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Two Modes of Asymmetric Polymerization of Phenylacetylene Having a L-Valinol Residue and Two Hydroxy Groups

Hongge Jia,[†] Masahiro Teraguchi,[†,‡,§] Toshiki Aoki,*[,†,‡,||] Yunosuke Abe,[†] Takashi Kaneko,[‡,§] Shingo Hadano,[§,||] Takeshi Namikoshi,[§,||] and Edy Marwanta[§,||]

Department of Chemistry and Chemical Engineering, Graduate School of Science and Technology, Center for Education and Research on Environmental Technology, Materials Engineering, Nanochemistry, Center for Transdisciplinary Research, and Venture Business Laboratory, Niigata University, Ikarashi 2-8050, Nishi-Ku, Niigata 950-2181, Japan

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Introduction. In 1993, the authors discovered an asymmetric-induced polymerization 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 discovery, 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 asymmetric-induced polymerization. For example, the homopolymers of (−)-*p*-(dimethyl(10-pinanyl)-silyl)phenylacetylene[2a] and (+)-*p*-(10-pinanyloxycarbonyl)-phenylacetylene[2g] obtained with a Rh complex showed strong CD absorptions similar to that of *p*-{L-(−)- menthoxycarbonyl}-phenylacetylene.[1] Similar results on such asymmetric polymerizations 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 1-, 3-, and/or 5-position 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 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 asymmetric-induced polymerization, the chiral group should be substituted at a position close to the polymerizable group in the monomers. In this asymmetric-induced polymerization, 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, i.e., the enantiomers PD and ML (or PL and MD),[4] could be obtained from the enantiomeric monomers. In other words, it was impossible to synthesize their diastereomers.

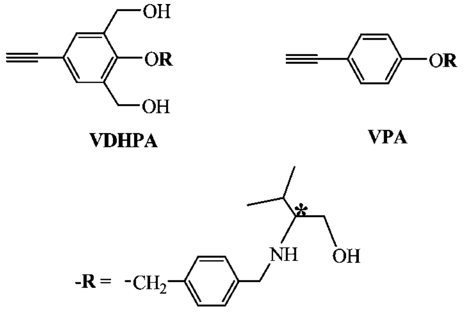
The authors have also found a simple and novel synthetic method for obtaining such a chiral polymer from an achiral substituted acetylene monomer using a chiral catalytic system.[5] In addition, the helical conformation was stable in solution. This is the first example of helix-sense-selective polymerization 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 (DHPA) 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 DHPA and (*R*)-PEA.[5a] On the other hand, no helix-sense-selective polymerizations occurred in the case of the corresponding monomers having no hydroxy groups. Therefore, two hydroxy groups were found to be necessary to realize the helix-sense-selective polymerization. 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.

In addition, these momomers described above were suitable only for the asymmetric-induced polymerization *or* the helix-sense-selective polymerization. There were no monomers which were suitable for both asymmetric polymerizations.

In order to develop a new monomer that can be used for both types of asymmetric polymerizations, i.e., the helix-sense-selective polymerization and asymmetric-induced polymerization, a new novel chiral monomer (VDHPA, Chart 1) was designed and synthesized. Monomer VDHPA contains two hydroxy groups and a chiral group, a L-valinol residue,[6] which was introduced via a relatively long spacer. To confirm the role of the two hydroxy groups, the corresponding monomer VPA which has the same substituent as monomer VDHPA, except for the absence of two hydroxy groups, was also synthesized and polymerized.

Experimental Part. The detailed procedures of synthesis of the monomers VDHPA and VPA are described in the Supporting Information (Scheme S1). An asymmetric-induced polymerization and a helix-sense-selective polymerization were carried out by an achiral catalyst, $(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$, and a chiral catalytic system, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene) and (*R*)- or (*S*)-PEA, respectively. The results of the polymerization are described in Table 1 and the Supporting Information. Poly(VDHPA)s were purified by precipitation of the THF solution into a large amount of acetone, and poly(VPA)s were precipitated in toluene and then dried in vacuum to give red polymers.

Chart 1. Chemical Structures of the New Chiral Monomers (VDHPA and VPA)



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* Corresponding author: Fax +81 25 262 7280; e-mail toshaoki@eng.niigata-u.ac.jp.

[†] Department of Chemistry and Chemical Engineering, Graduate School of Science and Technology.

[‡] Center for Education and Research on Environmental Technology, Materials Engineering, Nanochemistry.

[§] Center for Transdisciplinary Research.

[||] Venture Business Laboratory.

