3978 *Macromolecules* **2000,** *33,* 3978−3982

Effect of Chiral Substituents on the Helical Conformation of Poly(propiolic esters)

Hideo Nakako,[†] Yasushi Mayahara,[†] Ryoji Nomura,[†] Masayoshi Tabata,[‡] and Toshio Masuda*[,†]

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan, and Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Received February 2, 2000; Revised Manuscript Received March 28, 2000

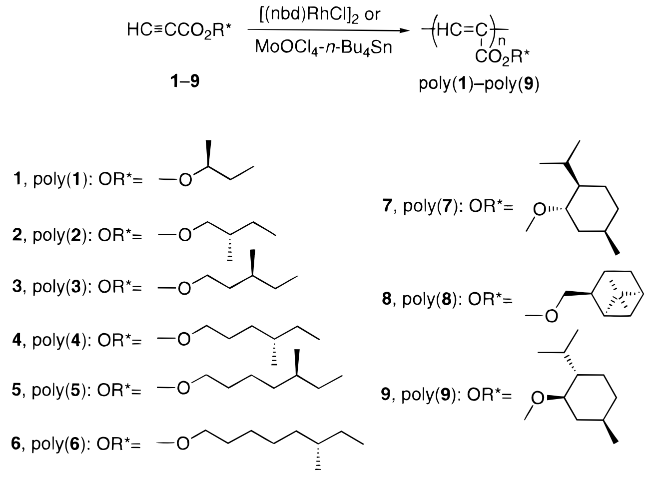
ABSTRACT: Propiolic esters having various chiral substituents, [HC≡CCO$_2$R*, R* = (S)-(CH$_2$)$_n$CHMeEt (n = 0−5), (1*S*,2*R*,5*R*)-isomenthyl, and (1*S*,2*S*,5*S*)-myrtanyl], were polymerized with [(nbd)RhCl]$_2$ or MoOCl$_4$−n-Bu$_4$Sn for the purposes of establishing the relationship between the helical conformations of the polymers and the structures of pendant chiral groups. In contrast to the poor stereoregularities of the polymers prepared with MoOCl$_4$−n-Bu$_4$Sn, [(nbd)RhCl]$_2$-catalyzed polymerizations resulted in polymers with high cis contents. These stereoregular polymers with 1−4 alkylene spacers displayed intense CD effects and large optical rotations as well as large band gap energy (ca. 3.2 eV), indicating that they possess restricted main-chain conjugation and exist in helical conformations with an excess of a one-handed screw sense. In contrast, the polymers without alkylene spacers possessed more extended coplanarity of the main chains and exhibited poorer chiroptical properties than those bearing alkylene spacers. The introduction of bulkier substituents to the polymers enhanced the persistence length of the one-handed helix, resulting in an increase in the magnitude of Cotton effects and optical rotations. Polymer stereoregularity remarkably influenced the polymer conformation, and no distinct CD signals were detected for polymers with alkylene spacers if polymerizations were performed with the Mo catalyst.

Introduction

A recent development in the field of polymer chemistry is the precise control of high-order structures of macromolecules. Especially, much attention has been paid to chiral polymers in which the chirality is mainly based on helical backbones with an excess of one-handed screw sense.[1] One goal in the study of helical polymers is to understand nature that elegantly utilizes self-organization processes to construct helical and multiple helical architectures such as α-helical polypeptides and nucleic acids. In addition to this, the excellent ability of helical polymers to recognize chiral molecules has led many chemists not only to the discovery of a variety of helical polymers but also to the development of new functions based on main-chain chirality.[1,2]

Among the helical polymers, π-conjugated helical polymers are very interesting since they are potentially useful as polarization-sensitive electrooptical materials, asymmetric electrodes, and so forth.[3] A representative example for such conjugated helical polymers is given by the polymers from monosubstituted acetylenes which are known to exist in helical conformations with an excess of a one-handed screw sense if appropriate chiral substituents are incorporated.[4] Disubstituted acetylenes bearing chiral substituents also provide polymers with very large chiroptical properties, probably due to main-chain chirality.[5] Even if substituted polyacetylenes have no chirality, single-handed helical conformations can be induced by strong complexation between pendant groups and chiral molecules.[6]

