Synthesis and Structure in Solution of Poly[(−)-menthyl propiolate] as a New Class of Helical Polyacetylene

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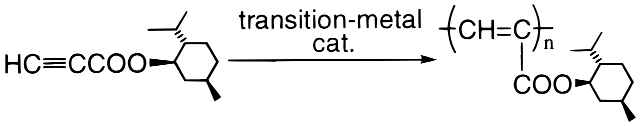
ABSTRACT: Polymerization of (−)-menthyl propiolate (MtPr) by $[(nbd)RhCl]_2$ and $MoOCl_4$−n-Bu_4Sn gave polymers in moderate yields. The ^1H NMR spectrum of the polymer formed with the Rh catalyst (PMtPr-Rh) showed a signal characteristic of the cis olefinic proton, meaning the high stereoregularity (cis) of PMtPr-Rh. In contrast, no clear signal attributable to the cis-olefinic proton was detected in the ^1H NMR spectrum of the polymer produced with the Mo catalyst (PMtPr-Mo), which indicates the geometrically irregular structure of PMtPr-Mo. PMtPr-Rh displayed much larger $[\alpha]_D$ and molar ellipticity $[\theta]$ than those of PMtPr-Mo, MtPr, and (−)-menthyl acrylate. This leads to conclusions that the main chain of PMtPr-Rh exists in a helical conformation with an excess of one-handed screw sense and that induction of the helical conformation requires the cis-transoidal structure of the main chain. No serious decrease in magnitude of CD effects of PMtPr-Rh was observed upon heating the polymer solution at 110 °C, indicating the high thermal stability of the helix of PMtPr-Rh in solution.

Introduction

Much attention has been paid to the synthesis of optically active polymers owing to their unique functions such as molecular recognition ability and catalytic activity for asymmetric synthesis.[1] Recent progress in polymer synthesis has enabled it to afford a variety of chiral polymers based on their one-handed helical conformations. Among them, optically active polymers with π-conjugation along the main chains are very interesting since they are potentially useful as polarization-sensitive electrooptical materials, asymmetric electrodes, and so on.[2] One of such conjugated polymers is represented by substituted polyacetylenes having chiral substituents that induce helical conformations to the main chains. For example, polymers from both aliphatic and aromatic monosubstituted acetylenes are known to exist in helical conformations with one-handed screw sense if appropriate chiral substituents are incorporated.[3] Even when substituted polyacetylenes have no chirality, single-handed helical conformations can be brought about when the polymers strongly complexes with chiral molecules.[4]

However, previous studies on the synthesis of substituted polyacetylenes with helical conformations have mostly dealt with ring-substituted phenylacetylenes as monomers. This is due to the following reasons: (i) essentially perfect stereoregularity (cis-transoidal structure) is readily attained from phenylacetylenes with Rh catalysts, and (ii) the stereoregular cis configuration is favorable for the induction of one-handed screw-sense conformation.[5] Despite these advantages, the chemical and thermal instability of poly(phenylacetylenes)[6] diminishes their utility in the practical use. Furthermore, the helical conformation of the conventional monosubstituted acetylene polymers is thermally unstable.[3a,b,d] For instance, the intensity of circular dichroism (CD) effects of helical polyacetylenes rapidly reduces when the solution is heated.

Scheme 1



Earlier, one of these laboratories showed that the polymerization of alkyl propiolates with a Rh catalyst gives polymers with high stereoregularity (cis).[7] It is interesting that the poly(alkyl propiolate)s are thermally quite stable compared with other polymers from monosubstituted acetylenes. Therefore, the polymerization of propiolates with chiral ester groups is expected to offer novel helical polymers with high stability, which would allow them to be applied as advanced functional materials. To the best of our knowledge, however, there have been no reports on the polymerization of alkyl propiolates with chiral substituents except our previous paper.[7]

In this study, we investigated the polymerization of (−)-menthyl propiolate (MtPr), a chiral acetylenic ester, by using various transition-metal catalysts (Scheme 1). The structures of resulting polymers in solution were also examined.

