Conformational Study of Helical Poly(propiolic esters) in Solution

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Abstract: Chiral and achiral propiolic esters [HC≡CCO$_2$R, where R = *n*-hexyl (HexPr), (CH$_2$)$_4$Cl (CBPr), (*R*)- and (*S*)-CH$_2$CHMeEt (MBPr), (1*S*,2*S*,5*S*)-myrtanyl (MyrtPr), and (1*R*,2*S*,5*R*)-menthyl (MentPr)] were copolymerized in the presence of [(nbd)RhCl]$_2$ in order to study the conformational properties of poly(propiolic esters). A clear cooperative effect on helical conformation was obtained in the copolymerization of CBPr with MyrtPr. A similar positive nonlinear relationship between the enantiomeric excess of MBPr and the observed chiroptical properties of copolymers was also recognized, which means a relatively long persistence length of the helix of poly(propiolic esters). In the copolymerization of HexPr with MentPr, on the other hand, randomly coiled (co)polymers were obtained when the MentPr content was around 60%. ^{1}H NMR spectra of poly-(propiolic esters) gave well-resolved two diastereotopic signals, attributed to the α-methylene protons in the side groups, owing to the slow helix−helix transformation on the NMR time scale. The energy barrier for the helix−helix transformation of poly(HexPr) was determined to be more than 18.5 kcal/mol by the variable-temperature NMR technique. The NMR study of the (co)polymers also enabled us to estimate the free energy difference between the helical and randomly coiled states (ΔG_r for poly(HexPr) = 1.59 ± 0.16 kcal/mol at 22 °C).

Introduction

Chiral polymers whose chirality is based on the helix of their main chains[1] have gathered great interest in the past two decades. Previous energetic efforts have made it possible to produce a variety of well-ordered helical polymers including polyisocyanates,[2] polyisocyanides,[3] polychloral,[4] poly(alkyl methacrylates),[5] polysilanes,[6] polyacetylenes,[7] polythiophens,[8] and so on. These helical polymers can be divided into two categories. One possesses a very stable helical structure whose helical sense is kinetically controlled. Therefore, the helix sense that is initially determined upon the polymerization can be maintained even in the absence of chiral information. Representative examples are given by polyisocyanides,[3] polychloral,[4] and poly(alkyl methacrylates)[5] with bulky substituents. The

rigidity of backbones and/or the steric repulsion of bulky pendants prevent these polymers from undergoing helix−helix or helix−random coil transformations, which enables the enantioselective formation of helical polymers with one-handed screw sense. The sense of the helix is defined by the chiral source at the initiating terminal or the appropriate chiral ligands on the propagation centers. The other category involves the polymers that undergo helix−helix interconversion due to the small energetic barriers for helix reversal. Polyisocyanates,[2] polysilanes,[6] and polyacetylenes[7] are known to belong to this type of polymers. Such polymers possess a stiff but not rigid main chain, allowing the presence of helix-reversal points along the polymer backbone. The screw sense is, therefore, thermo-dynamically determined, and, eventually, chiral information such as chiral substituents or solvents is required to provide an excess of one-handed helix sense.

As described above, substituted polyacetylenes are recognized to belong to the second category of helical polymers.[7] Namely, the helical backbone of substituted polyacetylenes readily undergoes helix reversal. Characteristic of the helix of substituted polyacetylenes is the very short persistence length of the helical domain. In other words, apart from the stiffness of the main chain of polyisocyanates that have a very long persistence

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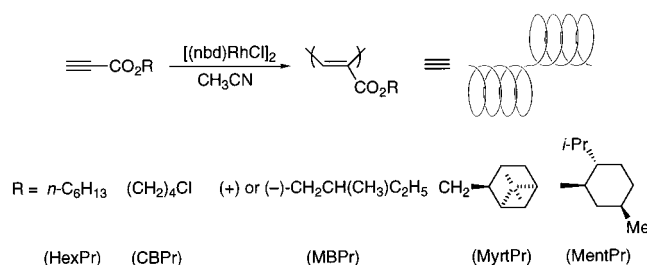
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Helical Poly(propiolic esters) in Solution

J. Am. Chem. Soc., Vol. 122, No. 37, 2000 8831

Scheme 1

length of the helical domain,[2] the backbone of substituted polyacetylenes is very flexible. For instance, as experimentally and computationally demonstrated by Yashima and co-workers,[7g] poly(phenylacetylene) has a very high population of the helix reversal point along the polymer backbone. Not only poly(phenylacetylenes) but also the other chiral polyacetylenes are likely to possess a high frequency of the helix reversal, which can be evidenced by the drastic increase in chiroptical properties of the polymers with a decrease in temperature.[7a,c]

We previously reported that stereoregular cis−transoidal poly-(propiolic esters) with chiral pendants take a helical conformation with an excess of one-handed screw sense.[9a] We also established a relationship between the polymer conformation and the structure of pendant groups.[9b,c] Our next questions involve the stability of the helix of poly(propiolic esters) that is the focus of the present work. To answer this question, we performed copolymerization of chiral with achiral comonomers because the helix stability is readily elucidated by this experimental technique. As described above, previous conformational studies of substituted polyacetylenes[7] suggest that poly(propiolic esters) also possess a very short helical persistence length, similar to the most of the substituted polyacetylenes. However, we found that, as demonstrated in the present study, propiolic esters derived from primary alcohols give helical polymers with long persistence length, even in the absence of a bulky pendant. We also show that, by using a simple ^1H NMR technique, the kinetic and thermodynamic parameters which govern the profile of helical structure of poly(propiolic esters) are readily accessible.