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Table 1. Polymerizations of the Chiral Monomers (VDHPA and VPA) with and without a Chiral Cocatalyst[a]

no.	chiral monomer	catalyst	chiral cocatalyst	yield (%)	M_w[b] ($\times 10^4$)	M_w/M_n[b]
1	VDHPA	$(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$	none	72.2	3.5	4.6
2[c]		$[Rh(nbd)Cl]_2$	(*R*)-PEA	14.5	6.9	4.7
3[c]		$[Rh(nbd)Cl]_2$	(*S*)-PEA	22.8	17.8	2.4
4	VPA	$(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$	none	71.9	2.7	1.7
5[d]		$[Rh(nbd)Cl]_2$	(*R*)-PEA	15.5	1.6	3.0
6[d]		$[Rh(nbd)Cl]_2$	(*S*)-PEA	12.3	0.9	4.0

[a] At room temperature in THF, [monomer] = 0.1 mol/L, [VDHPA]/[catalyst] = 250, [VPA]/[catalyst] = 100. The best condition was selected for each polymerization. [b] Determined by GPC correlating polystyrene standard with DMF eluent. [c] [Cocatalyst]/[catalyst] = 9300. [d] [Cocatalyst]/[catalyst] = 500.

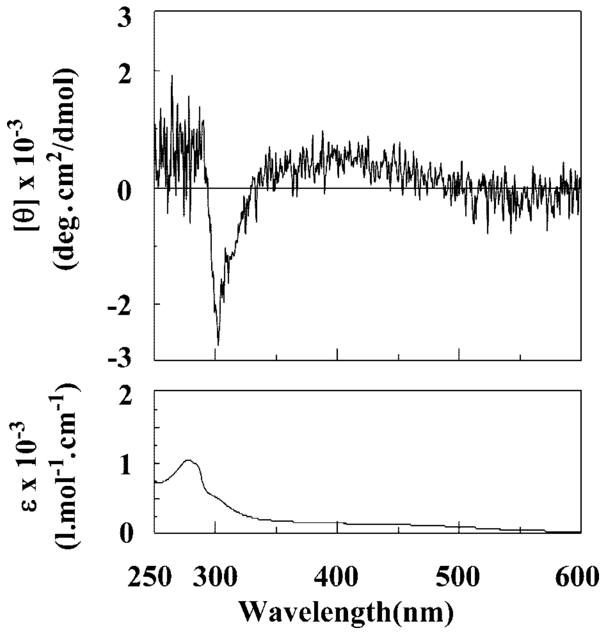

Figure 1. CD and UV/vis spectra of poly(VDHPA) prepared using a Rh catalyst without chiral cocatalysts (Table 1, no. 1).

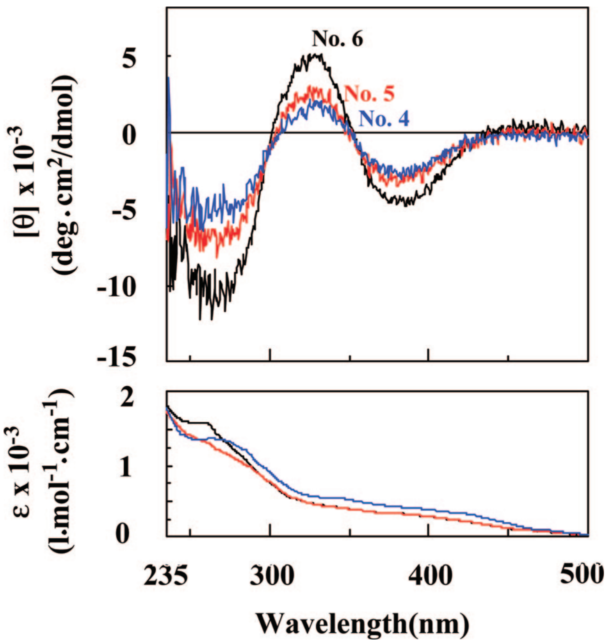

Figure 2. CD and UV/vis spectra of poly(VPA) prepared using Rh catalysts with and without chiral cocatalysts (Table 1, nos. 4−6).

Results and Discussion. *Asymmetric-Induced Polymerization.* We carried out polymerization of VDHPA using an achiral catalyst $(nbd)Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$ without the chiral cocatalyst to give polymers in high yields (Table 1, no. 1). The resulting polymer showed Cotton effects at wavelengths assignable to the main chain (Figure 1), indicating that the polymer adopted a one-handed helical conformation.[7] Poly(VPA) prepared by the achiral catalyst showed CD absorption bands at wavelengths assignable to the main chain (Table 1 and Figure 2, no. 4). A one-handed helical polymer of VPA was also obtained by the asymmetric-induced polymerization. It is noteworthy that VDHPA and VPA were suitable for the asymmetric-induced polymerization in spite of the relatively long distance between the chiral groups and the main chain. They were unexpected results. These may be because this spacer between the chiral group and the polymerizable group was more rigid than those composed of a siloxane chain we described in the Introduction and reported before.[2g] In case of the same spacer, the effectiveness on the chiral induction of the chiral groups must decrease with an increase in the distance.

