polymerization procedure was also applied. For example, a solution of (nbd)Rh$^+$[η^6-(C_6H_5)B$^-$(C_6H_5)$_3$] (0.24 mg, 0.52 μmol) and monomer **PDHPA** (50 mg, 0.12 mmol) in THF (1.17 mL) was stirred at room temperature for 4 h. During polymerization, the

TABLE 1 Polymerizations of **RDHPA**s and **VPA** by Using Achiral or Chiral Catalytic Systems[a]

No.	Chiral Monomer					Polymer						
		$[\alpha]_D^{20}$[b]			Chiral	Yield	M_w		$[\alpha]_D^{20}$[b]		$[\theta]_{310}$[d]	
	Code	THF	DMF	Catalyst	Cocatalyst	(%)	($\times 10^4$)[c]	M_w/M_n[c]	THF	DMF	THF	DMF
1	**ADHPA**	12	3.0	(nbd)$Rh^+[\eta^6$–$(C_6H_5)B^-(C_6H_5)_3]$	None	82.4	0.5	5.5	—[e]	−85	—[e]	0
2				$[Rh(nbd)Cl]_2$	(R)-PEA	5.0	6.2	1.2	—[e]	−24	—[e]	0
3				$[Rh(nbd)Cl]_2$	(S)-PEA	5.4	5.2	1.5	—[e]	−18	—[e]	0
4	**VDHPA**	−71	6.0	(nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$	None	72.2	3.5	4.6	−11	−15	−3	0
5				$[Rh(nbd)Cl]_2$	(R)-PEA	16.3	10.0	2.2	−28	−153	28	0
6				$[Rh(nbd)Cl]_2$	(S)-PEA	24.0	6.2	6.0	−12	−47	−28	0
7	**PDHPA**	−13	−15	(nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$	None	80.0	3.9	2.2	—[e]	−51	20[f]	0
8				$[Rh(nbd)Cl]_2$	(R)-PEA	8.0	3.7	4.3	—[e]	−85	—[e]	0
9				$[Rh(nbd)Cl]_2$	(S)-PEA	6.0	4.2	3.2	—[e]	−70	—[e]	0
10	**TDHPA**	−11	−17	(nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$	None	74.0	1.1	1.7	—[e]	−159	—[e]	0
11				$[Rh(nbd)Cl]_2$	(R)-PEA	4.0	3.1	9.9	—[e]	−147	—[e]	0
12				$[Rh(nbd)Cl]_2$	(S)-PEA	3.0	2.8	7.1	—[e]	−130	—[e]	0
13	**VPA**	−13	10	(nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$	None	71.9	2.7	1.7	−9	32	3	0
14				$[Rh(nbd)Cl]_2$	(R)-PEA	15.5	1.6	3.0	−11	30	3	0
15				$[Rh(nbd)Cl]_2$	(S)-PEA	12.3	0.9	4.0	−20	35	5	0

[a] At room temperature in THF, [monomer] = 0.1 molL^{-1}, [**RDHPA**]/[catalyst] = 250, [**VPA**]/[catalyst] = 100, [cocatalyst]/[catalyst] = 500.
[b] c = 0.1 g dL^{-1}.
[c] Determined by GPC correlating polystyrene standard with DMF eluent.
[d] $[\theta] = \times 10^{-3}$ (deg cm^2)/dmol, c = 1 mmolL^{-1}.
[e] Insoluble in THF.
[f] In THF solution before reprecipitation.

solution had been homogeneous. The formed polymer was purified by precipitation of the polymerization solution into a large amount of acetone and dried in vacuum to give a red polymer. For the other data such as yield, M_w, and CD, see Table 1 and Figure 3.

4. Polymerizations of **TDHPA**[5,6]
   A similar procedure as described for polymerization of **VDHPA** was applied. The formed polymer was purified by precipitation of the polymerization solution into a large amount of acetone and dried in vacuum to give a red polymer. For the other data such as yield, M_w and CD, see Table 1.
5. Polymerizations of **VPA**[5,6]
   A similar procedure as described for polymerization of **VDHPA** was applied. The formed polymer was purified by precipitation of the polymerization solution into a large amount of hexane and dried in vacuum to give a red polymer. For the other data such as yield, M_w and CD, see Table 1 and Figure 2.