Results and Discussion

Copolymerization. The monomers employed in the present study are 4-chlorobutyl propiolate (CBPr) and hexyl propiolate (HexPr) as achiral comononers, and (−)-myrtanyl propiolate (MyrtPr), (−)-menthyl propiolate (MentPr), and (+)- and (−)-2-methylbutyl propiolates (MBPr) as chiral comonomers (Scheme 1). The following comonomer combinations were examined: MyrtPr/CBPr, (−)-/(+)-MBPr, and MentPr/HexPr. The first and second combinations were chosen to explore the sergeants and soldiers rule[10] and the majority rule,[10a,11] respectively. The last combination is for elucidating the effects of alkylene spacers in comonomers on the conformation of copolymers.

Copolymerizations were conducted with [(nbd)RhCl]₂ (nbd = 2.5-norbornadiene) in acetonitrile because the Rh catalyst

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Table 1. Homo- and Copolymerizations of Various Chiral and Achiral Monomers with [(nbd)RhCl]₂ in CH₃CN at 30 °C[a]

monomer			polymer[b]				
M₁	M₂+	M₁/M₂	yield (%)	M₁/M₂[c]	M_n/10³ [d]	cis[e] (%)	[α]D[f] (°)
(−)-MyrtPr[g]	CBPr	100/0	28	100/0	2.4	68	+356
		75/25	25	80/20	13	100	+492
		50/50	73	62/38	21	83	+445
		25/75	26	30/70	47	84	+596
		10/90	43	11/89	58	65	+511
		5/95	31	6/94	51	71	+433
		2.5/97.5	33	5/95	65	70	+346
(−)-MBPr[h]	(+)-MBPr	100/0	36	100/0	80	72	−606
		75/25	55	nd[i]	46	86	−616
		60/40	49	nd[i]	39	76	−441
		55/45	53	nd[i]	40	90	−258
		52.5/47.5	47	nd[i]	43	71	−137
(−)-MentPr[j]	HexPr	100/0	27	100/0	110	82	+491
		90/10	26	87/13	11	nd[i]	+170
		80/20	24	76/24	13	82	+198
		69/31	10	60/40	120	100	+10.9
		51/49	18	45/55	130	nd[i]	+106
		39/61	21	43/57	720	100	+115
		24/76	37	26/74	37	nd[i]	+265
		20/80	37	22/78	220	97	+317
		10/90	55	10/90	40	nd[i]	+279
		0/100	38	0/100	78	100	

[a] [[(nbd)RhCl]₂] = 20 mM, [monomer]total = 2.0 M, 24 h. [b] Methanol-insoluble part. [c] Calculated by NMR and/or elemental analyses. [d] Estimated by GPC (THF, PSt). [e] Calculated by NMR and copolymer composition. [f] In CHCl₃ (c = 0.06−0.085 g/dL). [g] [α]D = −28° (CHCl₃, c = 0.20 g/dL). [h] [α]D = +5° (CHCl₃, c = 0.20 g/dL). [i] Not determined. [j] [α]D = −82° (CHCl₃, c = 1.0 g/dL).

can produce stereoregular polymers (cis−transoid)[12] and because the stereoregular main-chain structure is indispensable for the construction of well-ordered helical conformation.[9] The results of the copolymerizations are listed in Table 1. The copolymer compositions of the copolymers derived from MyrtPr and CBPr were determined by elemental analyses, while those of the copolymers of MentPr with HexPr were estimated by ^1H NMR spectra. The unit ratio was not determined for the copolymers of (+)-MBPr with (−)-MBPr. The plot of the copolymer composition versus feed composition for the MentPr/HexPr system indicated that the chiral units disperse randomly in the main chain of poly(MentPr-*co*-HexPr): the Fineman−Ross plot for the copolymerization of MentPr (M₁) with HexPr (M₂) clearly supported the randomness of the copolymerization (r_1 = 1.09 ± 0.07, r_2 = 1.04 ± 0.06).[13] In a similar way, the copolymerization of MyrtPr with CBPr has proven to be close to a random one (r_1 = 1.57 ± 0.01, r_2 = 1.19 ± 0.01, where M₁ = MyrtPr, M₂ = CBPr).[13] Since the reactivity ratio was not investigated for the *R/S* copolymerization, it is impossible to precisely discuss the randomness of the (+)-MBPr/(−)-MBPr copolymerizations. The monomer distribution in the copolymers of (+)-MBPr with (−)-MBPr is probably random because both monomers have identical steric hindrance.

As in the previous studies,[9,12] all of the (co)polymers showed clear signals due to the olefinic protons of the cis−transoidal main chain around 6.7−7.6 ppm, which means the formation of stereoregular (co)polymers. The cis content calculated using both or either the NMR data and the copolymer composition varied from 65% to 100%. Unfortunately, a systematic explanation cannot be made for the factors that influence the cis content.

