Review

Design and synthesis of semiflexible substituted polyacetylenes with helical conformation

Ryoji Nomura, Hideo Nakako, Toshio Masuda*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Abstract

In this review article, we summarize our recent efforts on the design and synthesis of helical polymers from propiolic esters. Stereoregular *cis*-transoidal poly(propiolic esters) prepared with Rh catalysts have proven to possess semiflexible main chain, which drives the main chain to the helical conformation with long persistence length. Based on the chiroptical properties of poly(propiolic esters) bearing various chiral pendants, we established the design strategy for the production of well-ordered helical poly(propiolic esters). NMR study of various poly(propiolic esters) enabled estimation of not only the activation energy of helix reversal, but also the free energy difference between the helical and disordered states. The helix sense of poly(propiolic esters) is determined by the configuration of the chiral center, structure of the pendant groups, temperature, and solvent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polyacetylenes; Helical polymers; Catalysts

1. Introduction

Much attention has been paid to the synthesis of helical polymers owing to their unique functions such as molecular recognition ability and catalytic activity for asymmetric syntheses [1–6]. Recent progress in polymer synthesis has enabled it to afford a variety of well-ordered helical polymers with an excess of one-handed screw-sense. Among them, helical polymers having π-conjugated main chain are very interesting since they are potentially useful as polarization-sensitive electrooptical materials, asymmetric electrodes, and so forth [1].

In most cases, the helicity of π-conjugated polymers originates from the aggregated forms. Therefore, large chiroptical properties are not obtained from chiral π-conjugated polymers in good solvents where they cannot aggregate. On the other hand, substituted polyacetylenes are exceptionally able to possess twisted main chain in solution, even if they do not aggregate, because of the steric repulsion between pendant groups. Especially, stereoregular *cis* polymers prepared with Rh or Fe catalysts, in which the repulsion between the pendant groups works well, can exist in the helical conformation based on the twist of the main chain [7–13]. However, in contrast to the stiffness of other helical polymers such as polyisocyanates, which possess a very large helical domain, the main chain of substituted polyacetylenes is rather flexible, and thus, they possess a very low population of helical domain. For example, the intensity of CD effects of Fe-based poly(1-alkynes) having chiral substituents drastically increases with decreasing temperature [7]. Another proof of the short persistence length of substituted polyacetylenes was given by the experimental and computational study on the conformation

* Corresponding author. Tel.: +81-75-753-5613;
fax: +81-75-753-5908.
E-mail address: masuda@adv.polym.kyoto-u.ac.jp (T. Masuda).

of poly(phenylacetylenes) demonstrated by Yashima et al. [12]. They showed that polyacetylenes cannot maintain the helical structure in solution unless they possess bulky substituents.

In 1997, we began a series of study on the synthesis of substituted polyacetylenes with well-ordered and stable helical conformation and found that, in contrast to most polymers from monosubstituted acetylenes, stereoregular *cis* poly(propiolic esters) possess semiflexible main chain. Resulting from the improved rigidity of the polymer backbone, they exist in the well-ordered helical conformation with long persistence length. Here, we briefly summarize our recent study on the synthesis and secondary structure of this new class of helical polymers.

2. Preparation and secondary structure of poly(propiolic esters)

Stereoregular polymerization of propiolic esters was first demonstrated by Tabata et al. They have shown that, although the polymer yield is not sufficiently high, Rh catalysts, especially [(nbd)RhCl]$_2$, gives stereoregularity (*cis*-transoidal) polymers from propiolic esters in protic solvents such as methanol and ethanol [14]. We investigated the Rh-catalyzed polymerization of propiolic esters and found that

the polymer yield as well as the molecular weight is improved by conducting the polymerization in acetonitrile (Scheme 1) [13].