Helix-Sense-Selective Polymerization. The monomer (VDHPA) was also polymerized 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. 2 and 3).[8] As shown in Figure 3, poly(VDHPA) (Table 1, nos. 2 and 3) showed absorption bands in CD at wavelengths around 430 and 306 nm, which are assigned to the 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.

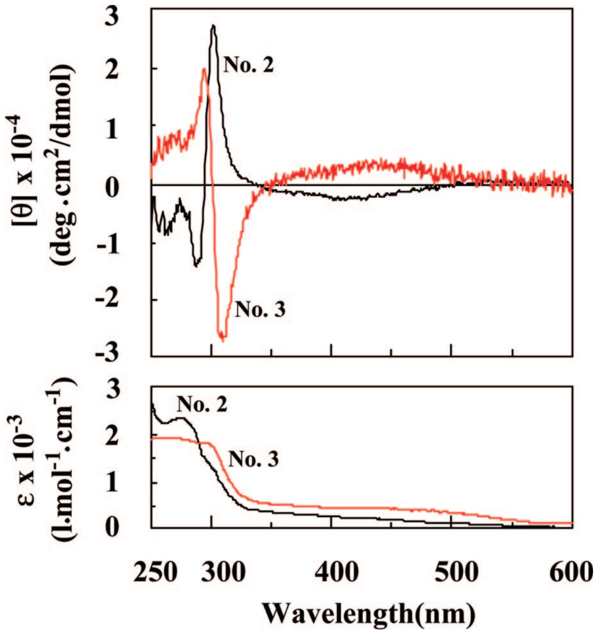

Figure 3. CD and UV/vis spectra of poly(VDHPA) using a Rh catalyst with chiral cocatalysts (Table 1, nos. 2 and 3).

In addition, positive and negative Cotton effects were observed for the polymers obtained using (*R*)-PEA and (*S*)-PEA, respectively (Table 1 and Figure 3, nos. 2 and 3). The handedness of the main chain was controlled not by the chiral substituent, but rather by the chiral cocatalyst. For all the asymmetric 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. We obtained the diastereomers (ML and PL)[4] first from the new monomer VDHPA described in this communication. This fact indicated that VDHPA was also suitable for the helix-sense-selective polymerization. Therefore, VDHPA was found to give one-handed helical polymers by both the helix-sense-selective polymerization and the asymmetric-induced polymerization. The $[\theta]$ value of the point of intersection of two CD peaks of the both polymers obtained by using (*S*)- and (*R*)-PEA was not zero but a positive value at 297 nm, and therefore, both peaks were not completely mirror images of each other (Figure 3, nos. 2 and 3). This may be because poly(VDHPA) contains chiral amino alcohol groups which can affect the asymmetric-induced polymerization. In addition, the chiral amino valinol residue can coordinate with the rhodium to affect the asymmetric induction.[9]

We also synthesized and polymerized the corresponding chiral monomer (VPA) lacking hydroxymethyl groups to compare with VDHPA. Poly(VPA)s prepared by the chiral catalytic system (Table 1, nos. 5 and 6) and the achiral catalyst (no. 4) showed similar Cotton effects at wavelengths around 382 and 327 nm in chloroform (Figure 2). The two polymers of VPA prepared by using (*R*)-PEA and (*S*)-PEA showed almost the same CD bands (Figure 2, nos. 5 and 6), although PEAs having opposite signs of configuration were used as a cocatalyst. Therefore, the chirality of the main chain of poly(VPA) was controlled only by the chiral valinol residue. This means VPA was not suitable for the helix-sense-selective polymerization, and two hydroxy groups were necessary.

In conclusion, we have synthesized a novel chiral phenylacetylene having a L-valinol residue and two hydroxymethyl groups. The monomer was suitable for both the helix-sense-selective polymerization with an chiral catalytic system and the asymmetric-induced polymerization with an achiral catalyst. This represents the first example of such a monomer, one with the possibility of synthesis of four chiral polymers, the diastereomers (PL, ML, PD, and MD).[4]

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Supporting Information Available: Experimental procedures for synthesis and polymerization of VDHPA and VPA. The material is available free of charge via the Internet at http://pubs.acs.org.

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(4) P and M mean a right- and left-handed helicity of main chains, respectively. D and L mean the chirality of the substituents which monomers have.

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(6) We selected L-valinol as one of the L-amino alcohols and introduced its residue to the monomers. We are now studying on several similar monomers containing residues of other L-amino alcohols in progress, and we will report them somewhere in the near future.

(7) The relatively weak CD is because the chiral group is located at a position far from the polymerizable group.

(8) The cis content of the polymer backbone could not be determined because its NMR peaks were so broad. However, since a NMR of a similar polymer prepared by the same helix-sense-selective polymerization showed high cis %, the present polymer may also have a high cis content. We will report the detail somewhere in the near future.

(9) This speculation is supported by our previous result.[5b] We reported a chiral amino alcohol was effective for the helix-sense-selective polymerization as a cocatalyst like (*R*)-PEA.

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