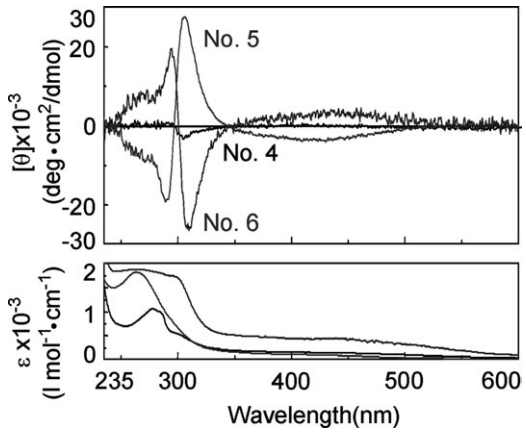


FIGURE 1 CD and UV/vis spectra of poly(**VDHPA**) in THF prepared by using (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ and $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA (Table 1, nos. 4–6).

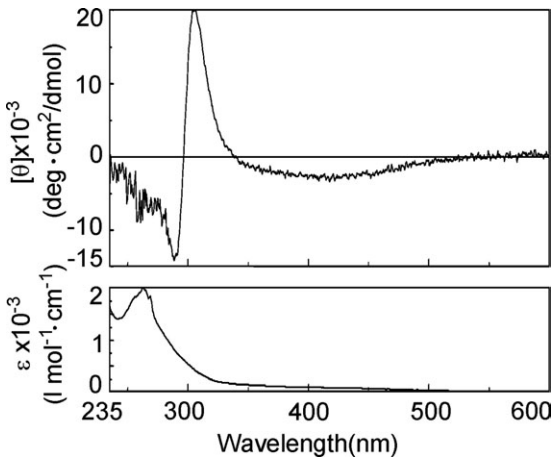


FIGURE 2 CD and UV/vis spectra of poly(**PDHPA**) in THF prepared by using (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ (Table 1, no. 7).

TABLE 2 Solubility of the Poly(**RDHPA**)s and Poly(**VPA**)[a]

polymer	$CHCl_3$	THF	Methanol	DMF	DMSO	Acetone	Hexane
Poly(**ADHPA**)	−	−	++	++	++	−	−
Poly(**VDHPA**)	−	+	+	+	+	−	−
Poly(**PDHPA**)	−	+	++	++	++	−	−
Poly(**TDHPA**)	−	−	++	++	++	−	−
Poly(**VPA**)	+	++	+	+	+	+	−

[a] ++: Soluble, +: partly soluble, −: insoluble.

Measurements

^{1}H NMR (270 MHz) spectra were recorded on a JEOL LEO-LEX-270 Spectrimeter. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography using Hitachi 655A-11 liquid chromatograph instruments (Polystyrene gel columns (Shodex GF-7M), DMF eluent, polystyrene calibration). CD spectra were recorded 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: 0.10–2.0 mM based on the monomer unit). The specific rotations were recorded with Polarimeter SEPA-200 (Horiba Co.). The infrared spectra were recorded on FT/IR-4200 (JASCO Co.).

RESULTS AND DISCUSSION

Effect of the Kind of Amino Alcohol Residues on Yields and M_w of Polymerizations and Solubility of the Resulting Polymers

The monomers (**ADHPA, VDHPA, PDHPA, TDHPA**, and **VPA**; Chart 1) were polymerized by using an achiral catalyst (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ and a chiral catalytic system $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA, and the results are summarized in Table 1.

VDHPA containing L-valinol residue was polymerized by using $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA as a chiral catalytic system to give polymers in 16.3% and 24.0% yields with 10.0 and 6.2 $\times$ 10^4 of M_w, respectively (Table 1, nos. 5 and 6).[12] Polymerizations of **ADHPA, PDHPA**, and **TDHPA** by using $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA as a catalytic system gave polymers in lower yields (3.0%–8.0%) with a lower molecular weight (2.8−6.2 $\times$ 10^4) (Table 1, nos. 2, 3, 8, 9, 11, and 12).[12]

The polymerizations of all the five chiral monomers (**RDHPA**s and **VPA**) were also performed by using an achiral catalyst (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ without the chiral cocatalyst to give polymers in high yields (71.9%–82.4%), which were much higher than those in polymerizations by using $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA as a catalytic system (Yields: 3.0%–24.0%, Table 1). The molecular weights of poly(**VDHPA**) and poly(**PDHPA**) were higher (3.5 and 3.9 $\times$ 10^4 in Table 1, nos. 4 and 7) than those of poly(**ADHPA**) and poly(**TDHPA**) (0.5 and 1.1 $\times$ 10^4 in Table 1, nos. 1 and 10). The differences may be because the amino groups of the monomers decreased the stability of Rh-PEA complex as an active species of the asymmetric polymerization. Stability of the active species may be weakened more strongly in the presence of highly polar monomers (**ADHPA** and **TDHPA**) than that in the presence of **VDHPA** and **PDHPA**, because the amino groups of the monomers coordinated probably with the rhodium. This speculation was supported by the following result we reported. A chiral amino alcohol was effective for the **HSSP** as a cocatalyst like (*R*)-PEA.[5(c)] However, the (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ was hardly affected. Therefore, the polymerization yields of all the monomers were high (71.9%–82.4%) by using (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ and low (3.0%–24.0%) by using $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA.