Chiroptical Properties of Copolymers. Figure 1 plots the optical rotation and molar ellipticity of the first Cotton effect

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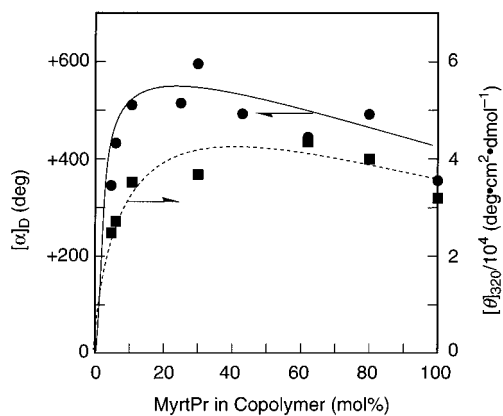
(13) See the Supporting Information.

Figure 1. Plot of the optical rotations ($\bullet$, $c = 0.06-0.08$ g/dL) and molar ellipticities at 323 nm ($\blacksquare$, $c = (4.3-8.6) \times 10^{-4}$ mol/L) of the copolymers of MyrtPr with CBPr versus copolymer composition at room temperature (in CHCl$_3$).

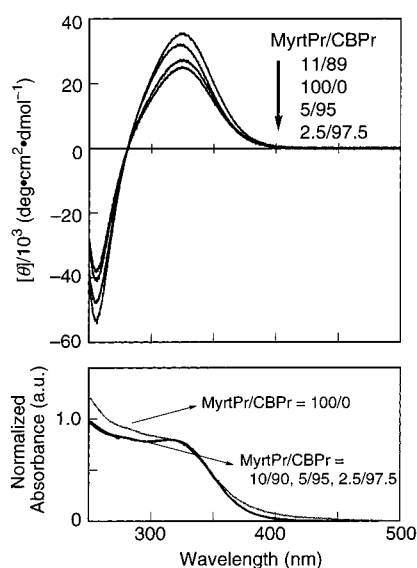**Figure 2.** CD and UV$-$visible spectra of the copolymers of CBPr with MyrtPr (in CHCl$_3$, $c = (3.8-6.8) \times 10^{-4}$ mol/L at room temperature).

for the copolymers of MyrtPr with CBPr versus the copolymer composition. A clear cooperative effect on the chiroptical properties can be seen from this figure. Thus, the presence of a 3$-$10% of chiral segment in the copolymer induced a large optical rotation which is comparable to that of a homopolymer from MyrtPr.[14] In a similar way, even a copolymer with a ratio of CBPr/MyrtPr = 89:11 showed very intense CD signals whose molar ellipticity was slightly larger than that of poly(MyrtPr) (Figure 2).[14] These results are in contrast to those of the copolymers from phenylacetylenes: for the poly(phenylacetylene)-based copolymers, 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.[7g] Therefore, one can conclude that poly-(propiolic esters) possess larger helical domain size than poly-(phenylacetylenes).

A similar chiral amplification phenomenon was observed in the copolymerization of (+)-MBPr with (−)-MBPr, as shown in Figure 3. Namely, there was a positive nonlinear relationship
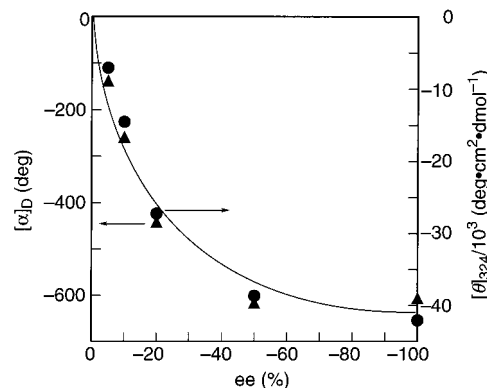
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(14) The reason is not clear for the lower chiroptical properties of the homopolymer of MyrtPr than those of the copolymers whose chiral comonomer contents were between 5 and 75%. The low molecular weight of poly(MyrtPr) may be responsible for this result.

Figure 3. Plots of the optical rotations ($\blacktriangle$, $c = 0.07$ g/dL) and molar ellipticity at 324 nm ($\bullet$, $c = (3.8-6.8) \times 10^{-4}$ mol/L) of the copolymers of (−)- with (+)-MBPr versus the enantiomeric excess of the monomer (in CHCl$_3$, at room temperature).
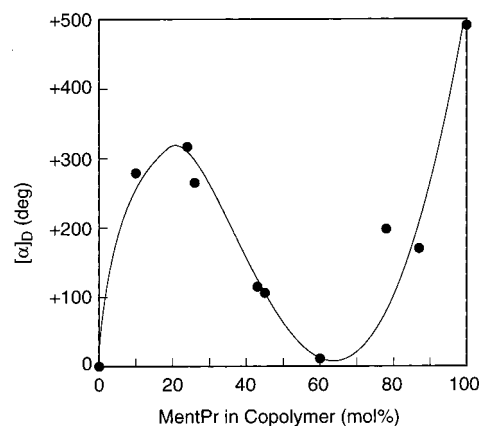