Scheme 1



Previous studies on polyacetylene-based helical polymers have mostly focused on poly(phenylacetylenes) with chiral substituents.[4d−g,6] This is because high stereoregularity (cis) is indispensable for the construction of well-ordered helical polymers from substituted acetylenes[4f,6b] and because stereoregular cis−transoidal poly(phenylacetylenes) are readily obtained using Rh catalysts.[7] This ability of Rh catalysts has been recently applied to the polymerization of propiolic esters by one of these laboratories, which provided a route to poly(propiolic esters) having excellent cis−transoidal stereoregularities.[8] Although this finding was deemed promising for the production of a new class of helical polymers based on poly(propiolic esters), no information was available on their secondary structures in solution. This background stimulated us to study the conformation of poly(propiolic esters), leading to the finding that a poly(propiolic ester) having chiral substituents possesses a helical structure with an excess of a one-handed screw sense in solution.[9] Namely, poly[(−)-menthyl propiolate] prepared with [(nbd)RhCl]$_2$ [poly(**9**)-Rh, Scheme 1][10] has high stereoregularity (cis 80%) and shows a large optical rotation and intense CD signals in the range of the absorption attributed to the main chain.[9]

[†] Kyoto University.
[‡] Hokkaido University.

10.1021/ma000191q CCC: $19.00

Table 1. Polymerizations of Propiolic Esters with Various Chiral Substituents[a]

monomer			polymer[b]			
	$[\alpha]_D$[c], deg	catalyst	yield, %	$M_n \times 10^{-3}$ [d]	cis content,[f] %	$[\alpha]_D$[e], deg
1	+18	Rh	36	21	75	+4
		Mo	43	130	*g*	−19
2	+5	Rh	36	80	100	−473
		Mo	56	12	*g*	−9
3	+11	Rh	37	24	100	−612
		Mo	52	18	*g*	0
4	+12	Rh	30	76	100	−418
		Mo	68	5.1	*g*	−4
5	+6	Rh	30	60	100	−358
		Mo	52	12	*g*	0
6	+8	Rh	33	60	100	−20
		Mo	42	3.3	*g*	−3
7	+20	Rh	33	8	75	−34
		Mo	35	7	*g*	−65
8	−28	Rh	15	99	91	−340
		Mo	84	8.1	*g*	−16
9[h]	−82[i]	Rh	34	250	80	+363[j]
		Mo	61	18	*g*	+39[j]

[a] Rh catalyst; in CH_3CN, 30 °C, 24 h; $[M]_0 = 1.0$ M, $[[(nbd)RhCl]_2] = 10$ mM. Mo catalyst; in toluene, 30 °C, 24 h; $[M]_0 = 0.50$ M, $[MoOCl_4] = [n\text{-}Bu_4Sn] = 20$ mM. [b] Methanol-insoluble part. [c] $c = 0.2$ g/dL, in $CHCl_3$. [d] By GPC ($CHCl_3$, PSt). [e] $c = 0.06$ g/dL, in $CHCl_3$. [f] Calculated by ^1H NMR. [g] No olefinic proton was clearly observed in ^1H NMR. [h] Data from refs 9 and 12. [i] $c = 1.0$ g/dL, in cyclohexane. [j] $c = 0.06$ g/dL, in cyclohexane.

The present study focuses on the effects of pendant groups on the secondary conformations of poly(propiolic esters) bearing chiral substituents. Obviously, the following two factors should play an important role in the polymer conformation. One is the distance between the ester groups and chiral carbons, and the other is the steric bulkiness of the pendant groups. From this point of view, we prepared various poly(propiolic esters) which are presented in Scheme 1. Poly(**1**)−poly(**6**), which possess different numbers of methylene spacers and the identical chirality and stereogenic units, were synthesized to elucidate the effect of distance between the main chain and the chiral group. Poly(**7**) and poly(**8**) were employed to estimate the effect of the bulkiness of the chiral substituent on the polymer conformation. Two kinds of catalysts, $[(nbd)RhCl]_2$ and $MoOCl_4$−n-Bu_4Sn, which are both effective for the polymerization of propiolic esters, were used to explore the influence of the main-chain structure because these catalysts are known to provide stereoregular (cis−transoid) and sterically irregular polymers, respectively.[8,11]

