# Helix Inversion of Poly(propiolic esters)

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ABSTRACT: The effects of temperature and solvents on the helical conformation of stereoregular cis−transoidal poly(propiolic esters) [(CH═CCO$_2$R*)$_n$] with various chiral side chains, which were prepared with [(nbd)RhCl]$_2$, were investigated using circular dichromism spectroscopy. CD effects of the polymers with short side chains, where R* = (*S*)-(CH$_2$)$_n$CH(CH$_3$)C$_2$H$_5$ ($n$ = 1−4), were only slightly amplified with decreasing temperature from +20 to −50 °C, and this behavior was independent of the solvents examined (CHCl$_3$, THF, and *n*-hexane). In contrast, although the temperature dependence of CD effects for polymers with long alkyl pendants [**5** and **6**, where R* = (*S*)-(CH$_2$)$_5$CH(CH$_3$)C$_2$H$_5$ and (*S*)-(CH$_2$)$_2$CH(CH$_3$)(CH$_2$)$_3$-CH(CH$_3$)$_2$, respectively] was similar in *n*-hexane to those for the other polymers, the Cotton effects of **5** and **6** in CHCl$_3$ decreased in intensity with decreasing temperature and inverted in sign between −30 and −40 °C. This CD inversion process was proved to originate from the thermally induced screw-sense inversion, and computational semiempirical calculation suggested that the transitions from M (left-handed) to P (right-handed) and from P to M helices took place for polymers **5** and **6**, respectively, with decreasing temperature. The screw-sense inversion driven by the change in solvent composition between *n*-hexane and CHCl$_3$ was also achieved at +20 °C for a copolymer of hexyl with (*S*)-2-methylbutyl propiolates.

## Introduction

Management of the three-dimensional structure of macromolecules, besides precise control of their first-order structure, is a key technology for the production of highly advanced polymers. The helical conformation is the most basic and simplest three-dimensional main chain structure and a very important component for natural macromolecules to yield their characteristic functions.

Recent development of the synthetic polymer chemistry has enabled us to provide well-defined helical polymers.[1] These polymers can adopt left- and right-handed helical conformations, and the helix sense can be controlled either thermodynamically or, in some cases, kinetically. Examples of the helical polymers whose screw sense is kinetically controlled are still quit limited to only a few polymers with excellent stereoregularity such as polychloral,[2] poly(alkyl methacrylates),[1e,f,3] and polyisocyanides.[4] These polymers possess a very large energy barrier for the transition between two helices or between helical and disordered conformations, due to the rigidity of the main chain. Thus, the helix sense initially determined by the polymerization process can be maintained even in solution. On the other hand, helical polymers with thermodynamically controlled helix sense, which are exemplified by poly(isocyanates),[5] polyacetylenes,[6] polysilanes,[7] poly(arylisocyanides),[8] etc., possess a semiflexible but not rigid main chain. Therefore, the helix−helix interconversion readily occurs due to the small energetic barrier for helix reversal. The helix sense is, thus, detemined by the free energy difference between two helices that originates from chiral source in the side chain, solvent, and so on. Since the free energy difference between the two helical conformations is appreciably small, the initially determined helix sense, in some cases, can be elegantly inverted into the counterpart by external stimuli. After the discovery of this helix sense inversion phenomenon in synthetic DNA[9] and poly(L-aspartic acid esters),[10] several artificial polymers[11] have been found to undergo helix-sense inversion, which is promoted by external stimuli such as the changes of temperature and solvent composition, chiral additives, the photoinduced isomerization of side chains, and so on.

Our recent interests have been placed on the understanding of the nature of the helical conformation based on poly(propiolic esters). We have demonstrated that stereoregular cis−transoidal poly(propiolic esters) with chiral pendants, prepared with Rh catalysts, take helical conformation with an excess of one-handed screw sense.[12] Our systematic study on the helical poly(propiolic esters) also revealed that polymers, especially those without branching at the α-position to the ester groups, adopt well-ordered helical structure with long persistence length.[12c] In the present study, we investigated the effects of temperature and solvents on the chiroptical property of poly(propiolic esters) with various chiral substituents (Scheme 1), which led to a finding that polymers having long alkyl side chains undergo helix-sense inversion driven by the change in temperature and also by the change in solvent composition.