As shown in Table 2, all the five polymers were soluble in polar solvents, such as methanol, DMF, and DMSO. The poly(**VDHPA**) and poly(**PDHPA**) were partly soluble in THF. However, poly(**ADHPA**) and poly(**TDHPA**) were totally insoluble in THF. Therefore, it was found that the kind of amino alcohol residues of the monomers affected yields, M_w, and solubility of the resulting polymers. The polarity of poly(**ADHPA**) having L-alaninol residue with a methyl group is higher than poly(**VDHPA**) containing L-valinol residue with an isopropyl group. The polarity of poly(**TDHPA**) containing L-tyrosinol residue with a hydroxylbenzyl group is higher than poly(**PDHPA**) having L-phenylalaninol residue with a benzyl group. Poly(**ADHPA**) and poly(**TDHPA**) are high polar, and therefore, they were insoluble in low polar solvent like THF and soluble in high polar solvents such as methanol, DMF, and DMSO (Table 2). In summary, the low polar monomers tended to give polymers with higher yields and M_ws.

Achievement of AIP of the Chiral Monomers Using an Achiral Catalytic System

We performed polymerization of **RDHPA**s using an achiral catalyst (nbd)$Rh^+[\eta^6$-$(C_6H_5)B^-(C_6H_5)_3]$ without chiral cocatalysts to give polymers in high yields (Table 1, nos. 1, 4, 7, and 10). The resulting poly(**VDHPA**) showed Cotton effects at wavelengths assignable to the main chain (Table 1, no. 4, Fig. 1), indicating that the polymer adopted a one-handed helical conformation. The intensity of the CD absorptions was relatively weak because the chiral groups were located at a position far from the main chain.[2(g)] Poly(**PDHPA**) obtained by using the achiral catalyst also showed CD absorption at wavelengths assignable to the main chain (Table 1, no. 7 and Fig. 2). The CD spectra of poly(**VDHPA**) and poly(**PDHPA**) were measured in THF and chloroform. However, the other two poly(**RDHPA**)s, that is, poly(**ADHPA**) and poly(**TDHPA**) were insoluble in THF and chloroform, and

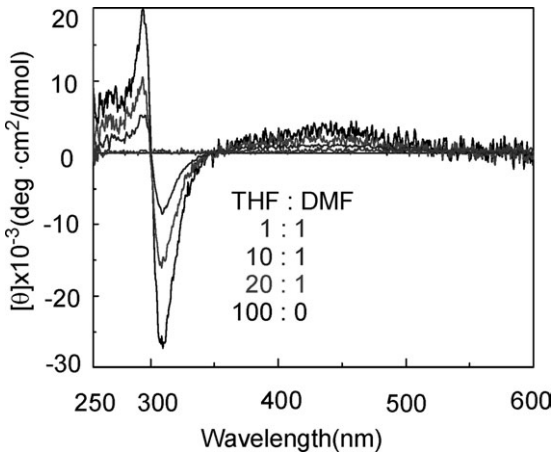


FIGURE 3 CD spectra of poly(**VDHPA**) in THF and DMF with various ratio prepared by using $[Rh(nbd)Cl]_2$/(*S*)-PEA (Table 1, no. 6).

soluble in polar solvents such as methanol, DMF, and DMSO, where they did not show CD absorptions. This was because intramolecular hydrogen bonds between hydroxyl groups of polyphenylacetylenes, which can maintain the one-handed helical conformation of the polymers, could not form in these polar solvents.[5(a, b)] In fact, all poly(**RDHPA**)s could not form stable one-handed helical conformations in polar solvents, such as methanol, DMF, and DMSO. The CD absorption of poly(**VDHPA**) decreased and disappeared with adding DMF to the solution of the polymers in THF (Fig. 3). In summary, the one-handed helical polymers of **VDHPA** and **PDHPA**, that is, relatively low polar monomer, were obtained by **AIP** with an achiral catalyst.