The most significant factors that influence the secondary conformation of poly(propiolic esters) is the structure of the α-carbon adjacent to the ester group [15]. This effect is clearly recognized by comparison of the chiroptical properties of poly(**1**) with those of poly(**2**)–(**5**) that possess an identical stereogenic group, but a different number of alkylene groups between the ester group and chiral center. For example, polymers that possess non-branched α-carbons, poly(**2**)–(**5**), display very large optical rotations ($[\alpha]_D = -340 - 612°$), while the $[\alpha]_D$ of the polymer having α-branched carbons, poly(**1**), is very small ($[\alpha]_D = +4°$). In a similar way, very intense CD signals are detected for poly(**2**)–(**5**), which is in contrast to the very weak Cotton effect of the CD spectrum of poly(**1**) (Fig. 1). The main chain of poly(**2**)–(**5**), therefore, exists in the helical conformation, and the domain size of one-handed helical conformation predominates over that of the counterpart. Emphasis should be placed on the difference in the CD pattern of poly(**1**) from those of poly(**2**)–(**5**): all the polymers without branched structure at the α-carbon show Cotton effects with different intensity but with identical patterns, whereas the CD effect of poly(**1**) significantly differs in shape from those of poly(**2**)–(**5**) as
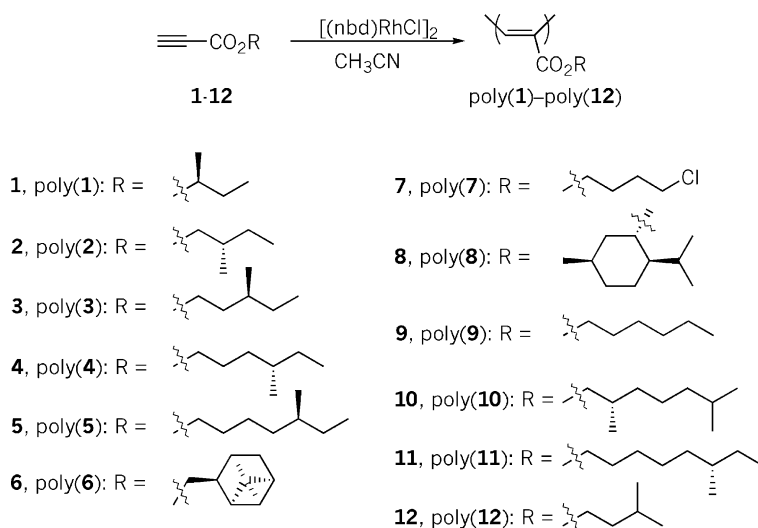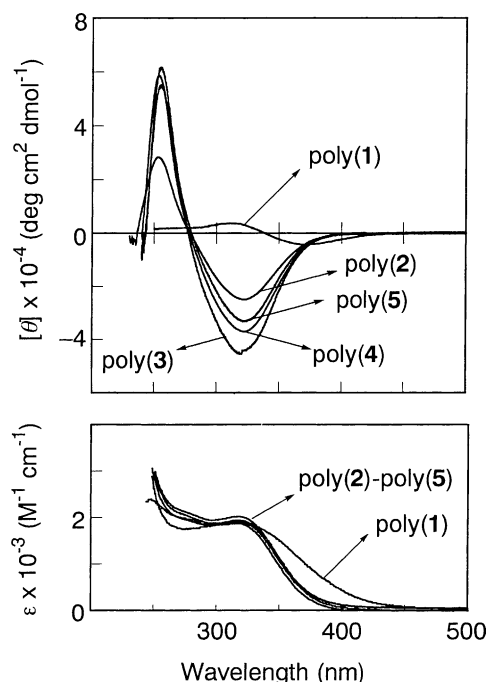

Scheme 1.

Fig. 1. (Top) CD and (bottom) UV–VIS spectra of poly(**1**)–(**5**) in CHCl$_3$.

shown in Fig. 1. Therefore, the secondary conformation of poly(**1**) is different from those of poly(**2**)–(**5**). As shown in Fig. 1, the UV–VIS absorption of poly(**1**) red shifts compared with the other polymers. Since the cut-off wavelength directly relates to band gap energy, i.e. the degree of main-chain conjugation, the red shift observed in poly(**1**) is attributed to its extended main-chain conjugation. In other words, the coplanarity of the polymer backbone is enhanced when the alkylene spacer is eliminated. The main chain of polymers with alkylene spacers is, thus, more tightly twisted from the planar structure, while the polymers with α-branching possess essentially a random conformation or helical one with a large pitch. This difference in secondary structure causes a difference in the shape of the CD signal of the polymers.

