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Synthesis and Chiroptical Properties of Poly(methylpropargyl ester)s Carrying Ferrocene Moieties

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Novel chiral methylpropargyl ester monomers containing ferrocene moieties, ferrocenecarbonyl-(*R*)-1-methylpropargyl ester were synthesized and polymerized with (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] to give the corresponding polymers with number-average molecular weights ranging from 7600 to 12 000 in 34–78% yields. The polymers were soluble in CHCl₃, CH₂Cl₂, and THF, but insoluble in hexane and diethyl ether. The specific rotation and circular dichroism (CD) spectroscopic studies revealed that polymers took predominantly one-handed helical structures in the solvents, and the helical structure of the polymers was stable to the addition of MeOH and heat. The cyclic voltammograms of the polymers indicated that the polymers exhibit electrochemical properties.

Keywords: Helical polymers, ferrocene, substituted polyacetylenes, electrochemical properties

1 Introduction

Ferrocene is widely used as a versatile building block in the construction of advanced functional materials due to the fact that it possesses unique thermal and electrochemical properties (1). Polymers containing ferrocene moieties in the main chain or side chain have attracted much attention because of their unique properties, including electronic and optical properties, which allow them to be applied to various photonic applications such as electrocatalysts, chemical sensors, modified electrodes, photoactive molecular devices, and medicine (2). On the other hand, substituted polyacetylenes possess alternating double bonds in the main chain, which endows them with unique properties such as semiconductivity, high gas permeability, nonlinear optical properties, and helix formation (3). Helical polyacetylenes gather interest not only from fundamental viewpoints regarding synthesis and properties, but also practical applications, because they exhibit useful functions resulting from the regulated secondary structure, which include chiral discrimination and catalytic activity for asymmetric synthesis (4). It is expected that ferrocene-containing helical polyacetylenes will combine these characteristics together and lead to the development of new functions materials.

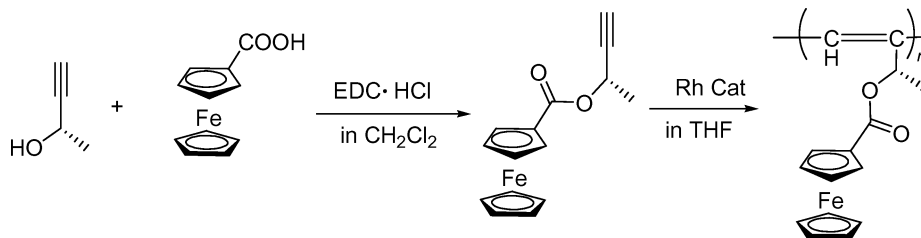
We have recently found that (*R*)- and (*S*)-1-methylpropargyl alcohols (5), and the ester derivatives undergo polymerization to give stable helical polymers carrying carbazole, triphenylamine, cholesteryl and pyrene moieties (6). They display electro-optical and liquid crystalline properties. Thus, (*R*)- and (*S*)-1-methylpropargyl alcohols are simple and powerful chiral sources for helical polyacetylenes. The present manuscript deals with the synthesis and polymerization of ferrocene-methylpropargyl esters (1 in Scheme 1), and examination of the chiroptical properties of the formed polymers [poly(1)].

2 Experimental

2.1 Measurements

¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded in CDCl₃ on a JEOL EX-400 spectrometer. IR spectra were measured using a JASCO FTIR-4100 spectrophotometer. The number- and weight-average molecular weights (*M_n* and *M_w*) of polymers were determined by gel permeation chromatography (GPC) on a JASCO Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using THF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40°C. Specific rotations ([α]_D) were measured on a JASCO DIP-1000 digital polarimeter with a sodium lamp as a light source. CD and UV-vis spectra were recorded in a quartz

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Sch. 1. Synthesis and polymerization of methylpropargyl ester carrying ferrocene.

cell (thickness: 1 cm) at room temperature using a JASCO J-820 spectropolarimeter.