## Results and Discussion

**Computational Calculation.** Chiroptical properties demonstrated by CD spectra and optical rotations enable us to discuss the secondary structure of chiral polymers. The existence of helical structure in the main chain can be confirmed by the intense CD effects and/or large optical rotations of polymers. However, the information on the detailed three-dimensional structure of main chain such as helix sense and pitch of the helix cannot be obtained only from the CD data. The most promising way to determine the main-chain structure is the isolation of oligomers and their X-ray crystal structure analysis. Unfortunately, selective formation of oligomers of propiolic esters is impossible at present because precise control of the polymerization has not

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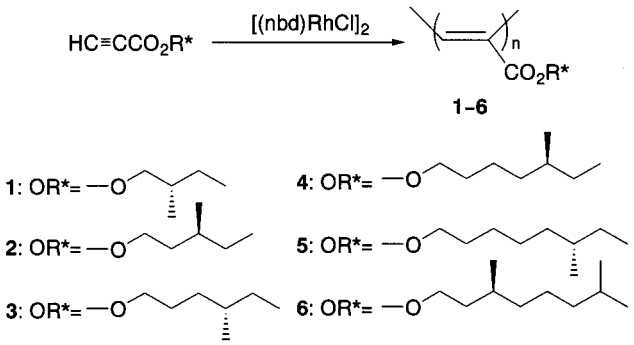
**Scheme 1**




been achieved. Therefore, prior to the discussion on the helix-sense reversal, we attempted the computational calculation of oligomers in order to gain approximate but experimentally unaccessible knowledge on the secondary structure of poly(propiolic esters).

We first constructed 12-mers of methyl propiolate as initial models. The dihedral angles around the double bonds were fixed at 180°, and the dihedral angles around the single bonds were varied from 90° to 175° by the step of 10°. The structural optimization was first carried out for these 12-mers by using the MM2 (Molecular Mechanics, version 2) method. Interestingly, irrespective of the initial dihedral angle about the single bonds of the initial models, all of the MM2 calculations gave similar results. Namely, regardless of the initial models, the computationally estimated most stable structure of the 12-mers was a right-handed helix, and the averaged dihedral angle around the double bonds was 103°. Further calculation was performed by using PM3 (Parametric Method, revision 3) method on the 30-mers of methyl propiolate, where the dihedral angles around the single bonds of the initial 30-mers were 103°. The stereoview for the most probable structure of 30-mers of methyl propiolate, optimized by the PM3 calculation, is illustrated in Figure 1, which suggests the helical main-chain conformation as the most stable secondary structure of poly(propiolic esters). The estimated dihedral angle about the single bonds was approximately 107°. Although the computational simulation does not always provide an actual structure, these results lead to a conclusion that, in comparison with poly(phenylacetylene), the main chain of poly(propiolic esters) more tightly twists.[13] Therefore, poly(propiolic esters) possess more limited main chain conjugation.

We next tried to estimate the plausible screw-sense of poly(propiolic esters) with chiral substituents by the PM3 semiempirical molecular orbital calculation. We chose 15-mers of **1** having various dihedral angles around the single bonds and dihedral angle at 180° around the double bonds and computationally optimized their side chain conformation with fixing the main-chain conformation by the MM2 calculation. After this process, the conformation of each model was optimized by PM3 fixing the dihedral angles around both single and double bonds in main chain, and potential energies were calculated. Figure 2 shows the dependence of the potential energy of 15-mers of **1** terminated with hydrogen on the C=C−C=C torsional angle. The potential curve had two energy minima at torsional angles of about 240° and 140°. These torsional angles correspond to the left-handed (M helix) and right-handed (P helix) helical structures, respectively. The potential barrier heights of M and P helices are 3.86 and 2.64