The precise secondary structure of poly(propiolic esters) is currently unknown because the isolation of well-defined oligomers for X-ray crystal structure analysis has not been achieved so far. Thus, we carried out computational calculation to gain approximate, but experimentally inaccessible knowledge on the secondary structure [16]. Fig. 2 illustrates the optimal

structure of 30-mer of poly(methyl propiolate) obtained by MM2 and PM3 methods, which clearly indicates that the helical conformation is the most stable secondary structure. The estimated dihedral angle about the single bonds is approximately 107°, which is much smaller than that of poly(phenylacetylene) (ca. 140°) calculated by the MM2 method [12]. The main chain of poly(propiolic esters) is, thus, tightly twisted compared with poly(phenylacetylene). A similar computational calculation of 15-mers of poly(**2**) gave the most stable conformation with the dihedral angle of the double bond of 240°. This value corresponds to the left-handed helical conformation. Therefore, the minus first Cotton effects suggest the excess of left-handed helical conformation. Since poly(**2**)–(**5**) exhibit negatively signed first Cotton effects, these polymers probably exist in the left-handed helical conformation.

3. Stability of helical conformation

As mentioned above, the helical conformation of poly(phenylacetylene), which is the most representative example for the helical polyacetylenes, is unstable. In other words, the population of helical domain is quite low, and the helix–helix or helix–random coil transition frequently occurs. However, the chiral/achiral and *R/S* copolymerizations, which are frequently performed to estimate the stability of helical conformation, clearly revealed that poly(propiolic esters) having α-methylene groups possess long persistence length of the helical domain [17]. The helix stability is nicely exemplified by the chiral amplification phenomenon in the copolymerization of (–)-myrtanyl propiolate (**6**) with 4-chlorobutyl propiolate (**7**). As illustrated in Fig. 3, the presence of 3–10 mol% of a chiral segment effectively leads to a large optical rotation of the copolymer that is comparable to that of the homopolymer from **6**. In a similar way, even a copolymer with the ratio of **7**/**6** = 89/11 shows very intense CD signals whose molar ellipticity is almost the same as that of poly(**6**). These results are in contrast to the copolymers from phenylacetylenes: no distinct CD signal is attainable from a copolymer containing 10% of a chiral comonomer, and bulky ring substituents are required to effectively achieve the sergeants-and-soldiers principle for the
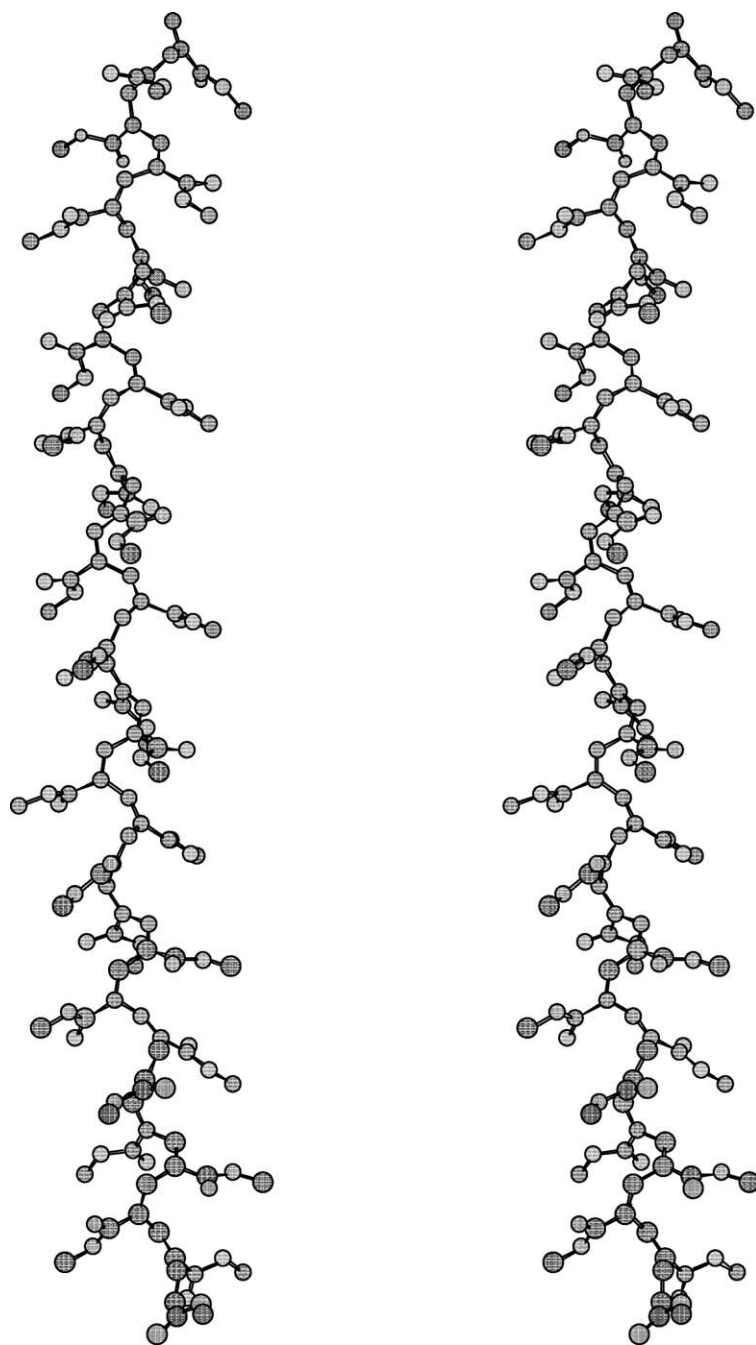
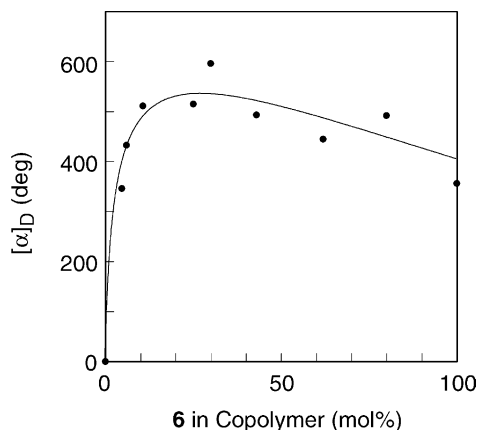Fig. 2. A stereoview of the optimized structures of 30-mer of methyl propiolate terminated by hydrogen.