2.2 Materials

(*R*)-(+)-1-Methylpropargyl alcohol (Aldrich), ferrocene carboxy acid (Wako), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl, Eiwiss), 4-dimethylaminopyridine (DMAP, Wako) were purchased and used without further purification. (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] [(nbd) = 2,5-norbornadiene] was prepared by the reaction of [(nbd)RhCl]₂ with NaB(C₆H₅)₄ as described in the literature (7). THF used for polymerization was purified by the standard methods.

2.3 Monomer Synthesis

Ferrocenecarbonyl-(*R*)-1-methylpropargyl ester (**1**) was prepared as follows: ferrocene carboxylic acid (2.07 g, 9.0 mmol) was added to a solution of EDC·HCl (1.90 g, 9.0 mmol) and DMAP (0.1 g, 0.90 mmol) in CH₂Cl₂ (45 mL) at room temperature. (*R*)-(+)-1-Methylpropargyl alcohol (0.50 g, 7.1 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (50 mL) three times, and the organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed on a rotary evaporator to afford the crude product. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate (4/1 volume ratio) as an eluent. Monomer **1** was obtained as a colorless liquid in 65% yield (1.28 g). [α]_D = +43° (*c* = 0.10 g/dL in THF). ¹H-NMR (400 MHz, CDCl₃): δ 1.60 (d, *J* = 6.8 Hz, 3H, COCHMe), 2.45 (s, 1H, -C≡CH), 4.20 (s, 5H, Fc), 4.30 (s, 2H, Fc), 4.50 (s, 2H, Fc), 5.64 (d, *J* = 4.8 Hz, 1H, COCHMe). ¹³C-NMR (100 Hz, CDCl₃): δ 21.4 (COCHMe), 60.07 (COCHMe), 70.0, 70.5, 70.8, and 71.8 (Fc), 72.7 (-C≡CH), 82.5 (-C≡CH), 166 (>C=O). IR (cm⁻¹, KBr): 3374, 3297 (≡C-H), 3085, 2121 (-C≡C-), 2981, 2938, 1708, 1516, 1454, 1369, 1254, 1169, 1030, 830, 770, 740, 532. Anal. Calcd for C₁₅H₁₄FeO₂: C 63.86, H 5.0. Found: C 63.50, H 5.39.

2.4 Polymerization Procedure

The polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. A so-

lution of a monomer in THF ([M]₀ = 0.50 M) was added to a solution of (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] in THF ([M]₀/[cat] = 100) under nitrogen, and the solution was kept at 30°C for 24 h. The polymerization mixture was poured into a large amount of hexane to precipitate the formed polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A), and dried under reduced pressure.

2.5 Spectroscopic Data of the Polymers

Poly(**1**): ¹H-NMR (400 Hz, CDCl₃): δ 0.80–1.60 (br, 3H OCHCH₃), 4.0–4.5 (br, 9H, Fc), 5.93 (br, 2H, OCHCH₃, -C=CH<), 6.51 (br, 1H, >C=CH-). IR (cm⁻¹, KBr): 3374, 3085, 2981, 2935, 1716, 1511, 1454, 1369, 1253, 1169, 1061, 856, 830, 770, 740.

3 Results and Discussion

3.1 Monomer Synthesis and Polymerization

Scheme 1 illustrates the synthetic routes for the ferrocene containing monomer **1**. It was synthesized by the condensation of the ferrocene carboxylic acid with (*R*)-(+)-1-methylpropargyl alcohol using EDC·HCl and DMAP as condensation agents. The structures of the monomers were confirmed by IR, ¹H, and ¹³C NMR spectroscopies besides elemental analysis.

