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# Chiral Teleinduction in Asymmetric Polymerization of 3,5-Bis(hydroxymethyl)phenylacetylene Having a Chiral Group via a Very Long and Rigid Spacer at 4-Position

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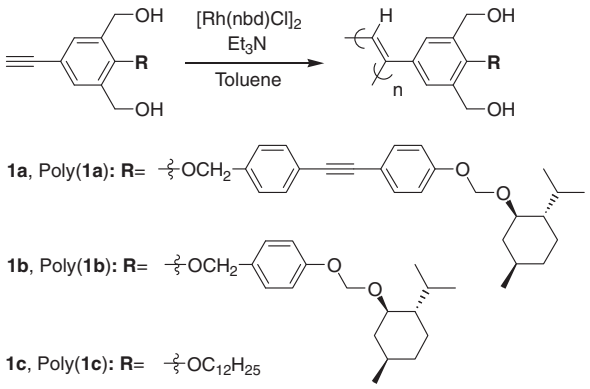
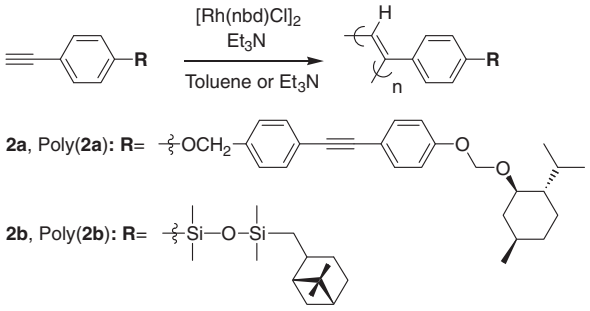
A new polymer prepared by polymerization of 3,5-bis-(hydroxymethyl)phenylacetylene having a chiral menthyl group via a very long and rigid spacer by an achiral rhodium complex with triethylamine as an initiator showed strong CD absorptions assigned to the main chain in spite of the long distance (23 Å) between the chiral group and the polymerizing group in the monomer. This distance is the longest to the best of our knowledge. In addition, switching between the two chiralities of the resulting polymer was realized in the CD spectrum.

Many kinds of chiral poly(substituted acetylene)s have been reported because they have unique properties such as enantio-selective recognition.[1] There are two methods for synthesizing them. One is polymerization of chiral monomers by achiral initiators, asymmetric-induced polymerization (AIP)[2] that we reported for the first time and then many other chemists have reported,[3] and the other is polymerization of achiral monomers by chiral initiators, helix-sense-selective polymerization (HSSP)[4] we reported first. The AIP was simple and many kinds of chiral monomers were suitable for AIP, while the HSSP needed two hydroxy groups in the monomers and, therefore, structures of monomers suitable for HSSP are limited. Many AIP's of many kinds of chiral monomers were reported which were not only substituted acetylenes but also other types of chiral monomers.[5] However, to realize AIP effectively, the distance between the chiral group and the polymerizing group in the monomers for AIP should be small. For example, in chiral arylisocyanates (**S1** in Supporting Information),[6] propiolic esters (**S2**),[7] and bulky vinyl monomers (**S3**),[8] the longest values for their distances in the monomers which were suitable for AIP were 9, 11, and 12 Å respectively (See Table S1 in SI[15]). Since the distances must be small, variation of structures of monomers for AIP was limited.