Fig. 3. Plot of the optical rotation ($c = 0.06$–0.08 g/dl) of the copolymers of **6** with **8** vs. copolymer composition at room temperature (in CHCl$_3$).

poly(phenylacetylene)-based copolymers [12]. A similar chiral amplification is observed in the polymerization of **2** with various optical purities. Poly(propiolic esters), thus, possess a larger helical domain size than poly(phenylacetylenes).

As mentioned above, there exists a distinct difference in the secondary structure of the polymers with and without an alkylene spacer. This structural difference causes very unique behavior of the copolymerization of (–)-menthyl propiolate (**8**) with hexyl propiolate (**9**) [17]. As illustrated in Fig. 4, the
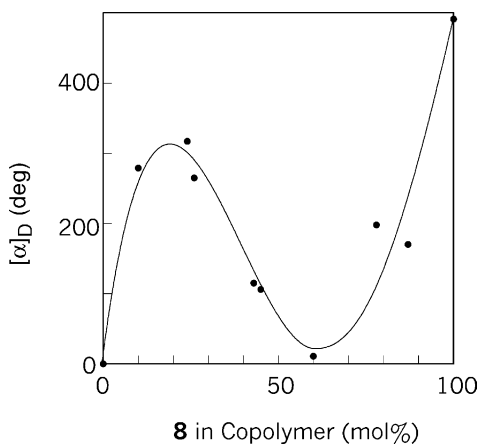