Results and Discussion

Polymerization. The results for the polymerization of monomers **1**−**8** with $[(nbd)RhCl]_2$ and $MoOCl_4$−n-Bu_4Sn are summarized in Table 1. Both the Rh and Mo catalysts gave polymers in moderate to good yields. The use of the Rh catalyst generally tended to increase the molecular weight of the polymers. The polymers prepared with the Rh catalyst showed a well-resolved signal based on the olefinic protons of the main chain in the range of 6.7−7.6 ppm in ^1H NMR spectra. This resonance is assignable to the olefinic protons of the cis−transoidal main chain,[8] and the cis contents of the polymers were calculated by comparison of the integrated intensities of the methylene or methine protons adjacent to the ester groups with those of the olefinic protons. The Rh-catalyzed polymerization gave polymers with high stereoregularities (cis−transoid), which is consistent with earlier results.[8] Especially, polymers with alkylene spacers between the ester group and the chiral carbon possessed a quantitative cis content except for poly(**8**)-Rh, which has bulky substituents. The cis contents of the polymers without alkylene spacers [(poly(**1**)-Rh and poly(**7**)-Rh] were lower than those of the other polymers. In contrast to the Rh-catalyzed polymerization, no clear signal due to the main-chain olefinic protons was detected in the ^1H NMR spectra of the polymers prepared with $MoOCl_4$−n-Bu_4Sn. This suggests an ill-defined microstructure for the main chain of the Mo-based polymers.

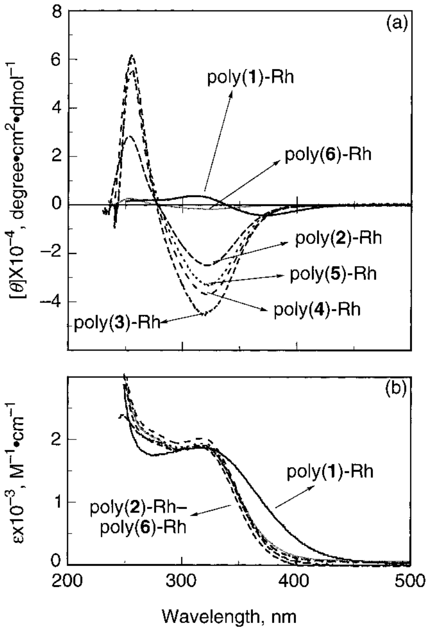


Figure 1. (a) CD and (b) UV−vis spectra of poly(**1**)-Rh−poly(**6**)-Rh in $CHCl_3$ ($c = 6.0 \times 10^{-4}$ mol/L, 20 °C).

Effect of Alkylene Spacers. To evaluate the effect of the length of alkylene spacers, poly(**1**)−poly(**6**) prepared with the Rh catalyst were employed for comparison since they possess the same stereogenic unit but have different alkylene spacers. Figure 1 illustrates the CD and UV−vis spectra of poly(**1**)-Rh−poly(**6**)-Rh. Emphasis should be placed on the UV−vis spectra of the polymers where one can recognize the longer cutoff wavelength for poly(**1**)-Rh than those for the other polymers. Namely, the cutoff wavelength of poly(**1**)-Rh reached 420 nm, whereas those of the others were below 390 nm. Since the cutoff wavelength directly relates to band gap energy, i.e., the degree of main-chain conjugation, the red shift observed for poly(**1**)-Rh is attributed to its extended main-chain conjugation. In other words, the coplanarity of the polymer backbone is enhanced by eliminating the alkylene spacer. The higher order of main-chain conjugation of poly(**1**)-Rh could be due to a lower cis content. However, comparison of the UV−vis spectrum of a less stereoregular poly(**2**)-Rh (cis 72%)[12] with that of the present sample of poly(**2**)-Rh concluded that such a small decrease in the cis content essentially causes no effect on the absorption behavior of the polymers. This means that the red shift observed for poly(**1**)-Rh does not originate from its low cis content. Therefore, the higher degree of main-chain conjugation of poly(**1**)-Rh than in the other polymers results from the larger dihedral angles of the double bonds from planarity. The main chains of polymers fitted with alkylene spacers are, thus, more tightly twisted from a planar structure.

The degree of twist of the main chain remarkably influenced the chiroptical properties of the polymers. As seen in Table 1, the optical rotations ($[\alpha]_D$) of poly(**2**)-Rh−poly(**5**)-Rh were very large and opposite in sign to those of the corresponding monomers. In a similar way, very intense CD signals were recognized for poly(**2**)-Rh−poly(**5**)-Rh in the range of the absorption due to the $\pi-\pi^*$ electronic transitions of the conjugated polyene chromophores (Figure 1a). The chirality is, thus, attributed to the main chain of the polymers. In other words, the main chains of polymers having 1−4 methylene spacers exist in helical conformations, and the domain size of one-handed helical conformation predominates over that of the counterpart. On the contrary, poly(**1**)-Rh showed a negligibly small $[\alpha]_D$ whose sign was the same as for the monomer. Moreover, a remarkable difference in the chiroptical properties of poly(**1**)-Rh from those of the other polymers can be found in the shape of CD spectra: all the polymers with alkylene spacers, poly(**2**)-Rh−poly(**6**)-Rh, displayed identical signal patterns, whereas the CD effects of poly(**1**) differed in shape from those of poly(**2**)-Rh−poly(**6**)-Rh as shown in Figure 1a. A plausible explanation for this phenomenon is given by the different secondary structure of poly(**1**)-Rh from those of the polymers with alkylene spacers. As discussed above, the lower band gap energy of poly(**1**)-Rh (2.95 eV) than those for poly(**2**)-Rh−poly(**6**)-Rh (ca. 3.2 eV) suggests that poly(**1**)-Rh possesses a more planar backbone. It is, therefore, plausible that the helix pitch of poly(**1**)-Rh is larger than those of the other polymers. Such a conformational difference appears to contribute to the poorer chiroptical properties of poly(**1**)-Rh.[13]