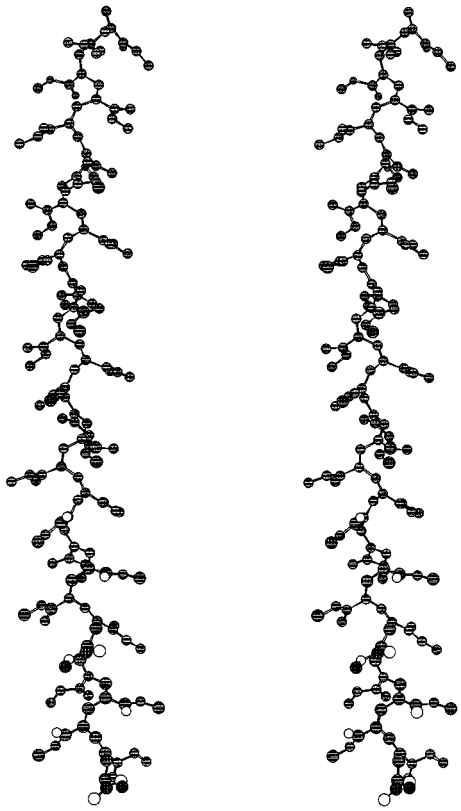


**Figure 1.** A stereoview of the optimized structures of 30-mer of methyl propiolate terminated by hydrogen.

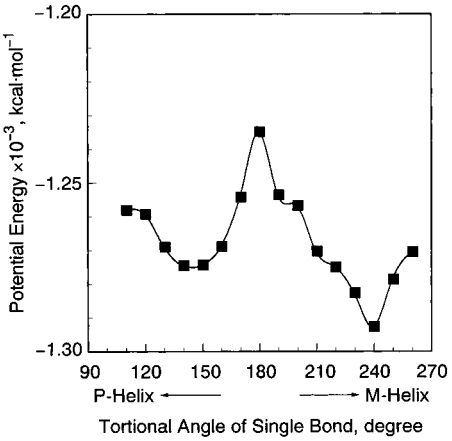



**Figure 2.** PM3 calculation. The C=C−C=C torsional angle dependence of the potential energy of 15-monomer units of **1** terminated with hydrogen. The C−C=C−C torsional angle was fixed at 180°.

kcal/mol per repeat unit, respectively. The global energy minimum at 240° means that the M helical structure is preferred to the P helix by 1.22 kcal/mol per repeat unit. Therefore, polymer **1** appears to possess the M helical structure predominantly. By comparison with the results from CD measurements,[12b] we assume that poly(propiolic esters) with left-handed helical structure (M helix) display a minus first Cotton effect in a range of 300−400 nm. Accordingly, a plus first Cotton effect at the main-chain absorption band implies an excess of right-handed helical conformation.

**Thermally Driven Helix-Sense Inversion.** Poly(propiolic esters) with chiral substituents show large Cotton effects around 320 nm corresponding to the UV absorption bands of the main chain.[12] Figure 3 plots the

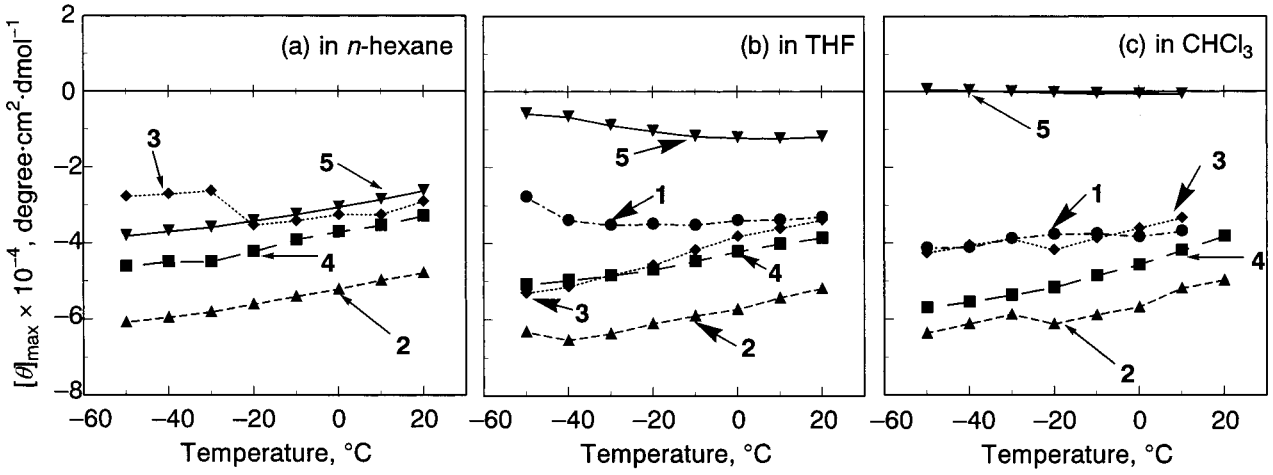



**Figure 3.** Temperature dependence of $[\theta]_{max}$ of the first Cotton effect for **1**−**5** in (a) *n*-hexane, (b) THF, and (c) chloroform ($c = 6.0 \times 10^{-4}$ mol/L).