Table 1 summarizes the results of the polymerization of ferrocene-based monomer catalyzed by Rh⁺(nbd)[η⁶-C₆H₅B⁻(C₆H₅)₃]. Monomer **1** satisfactorily underwent polymerization to afford brown polymers [poly(**1**)] with *M_n*'s ranging from 7600 to 12 000 in 34–78% yields. The polymers were soluble in CHCl₃, CH₂Cl₂, and THF, but insoluble in hexane and diethyl ether. The polymers displayed a unimodal GPC chromatogram, indicating that the polymerization proceeded through a single propagating species.

The structure of poly(**1**) was examined by IR and ¹H-NMR spectroscopies. The monomers exhibited IR absorption peaks around 3 297 and 2 121 cm⁻¹ associated with the ≡C-H and -C≡C- stretching vibrations, respectively, while the polymers did not exhibit these peaks. Accordingly, the polymers displayed no ¹H-NMR signal at 2–3 ppm

Table 1. Polymerization of **1**^a

Run	$[M]_0$	Yield ^b (%)	M_n^c	M_w/M_n^c	Cis Content ^d (%)	$[\alpha]_D^e$ (deg)
1	0.2	34	7 600	1.68	— ^f	—
2	0.5	65	8 900	1.95	—	—
3	1.0	78	12 000	2.27	85	-543

^aCatalyst (nbd)Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃], $[M]_0/[Rh] = 100$, in THF, 30°C, 24 h.

^bHexane-insoluble part.

^cDetermined by GPC in THF on the basis of a polystyrene calibration.

^dDetermined by the integration ratios of the cis vinyl proton signal at 6.5 ppm and the other proton signals in the ¹H-NMR spectra.

^eMeasured by polarimetry ($c = 0.1$ g/dL in THF).

^fNot determined.

assignable to an ethynyl proton as show in Figure 1. The results clearly indicate that the acetylene polymerization took place to form polymers containing alternating single and double bonds along the main chain. Commonly, the Rh zwitterion complex efficiently catalyzes the polymerization of monosubstituted acetylenes by the insertion mechanism to give *cis*-stereoregular polyacetylenes. In the present study, the steric structure of the polymers is also the case, the cis content was about 85% as listed in Table 1.

3.2 Secondary Structure of the Polymers

The secondary structure of poly(**1**) was examined by polarimetry, CD, and UV-vis spectroscopies. As listed in Table 1, the polymers displayed large optical rotations

($[\alpha]_D = -543$, run 3) in THF compared to the corresponding monomers (**1**: +45°), suggesting that it took a helical structure with predominantly one handed screw sense in the solvent. We also measured the specific rotations of poly(**1**) in

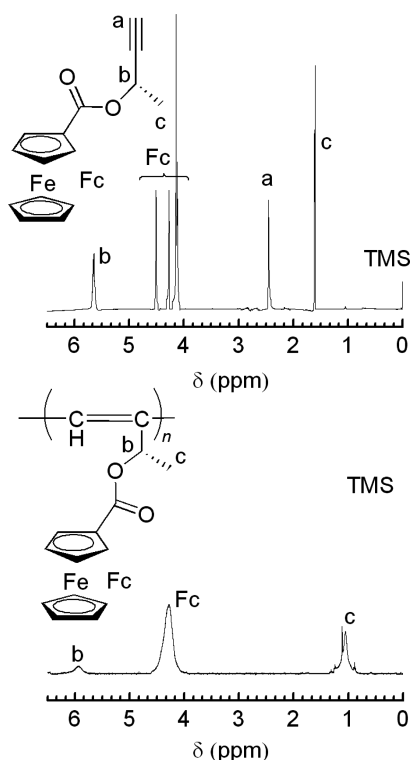


Fig. 1. ¹H-NMR spectra (400 MHz, CDCl₃) of **1** and poly(**1**). Polymer samples: runs 3 in Table 1.