Amabilino et al.[9] reported AIP of a chiral isocyanide (**S4**) where the distance between the chiral group and the polymerizing group was 21 Å and [$\theta$] for the resulting polymers was only 990. They called it *chiral teleinduction*. Percec et al.[10] reported AIP of chiral phenylacetylenes having dendron structure as a spacer (**S5**). The distance between the chiral group and the polymerizing group was 21 Å and [$\theta$] for the resulting polymers was less than 2500. Therefore, to our knowledge, 21 Å is the longest distance between the chiral group and the polymerizing group in monomers suitable for AIP. Here in this paper we call asymmetric induction in polymerization of chiral monomers where the distance between the chiral group and the polymerizing group are more than 21 Å, *chiral teleinduction*. In order to realize *chiral teleinduction*, we selected 3,5-bis(hydroxymethyl)phenylacetylene (**1a** in Scheme 1) having a chiral menthyl group[11] via a very long (23 Å)[12] and rigid spacer as a chiral monomer for AIP (Scheme 1). The two hydroxy groups are expected to make the backbone of the resulting polymer more rigid. In addition, switching between the two chiralities will be reported in CD spectra. To investigate effect of the length of the spacers on AIP, **1b** which has a shorter spacer (16 Å) than **1a** was synthesized (Scheme 1). To investigate the effect of the two hydroxy groups on AIP, **2a** (Scheme 2) which has the same spacer as **1a** but no hydroxy groups was synthesized. In addition, to compare the effect of rigidity of the spacers on AIP, **2b** was used which has a very flexible spacer. The distances between the chiral group and the polymerizing group of **1a**, **1b**, **2a**, and **2b** were 23, 16, 23, and 10 Å, respectively (Table 1 and Scheme 2).[12]




**Scheme 1.** Synthesis of poly(**1a**) and poly(**1b**) having hydroxymethyl groups at 3,5-positions.




**Scheme 2.** Synthesis of poly(**2a**) and poly(**2b**) without hydroxymethyl groups at 3,5-positions.

**Table 1.** Chiral teleinduction in asymmetric-induced polymerization of chiral phenylacetylenes[a]

| Code | Monomer | | Polymer | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ [b] /° | Distance[c] /Å | Yield[d] /% | $M_w$[e] $/\times10^5$ | $M_w/M_n$[e] | $[\alpha]_D^{20}$ [b] /° | $[\theta]_{435}$ $/\times10^3$ deg cm$^2$ dmol$^{-1}$ | $g_{435}$[f] $/\times10^{-8}$ |
| **1a** | −61.9 | 23 | 90.4 | 21 | 3.8 | −188 | 8.17 | 191 |
| **1b** | −58.2 | 16 | 98.6 | 44 | 6.5 | −291 | 22.7 | 768 |
| **2a** | −63.1 | 23 | 91.4 | 11 | 8.2 | −88.5 | 0.206 | 2.1 |
| **2b**[g] | −2.6 | 10 | 87.5 | 8.6 | 2.3 | −0.39 | 0 | 0 |

[a]Monomers **1a**, **1b**, and **2a**: at room temperature for 6 h in toluene. [monomer] = 0.1 mol L$^{-1}$, [monomer]/[[Rh(nbd)Cl]$_2$] = 100, **2b**: at room temperature for 4 h in $Et_3N$; [**2b**] = 0.2 mol L$^{-1}$, [**2b**]/[[Rh(nbd)Cl]$_2$] = 200. [b]In $CHCl_3$. [c]Distances between an asymmetric carbon and an ethynyl group were calculated by MMFF. [d]Methanol insoluble part. [e]By GPC. [f]$g = ([\theta]/3300)/\varepsilon$. [g]From ref. 3n.