maximum molar ellipticity ($[\theta]_{max}$) of the first Cotton of polymers **1**−**5** in *n*-hexane, THF, and chloroform in a temperature range of +20 to −50 °C. These polymers **1**−**5** possess chiral side chains with (*S*)-configuration and exhibited a negative first Cotton effects at +20 °C, which means that all the polymers exist in an excess of left-handed helical conformation at +20 °C. In *n*-hexane, polymers **2**−**5** showed intense CD effects even at +20 °C (Figure 3a).[14] The intensity of these CD effects only slightly increased with decreasing temperature.[15,16] As temperature was decreased, the shapes of CD spectra of the polymers did not change at all. These results were interpreted by the idea that the main chain of **2**−**5** takes almost one-handed (left-handed) helical structure even at ambient temperature, and the persistence length of helical domain only slightly increases with decreasing temperature. This is in contrast to the previous results that the intensities of CD effects and/or specific rotations of polymers from optically active 1-alkynes and phenylacetylenes drastically increases as temperature is decreased.[6a,d] This is because the main chain of these polymers is quite flexible so that the regular helical form is readily transformed to an irregular structure by thermal stimuli. On the other hand, poly(propiolic esters) possess a semiflexible main chain, and eventually, the helix of poly(propiolic esters) is more thermally stable than that of other substituted polyacetylenes.[12c] This profile contributed to the small effect of temperature on the CD effect of poly(propiolic esters) as demonstrated above.

The temperature variable CD spectra in THF also gave a similar tendency. The $[\theta]_{max}$ values of polymers **1**−**4** were intense even at +20 °C, and the magnitudes only slightly increased with decreasing temperature (Figure 3b). However, the $[\theta]_{max}$ of **5** was smaller than that in *n*-hexane. Our previous study has shown that poly(propiolic esters) without branching at the α-position of the ester groups exist in well-ordered helical conformation even if they do not possess sterically demanding substituents.[12b,c] It is, therefore, reasonable to assume that **5** adopts a helical structure, but in THF, this polymer possesses reduced ability to bias the screw sense due to the long distance from the chiral center to the main chain. Here, it should be noted that, in contrast to polymers **2**−**5** in *n*-hexane and to polymers **1**−**4** in THF, the magnitude of the CD effects of polymer **5** decreased with decreasing temperature in THF. Such a tendency was more clearly observed in chloroform. In chloroform, the $[\theta]_{max}$ of **1**−**4** was very large at +20 °C, and only a slight increase in the intensity was observed as temperature was lowered from +20 to −50 °C (Figure 3c). The intensity of $[\theta]_{max}$ of polymer **5** was also quite small compared with that of the other polymers **1**−**4** and gradually decreased with decreasing temperature. These results are in good agreement with those observed in THF. Emphasis should be placed on the fact that, in chloroform, the sign of the Cotton effect of polymer **5** was inverted at around −30 °C, and the CD spectrum of **5** at +20 °C was the mirror image to that at −50 °C.

In summary, polymers **1**−**4** which possess short pendant groups exist in a regular left-handed helical structure irrespective of solvents, and their intensity only slightly increased with decreasing temperature, maintaining their signal patterns. This means that the conformation of polymers **1**−**4** does not change upon the change of temperature, except for the slight increase in the persistence length of the helical domain. From the magnitude of $[\theta]_{max}$ of these polymers, the persistence length of the helical domain appears to decrease in the order of *n*-hexane > THF > $CHCl_3$. In contrast to polymers **1**−**4**, the chiroptical property of polymer **5**, which has a long alkyl pendant, showed a strong dependence on solvents, and CD inversion driven by temperature change occurred in chloroform.

The above-denoted results led to a hypothesis that poly(propiolic esters) having long alkyl side chains yield the CD-inversion phenomenon. To prove this hypothesis, we next investigated the temperature dependence of the CD effect of poly[(*S*)-3,7-dimethyloctyl propiolate] (**6**) because this polymer possess long alkyl side chains and also because the closely located chiral center to the main chain induces intense CD effects. As shown in Figure 4, polymer **6** displayed a large Cotton effect at +20 °C in chloroform. When temperature was lowered, the magnitude of the Cotton effect decreased, and the inversion of the sign occurred between −30 and −40 °C.[17] A plot of $[\theta]_{max}$ vs temperature indicated that the transition temperature was about −37 °C.[17] Although the chiral centers are located at different positions for polymers **5** and **6**, the CD inversion took place for both polymers. Furthermore, polymer **2**, which possess the chiral center at the γ position like polymer **6**, did not show the CD-inversion phenomenon. Therefore, the distance from the chiral center to the main chain does not influence the CD inversion. All these results suggest that polymers with long alkyl side chains achieve the