Figure 4. Plot of the optical rotations versus the segment ratio for the copolymerization of HexPr with (−)-MentPr (in CHCl$_3$, $c = 0.06$ g/dL at room temperature).

between the enantiomeric excess of monomer and the observed optical rotation as well as the ellipticity of the Cotton effects. This observation also supports the large helical domain of poly-(propiolic esters). However, the persistence length of helical structure of poly(propiolic esters) is apparently shorter than that of polyisocyanates, judging from the results of the *R/S* copolymerization of isocyanates. For instance, in the case of poly-(propiolic esters), approximately 40$-$50% enantiomeric excess is necessary to obtain copolymers with chiroptical properties similar to those of the corresponding homopolymers. On the other hand, polyisocyanates respond very sharply to a slight difference in the concentration of enantiomers: the absolute value of optical rotation of the polymer from 2,6-dimethylheptyl isocyanate with 20% enantiomeric excess is almost identical to that of the polymer from the pure enantiomer.[10a] This means that, compared with polyisocyanates, the backbone of poly-(propiolic esters), at least that of sterically less demanding polymers, is not stiff enough to provide a very large helical domain.

In contrast to the ordinary chiral amplification phenomena as seen in the above systems, copolymers obtained from HexPr and MentPr showed a very unique behavior in their chiroptical properties. As shown in Figure 4, the optical rotation rapidly increased as the proportion of the chiral segment increased, which is a behavior similar to that observed in the copolymerization of the other monomer combinations. In other words, the copolymer displays a cooperative nature of the chiroptical property at low chiral comonomer contents. However, when the chiral comonomer content exceeded 20%, the increase in the

Helical Poly(propiolic esters) in Solution

J. Am. Chem. Soc., Vol. 122, No. 37, 2000 8833
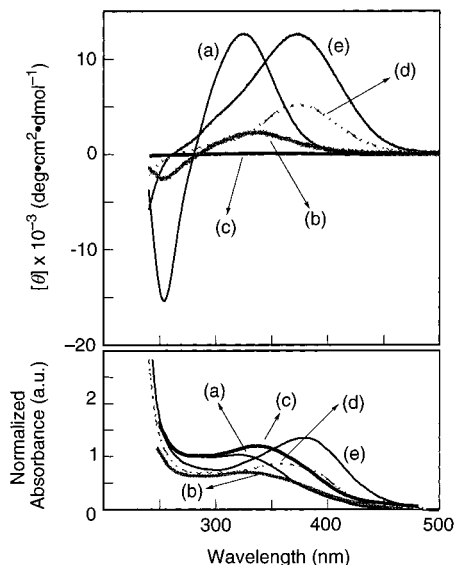
Figure 5. CD and UV−visible spectra of the copolymers of HexPr with MenPr (in CHCl₃, $c = 0.012$ g/dL at room temperature). MentPr/HexPr = (a) 22/78, (b) 55/45, (c) 60/40, (d) 76/24, (e) 100/0.

Figure 6. Mark−Hauwink−Sakurada plots of (a)−(e) poly(HexPr-*co*-MentPr) and (f) polystyrene. MentPr/HexPr = (a) 0/100, (b) 22/78, (c) 60/40, (d) 87/13, (e) 100/0.

chiral unit led to a decrease in the optical rotation of the copolymer, and almost no chirality was recognized when the ratio of MentPr/HexPr was 60:40 ($+10.9°$ in CHCl₃, $c = 0.066$ g/dL). The $[\alpha]_D$ again increased and reached a very large value as the content of chiral unit was further increased. A similar phenomenon was observed in the CD spectra of the copolymers (Figure 5). The intensity of CD decreased with an increase in the chiral segment (Figure 5a,b), and no CD effect was obtained when 60% MentPr was incorporated into the copolymer (Figure 5c). The magnitude of the CD signal increased again as the content of MenPr increased further (Figure 5d,e). Simultaneously, the shape of the CD signal remarkably changed, and the peak top of the CD band shifted toward the long-wavelength region (Figure 5a versus 5e). The shape of the CD spectra of the copolymers with low chiral component (Figure 5a,b) was completely identical to or the mirror-image of those of homopolymers from chiral monomers with alkylene spacers between the chiral centers and ester groups.[9b,c] On the other hand, the chiral segment-rich copolymers showed CD signals which were very close in shape to that of poly(MentPr) (Figure 5d,e).[9a]

The poor chiroptical property of the MentPr/HexPr = 60:40 copolymer is not due to the lack of stereoregularity because this copolymer was confirmed to possess perfect stereoregularity (cis) by the ¹H NMR spectrum in CD₂Cl₂ (Table 1). This could be explained by assuming that the MentPr and HexPr units prefer the opposite helix sense to each other and that the presence of the same amount of both helix senses might cancel the CD effects. Such a phenomenon has been observed in the copolymerization of chiral with achiral phenyl isocyanates.[15] However, if the helix senses of MentPr and HexPr differ from each other, the signs of optical rotations of HexPr-rich copolymers should differ from those of MentPr-rich copolymers. This hypothesis is, therefore, negligible because there is no difference in the sign of optical rotation between MentPr-rich and HexPr-rich copolymers. Thus, the poor chiroptical property of the copolymer MenPr/HexPr = 60:40 originates from its randomly coiled, disordered conformation.