It is noteworthy that **VDHPA** and **PDHPA** were suitable for the **AIP** despite the relatively long distance between the chiral groups and the main chain. These may be because this spacer between the chiral group and the polymerizable group was relatively rigid, at least more rigid than those composed of a siloxane chain we described in the Introduction section and reported before.[2(g)]

Achievement of HSSP of the Chiral Monomer Using a Chiral Catalytic System

The monomer (**VDHPA**) was also polymerized by using $[Rh(nbd)Cl]_2$ catalyst in the presence of a chiral amine cocatalyst, (*R*)- or (*S*)-PEA, to give polymers having a moderate molecular weight in moderate yields (Table 1, nos. 5 and 6). As shown in Figure 1, the resulting poly(**VDHPA**) showed absorption bands in CD at wavelengths around 430 and 306 nm, which are assigned to the one-handed helical main chain and the chiral position between pendant groups, respectively. These findings indicated the presence of an excess of a one-handed helical polyacetylene backbone.

In addition, positive and negative Cotton effects were observed for the polymers obtained using (*R*)-PEA and (*S*)-PEA, respectively (Table 1 and Fig. 1, nos. 5 and 6). Therefore, the handedness of the main chain was controlled not by the chiral substituents but by the chiral cocatalyst. For all the polymerizations 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 (ML or PL)[4] could be synthesized. However, as chiral **VDHPA** was suitable for the **HSSP**, the diastereomers (ML and PL)[4] can be obtained from the chiral monomer **VDHPA**.

The [θ] value of the point of intersection of the two CD peaks of the both polymers obtained by using (*R*)- and (*S*)-PEA was not zero but a positive value at 297 nm, and therefore, both the peaks were not completely mirror images of each other (Fig. 1, nos. 5 and 6). This may be because poly(**VDHPA**) contains chiral amino alcohol residues, which can affect the main-chain chirality. In addition, the chiral valinol residue can coordinate with rhodium to affect the chiral induction.[5(c)]

The CD spectra of the other three poly(**RDHPA**)s, that is, poly(**ADHPA**), poly(**PDHPA**), and poly(**TDHPA**) could not be detected, because those were insoluble in THF and chloroform. In addition, these polymers did not show CD absorptions in polar solvents such as methanol, DMF, and DMSO, because hydrogen bonds could not form in the solvents. Therefore, they were not suitable to **HSSP**.

In conclusion, only **VDHPA** of these four monomers (**RDHPA**s) was suitable to both the **HSSP** by using the chiral catalytic system and the **AIP** by using the achiral catalytic system (Table 3). In other words, it polymerized in two modes.

Role of the Two Hydroxyl Groups of Monomers (RDHPAs)

We also synthesized and polymerized the corresponding chiral monomer (**VPA**) of **VDHPA** lacking hydroxymethyl groups (Chart 1). Poly(**VPA**) prepared by the achiral catalyst showed CD absorption bands at wavelengths assignable to the main chain (Table 1, no. 13 and Fig. 4). **AIP** of **VPA** was also achieved. Poly(**VPA**)s prepared by the chiral catalytic system (Table 1, nos. 14 and 15) and the achiral catalyst (Table 1, no. 13) showed similar Cotton effects at wavelengths around 382 and 327 nm in chloroform (Fig. 4). The two polymers of **VPA** prepared by using (*R*)-PEA and (*S*)-PEA showed almost the same CD bands (Fig. 4, nos. 14 and 15), although PEAs having opposite signs of configuration were used as a

TABLE 3 Suitability of **RDHPA**s and **VPA** for Asymmetric Polymerizations[a]

Monomer	HSSP[b]	AIP[c]
ADHPA	−	−
VDHPA	+	+
PDHPA	−	+
TDHPA	−	−
VPA	−	+

[a] +: Suitable, −: unsuitable.
[b] **HSSP**: Helix-sense-selective polymerization.
[c] **AIP**: Asymmetric-induced polymerization.

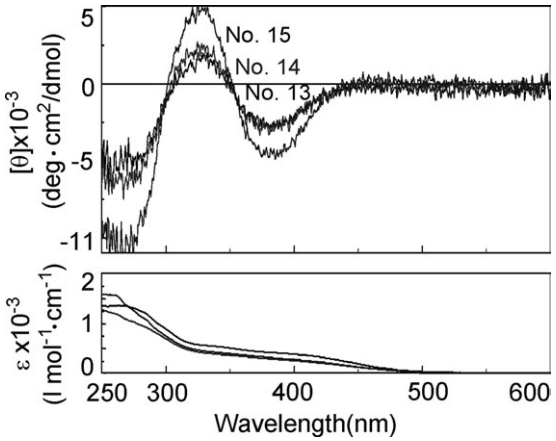


FIGURE 4 CD and UV/vis spectra of poly(**VPA**)s in chloroform prepared by using (nbd)$Rh^{+}[\eta^{6}$-$(C_6H_5)B^{-}(C_6H_5)_3]$ and $[Rh(nbd)Cl]_2$/(*R*)- or (*S*)-PEA (Table 1, nos. 13–15).