Results and Discussion

Polymerization. Polymerization of MtPr was briefly documented in our previous paper, where the (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ($[(nbd)RhCl]_2$) has proven to be active for the polymerization of MtPr in methanol.[7] However, the molecular weight of the polymer (PMtPr) is not satisfactory (M_n ∼6000). Thus, we first investigated the polymerization of MtPr with $[(nbd)RhCl]_2$ in various solvents to optimize the reaction conditions (Table 1). It turned out that acetonitrile is a better solvent for the Rh-catalyzed polymerization of MtPr than methanol. For example, at high

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Table 1. Polymerization of MtPr by $[(nbd)RhCl]_2$ in Various Solvents[a]

solvent	$[MtPr]_0$, M	polymer[b] yield, %	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
MeOH	0.50	8	6.0	5.8
MeOH	2.0	17	6.2	9.4
MeCN	0.50	13	15	15.3
MeCN	2.0	34	250	1.9
THF	0.50	15	26	10.5
THF	2.0	5	11	6.5
PhCN	0.50	6		
DMF	0.50	4		

[a] Polymerized at 40 °C for 24 h; $[MtPr]_0/[Rh] = 100$. [b] Methanol-insoluble product. [c] Estimated GPC ($CHCl_3$, PSt calibration).

Table 2. Polymerization of MtPr by Various Transition-Metal Catalysts[a]

catalyst	solvent	$[MtPr]_0$	polymer[b] yield, %	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
$PdCl_2$	MeOH	1.0	7	1.6	1.1
WCl_6—n-Bu_4Sn	toluene	0.50	0		
$WOCl_4$—n-Bu_4Sn[e]	toluene	0.50	18	1.9	1.4
$MoCl_5$—n-Bu_4Sn[d]	toluene	0.50	14		
$MoOCl_4$—n-Bu_4Sn[e]	toluene	0.50	61	18	1.9

[a] Polymerized at 60 °C for 24 h; [cat] = 20 mM. [b] Methanol-insoluble fraction. [c] Estimated by GPC ($CHCl_3$, PSt calibration). [d] $[n\text{-}Bu_4Sn] = 30$ mM. [e] $[n\text{-}Bu_4Sn] = 20$ mM.

concentration of MtPr (2.0 M) in acetonitrile, a polymer with quite high molecular weight (M_n 2.5×10^5) was obtained in a relatively good yield. This polymer (denoted as PMtPr-Rh) was used for characterization stated below. The use of other solvents such as THF, PhCN, and DMF did not improve the yield.[8]

Various transition-metal catalysts, which are active for the polymerization of substituted acetylenes,[5] were next employed for the polymerization of MtPr (Table 2). $PdCl_2$, WCl_6—n-Bu_4Sn, and $MoCl_5$—n-Bu_4Sn were hardly or not effective for the polymerization. On the other hand, the polymerizations with $WOCl_4$—n-Bu_4Sn and $MoOCl_4$—Bu_4Sn gave polymers (denoted as PMtPr-W and PMtPr-Mo, respectively) in clearly better yields than those with WCl_6- and $MoCl_5$-based catalysts. This is probably due to the reduced acidity of $WOCl_4$ and $MoOCl_4$ compared with that of WCl_6 and $MoCl_5$. All of PMtPr-Rh, PMtPr-W, and PMtPr-Mo were pale yellow solids. These polymers were soluble in toluene, n-hexane, cyclohexane, chloroform, and THF but insoluble in methanol, acetonitrile, and water.

Geometrical Structure. ^1H NMR spectra of the resulting polymers, PMtPr-Rh, PMtPr-W, and PMtPr-Mo, are illustrated in Figure 1. The spectrum of PMtPr-Rh showed a sharp singlet signal at δ 7.7 ppm and a broad singlet signal around δ 5.0 ppm. The former is assigned to the olefinic proton of the main chain having the cis—transoidal structure. The latter is the methyne proton adjacent to the ester group. By comparison of integrated intensity of both protons, the content of the cis—transoidal structure was estimated to be 80% for PMtPr-Rh. This result is in good agreement with the general feature of Rh-catalyzed polymerization of acetylenes, where high contents of cis—transoidal segment are attainable.[5] On the other hand, no sharp signal attributable to the cis—transoidal olefinic proton was detected in the cases of PMtPr-Mo and PMtPr-W. This means that the polymers produced with Mo and W catalysts have geometrically irregular structures. This idea is also supported by the thermal isomerization behavior of PMtPr.[9] Thus, the olefinic signal observed at 7.7 ppm in the ^1H NMR of PMtPr-Rh completely disappeared when PMtPr-Rh was treated at 150—200 °C for 15 min under nitrogen, and this thermally treated polymer (PMtPr-Δ) displayed very similar signals to those of PMtPr-Mo (Figure 1).