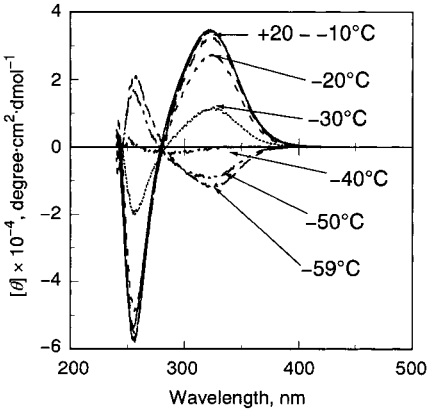



**Figure 4.** CD spectra of **6** at various temperatures in chloroform ($c = 6.0 \times 10^{-4}$ mol/L).

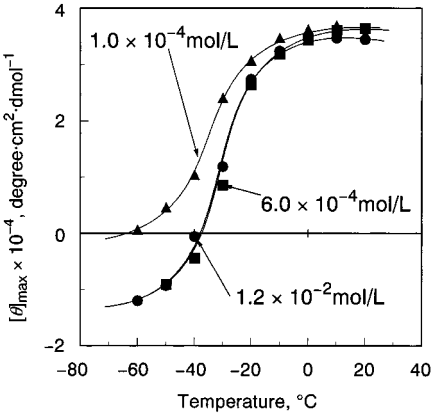



**Figure 5.** Temperature dependence of $[\theta]_{max}$ of the first Cotton effect for **6** in chloroform at various concentrations ($c = 1.2 \times 10^{-2}$, $6.0 \times 10^{-4}$, and $1.0 \times 10^{-4}$ mol/L).

inversion of their CD effects.

Although the absolute intensity of the CD signal of **6** at −59 °C was smaller than that at +20 °C, the shape of the CD spectrum at −59 °C was just mirror imaged. In addition, no change was observed in the UV−vis spectrum of **6** upon the change in temperature. These results imply that the CD inversion does not cause the change of conformation such as screw pitch. One of the probable origins for the CD inversion might be from the aggregation of the polymer chains. Such a phenomenon often induces helical structure to conjugated polymers such as polythiophenes[11h,18] and poly(phenylenes)[19] and is claimed to cause helix inversion of the polymers,[11h] resulting in the inversion of the CD signals. Poly(propiolic esters) can also aggregate into a hexagonal packing suprastructure in the solid state.[20] It is known that the aggregation behavior is strongly affected by the concentration of the polymers and that the increase in the concentration generally promotes the aggregation. However, the increase in the concentration of **6** did not affect the CD-inversion phenomenon (Figure 5). For example, at a 20 times concentration ($1.2 \times 10^{-2}$ mol/L), the CD spectrum of **6** at +20 °C was identical in shape and also in intensity to that at a concentration of $6.0 \times 10^{-3}$ mol/L. Under this concentrated condition, the plot of $[\theta]_{max}$ vs temperature gave an identical curve to that obtained at the standard concentration ($6.0 \times 10^{-4}$ mol/L). On the other hand, the temperature dependence of CD intensity was influenced at a very low concentration ($1.0 \times 10^{-4}$ mol/L), and the CD signal disappeared at about −59 °C, which was lower than the transition temperature at the standard concentration. However, it should be emphasized that even under this very diluted condition, the intensity of the CD effect was reduced with decreasing temperature. Therefore, we assume that, although polymer **6** may, to some extent, form an aggregated structure, the aggregation phenomenon does not mainly contribute to the CD inversion.

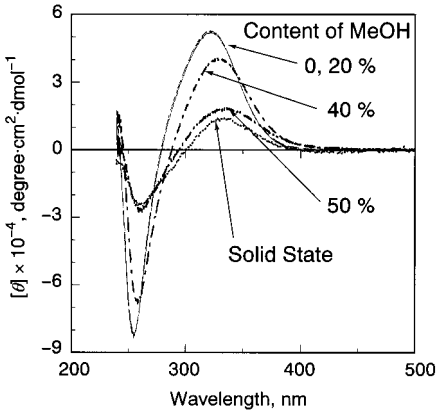



**Figure 6.** CD spectra of **6** in chloroform/methanol (20 °C, $c = 6.0 \times 10^{-4}$ mol/L) and in the solid state (20 °C).