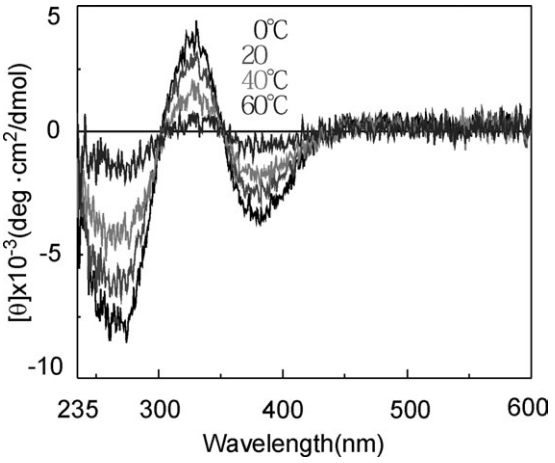


FIGURE 6 CD spectra of poly(**VPA**) versus various temperatures in chloroform prepared by using $[Rh(nbd)Cl]_2$/(*R*)-PEA (Table 1, no. 14).

cocatalyst. Therefore, the chirality of the main chain of poly(**VPA**) was controlled only by the chiral valinol residues. This means **VPA** was not suitable for the **HSSP**. Therefore, the two hydroxy groups were necessary to realize **HSSP** and not necessary to **AIP**.

Cotton effects of poly(**VDHPA**) containing two hydroxyl groups hardly decreased as the measuring temperature was raised from 0 to 60 °C (Fig. 5). On the other hand, CD absorptions of poly(**VPA**) without hydroxyl groups decreased largely as the measuring temperature was raised from 0 to 60 °C (Fig. 6). These results indicated that the helical conformation of poly(**VDHPA**) was more stable than that of poly(**VPA**). We can conclude that two hydroxyl groups of **VDHPA** played a very important role in the stability of helical structure by intramolecular hydrogen bonds. It is similar as our previous study, the chiral helical conformation of poly(**DoDHPA**) was stabilized by intramolecular hydrogen bonds between two hydroxyl groups of the achiral monomer units.[5(a,b)]

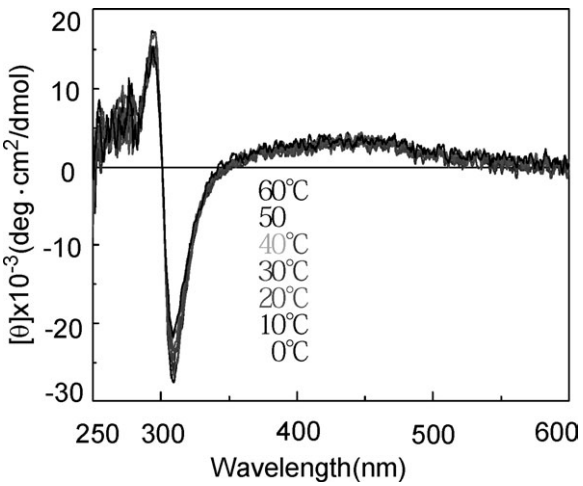


FIGURE 5 CD spectra of poly(**VDHPA**) versus various temperatures in THF prepared by using $[Rh(nbd)Cl]_2$/(*S*)-PEA (Table 1, no. 6).

In conclusion, the two hydroxyl groups played an important role on both the asymmetric polymerization and the stability of one-handed helical conformation.

CONCLUSIONS

We have synthesized a novel four chiral phenylacetylenes having an L-amino alcohol residue and two hydroxymethyl groups. The monomer **VDHPA** only was suitable for both the **HSSP** with a chiral catalytic system and the **AIP** with an achiral catalyst. This means the possibility of synthesis of four chiral polymers, the diastereomers (PL, ML, PD, and MD) form the chiral monomer from the chiral monomer.[4] It was found that the kind of amino alcohol residues of the monomers affected asymmetric polymerization and solubility of the resulting polymers. The two hydroxy groups in the monomer were necessary to realize the **HSSP** of **VDHPA**. The two hydroxyl groups played an important role on both the asymmetric polymerization and the stability of one-handed helical conformation.

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