The magnitude of the Cotton effects increased with an increasing number of methylene spacers and showed a maximum value when the pendants had ethylene spacers. This suggests that the persistence length of the helical domain of poly(**3**)-Rh is the largest among poly(**1**)-Rh−poly(**6**)-Rh, and the chiral information within the ϵ-carbon in the pendant is able to effectively conduct the screw sense. On the other hand, the CD signals and $[\alpha]_D$ of poly(**6**)-Rh were negligibly small. This means either that poly(**6**)-Rh occupies a random coil geometry rather than a helical conformation or that poly(**6**)-Rh exists in a helical conformation with an ill-controlled screw sense. It should be noted that the CD pattern of poly(**6**)-Rh is identical to those of poly(**2**)-Rh−poly(**5**)-Rh. Additionally, our recent studies revealed that poly(propiolic esters) with achiral substituents possess a helical conformation with a relatively large helical domain size in solution even if they do not bear bulky substituents.[14] The former possibility is, thus, ruled out. Similarly to poly(**2**)-Rh−poly(**5**)-Rh, poly(**6**)-Rh adopts a helical structure, but the helix sense is ill-defined.

All the stereogenic units in monomers **2**−**6** possess (*S*)-configuration, and all the corresponding polymers prepared with the Rh catalyst showed identical CD patterns with the same sign. This is indicative of the formation of helical polymers with an identical screw sense from monomers **2**−**6**, which contrasts to the observation of odd−even rules in the chiroptical properties for several chiral polymers such as polythiophenes[15] and polyisocyanides.[16] For example, the helix sense of polythiophenes having identical stereogenic units alternates upon sequential variation of the number of methylene spacers.[15] Such an effect was not observed in the present system at the temperature measured (20 °C).

Effect of Bulkiness of Substituents. A comparison of the CD spectra for poly(**2**)-Rh with that for poly(**8**)-Rh was next made to estimate the effect of bulkiness of substituents on the conformation of the polymers with alkylene spacers. As can be seen in Figure 2a, although both pendant groups possess (*S*)-configurations with respect to the β-carbons, the CD spectrum of poly(**8**)-Rh is mirror-imaged to that of poly(**2**)-Rh, meaning that these polymers possess opposite screw senses from each other. Thus, the chirality that positions at γ and ϵ carbons also stirs the helix sense. Emphasis should be placed on the fact that no difference in the CD signal pattern was observed between these two polymers. This means that the stereochemistry on remote carbons influences the screw sense but does not effect the secondary conformation of poly(propiolic esters) with alkylene spacers. On the other hand, the absolute value of $[\theta]$ for the first Cotton of poly(**8**)-Rh is larger than that of poly(**2**)-Rh (Figure 2a) although poly(**8**)-Rh has a slightly lower cis content than poly(**2**)-Rh. Because the limited availability of chiral alcohols prohibits providing systematic information on the effect of the shape of pendant groups, it may be hazardous to establish a conclusion by using only the above results. However, in addition to the above observations, a general dependence of the persistence length of helical domain of poly(phenylacetylenes) on the bulkiness of ring substituents[4g] can lead to a conclusion that bulky substituents increase the persistence length of the helical domain of poly(propiolic esters) but do not influence the conformation of the helix if pendants possess alkylene spacer.