Fig. 4. Plot of optical rotation versus segment ratio for the copolymerization of **8** with **9** (in CHCl$_3$, $c = 0.06$ g/dl at room temperature).
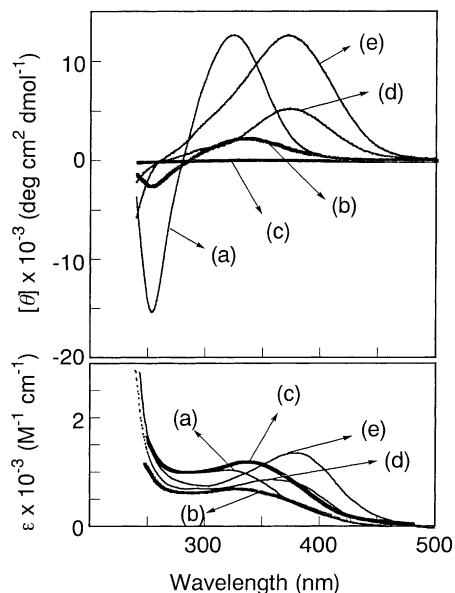

Fig. 5. CD and UV–VIS spectra of the copolymers of **8** with **9** (in CHCl$_3$, $c = 0.012$ g/dl at room temperature). Copolymers **8/9** = (a) 22/78, (b) 55/45, (c) 60/40, (d) 76/24, (e) 100/0.

copolymer of **8** with **9** shows a nonlinear effect of the chiroptical properties at low chiral contents. However, when the chiral comonomer content exceeds 20%, the increase in the chiral unit leads to a decrease in the optical rotation of the copolymer, and almost no chirality is recognized when the ratio of **8/9** is 60/40 ($+10.9°$ in CHCl$_3$, $c = 0.066$ g/dl). The $[\alpha]_D$ again increases as the content of the chiral unit is further increased. A similar phenomenon is observed in the CD spectra of the copolymers (Fig. 5). The intensity of CD steeply decreases with an increase in the chiral segment (Fig. 5a and b), and no CD effect was obtained when 60% of **8** is incorporated to the copolymer (Fig. 5c). The magnitude of the CD signal increases again as the content of **8** increases (Fig. 5d and e). Simultaneously, the shape of CD remarkably changes, and the peak top of the CD band shifts toward a long wavelength region. The shape of the CD spectra of the copolymers with low chiral component (Fig 5a and b) is just mirror-imaged to those of homopolymers from chiral monomers, **2**–**5**. On the other hand, the chiral segment-rich copolymers show CD signals that are very close in shape to that of poly(**8**) (Figs 5d and e).

The poor chiroptical property of the **8/9** $= 60/40$ copolymer is not due to lack of stereoregularity

because this copolymer is confirmed to possess perfect stereoregularity (*cis*) by the ^{1}H NMR spectrum in CD_2Cl_2. A hypothesis that the opposite preferences of **8** and **9** in the screw-sense give the same amount of both helix senses is also ruled out because there is no difference in the sign of optical rotation between **8**- and **9**-rich copolymers. Thus, the poor chiroptical property of the copolymer originates from its randomly coiled, disordered conformation, which results from the difference in the secondary structure between these homopolymers. This conclusion is also supported by the relationship between the molecular weight and [*n*] of these copolymers. Specifically, the slope of the Mark–Hauwink–Sakurada plot gradually decreases from 1.233 to 0.534 when the chiral content is increased from 0 to 60%. This clearly means that poly(**9**) possesses a stiff main chain due to its well-ordered helical structure and that the copolymer of **8** with **9** (**8**/**9** = 60/40) exists in a randomly coiled conformation. The slope of the Mark–Hauwink–Sakurada plot of poly(**8**) (0.66) is unexpectedly small. This suggests that, at least, poly(**8**) does not possess well-ordered helical conformation with long persistence length, which is in consistence with poly(**9**). However, the very large $[\alpha]_D$ (+491°) and intense CD effects of poly(**8**) ($[\theta]_{max}$ = 12000° cm²/dmol) cannot be explained without assuming that poly(**8**) possesses a helical structure. Thus, the large chiroptical properties of poly(**8**) are explained by helical conformation but the helical domain size is probably quite small.