Further evidence that supports the above idea was obtained by the CD measurements performed in mixed solvents comprising chloroform as a good solvent and methanol as a poor solvent (Figure 6). The chloroform/methanol composition was varied from 100/0 to 50/50. The CD spectrum of a film of **6** cast from a chloroform solution on a quartz plate is also illustrated in Figure 6.[21] The CD spectrum in an 80% chloroform solution was almost identical to that in a 100% chloroform solution. When the methanol fractions were 40% and 50%, the CD spectra were slightly red-shifted, and the CD spectrum in 50% chloroform was identical to that in the solid state. Since poly(propiolic esters) form an aggregated structure in the solid state,[20] it can be reasonably concluded that this red shift is due to the aggregation phenomenon. Therefore, the suspension in chloroform/methanol (50/50) involves an aggregated structure. It should be emphasized that no CD inversion took place in a high composition of the poor solvent and also in the solid state. Thus, we can conclude that the main-chain aggregation does not trigger off the CD inversion. In other words, helix-sense inversion of individual polymer chain, driven by thermal stimuli, causes the inversion of the CD effect. It has been reported that, for the helix-sense inversion of polyisocyanates[11f] and polysilanes,[11g] the entropy term in the free energy difference between two helices plays an important role. Like these systems, the entropy term is probably responsible for the thermally driven helix-sense inversion of poly(propiolic esters).

**Solvent-Driven Helix Inversion.** As described above, the side chain length is the most important factor for the helix-sense inversion of poly(propiolic esters), and the polymers that have long alkyl side chains tend to undergo thermally driven helix-sense inversion. Unfortunately, chiral primary higher alcohols are not readily available, which inhibits to systematically investigate this factor. However, as described in our previous paper, we are able to construct poly(propiolic esters) with an excess of one-handed helical structure from achiral monomers by copolymerizing with a small amount of chiral comonomers because the persistence length of the helical domain of poly(propiolic esters) is

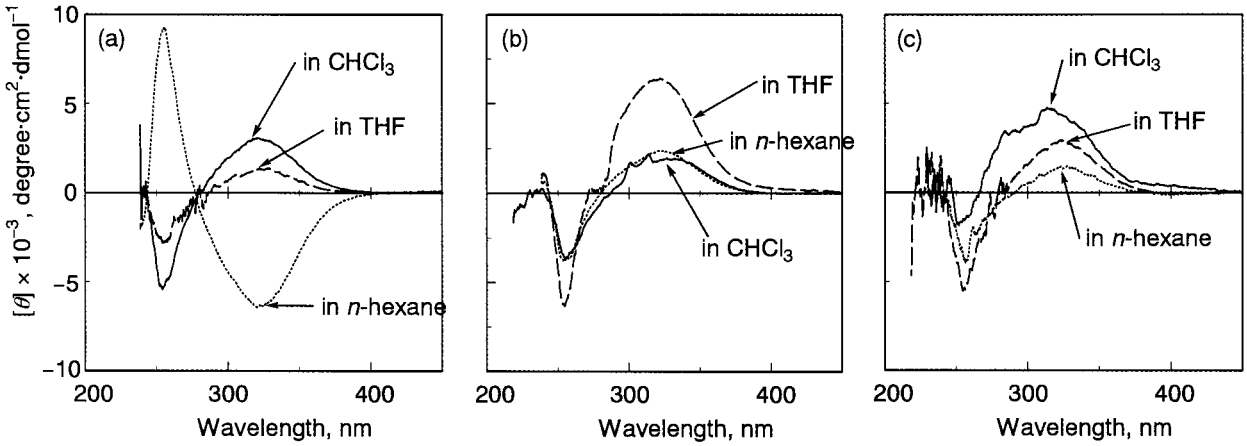



**Figure 7.** CD spectra of (a) **7**, (b) **8**, and (c) **9** in chloroform, THF, and *n*-hexane (20 °C, $c = 6.0 \times 10^{-4}$ mol/L).

long enough to achieve the so-called sergeant-and-soldier principle.[12c] For example, polymers that are identical in the secondary conformation to a homopolymer from enantiometrically pure chiral monomer can be obtained even if an achiral monomer is copolymerized with a 10 mol % of chiral monomer.[12c]