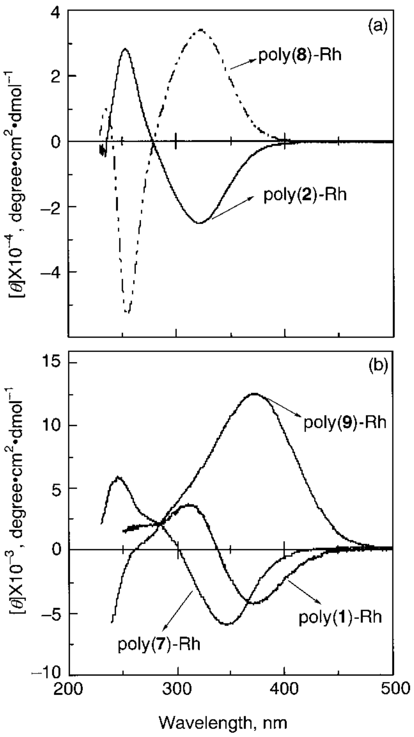


Figure 2. CD spectra of (a) poly(**2**)-Rh, poly(**8**)-Rh and (b) poly(**1**)-Rh, poly(**7**)-Rh (in $CHCl_3$, $c = 6.0 \times 10^{-4}$ mol/L, 20 °C).

In contrast, in the case of the polymers without alkylene spacer, the effect of both bulkiness and stereochemistry of remote carbons is very complicated. As shown in Table 1, poly(**9**)-Rh exceptionally showed a large $[\alpha]_D$, while the absolute values of $[\alpha]_D$ for poly(**1**)-Rh and poly(**7**)-Rh were very small. Judging from the extremely large optical rotation and intense CD effect of poly(**9**)-Rh (Figure 2b), it is reasonable to conclude that poly(**9**) exists in helical conformation. On the other hand, the chiroptical properties of poly(**1**)-Rh were poorer than those of poly(**9**)-Rh and poly(**7**)-Rh. In addition to the completely different shape of the CD spectrum for poly(**1**)-Rh from those for poly(**7**)-Rh and poly(**9**)-Rh, the agreement of the signs of $[\alpha]_D$ between **1** and poly(**1**)-Rh indicates that poly(**1**)-Rh essentially adopts a random coiled conformation. Thus, the introduction of bulky substituents appears to promote the main chain to adopt helical conformation. However, the absolute value of $[\alpha]_D$ and the intensity of CD spectrum of poly(**7**)-Rh were smaller than those of poly(**9**)-Rh despite the similarity in bulkiness between their pendant groups. Furthermore, their exists a difference in CD signal pattern between poly(**7**)-Rh and poly(**9**)-Rh as shown in Figure 2b: the shape of CD signals of poly(**7**)-Rh is close to that of the polymers with alkylene spacers, and its absorption is blue-shifted compared with that of poly(**9**)-Rh. These results were undoubtedly brought about only by the difference in stereochemistry with respect to the γ carbon. In other words, in contrast to the polymers bearing alkylene spacers, not only the bulkiness of the pendant but also the stereochemistry of remote carbon remarkably affect the second-order conformation of the polymers having branching at the α-carbon of pendant group.

Effect of Catalyst Type. As described above, the Mo catalyst gave sterically irregular polymers, which is supported by the lack of signals attributed to the main-chain olefinic protons in their ^{1}H NMR spectra. The polymers prepared with the Mo catalyst generally displayed reduced chiroptical properties compared with those prepared with the Rh catalyst.[17] This tendency is outstanding in the case of polymers with spacing groups: the optical rotations of spacer-containing Mo-based polymers were quite small and at times negligible (Table 1). A more pronounced influence of the catalyst type is seen in the CD spectra of the polymers having alkylene spacers, where no distinct CD effects were obtained for poly(**2**)-Mo–poly(**6**)-Mo and poly(**8**)-Mo (Figure 3a). Similarly, in the CD spectra of poly(**1**) and poly(**7**) which have no alkylene spacer, the smaller intensity of Cotton effects is recognized for the Mo-based polymers (Figure 3b). It can be, therefore, concluded that the use of Rh catalyst to form a highly stereoregular polymer is indispensable for the effective construction of helical polymers from propiolic esters.[18] However, a reasonable explanation cannot be given for the larger optical rotation of Mo-based poly(**1**) than that of Rh-based one (Table 1). A similar tendency was also recognized in the case of poly(**7**). As described above, it is plausible that poly(**1**)-Rh exists in a randomly coiled conformation rather than well-ordered helical structure. Thus, the poor chiroptical properties including optical rotation and molar ellipticity for poly(**1**)-Rh and poly(**1**)-Mo may not originate from the chirality based on the helical main chains. A similar conclusion may be applicable to poly(**7**).

