

NOTES

Polymerization of 1-Ferrocenyl-1-propyne by WCl_6 -Based Catalysts[†]

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Since ferrocene-containing polymers often show characteristics such as electrical conductivity, heat resistance and redox properties, various ferrocene-containing polymers have been synthesized [*e.g.*, poly(vinylferrocene),² poly(ferrocenylene)³].

Because the polymers obtained from ferrocene-containing acetylenes possess a unique structure having alternating double bonds in their backbone and ferrocenes as pendant groups, they are expected to show interesting properties. Though the polymerization of ethynylferrocene ($HC\equiv CFc$; Fc, ferrocenyl) has been examined by various methods, the molecular weight of the polymer is no more than ~ 3000 .⁴⁻⁸ For more than a decade, we have studied the Mo- and W-catalyzed polymerization of various substituted acetylenes.⁹ The molecular weight of poly(ethynylferrocene) obtained with Mo and W catalysts was also only ~ 3000 .¹⁰

This note deals with the polymerization of 1-ferrocenyl-1-propyne ($CH_3C\equiv CFc$) by W-based catalysts. Poly(1-ferrocenyl-1-propyne) whose molecular weight is higher than 1×10^4 was obtained. The polymer showed fairly high thermal stability and relatively high electrical conductivity ($\sigma = 10^{-11}$ S cm^{-1}).

EXPERIMENTAL

The monomer was prepared by the following method with reference to that of Schlögl method:¹¹ Ferrocene (50 g) was reacted with a mixture of propionic anhydride (250 ml) and phosphoric acid (15 ml) at 120°C for 3 h. Neutralization of the reaction mixture with sodium carbonate followed by extraction with ether afforded propionylferrocene: yield 76%. The Vilsmeier reagent, prepared by adding phosphorous oxychloride (21.3 ml) dropwise to *N,N*-dimethylformamide (35.6 ml) at 0°C under nitrogen, was added dropwise to propionylferrocene (30 g) in *N,N*-dimethylformamide, and the mixture was stirred at 20°C for 5 h. An aqueous solution of sodium hydroxide (NaOH 24 g, water 600 ml) was added to terminate the reaction. Extraction with ether gave 1-ferrocenyl-1-chloro-1-propene: yield 87%. The addition of 1-ferrocenyl-1-chloro-1-propene to sodium hydride, beforehand suspended in dimethyl sulfoxide and treated with an equimolar amount of water, provided 1-ferrocenyl-1-propyne. The crude monomer was sublimed twice for purification: yield 14%.

Catalysts and cocatalysts were used without further purification. Solvents for polymeri-

[†] Part V of "Polymerization of Heteroatom-Containing Acetylenes." For Part IV, see ref 1.

zation were purified by standard methods. All polymerizations were carried out under nitrogen. The polymers formed were isolated by precipitating into acetone (when methanol was used as precipitant, the polymer was contaminated by oligomers; thus methanol was not used as precipitant). Conversions were determined by gas chromatography (silicone DC-550 3 m, 200°C), and polymer yields were measured by gravimetry.

RESULTS AND DISCUSSION

Polymerization of 1-Ferrocenyl-1-propyne by MoCl₅- and WCl₆-Based Catalysts

Table I shows results for the polymerization of 1-ferrocenyl-1-propyne by WCl₆- and MoCl₅-based catalysts. Polymerization was carried out in toluene at 60°C for 24 h. Since the monomer was not consumed at all by MoCl₅ or WCl₆ alone, mixtures of these metal halides with organometallics serving as weak reducing agents were employed as catalyst systems. When a 1:1 mixture of WCl₆ with tetraphenyltin (Ph₄Sn) was used as catalyst, an acetone-insoluble polymer was obtained in a high yield up to about 60%. On the other hand, MoCl₅-Ph₄Sn, the corresponding Mo catalyst, hardly formed the polymer. NbCl₅- and TaCl₅-based catalysts, which are capable

of polymerizing some disubstituted acetylenes,^{1,12} were also ineffective to this monomer.