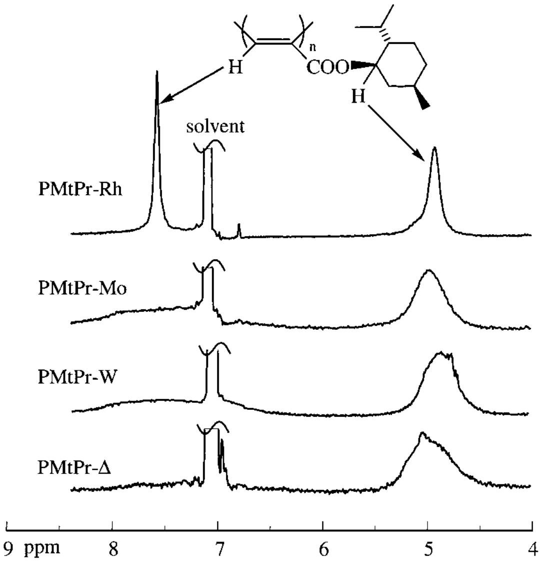

Figure 1. ^1H NMR spectra of PMtPr-Rh, PMtPr-Mo, PMtPr-W, and PMtPr-Δ in d_6-benzene (27 °C).

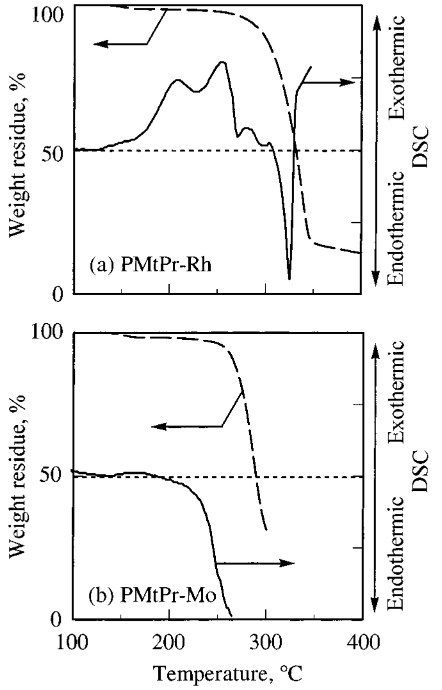

Figure 2. DSC and TGA curves of (a) PMtPr-Rh and (b) PMtPr-Mo (heating rate 10 °C/min).

Differential scanning calorimetric (DSC) analyses of PMtPr-Rh and PMtPr-Mo also clearly supported the idea regarding the steric structure of the polymers (Figure 2). The DSC curve of MtPr-Rh exhibited exothermic peaks at 180—255 °C. These peaks were observed below the decomposition temperature (>270 °C) of the polymer. Thus, it is reasonable to consider that these exothermic peaks stem from thermal isomerization from cis to trans structure. Such a thermal behavior is often observed for cis-transoidal polymers produced

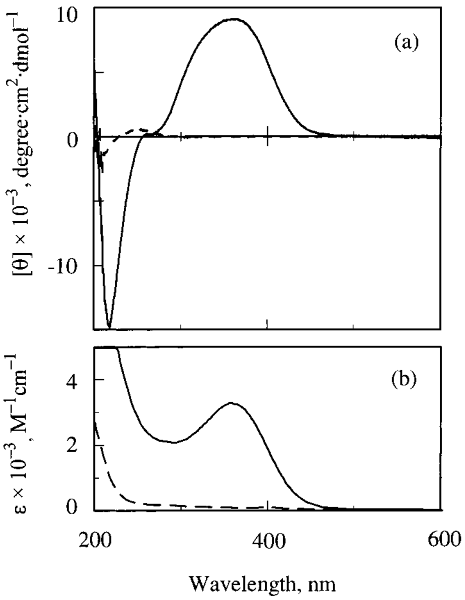

Figure 3. (a) CD and (b) UV−visible spectra of PMtPr-Rh (—) and (−)-menthyl acrylate (- - -) in cyclohexane (c = 6 × 10^{-4} M).

with Rh catalysts.[10] This result manifests that the steric structure of PMtPr-Rh is mainly composed of the cis structure. On the other hand, no exothermic peak was detected in PMtPr-Mo. In other words, PMtPr-Mo exists in sterically irregular structure and possesses a lower cis content than those of PMtPr-Rh.

Conformation in Solution. Stereoregular cis−transoidal polyacetylenes with chiral substituents often show large optical rotations ($[\alpha]_D$) and intense CD effects in the absorption region of polymer backbone.[3,4] This is caused by an excess of one-handed helical conformation of polymers. Similarly to these cases, PMtPr-Rh has proven to exist in a helical conformation with an excess of one-handed screw sense. For example, the sign of $[\alpha]_D$ reversed after the polymerization of MtPr with Rh, and the absolute value of $[\alpha]_D$ of PMtPr-Rh [+363° (c = 0.06, cyclohexane)] was much larger than that of the (−)-menthyl acrylate [−89° (c = 0.06, cyclohexane)] and that of the monomer [−82° (c = 1.0, chloroform)]. The CD spectra of PMtPr-Rh and (−)-menthyl acrylate which mimics the repeating unit of the polymer are illustrated in Figure 3. The CD spectrum of PMtPr-Rh exhibited a large molar ellipticity [θ] in the UV absorption region of the polymer main chain. In contrast, no such large CD effects were detected in the range of the absorption of (−)-menthyl acrylate. These results lead to a conclusion that the main chain of PMtPr-Rh exists in a helical conformation with an excess of one-handed screw sense.