Experimental Section

Materials. All the solvents were distilled by the standard procedures. Commercial $[(nbd)RhCl]_2$ (Aldrich) and $MoOCl_4$ (Strem) were used without further purification. *n*-Bu_4Sn was purchased from Tokyo Kasei, distilled under reduced pressure from calcium hydride, and stored as a toluene solution (100 mmol/L).

All propiolic esters were prepared by the condensation of the corresponding alcohols with propiolic acid in the presence of *p*-toluenesulfonic acid. Purification of **1** was performed by distillation. The other monomers were purified by flash column chromatography (Al_2O_3, eluent; ether/hexane). (*S*)-5-Methyl-1-heptanol was prepared by the reaction of formaldehyde with (*S*)-4-methyl-1-hexylmagnesium bromide. (*S*)-4-Methyl-1-hexyl bromide was synthesized by the reaction of (*S*)-4-methyl-1-hexanol with HBr in the presence of H_2SO_4. Spectral data of the new monomers are as follows:

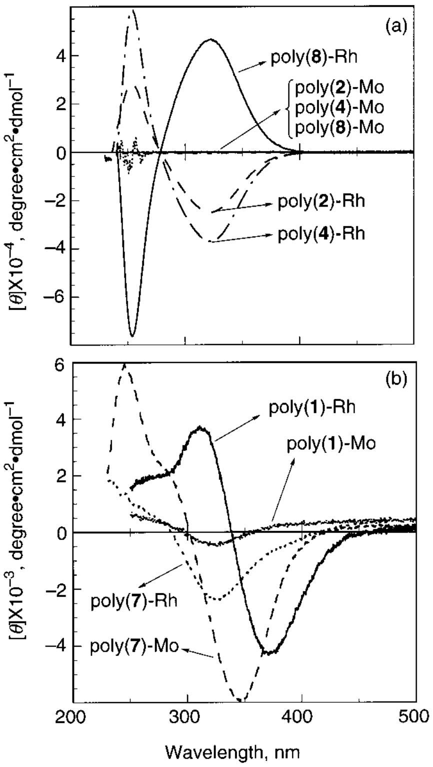


Figure 3. CD spectra of (a) poly(**2**), poly(**4**), poly(**8**) and (b) poly(**1**), poly(**7**) (in $CHCl_3$, $c = 6.0 \times 10^{-4}$ mol/L, 20 °C).

(*S*)-2-Butyl propiolate (**1**): Yield 30%, colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.00–4.90 (m, 1H), 2.86 (s, 1H), 1.64–1.53 (m, 1H), 1.30 (d, 3H, $J = 7.0$ Hz), 0.95 (t, 3H, $J = 8.0$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.4, 74.8, 74.7, 74.4, 28.3, 18.9, 9.3. IR (neat): 3260, 2965, 2120, 1709, 1455, 1309, 1236, 981, 756 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) +18°. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.76; H, 7.94.

(*S*)-2-Methyl-1-butyl propiolate (**2**): Yield 12%, colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.14–3.92 (m, 2H), 2.90 (s, 1H), 1.84–1.68 (m, 1H), 1.54–1.37 (m, 2H), 0.88–1.02 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 74.8, 74.7, 70.5, 34.0, 25.6, 16.0, 11.0. IR (neat): 3264, 2967, 2120, 1717, 1466, 1385, 1229, 980, 756 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) +5°. Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.46; H, 9.06.

(*S*)-3-Methyl-1-pentyl propiolate (**3**): Yield 55%, colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.31–4.19 (m, 2H), 2.87 (s, 1H), 1.79–1.67 (m, 1H), 1.55–1.44 (m, 2H), 1.44–1.32 (m, 1H), 1.27–1.14 (m, 1H), 1.00–0.82 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 76.7, 74.4, 65.0, 34.7, 31.2, 29.3, 18.9, 11.2. IR (neat): 3264, 2965, 2122, 1717, 1464, 1381, 1238, 968, 756 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) +11°. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.82; H, 8.92.

(*S*)-4-Methyl-1-hexyl propiolate (**4**): Yield 69%, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.99 (t, 2H, $J = 6.0$ Hz), 2.85 (s, 1H), 1.79–1.58 (m, 2H), 1.42–1.27 (m, 3H), 1.23–1.15 (m, 2H), 0.95–0.80 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 74.8, 74.4, 64.9, 36.9, 35.1, 29.2, 23.2, 19.0, 11.3. IR (neat): 3264, 2120, 1716, 1232, 756 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) +12°. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.61; H, 9.82.