The above conclusion is further supported by the analysis of the Mark−Hauwink−Sakurada (MHS) plots of the logarithm
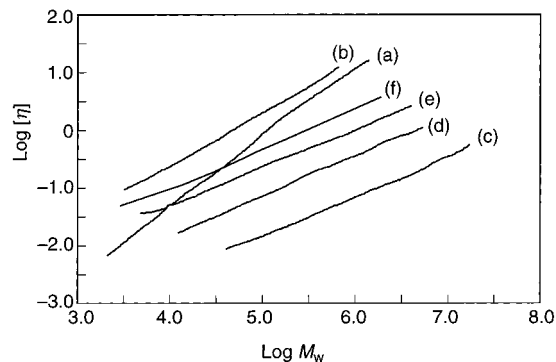
of the intrinsic viscosity $[\eta]$ against the logarithm of the molecular weight (M_w) of the copolymers. Figure 6 shows the plots for the five copolymers along with that for a polystyrene sample as a reference. We note here that the units of both abscissa and ordinate in each sample are arbitrary, as mentioned in the Experimental Section. However, what should be considered in the present study is the magnitude of the slopes of the plots; therefore, the location of the plots is immaterial. As seen in Figure 6, poly(HexPr) showed the maximum slope (log $[\eta]$/log $M_w = 1.2$), and this value is comparable to that of poly-(hexyl isocyanate) (1.2 in hexane, and 1.4 in butyl chloride).[16] This result verifies the stiff or semiflexible main chain of poly-(HexPr).[17] Combination of these data with the large chiroptical properties of the polymers with alkylene spacers between the chiral carbons and ester groups[9b,c] suggests the well-ordered helical conformation of poly(HexPr). This means that poly-(propiolic esters) without branching at the α-carbon adopt helical conformation, even in the absence of bulky and/or chiral substituents.

To the contrary, the slope gradually decreased from 0.92 to 0.68 with an increase in the chiral unit from 22 to 40%, and the slope of the MHS plot of the copolymer (HexPr/MentPr = 40:60) was almost the same as that of polystyrene (0.68). This result is a clear indication of the very flexible main chain of the copolymer with 60% of MentPr unit. As denoted above, it is not plausible that the same population of two helix senses might contribute to the poor chiroptical properties of poly-(HexPr-*co*-MentPr) (HexPr/MentPr = 40:60). Thus, the small value of the MHS plot of this copolymer is an indication of its randomly coiled conformation.

It was unexpected that further increases in the chiral content did not enhance the slope of the MHS plot. Even the homopolymer of MentPr displayed essentially the same degree of main-chain flexibility (log $[\eta]$/log $M_w = 0.66$) as that of polystyrene. The copolymers with chiral content more than 60%, thus, also exist in a randomly coiled conformation. However, the large optical rotation of poly(MentPr) ($+491°$ in CHCl₃) undoubtedly originates from the helical structure with an excess of one-handed screw sense. Thus, poly(MentPr) exists in a helical conformation but appears to possess a very short persistence length, like poly(phenylacetylene). As observed in the CD spectra of poly(HexPr-*co*-MentPr), the red-shifted absorption of poly(MentPr) compared with that of poly(HexPr), indicates

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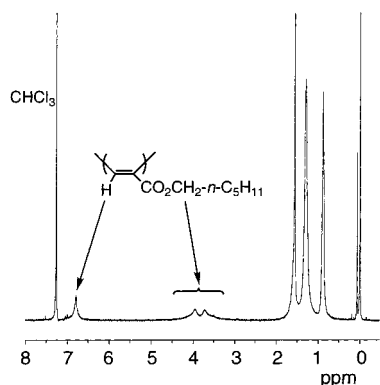
Figure 7. ^{1}H NMR spectrum of poly(HexPr) in CDCl$_3$ (400 MHz).

Figure 8. Expanded ^{1}H NMR spectra of (a) poly(MentPr), (b) copolymer of MentPr with HexPr (MentPr/HexPr = 60:40), and (c) poly(HexPr) in CDCl$_3$ (400 MHz).

Figure 9. Expanded ^{1}H NMR spectra of (a) poly[(−)-MBPr] and (b) a copolymer from MBPr with an enantiomeric excess of −50% (in CDCl$_3$, 400 MHz).

the enhanced coplanarity of the main chain of poly(MentPr). In other words, the pitch of the helix of poly(MentPr) seems to be larger than that of poly(HexPr). Such a remarkable difference in secondary structure between the polymers with and without an α-methylene group pendant leads to the disordered conformation of the copolymers when the content of MentPr is close to that of HexPr.