The stability of the helical conformation can be qualitatively discussed by the aforementioned copolymerization technique. However, quantitative elucidation of the helix stability is quite difficult. The most characteristic feature of poly(propiolic esters) is that the thermodynamic stability as well as the kinetic one is readily estimated by a simple NMR technique. That is, not only the activation energy for the interconversion process between right- and left-handed helices ($\Delta G^{\ddagger}$), but also the free energy difference between the helical and helix reversal states (ΔG_r) can be determined by NMR spectra [17].

The determination of $\Delta G^{\ddagger}$ for various poly(propiolic esters) is based on a result that all poly(propiolic esters) having α-methylene groups show two diastereotopic signals due to the α-methylene protons (Fig. 6c). This peak separation is reasonably explained
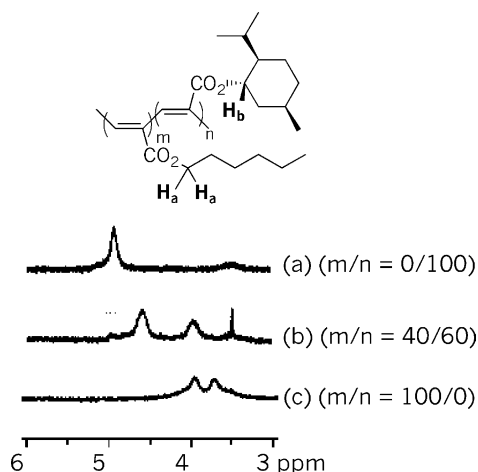

Fig. 6. ^{1}H NMR spectrum (expanded) of poly(**9**) in $CDCl_3$ (400 MHz).

by the slow process of the interconversion between right- and left-handed helices on the NMR time-scale at ambient temperature. The clearest proof is that the α-methylene proton is not diasterotopic when the polymer exists in disordered conformation. Namely, the copolymer (**8**/**9** = 60/40) with random conformation shows α-methylene protons as one broad resonance (Fig. 6b), while this signal attributed to the α-methylene protons in helical poly(**9**) is clearly separated (Fig. 6c). The variable temperature ^{1}H NMR technique, thus, permits estimation of $\Delta G^{\ddagger}$ for various polymers. As seen in the NMR spectra of poly(**9**), two broad but clearly separated signals at 22 °C coalesce at 110 °C, and this process is reversible (Fig. 7). From the coalesced temperature and the difference in the chemical shifts at 22 °C, $\Delta G^{\ddagger}$ is readily calculated to be 18.5 kcal/mol, which means the helix–helix transition occurs at ambient temperature.

Since the peak separation of the α-methylene signal is attributed to the slow interconversion between two helices, the integrated intensities of these two signals should be identical unless two methylene protons possess unexpectedly different relaxation time. However, Fig. 7 apparently exhibits a difference in the intensity between the two signals. At every temperature the peak at lower magnetic field has larger intensity, and an increase in temperature leads to an increase in the difference in the peak intensity. This is due to the overlapping of the signal attributed to the α-methylene
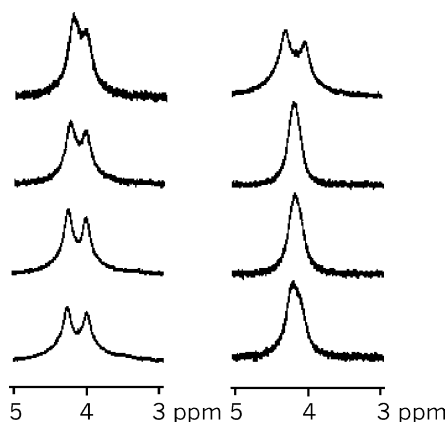
Fig. 7. Expanded ^{1}H NMR spectra of (a) poly(**8**), (b) poly(**8**-*co*-**9**) (**8**/**9** = 60:40) and (c) poly(**9**) in CDCl$_3$ (400 MHz).