(*S*)-5-Methyl-1-heptyl propiolate (**5**): Yield 80%, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.20 (t, 2H, $J = 7.0$ Hz), 2.87 (s, 1H), 1.72–1.61 (m, 2H), 1.45–1.22 (m, 5H), 1.20–1.07 (m, 2H), 0.93–0.78 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 74.4, 74.3, 66.4, 36.0, 34.2, 29.2, 28.6, 23.2, 19.0, 11.3. IR (neat): 3264, 2934, 1716, 1464, 1379, 1238, 756 cm^{-1}. $[\alpha]_D$ (*c*

= 0.20 g/dL, $CHCl_3$) +6°. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.47; H, 10.13.

(*S*)-6-Methyl-1-octyl propiolate (**6**): Yield 49%, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.20 (t, 2H, $J = 7.0$ Hz), 2.89 (s, 1H), 1.94−1.62 (m, 2H) 1.40−1.23 (m, 7H) 1.20−1.07 (m, 2H), 0.86 (t, 3H, $J = 7.0$ Hz) 0.84 (d, 3H, $J = 7.0$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 76.7, 74.8, 66.5, 36.3, 34.3, 29.4, 28.3, 26.6, 26.1, 19.1, 11.4. IR (neat): 3304, 2934, 1709, 1464, 1379, 1232, 756 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) +8°. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.42; H, 10.45.

(1*S*,2*R*,5*R*)-Isomenthyl propiolate (**7**): Yield 33%, a white solid; mp 52−54 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.21−5.10 (m, 1H), 2.88 (s, 1H), 2.02−1.17 (m, 9H), 1.01−0.82 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.0, 75.2, 74.9, 74.0, 45.4, 35.1, 30.0, 27.2, 26.1, 20.9, 20.8, 20.2, 18.9. IR (KBr): 3260, 2960, 1710, 1465, 1230, 1160, 1030, 950, 755, 690 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) −82°. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.73; H, 9.98.

(1*S*,2*S*,5*S*)-Myrtanyl propiolate (**8**): Yield 54%, a white solid; mp 41−44 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.18−3.95 (m, 2H), 2.87 (s, 1H), 2.51−2.31 (m, 1H), 2.26−1.57 (m, 6H), 1.53−1.17 (m, 5H), 0.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 74.8, 74.4, 64.9, 63.1, 39.1, 37.1, 35.5, 29.8, 27.9, 24.5, 22.6, 19.4. IR (KBr): 3264, 2930, 1710, 1460, 1250, 970, 758 cm^{-1}. $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) −28°. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.44; H, 9.06.

Measurements. The molecular weights and polydispersities of the polymers were determined by using gel permeation chromatography (eluent, chloroform; Shodex columns K804, K805, and K806; calibrated by polystyrene standards). ^{1}H NMR spectra were recorded with a JEOL EX-400 spectrometer using $CDCl_3$ as a solvent. CD spectra were measured in a quartz cell (thickness 1 cm) at 20 °C using a Jasco J600 spectropolarimeter. Specific rotations were determined with a Jasco V-530 spectropolarimeter. UV−vis and IR spectra were recorded with Shimadzu UV-2200 and Shimadzu FTIR-8100 spectrophotometers, respectively. Melting points were measured on a Yanaco micromelting point apparatus and were not corrected.

Polymerizations with $[(nbd)RhCl]_2$. A typical procedure is as follows: a solution of a monomer (2.00 mmol) in CH_3CN (1 mL) was added to a solution of $[(nbd)RhCl]_2$ (18.4 mg, 40 μmol) in CH_3CN (1 mL) at 30 °C under nitrogen. The solution was kept at 30 °C for 24 h. The resulting suspension was dissolved in toluene (ca. 10 mL) and poured into a large excess of methanol to precipitate the polymer. The polymer was filtered with a sintered glass (G3) and dried under reduced pressure.

Polymerizations with $MoOCl_4$−*n*-Bu_4Sn. Following is a typical procedure: A 200 mM solution (0.2 mL) of *n*-Bu_4Sn in toluene was added to a 50 mM solution (0.8 mL) of $MoOCl_4$ in toluene, and the resulting solution was kept at 30 °C for 10 min. A solution (1 mL) of monomer (1.00 mmol) in toluene was added to the catalyst solution, and the solution was kept at 30 °C for 24 h. The isolation and purification of polymer were carried out in a similar way to the Rh-catalyzed polymerizations as stated above.

Acknowledgment. We acknowledge Professor Shunsaku Kimura and Professor Shiro Kobayashi for the permission of the use of a CD spectropolarimeter. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, Culture, and Sports, Japan.