NMR Study of the Conformation of Poly(propiolic esters). The ^{1}H NMR study of the produced (co)polymers gave very interesting information on the nature of helical structure. The ^{1}H NMR spectrum of poly(HexPr) is presented in Figure 7 as a typical example. Interestingly, the α-methylene protons were observed as two broad but clearly separated signals with almost identical intensity at 3.65 and 3.95 ppm. The large difference in the chemical shift between these signals (>100 Hz) readily excludes the hypothesis that the peak separation is derived from the geminal coupling between two methylene protons. In other words, the two α-methylene protons are diastereotopic. The following experimental results led to a conclusion that the nonequivalence of the α-methylene protons stems from the slow process of the helix inversion on the NMR time scale at ambient temperature.[18]

First, it was confirmed by ^{1}H NMR spectroscopy that the stereoregularity (cis−transoidal) of the present sample of poly-(HexPr) is almost quantitative (Table 1). This was also supported by the ^{13}C NMR spectrum, where every carbon of poly(HexPr) provided only one very sharp signal at ambient temperature. Therefore, the possibility that poor stereoregularity causes the separation of the α-methylene signal is denied. The ^{13}C NMR data also rule out the possibility that the peak separation is due to the slow change between the s-trans and s-cis configurations with respect to the carbonyl group. Second, the ^{1}H NMR spectrum of poly(ethyl propiolate) exhibited a similar diastereotopic resonance for the α-methylene protons, which excludes the idea that the peak separation might arise from the hindered rotation of the pentyl residues in the side chain of poly(HexPr). Further evidence was obtained by the ^{1}H NMR spectrum of a copolymer of HexPr with MenPr having random conformation; i.e., in the ^{1}H NMR spectrum of the randomly coiled copolymer (MentPr/HexPr = 60/40) (Figure 8b), the α-methylene protons in the hexyl group are not diastereotopic, and only a broad signal was observed. All these data rule out the possibility that the magnetically nonidentical environment for the α-methylene protons in poly(HexPr) is dependent on the primary structure of the polymer. In other words, the secondary structure, i.e., helical structure, contributes to this phenomenon, and the slow

interconversion process between right- and left-handed helical conformations on the NMR time scale allows the α-methylene protons to exist in magnetically nonequivalent environments.

This result nicely explains the complicated ^{1}H NMR spectrum of the copolymers from (−)- and (+)-MBPr. As illustrated in Figure 9a, α-methylene protons of the homopolymer of (−)-MBPr gave two signals.[19] This is due to the slow interconversion process between the two helices, as described above. On the other hand, their copolymers exhibited four signals attributed to the α-methylene protons, as exemplified by the copolymer from the 50% ee monomer (Figure 9b). Because the chiroptical properties of this copolymer are almost the same as those of poly[(−)-MBPr], both polymers possess the same ratio of one-handed helix to its counterpart. Furthermore, both homo- and copolymers showed completely identical ^{13}C NMR spectral patterns, where every carbon appeared as a sharp, well-resolved single peak.[20] This means that there is no difference in the magnetic environment for the α-methylene carbons between these homo- and copolymers. Therefore, with respect to the α-methylene protons, there is a diastereotopic relationship between the (−)- and (+)-MBPr units. In other words, the α-methylene signals attributed to the two enantiomers can be distinguished by ^{1}H NMR; the couple of the signals at 3.73 and 3.60 ppm and the other couple of the resonance at 3.93 and 3.43 ppm can be assigned to the α-methylene protons from (−)-(S)-MBPr and (+)−(R)-MBPr, respectively.

Stability of the Helical Conformation of Poly(propiolic esters). In the case of a helical polymer that undergoes helix

(18) A similar effect has been observed in several polymers and oligomers. See: Ute, K.; Fukunishi, Y.; Jha, S. K.; Cheon, K. S.; Muñoz, B.; Hatada, K.; Green, M. M. *Macromolecules* **1999**, *32*, 1304−1307 and references therein.
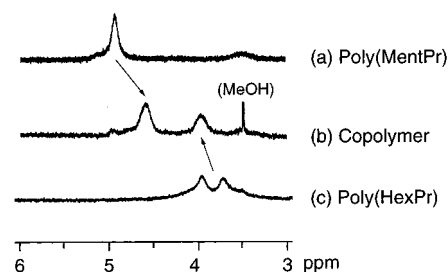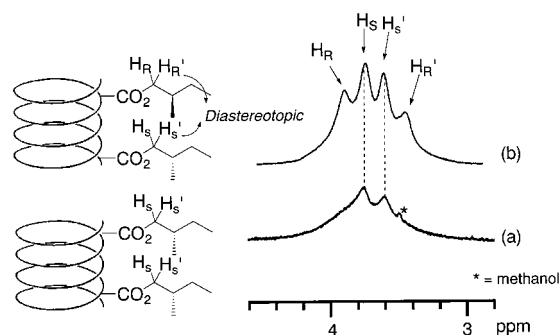
(19) All of the polymers from chiral monomers with alkylene spacers, which were used in ref 9b, gave similar diastereotopic signals for the α-methylene protons. In a similar way, the diastereotopic peak separation of α-methylene protones was observed for the achiral polymers listed in the table in the Supporting Information. Thus, the peak separation of α-methylene protons of poly[(−)-MBPr] is not due to the secondary butyl residue.