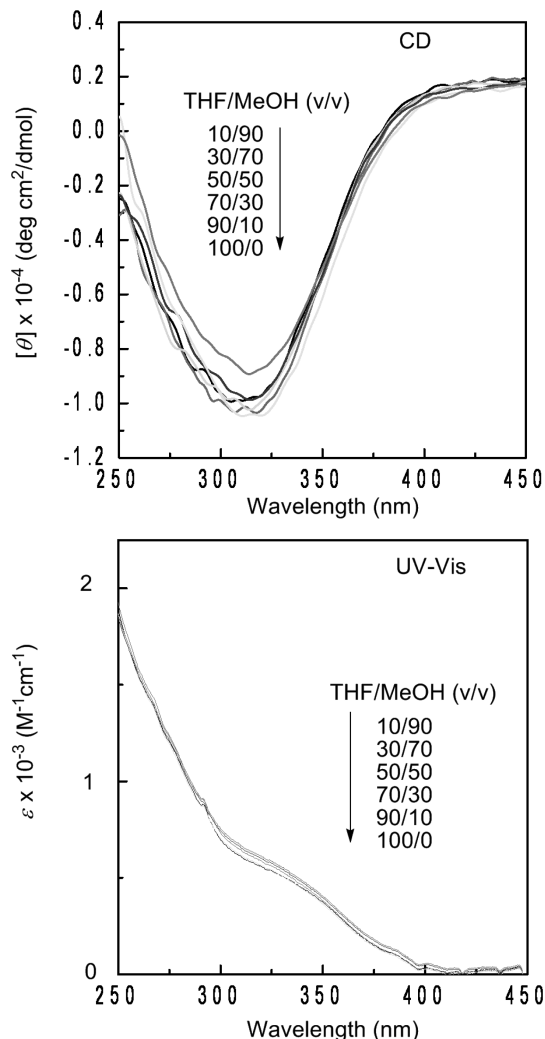


Fig. 2. CD and UV-vis spectra of poly(**1**) measured in THF/MeOH with various compositions (100/0–10/90, v/v) at 20°C ($c = 3.54 \times 10^{-4}$ M). Polymer samples: runs 3 in Table 1.

CHCl_3 and CH_2Cl_2 to find that the $[\alpha]_D$ values were almost the same as those in THF.

Figure 2 depicts the CD and UV-vis spectra of poly(**1**) measured in THF. Although monomers **1** were CD inactive (not shown), poly(**1**) showed strong minus signed Cotton effects around 305–325 nm, unambiguously proving that these polymers adopt a preferably one-handed helical conformation. We further measured the CD and UV-vis spectra of the polymers in THF/MeOH with various compositions. No significant dependence was observed on the solvent compositions as shown in Figure 2. The helical structure of the polymers was very stable to addition of MeOH, which is quite different from poly(*N*-propargylamide)s that utilize intramolecular hydrogen bond to stabilize the helical structure (8).

Figure 3 depicts the temperature dependence of the CD and UV-vis spectra of poly(**1**) measured in THF. The magnitude of Cotton effect also only slightly changed in THF at