On the other hand, PMtPr-Mo showed a smaller $[\alpha]_D$ [+39° (c = 0.06, cyclohexane)] than did PMtPr-Rh, and the sign of $[\alpha]_D$ of PMtPr-Δ [−20° (c = 0.06, cyclohexane)] agreed with that of (−)-menthyl acrylate. Similarly, the CD effects of PMtPr-Mo ($[\theta]_{max}$ = 6400) and PMtPr-W ($[\theta]_{max}$ = 900) were smaller than that of PMtPr-Rh ($[\theta]_{max}$ = 9100) (Figure 4). Furthermore, the thermally treated polymer, PMtPr-Δ, displayed no CD effects. Therefore, it can be concluded that the induction of helical conformation requires the stereoregular cis−transoidal structure of the main chain.

As mentioned above, when the polymer solutions are heated, the CD effects of conventional helical polyacetylenes generally reduce owing to the facile transformation from helices to random coils.[3a,b,d] For example, $[\alpha]_D$ of poly(phenylacetylene) having (−)-menthoxylcarbonyl group rapidly decreases from −680° to −630° when its solution is warmed from 20 to 45 °C.[3d] Ciardelli et al. also showed the increase in ellipticity of poly[(+)-3-methylpentyne] by lowering the temperature.[3a] These observations mean that the helices of such polyacetylenes are not rigid enough to maintain their helical structure in solution at high temperature. It is noteworthy that the helical conformation of PMtPr-Rh is thermally quite stable in solution compared with those of previously prepared polyacetylenes. When the measuring temperature was raised from 20 to 80 °C, the intensity of the CD hardly changed (Figure 5). Only a slight decrease in magnitude of CDs was observed even though the solution was heated at 110 °C.[11] These results imply that the helix sense of this polymer backbone is highly stable against heating in solution. The slight decrease in the intensity of CD effects is probably due to the isomerization because the intensity of CD of the original PMtPr-Rh was not recovered after the solution was cooled to 20 °C. This was also sup-

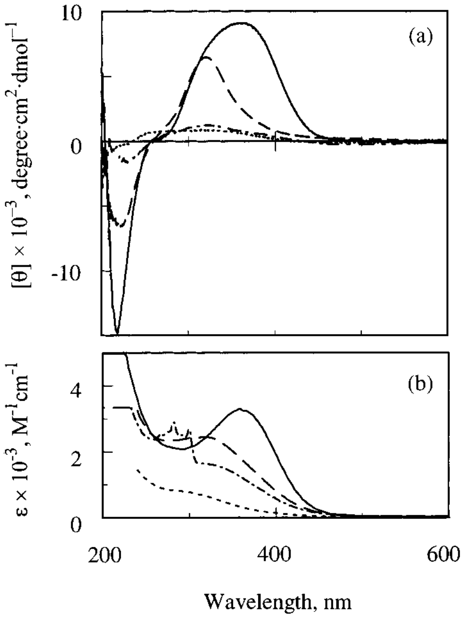

Figure 4. (a) CD and (b) UV−visible spectra of PMtPr-Rh (—), PMtPr-Mo (- - -), PMtPr-W (- • -), and PMtPr-Δ (···) in cyclohexane (c = 6 × 10^{-4} M).

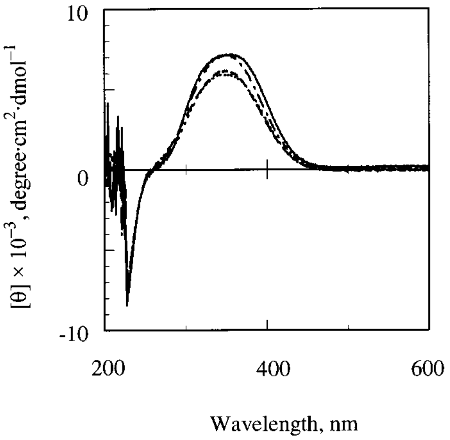

Figure 5. CD spectra of PMtPr-Rh [in decalin (c = 6 × 10^{-4} M) at 20 (—), 80 (- • -), 110 (- - -), and 20 °C (···) after heating at 110 °C.

ported by the fact that the decrease in the cis content was recognized in the ^{1}H NMR spectrum when PMtPr-Rh was treated at 120 °C for 2 h. In other words, the produced polymer does not undergo helix−random coil transformation at the temperature examined.