(20) Although α-methylene carbon of 50% ee copolymer may theoretically display two peaks, we observed it as a single peak in the ^{13}C NMR. This may be because the chemical shifts of α-methylene carbons of *R* and *S* pendants are incidentally identical.
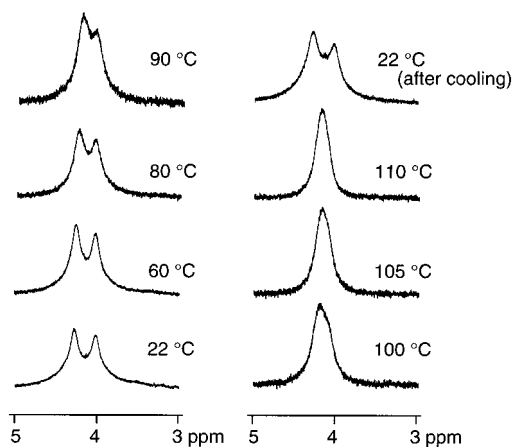
Figure 10. Variable-temperature ^{1}H NMR spectra (expanded) of poly-(HexPr) in toluene-d_6 (400 MHz).

reversal, the polymer chain is comprised of both helical and disordered domains. When the helix sense is inverted through the disordered state, this disordered state is regarded as a helix reversal point. The stability of the helical conformation of achiral polymers is governed by the population of the disordered state and by the speed of the transformation between the helical and disordered states. The former is determined by the free energy difference (ΔG_r) between the helical and disordered states, and the latter depends on the energy barrier ($\Delta G^{\ddagger}$) of the process from the helical to disordered states.[21,22] Interestingly, the variable-temperature NMR technique proved to readily allow the estimation of not only $\Delta G^{\ddagger}$ but also ΔG_r for poly(propiolic esters).

As described above, the peak separation of the α-methylene signals is caused by the slow transformation from one helix to the other. Therefore, the integrated intensities of these two signals should be identical unless these two methylene protons possess remarkably different relaxation times. However, careful investigation of the spectrum measured at 22 °C suggests that these two peaks possess different integrated intensities (Figure 10). A much clearer example is provided by the spectrum at 90 °C. At every temperature, the intensity of the lower magnetic field peak is larger than that of the other peak. This means that the signals appearing around 3.5−5 ppm include some other protons in addition to α-methylene protons in the helical state. Again, the stereoregularity of the present sample of poly(HexPr) was perfect, which concludes that the concealed peak is not caused by the irregular first-order microstructure. In other words, a second-order conformation other than the helical structure contributes to the difference in the integrated intensities between the two signals. Here, emphasis should be placed on the fact that, as shown in Figure 8, the chemical shift of the α-methylene protons in the disordered state (Figure 8b) is completely identical

to that of the lower magnetic field peak of the α-methylene protons in the helical state (Figure 8c). These results suggest that a peak for the α-methylene protons of poly(HexPr) in the disordered state overlaps with the lower magnetic field signal for the α-methylene proton in the helical state.[23] The observed temperature dependence of the integration ratio between the two α-methylene signals (Figure 10) can be reasonably explained by the increasing population of the disordered state with an increase in temperature. A computational deconvolution of the signals based on the α-methylene protons into two separate Lorentzian functions gave the proportion of the helical to disordered conformations. Through this process, the free energy difference between the helical and disordered states (ΔG_r) was readily estimated to be 1.59 ± 0.16 kcal/mol at 22 °C and 0.55 ± 0.06 kcal/mol at 90 °C for the present sample of poly(HexPr).

The energy barrier ($\Delta G^{\ddagger}$) for the interconversion between the two helical conformations was readily obtained in a similar manner as that applied in the study of several helical polymers and oligomers.[18] As shown in Figure 10, ^{1}H NMR spectra of poly(HexPr) in toluene-d_8 at various temperatures showed that the diastereotopic signals for the α-methylene proton coalesced at 110 °C. This phenomenon was reversible: the diastereotopic protons were observed again after cooling of the sample to 22 °C. This means that, at ambient temperature, the rate of the interconversion is slow on the time scale of NMR. Lowering the temperature below 20 °C caused no change in the NMR spectrum. From the coalesced temperature and the difference of the chemical shifts at 22 °C, $\Delta G^{\ddagger}$ of the present sample of poly(HexPr) was estimated to be 18.5 kcal/mol, which is comparable to that of poly(2-butylhexyl isocyanate).[18] This observed value of $\Delta G^{\ddagger}$ for poly(HexPr) is apparently underestimated because, at elevated temperature, the unavoidable cis-to-trans isomerization in part took place to reduce the stereoregularity of the polymer. Indeed, the cis content of poly(HexPr) decreased to 89% after the variable-temperature NMR measurement.

Summary

The purpose of the present study is to elucidate the nature of the helical conformation of poly(propiolic esters). Emphasis should be placed on the fact that the two parameters, ΔG_r and $\Delta G^{\ddagger}$, governing the nature of helical structure can be estimated by an NMR technique. By using these parameters, one can draw the profile of the helical conformation of poly(propiolic esters). The helical reversal free energy (ΔG_r) was of the order of 1 kcal/mol, which is quite small compared with that of polyisocyanates (3−4 kcal/mol). This means that there is a higher population of helix reversal state along the backbone of poly-(propiolic esters). However, as demonstrated by the chiral/achiral and *R/S* copolymerizations, the persistence length of the helix of poly(propiolic esters) is apparently large in comparison with those of the other polymers from monosubstituted acetylenes. The speeds of helix inversion and, in turn, activation energy for the interconversion between the two opposite helices are comparable to those of polyisocyanates. Inversion of the helix of poly(propiolic esters), thus, readily occurs at ambient

(21) (a) Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc*. **1989**, *111*, 8850−8858. (b) Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C.; Peterson, N. C.; Lifson, S. *Macromolecules* **1995**, *28*, 1016−1024. (c) Okamoto, N.; Mukaida, F.; Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M. *Macromolecules* **1996**, *29*, 2878−2884. (d) Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Jha, S. K.; Andreola, C.; Reidy, M. P. *Macromolecules* **1998**, *31*, 6362−6368. (e) Gu, H.; Sato, T.; Teramoto, A.; Varichon, L.; Green, M. M. *Polym. J.* **1997**, *29*, 77−84. See also ref 2b.