To estimate the effect of the side chain length on the helix-sense inversion, *n*-hexyl, *n*-octyl, and *n*-dodecyl propiolates were copolymerized with a small amount of (*S*)-2-methylbutyl propiolate at the feed content of chiral/achiral copolymers of 10/90.[22] The CD spectra of these copolymers based on *n*-hexyl (**7**), *n*-octyl (**8**), and *n*-dodecyl propiolates (**9**) in chloroform, THF, and *n*-hexane at +20 °C are presented in Figure 7. These copolymers should take the same screw sense as that of homopolymer **1** according to the sergeant-and-soldier rule, if the helix inversion driven by thermal stimuli does not take place. The helix sense of **7**−**9** should be, thus, left-handed because polymer **1** shows a negative first Cotton effect irrespective of solvent. In *n*-hexane, in which no helix-sense inversion was observed for all the homopolymers used in the present study, the CD spectrum of **7** was the same in sign as that of **1** and showed a minus first Cotton effect (Figure 7a). This is because the bias of the screw sense is governed by the helix preference of (*S*)-2-methylbutyl propiolate. In contrast, the CD spectra of **7** in chloroform and THF were plus in sign of the first Cotton effects and mirror-imaged to that of **1**. This means that the helix sense was reversed to the opposite one by changing solvent. This phenomenon is very interesting because the helix inversion occurs above +20 °C. In other words, the transition temperature of helix inversion is higher than +20 °C in chloroform and THF for copolymer **7**. Such a tendency was more clearly demonstrated by increasing the length of alkyl chain. Polymers **8** and **9,** which have very long alkyl side chains, showed plus first Cotton effects even in *n*-hexane in which helix inversion does not occur for polymers **1**−**7** (Figure 7b,c). This clearly reveals that increasing the length of the side chain facilitates the helix-sense inversion. These results also suggest that polymers having linear, no-branching side chains prefer helix-sense inversion at high temperature.

As shown in Figure 7a, the Cotton effects of **7** were opposite in sign to each other in chloroform and *n*-hexane at +20 °C. In other words, biased helix sense was opposite between these two solvents. Therefore, it is expected that the helix-sense inversion occurs by changing the solvent composition. Such examples have been reported for only poly(L-aspartic acid esters) in chloroform/organic acid[10,23] and for the aggregated form of stereoregular poly(thiophene) in chloroform/methanol.[11i] Figure 8, which shows the solvent-composition dependence of the CD spectrum of copolymer **7**, clearly demonstrates the helix-sense inversion driven by the change in solvent composition between chloroform and *n*-hexane. Namely, the intensity of the negative-signed CD effect in 100% *n*-hexane decreased with increasing content of chloroform, and the CD effect was inverted between 60% and 80% contents of chloroform.

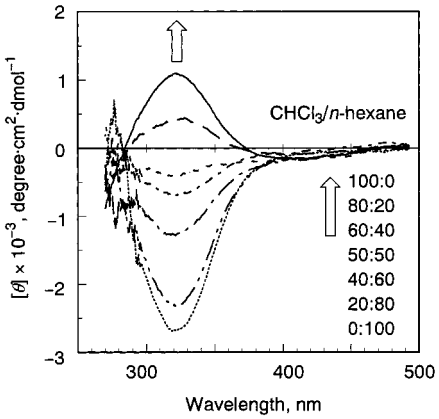



**Figure 8.** CD spectra of **7** in chloroform/*n*-hexane (20 °C, $c = 6.0 \times 10^{-4}$ mol/L).

## Conclusions

In this paper, we have demonstrated that the helix sense of poly(propiolic esters) depends not only on the configuration of the chiral center but also on the structure of the side chain, temperature, and solvent. When the polymers possess short alkyl pendants, the helix sense, initially determined by the configuration of chiral center, is not influenced by thermal stimuli irrespective of solvent. On the other hand, polymers with long alkyl chains readily invert their helix sense with thermal stimuli in chloroform, and linear, long alkyl side chains tend to increase the helix-sense transition temperature. Therefore, if the length of the alkyl side chain is properly controlled, the helix inversion can be driven by the change of solvent even at ambient temperature. In other words, it is now possible to tune the helix sense of poly(propiolic esters) not only by the configuration of the chiral center but also by solvent, by temperature, and by the side-chain skeleton.

**Table 1. Characterization Data for the Polymers Used in the Present Study**

| (co)polymer | yield,[a] % | $M_n \times 10^{-3}$ [b] | PDI[b] | cis content,[c] % | $[\alpha]_D$,[d] deg |
|---|---|---|---|---|---|
| **1** | 36 | 80 | 3.3 | 100 | −473 |
| **2** | 37 | 24 | 2.0 | 100 | −612 |
| **3** | 30 | 76 | 3.2 | 100 | −418 |
| **4** | 30 | 60 | 1.7 | 100 | −358 |
| **5** | 33 | 60 | 3.1 | 100 | −20 |
| **6** | 17 | 8.5 | 3.0 | 100 | +485 |
| **7** | 20 | 140 | 1.5 | 100 | +54 |
| **8** | 15 | 200 | 3.2 | 100 | +40 |
| **9** | 16 | 140 | 1.7 | 100 | +13 |

[a] Methanol-insoluble part. [b] Number-average molecular weight and polydispersity index; by GPC ($CHCl_3$, PSt). [c] Calculated by $^1$H NMR. [d] $c = 0.2$ g/dL, in $CHCl_3$.