References and Notes

(1) For recent reviews of the synthesis of helical polymers, see: (a) Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 63−68. (b) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349−372. (c) Qin, M.; Bartus, J.; Vogl, O. *Macromol. Symp.* **1995**, *12*, 387−402. (d) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, 11−19.

(2) (a) Okamoto, Y.; Hatada, K. In *Chromatographic Chiral Separations*; Zief, M., Crane, L. J., Eds.; Marcel Dekker: New York, 1988; p 199. (b) Pu, L. *Tetrahedron: Asymmetry* **1998**, *9*, 1457−1477.

(3) For a review of chiral conjugated polymers, see: Pu. L. *Acta Polym*. **1997**, *48*, 116−141.

(4) (a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *7*, 174−179. (b) Tang, B. Z.; Kotera, N. *Macromolecules* **1989**, *22*, 4388−4390. (c) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704−1712. (d) Yamaguchi, M.; Omata, K.; Hirama, M. *Chem. Lett.* **1992**, 2261−2262. (e) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009−2012. (f) Yashima, E.; Huang, S.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1811−1812. (g) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184−4193. (h) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662−6666.

(5) (a) Aoki, T.; Shinohara, K.; Kaneko, T.; Oikawa, E. *Macromolecules* **1996**, *29*, 4129−4198. (b) Aoki, T.; Kobayashi, Y.; Kaneko, T.; Oikawa, E.; Yamamura, Y.; Fujita, Y.; Teraguchi, M.; Nomura, R.; Masuda, T. *Macromolecules* **1999**, *32*, 79−85.

(6) (a) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449−451. (b) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345−6359.

(7) For recent reviews of the polymerization of substituted acetylenes, see: (a) Masuda, T. *Catalysis in Precision Polymerization*; Kobayashi, S., Ed.; Wiley: Chichester, 1997; Chapter 2.4. (b) Masuda, T. *Polymeric Material Encyclopedia*; Salamone, J. C., Ed.; CRC: New York, 1996; Vol. 1, pp 32−39.

(8) Tabata, M.; Inaba, Y.; Yokota, K.; Nozaki, Y. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 465−475.

(9) Nakako, H.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **1999**, *32*, 2861−2864.

(10) We denote the polymers with number and the catalyst used for convenience. For example, poly(**1**) prepared with Rh catalyst is described as poly(**1**)-Rh.

(11) Masuda, T.; Kawai, M.; Higashimura, T. *Polymer* **1982**, *23*, 744−747.

(12) Nomura, R.; Fukushima, Y.; Nakako, H.; Masuda, T. *J. Am. Chem. Soc.*, submitted.

(13) It is also plausible that the ill-defined screw sense caused the poor chiroptical properties of poly(**1**)-Rh.

(14) A copolymer consisting of an achiral propiolic ester, 4-chlorobutyl propiolate, and only 11 mol % of chiral comonomer **8** exhibited very large chiroptical properties comparable to those of poly(**8**)-Rh. This suggests a relatively large helical domain size of poly(propiolic esters). Further, NMR study on the conformation of poly(propiolic esters) also revealed that achiral polymers having alkylene spacers adopt helical conformation even in the absence of bulky side groups. See ref 12.

(15) Lermo, E. R.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *Chem. Commun.* **1999**, 791−792.

(16) Amabilino, D. B.; Ramos, E.; Serrano, J. L.; Sierra, T.; Veciana, J. *J. Am. Chem. Soc.* **1998**, *120*, 9126−9134.

(17) We recently determined the persistence length of the helical domain for poly(propiolic esters) with alkylene spacers to be approximately 15−20 monomer unit length. Thus, all of the polymers prepared in the present study have large molecular weight enough to ignore the effect of molecular weight on the chiroptical properties of polymers.

(18) It should be noted that poly(**1**) and poly(**7**) prepared with the Mo catalyst showed blue-shifted absorptions compared with those prepared with the Rh catalyst. The CD spectra presented in Figure 3a also clearly display this phenomenon. This blue shift suggests the tightly twisted main chain of the Mo-based polymers compared with the Rh-based polymers. This suggestion conflicts with the above-described conclusion that the less conjugated main chain twists more tightly. However, quite limited availability of the information on the structure of Mo-based polymers[11] does not allow to exclude a possibility that contamination of irregular microstructure such as head-to-head and tail-to-tail forms hinders the main-chain conjugation to result in the blue shift. Therefore, detailed discussion on the difference in the degree of main-chain conjugation cannot be made only on the basis of the results from UV−vis spectra if the polymerization is conducted with different catalysts.

MA000191Q