(22) The helix reversal state is defined as a disordered structure interposed between two helices with opposite sense. Therefore, the parameters (ΔG_r and $\Delta G^{\ddagger}$) used in the present study do not rigorously correspond to those previously defined[18] because the disordered structure of poly(propiolic esters) has not been confirmed to function as the helix reversal state. However, we believe that the two energy parameters determined in the present study are essentially identical to the actual ΔG_r and $\Delta G^{\ddagger}$.

(23) An attempt unfortunately failed to isolate the signal in the helix reversal state by controlling the interval between the 180° and 90° pulses. This is probably because α-methylene protons have similar relaxation times regardless of the conformations and/or because the population of helix reversal state is not large enough to be detected at ambient temperature. A similar NMR experiment at elevated temperature, which would increase the proportion of helix reversal state and eventually facilitate the detection of helix reversal points, was not carried out due to the unavoidable cis-to-trans isomerization of the polymer.

temperature. Kinetic control of the helix sense is impossible even if poly(propiolic esters) possess very bulky pendant groups.[24] As seen in the very limited case of a poly(phenylacetylene) derivative,[25] introduction of elegantly designed functional groups that can fix the helix sense through the large interaction between pendants is necessary to achieve the screw-selective production of chiral polymers from achiral propiolic esters.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. The molecular weights of the present polymer samples listed in Table 1 were determined with a GPC equipped with two Shodex KF 508L columns (eluent, THF) after calibration with standard polystyrenes. CD spectra were recorded in a quartz cell (thickness 1 cm) at room temperature using a Jasco J600 or J750 spectropolarimeter. Specific rotations were obtained with a Jasco V-530 polarimeter. UV−visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. Acetonitrile was dried over CaH_2 and distilled under nitrogen. All the other reagents were used without purification. 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 of 4-chlorobutyl propiolate are as follows: bp 73 °C (6 mmHg); ^{1}H NMR (CDCl3) δ 1.81−1.96 (m, 4H), 2.91 (s, 1H), 3.58 (t, 2H, $J = 8.0$ Hz), 4.26 (t, 2H, $J = 8.0$ Hz); ^{13}C NMR (CDCl3) δ 25.7, 28.8, 44.2, 65.4, 74.5, 74.8, 152.6; IR (neat) 3283, 2963, 2120, 1725, 1275, 754 cm^{-1}. Anal. Calcd for $C_7H_9O_2Cl$: C, 52.35; H, 5.65; Cl, 22.08. Found: C, 52.07; H, 5.62; Cl, 22.34.

(Co)polymerizations. An acetonitrile solution (1 mL) of the monomers (total 4 mmol) was added to the solution of [(nbd)RhCl]2 (40 μmol) in acetonitrile (1 mL), and the solution was kept for 24 h at 30 °C. After the solvent was removed under 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.

Mark−Hauwink−Sakurada Plot. The data used in the Mark−Hauwink−Sakurada plots of the copolymers were kindly supplied by Asahi Techneion Co. Ltd. using a TDA 300 GPC system (Viscotek Co.) equipped with two TSKgel GMHXL columns (eluent, THF). The refractive index and the relative viscosity η_r of the eluate were simultaneously recorded with this apparatus. The former quantity was converted to the mass concentration c of the eluted copolymer by using the refractive index increment $\partial n/\partial c$ of the copolymer. [η] was approximately evaluated by dividing $\eta_r - 1$ by c. The M_w of the eluted copolymer was estimated on the assumption that the hydrodynamic volume of the copolymer, defined by [η]M_w, is given by the universal function of elution time. However, since the exact value of $\partial n/\partial c$ was not determined for the individual copolymer, the calculated c is only an apparent one proportional to the absolute c. The obtained data, thus, cannot give the correct abscissa and ordinate in the MHS plots of the present copolymers. However, it is reasonably possible to discuss the stiffness of the main chain of copolymers on the basis of the slopes of the MHS plots.

Supporting Information Available: Composition curves and Fineman−Ross plots for the copolymerizations of MentPr with HexPr and of MyrtPr with CBPr, and a list of $\Delta G^{\ddagger}$ of several poly(propiolic esters) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The $\Delta G^{\ddagger}$ of poly(propiolic esters) was almost independent of the bulkiness of the pendant. See the Supporting Information.

(25) Sumi, A.; Maruyama, N.; Aoki, T.; Kaneko, T.; Oikawa, E. *Polym. Prepr. Jpn.* **1999**, *48*, 1872−1873.