## Experimental Section

**General.** $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL EX-400 spectrometer. CD spectra were recorded on a Jasco J600 spectropolarimeter equipped with a quartz cell (thickness 1 cm or 1 mm) in a cryostat. Specific rotations were obtained with a Jasco V-530 polarimeter. UV−vis spectra were recorded with a Shimadzu UV-2200 spectrophotometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. The molecular weights of the present polymer samples were determined by gel permeation chromatography (eluent, chloroform; Shodex columns K804, K805, and K806; calibrated by polystyrene standards). Acetonitrile was dried over $CaH_2$ and distilled under nitrogen. All the other reagents were used without purification. (*S*)-3,7-Dimethyl-1-octanol was obtained by the hydrogenation of (*S*)-(−)-citronellol with Pd/C. All of the monomers were prepared by the condensation of propiolic acid with the appropriate alcohols in the presence of *p*-toluenesulfonic acid or sulfuric acid. Spectral data for the new monomer, (*S*)-3,7-dimethyl-1-octyl propiolate, were as follows: $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 4.22 (m, 2H), 2.86 (s, 1H), 1.71 (m, 1H), 1.52 (m, 3H), 1.28 (m, 2H), 1.14 (m, 4H), 0.91 (d, 3H, $J = 3.1$ Hz), 0.85 (d, 6H, $J = 3.4$ Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 152.8, 74.8, 74.3, 64.9, 39.1, 37.0, 35.1, 29.7, 27.9, 24.5, 22.7, 22.6, 19.4; IR 3306, 2930, 1717, 1468, 1385, 1232, 756 cm$^{-1}$; $[\alpha]_D$ ($c = 0.20$ g/dL, $CHCl_3$) +2°. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24%; H, 10.54%. Found: C, 74.27%; H, 10.83%.

**(Co)polymerizations.** An acetonitrile solution (1 mL) of the monomers (total 4 mmol) was added to a solution of $[(nbd)RhCl]_2$ (40 $\mu$mol) in acetonitrile (1 mL), and the mixture was kept for 24 h at 30 °C. After the solvent was removed under a reduced pressure, the resulting precipitates were dissolved in toluene and then poured into a large amount of methanol to precipitate the polymers. The polymers were isolated by filtration, and the reprecipitation procedure was carried out again. The polymers were collected by filtration and dried under reduced pressure. The data for the produced polymers are summarized in Table 1.

**Computational Calculation.** Semiempirical calculations were performed using the MOPAC 2000 developed by Fujitsu and Dr. J. J. P. Stewart running on the Pentium-based IBM PC-AT compatible machine with windows NT4.0. The used semiempirical Hamiltonian was PM3 with MOZYME algorithms. Initial models were constructed with FREE WHEEL (Butch Software Studio) and CS Chem3D Pro (version 5.0, CambridgeSoft Corporation). MM2 calculations were carried out by using CS Chem3D Pro.

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**Supporting Information Available:** Temperature and solvent dependence of the intensity of the first Cotton effect of polymer **6.** This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

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(13) The dihedral angles around the single bonds of the most preferred structure of the phenylacetylene 20-mer was computationally estimated to be 140°. See ref 6f.

(14) **1** was not soluble in *n*-hexane.

(15) The intensity of the CD effects of polymer **3** steeply changed between −20 and −30 °C. Similarly, the CD effects of polymers **3** and **2** in $CHCl_3$ increased when the temperature was lowered from −20 to −30 °C. The reason for these phenomena is unclear at present. The aggregation phenomenon of polymer chains might contribute to this behavior.

(16) The decrease in temperature causes the increase in the density of solvents. Therefore, the concentration of polymers should increase with decreasing temperature. We did not correct this temperature effect in the present study.

(17) Temperature and solvent dependences of CD effects of polymer **6** were similar to those of polymer **5**, where the intensity of CD spectra slightly increased in *n*-hexane but decreased in THF with decreasing temperature. See the Supporting Information.
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(21) The 100% and 80% chloroform solutions were transparent, but the 60% chloroform solution was somewhat translucent. Polymer **6** precipitated in the 50% chloroform solution. The intensity of CD spectra was corrected by estimating the concentrations of these samples using the voltage of photomultiplier that corresponds to the UV−vis spectra. Thus, the intensity of the CD spectra in Figure 6 is in arbitrary units and cannot be discussed precisely.
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