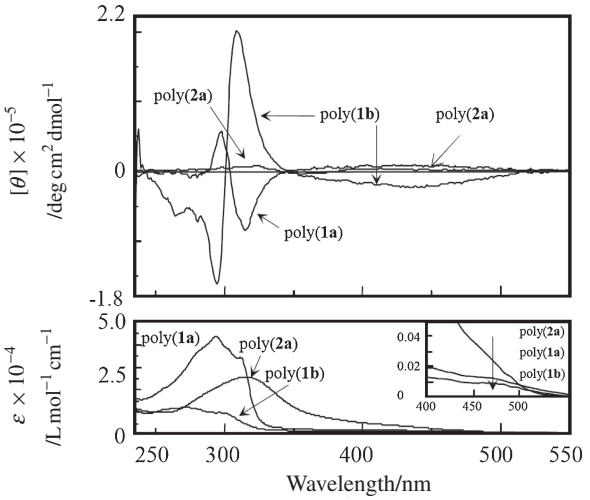



**Figure 1.** CD and UV–vis spectra of poly(**1a**), poly(**1b**), and poly(**2a**) in $CHCl_3$.

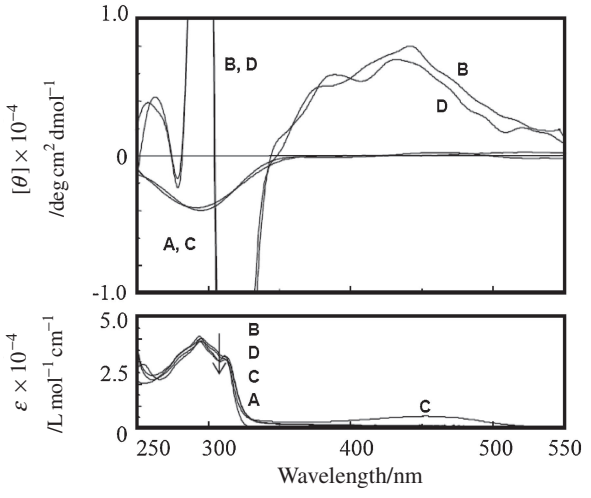



**Figure 2.** CD and UV–vis spectra of (A) **1a** in $CHCl_3$, and poly(**1a**) in (B) $CHCl_3$, (C) $CHCl_3$/DMSO = 45/55 (v/v) and (D) $CHCl_3$/DMSO = 95/5 ((D) was the solution prepared by addition of $CHCl_3$ to the solution C).

These chiral monomers were polymerized by an achiral rhodium complex ([Rh(nbd)Cl]$_2$) to yield high MW (=$10^6$) polymers in high yields as shown in Table 1. Since specific rotation values for poly(**1a**) and poly(**1b**) were much higher than those of the corresponding monomers, chiral inductions to the main chains were suggested. In addition, since CD signals assigned to their main chain were observed for poly(**1a**) and poly(**1b**), chiral induction to the main chains was confirmed (Figure 1). Therefore, AIP of **1a** where the distance between the chiral group and the polymerizing group is 23 Å was realized, i.e., *chiral teleinduction* in AIP of **1a** was achieved. In addition, the $[\theta]$ value was large (=8170) and much larger than those of poly(**S4**) and poly(**S5**).

The value of $g$ for poly(**1a**) was 100 times higher than that for poly(**2a**), although they had the same spacers and chiral groups. The difference between the two monomers was that **1a** has two hydroxy groups and **2a** does not. The two hydroxy groups in the monomer unit can make the backbone of the resulting polymer more rigid by making intramolecular hydrogen bonds, judging from our previous results that phenylacetylene monomers having two hydroxy groups (**1c**) yielded very rigid polymers having one-handed helical backbone maintained by intramolecular hydrogen bonds.[4,13] Judging from similarity of the CD and UV spectra for poly(**1a**) (Figure 1) and poly(**1c**) (Figure S1[15]), the backbone of poly(**1a**) was maintained by intramolecular hydrogen bonds.[4] Rigid backbones can accept chiral information more effectively from the pendant chiral groups.[14] Therefore, poly(**1a**) showed much higher $g$ values than poly(**2a**) (Table 1). Poly(**2b**) having a short spacer (10 Å) showed no CD although poly(**2a**) having a longer spacer (23 Å) showed CD. It was thought that **2b** was not suitable for AIP because the spacer in **2b** was so flexible that chiral induction was difficult. In summary, **1a** was suitable for AIP in spite of the long distance of the spacer because of rigidity of the spacer and the main chain. *Chiral teleinduction* in AIP was achieved.