In summary, we have achieved the synthesis of a new substituted polyacetylene with helical conformation. (−)-Menthyl propiolate gave polymers in the presence of $[(\mathrm{nbd})\mathrm{RhCl}]_2$ and $\mathrm{MoOCl_4}$−*n*-$\mathrm{Bu_4Sn}$ in moderate yields. The polymer obtained with the Rh catalyst had a high cis-transoidal content and showed intense CD effects and a large $[\alpha]_D$, meaning that this polymer takes a predominant one-handed helical conformation in solution. The helical conformation was thermally stable in solution, which can inhibit the helix−random coil transformation even at high temperature. Synthesis of various of poly(propiolate)s with chiral substituents and investigation of their conformations are now in progress.

Experimental Section

Materials. (−)-Menthyl propiolate was prepared by the condensation of *l*-(−)-menthol with propiolic acid in the presence of *p*-toluenesulfonic acid and purified by flash chromatography ($\mathrm{SiO_2}$, eluent; ether/hexane) and the subsequent recrystallization from ether; yield 45%, mp 87−88 °C, $[\alpha]_D$ −82° (c = 1.0, $\mathrm{CHCl_3}$). All the solvents were distilled by the standard procedures. Commercial $[(\mathrm{nbd})\mathrm{RhCl}]_2$ (Aldrich), $\mathrm{MoOCl_4}$ (Strem), $\mathrm{MoCl_5}$ (Aldrich), $\mathrm{WCl_6}$ (Aldrich), $\mathrm{WOCl_4}$ (Aldrich), and $\mathrm{PdCl_2}$ (Nacalai Tesque) were used without further purification. *n*-$\mathrm{Bu_4Sn}$ was purchased from Tokyo Kasei, distilled under reduced pressure from calcium hydride, and stored as a toluene solution (200 mmol/L).

Measurements. The molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (eluent, chloroform; Shodex columns K804, K805, and K806; calibrated by polystyrene standards). ^{1}H NMR spectra were recorded with a JEOL GSX-270 spectrometer in d_6-benzene. TGA measurements were done with a Perkin-Elmer TGA7 thermal analyzer in nitrogen. DSC analyses were carried out with a MAC science DSC3100 calorimeter in air. CD spectra were recorded with a Jasco J600 spectropolarimeter in a quartz cell (thickness 1 cm) at 20 °C. Specific rotations were obtained with a Jasco V-530 spectropolarimeter. UV−visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer. Melting points were measured with a Yanaco micro melting point apparatus.

Polymerization with $[(\mathrm{nbd})\mathrm{RhCl}]_2$. A typical procedure was as follows. A solution of MtPr (833 mg, 4.00 mmol) in $\mathrm{CH_3CN}$ (1 mL) was added to a solution of $[(\mathrm{nbd})\mathrm{RhCl}]_2$ (18.4 mg, 0.0400 mmol) in $\mathrm{CH_3CN}$ (1 mL) at 40 °C under nitrogen. The solution was kept at 40 °C for 24 h. The resulting suspension was dissolved with toluene (ca. 10 mL) and poured into a large excess of methanol to precipitate the polymer. The polymer was filtered with a sintered glass (G3) and dried under reduced pressure. The polymerization with $\mathrm{PdCl_2}$ was carried out in a similar way (in methanol, 60 °C, 24 h; [MtPr] = 0.50 M, [Pd] = 20 mM).

Polymerization with Mo and W Catalysts. A typical procedure was as follows. A 200 mM solution (0.2 mL) of *n*-$\mathrm{Bu_4Sn}$ in toluene was added to a 50 mM solution (0.8 mL) of $\mathrm{MoOCl_4}$ in toluene, and the resulting solution was at 60 °C for 10 min. A solution (1 mL) of MtPr (208 mg, 1.00 mmol) in toluene was added to the catalyst solution. The solution was kept at 60 °C for 24 h. The resulting solution was diluted with toluene (ca. 10 mL) and poured into a large excess of methanol to precipitate the polymer. The polymer was filtered with a sintered glass (G3) and dried under reduced pressure. Polymerization runs using $\mathrm{MoCl_5}$, $\mathrm{WCl_6}$, and $\mathrm{WOCl_4}$ were carried out in a similar way.

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(11) No significant decrease in the CD effects of PMtPr-Rh was observed even when the solution was heated at 110 °C for 2 h in decalin.

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