Fig. 8. CD spectra of poly(**10**) at various temperatures in CHCl$_3$ ($c = 6.0 \times 10^{-4}$ mol/l).

proton in disordered conformation. This idea is supported by the fact that the resonance due to the α-methylene proton of randomly coiled poly(**8**-*co*-**9**) (**8**/**9** = 60/40) is observed in the same region as the lower magnetic field peak of the α-methylene signal in the helical state (Fig. 6). The temperature dependence of the variation of the integrated intensity ratio is reasonably explained by the increasing population of the disordered state with increasing temperature. The computational peak deconvolution of the diastereotopic two signals into two Lorentzian functions allows the estimation of the ratio of the helical and disordered states, which consequently gives the free energy difference between these two states. The estimated value, 1.59 ± 0.16 kcal/mol at 22 °C and 0.55 ± 0.66 kcal/mol at 90 °C for the present sample of poly(**9**), corresponds to ΔG_r because the disordered states can act as the helix reversal state interposed between two helices with opposite screw-sense. This is the first example for the spectroscopic determination of the thermodynamic parameters governing the helix stability.

4. Helix Inversion

Poly(propiolic esters) readily undergo helix–helix interconversion at ambient temperature due to the small energetic barrier for helix reversal. Thus, the helix sense is determined by the free energy difference 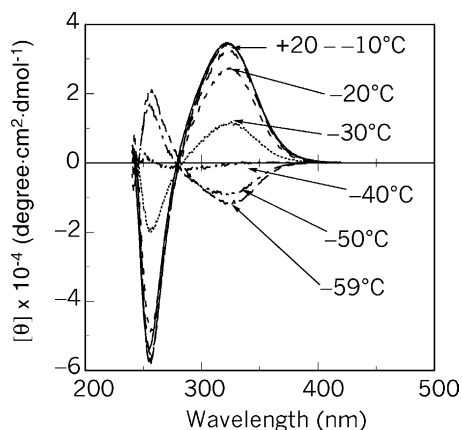between two helices (ΔG_h) that is generated by the chiral information in the side chain. Since the value of ΔG_h is appreciably small, the helix sense initially determined by the chirality in the side chain, in some cases, can be elegantly inverted into the counterpart by external stimuli. Such phenomena are also observed for poly(propiolic esters) [16]. A representative example is given by the temperature variable CD spectra of poly(**10**) (Fig. 8); the CD effects of poly(**10**) decreases in intensity with decreasing temperature, and inverted in sign at around −40 °C. The CD spectrum at −50 °C is mirror-imaged to that at 20 °C. Because the change in the CD spectra upon temperature change is independent of the polymer concentration, and because the addition of a poor solvent (methanol) into a CHCl$_3$-solution of poly(**10**) causes no CD-inversion, the CD inversion does not result from the aggregation of the polymer chain. In other words, the helix-sense inversion occurs upon the temperature change. The inversion of the positively signed first Cotton effects into the negatively signed one means the conversion from right- to left-handed helical conformations. The helix inversion takes place only in CHCl$_3$, while, in other solvents (hexane and THF), CD effects only slightly increase in magnitude with decreasing temperature.

Detailed investigation of the temperature effects on the CD spectra of various chiral polymers, poly(**2**)–(**5**), poly(**10**) and poly(**11**), revealed that polymers having long alkyl side chains such as poly(**10**) and (**11**) undergo the helix inversion, while other polymers with short side chains do not significantly change in the
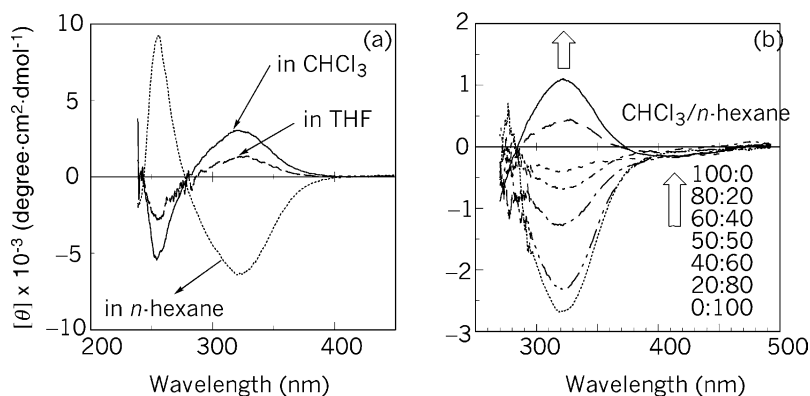
Fig. 9. (a) CD spectra of poly(2-co-9) (2/9 = 10/90 in feed) in CHCl₃, THF, and hexane, at 20 °C and (b) CD spectra of poly(2-co-9) in a mixed solvent comprising CHCl₃ and hexane at 20 °C.