When DMSO as a polar solvent was added to a chloroform solution of poly(**1a**) and poly(**1b**) showing CD around 435 nm assigned to the main chain (Figures 2B and S2A,[15] respectively), the CD disappeared and the UV band shifted to longer wavelengths (Figures 2C and S2B,[15] respectively), because the intramolecular hydrogen bonds were broken, the helical conjugated conformation was extended, and the one-handed conformation was racemized (Similar phenomenon in poly(**1c**) was reported by our group (Figure S1[15])).[4] This was supported by the fact that poly(**2a**) having no hydroxy groups showed no change when DMSO was added (Figure S3[15]).

In the case of poly(**1a**), when the CD around 435 nm assigned to the main chain disappeared (Figure 2C), a new CD signal appeared at 300 nm. Since this signal was identical to that for the corresponding monomer, **1a** (Figure 2A), this was assigned to a chiral structure of the monomer unit. When to the solution of chloroform/DMSO (45/55 (v/v)) (Figure 2C) chloroform was added, the resulting solution of chloroform/DMSO (95/5 (v/v)) showed almost the same CD signals (Figure 2D) as the original solution of chloroform (Figure 2B). Therefore, change in CD by changing polarity of solvents was reversible (Figure S4[15]). In conclusion, chiral switching between two kinds of chiral structures, one handed helical backbone and chiral pendant groups has been realized for the first time. On the other hand, in the case of poly(**1b**) having the same chiral groups and shorter spacers, when the CD around 435 nm assigned to the main chain disappeared, no new CD signals appeared (Figure S2B[15]). When to the solution of chloroform/DMSO (55/45 (v/v)) chloroform was added, the resulting solution of chloroform/DMSO (95/5 (v/v)) showed almost the same CD signals (Figure S2C[15]) as the original solution in chloroform (Figure S2A[15]). Therefore, the change in CD by changing polarity of solvents was reversible (Figure S5[15]). In summary, chiral switching between on and off in CD signals for one handed helical backbone was observed (Figure S2[15]) similarly to the findings we reported for poly(**1c**) before (Figure S1[15]).[4] In the case of poly(**2a**) having no hydroxy groups, no response by changing polarity of the solvent was observed (Figure S3[15]). Therefore, only in poly(**1a**) reversible response of their CD between two kinds of chiralities by changing polarity of the solvents was observed because the one-handed helicity was kept by their intramolecular hydrogen bonds and the chiral phenylethynylphenyl group absorbed at a more than 250 nm where **1b** did not have any absorbance.

In conclusion, a new polymer prepared by polymerization of a chiral phenylacetylene having two hydroxy groups and a chiral menthyl group via a very long and rigid spacer by an achiral rhodium complex with triethylamine as an initiator showed strong CD absorptions assigned to the main chain in spite of the long distance (23 Å) between the chiral group and the polymerizing group in the monomer. Therefore, chiral teleinduction was achieved. This distance is the longest in AIP to the best of our knowledge. In addition, reversible switching in CD between one-handed helical backbone and chiral pendant groups by changing polarity of the solvent has been realized for the first time.

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11 In our previous reports on the AIP, we found polymers having menthyl groups[2] had tendency to show stronger CD peaks than others such as pinanyl groups.[3l,3n]

12 Distances between a polymerizable group and an asymmetric carbon of all the compounds in this report were calculated by MMFF.

13 When we attempted the HSSP of phenylacetylenes having two methoxymethyl,[4a] hydroxy, hydroxyethyl, or hydroxybutyl groups instead of the two hydroxymethyl groups, the resulting polymers had no CD. Therefore, the two hydroxymethyl groups were found to be very important.

14 Since the CD spectra for **1a** (Figure 2A) and the pendant groups (Figure 2C) in poly(**1a**) were the same, the effect of interaction between the chiral pendant groups on the chiral teleinduction to the main chain was thought to be small.

15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.


  