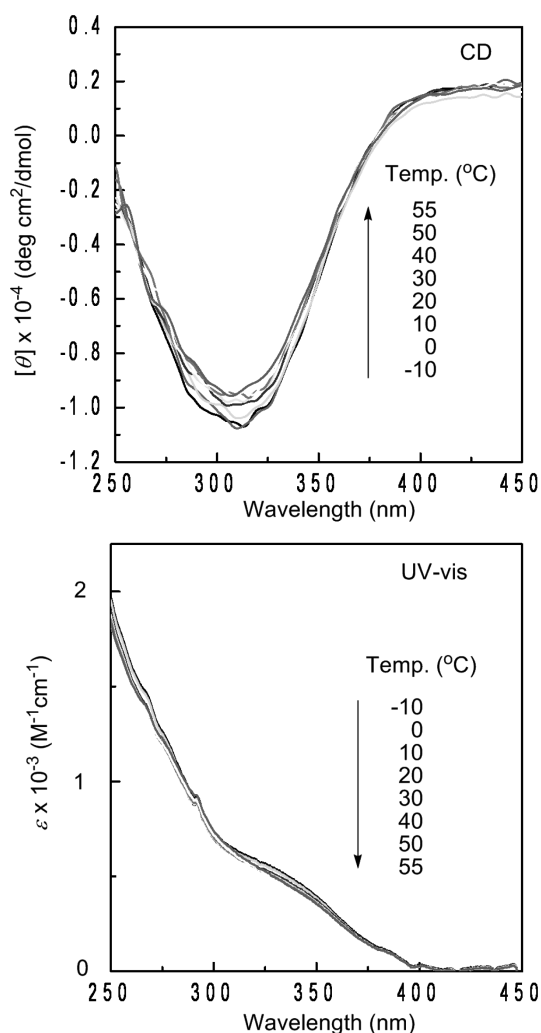


Fig. 3. Temperature-variable CD and UV-vis spectra of poly(**1**) measured in THF ($c = 3.54 \times 10^{-4}$ M). Polymer samples: runs 3 in Table 1.

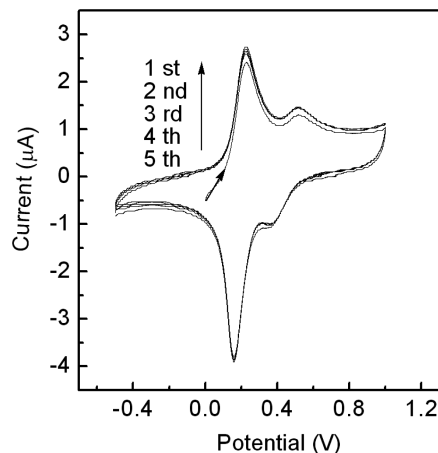


Fig. 4. Cyclic voltammograms of poly(**1**) (1 mM) dissolved in THF with TBAP (0.1 M) with consecutive scan at 0.1 V/s. Polymer samples: runs 3 in Table 1.

the temperature range of -10 to 55°C . It is considered that the helical structure of the polymers was thermally very stable at the temperature range from -10 to 55°C . The tolerance of the helicity to heat of the present polymers is remarkably high among helical polyacetylenes, which commonly transform into random coil at this temperature.

Figure 4 depicts the cyclic voltammetric (CV) curves of poly(**1**). Reversible oxidation and reduction based on the ferrocene unit are observed for the polymer. Poly(**1**) exhibits two oxidation peaks at about 0.25 and 0.56 V, and responding reduction peaks at 0.19 and 0.42 V, indicating ferrocene carrying polymer displays reversible redox properties, and the two redox peaks associated with the stepwise, one-electron oxidation of the iron centers in the ferrocene units (9). It is noted that the distances between the first oxidation and responding reduction peak potentials of polymers are 0.060 V at a sweep rate of 0.01 V/s, which are by far smaller than those of other electroactive organic materials such as PTMA (ca. 0.146 V), disulfide compounds (ca. 0.10–0.20 V) and conducting polymers (ca. 0.20–0.80 V) (10). The small gaps between the reduction and oxidation peaks generally imply large electrode reaction rates of the polymers, which suggest that these polymers will exert high power rates in the charge/discharge processes of battery under the constant battery process conditions. Although CV scans were continued in five cycles, the oxidation and reduction peaks of polymer scarcely changed, indicating that the electrochemical properties of these ferrocene-containing polymers are sufficiently stable.

4 Conclusions

In this research, we have synthesized and polymerized ferrocene-based optically active novel acetylene monomer **1** to obtain polymers with moderate molecular weights in

good yields. Poly(**1**) took a predominantly one-handed helical structure in CHCl_3 , CH_2Cl_2 , and THF. The helical conformation of poly(**1**) was stable to addition of MeOH and heat. The polymer exhibit electrochemical properties base on ferrocene unit.

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