CD effects upon the temperature change. This tendency can be applied to copolymers based on achiral monomers having long alkyl chain. For example, the copolymer of **9** with **2** (**9**/**2** = 90/10 in feed) shows the negatively signed first Cotton effect in hexane, meaning an excess of the left-handed helical conformation (Fig. 9a). This is because the small amount of the chiral segment (**2**) is able to govern the screw sense. However, the first Cotton effect is positively signed in THF and CHCl₃, meaning that right-handed helical conformation predominates over the counterpart. This indicates that the transition temperature of helix-sense inversion is higher than +20 °C in chloroform and THF for this copolymer.

The helix-sense inversion is also driven by the change of the solvent composition. As demonstrated in Fig. 9b, poly(**9**-co-**2**) shows negatively signed first Cotton effect in hexane at +20 °C because this copolymer exists in an excess of left-handed helical conformation. However, the addition of CHCl₃ leads to the gradual decrease of the intensity, and the Cotton effect inverts its sign when the content of CHCl₃ exceeds about 70 vol.%. These results mean that the screw sense is controlled not only by the configuration of the chiral center but also by temperature, length the pendant groups, and solvent.

5. Intermolecular chiral amplification

As demonstrated in the chiral/achiral copolymerization, the high stability of the helical conformation

of poly(propiolic esters) allows the formation of copolymers having an excess of one-handed helical conformation even if the chiral content of the side chain is small. This is because intramolecular chiral amplification takes place, which is so-called the "Sergeant and Soldiers Rule". It is quite interesting that intermolecular chiral amplification also occurs for poly(propiolic esters) [18]. This phenomenon is observed in the solid state. As Tabata et al. demonstrated, stereoregular polyacetylenes such as poly(phenylacetylenes) and poly(propiolic esters) self-organize and form the ordered, hexagonal suprastructure in the solid state. When an achiral polymer such as poly(**12**) is mixed with the corresponding
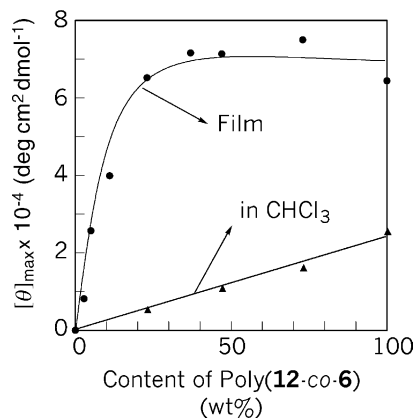

Fig. 10. Plot of the molar ellipticity of the first Cotton effect of the mixture of poly(**12**) with poly(**12**-co-**6**) in CHCl₃ and in the solid state.

chiral copolymer, poly($\mathbf{12}$-*co*-$\mathbf{6}$) ($\mathbf{12}/\mathbf{6}$ = 88/12, $[\alpha]_D = +373°$) in CHCl$_3$, the magnitude of the Cotton effects linearly increases with increasing content of the chiral copolymer (Fig. 10). This is simply because the chiroptical property originates only from the copolymer and no chiral amplification occurs. In contrast, when the solution is cast on a quartz cell, the resulting polymer film shows intense CD effects, and the intensity of the CD effects of that film is larger than that linearly calculated from the chiral copolymer content. The CD spectra in the solid state contain no artifacts, which was evidenced by the solid-state specific CD spectrophotometer. This means that the chirality of the copolymer is amplified intermolecularly upon the self-organization of the polymer chain.

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