Various organo-tin, -silicon, and -bismuth compounds were employed as cocatalysts. Except for Ph₄Sn, however, only tetramethyltin showed moderate activity (see Table I).

Number-average molecular weights of the poly(1-ferrocenyl-1-propyne) formed were determined by GPC (JASCO FLC-700, calibrated by standard polystyrenes). The values were 15000—16000, being higher than those ever reported for poly(ethynylferrocene).

Effects of Reaction Conditions on the Polymerization of 1-Ferrocenyl-1-propyne

The polymerization of 1-ferrocenyl-1-propyne by WCl₆-Ph₄Sn (1:1) was examined in various solvents (Table II). The monomer was hardly consumed in cyclohexane owing to the low solubility of the catalyst and polymer. In halogenated hydrocarbons such as chlorobenzene and 1,2-dichloroethane, polymerization proceeded to some extent. Among oxygen-containing solvents, anisole proved somewhat useful, whereas dioxane was hardly effective. Eventually, toluene achieved the highest polymer yield and molecular weight among the solvents examined.

Table I. Polymerization of 1-ferrocenyl-1-propyne by MoCl₅- and WCl₆-based catalysts^a

Catalyst	Conv'n	Polymer ^b	
	%	Yield/%	M_n^c
WCl ₆ -Ph ₄ Sn	73	61	16000
MoCl ₅ -Ph ₄ Sn	—	~0	—
WCl ₆ -Me ₄ Sn	36	30	15000
WCl ₆ -Ph ₃ Bi	12	~0	—
WCl ₆ -Et ₃ SiH	13	~0	—

^a Polymerized in toluene at 60°C for 24 h: [M]₀ = 0.50 M, [Cat] = [Cocat] = 30 mM.

^b Acetone-insoluble part.

^c Determined by GPC.

Table II. Solvent effects on the polymerization of 1-ferrocenyl-1-propyne^a

Solvent	Conv'n	Polymer ^b	
	%	Yield/%	M_n^c
Toluene	73	61	16000
Cyclohexane	15	~0	—
C ₆ H ₅ Cl	66	31	6300
(CH ₂ Cl) ₂	31	11	—
C ₆ H ₅ OCH ₃	65	24	7400
1,4-Dioxane	9	6	—

^a Polymerized by WCl₆-Ph₄Sn at 60°C for 24 h: [M]₀ = 0.50 M, [Cat] = [Cocat] = 30 mM.

^b Acetone-insoluble part.

^c Determined by GPC.

Effects of temperature, monomer concentration and catalyst concentration were studied for the polymerization in toluene by WCl_6-Ph_4Sn (1:1) (see Table III). The polymer yield was about 25% at 30 or 80°C but reached a maximum (~60%) at 60°C. Polymer yield increased when the initial monomer concentration was reduced, or when the catalyst concentration was enhanced. The molecular weight of the polymer was essentially independent of these conditions, and ranged from 11000 to 16000.

Structure and Properties of the Polymer

No apparent change in the structure or

Table III. Effects of temperature and monomer and catalyst concentrations on the polymerization of 1-ferrocenyl-1-propyne^a

Temp	[M] ₀	[Cat]	Convsn	Polymer ^b	
°C	M	mM	%	Yield/%	<i>M_n</i> ^c
60	0.50	30	73	61	16000
80	0.50	30	48	28	10800
30	0.50	30	—	25	13400
60	1.0	30	49	26	13000
60	0.25	30	100	65	13000
60	0.50	10	56	43	12000

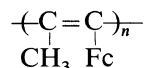
^a Polymerized by WCl_6-Ph_4Sn (1:1) in toluene for 24 h.

^b Acetone-insoluble part.

^c Determined by GPC.

properties of the polymer under the present polymerization conditions was observed. Thus, the polymer sample obtained by WCl_6-Ph_4Sn in toluene shown in Table I was analyzed in detail.

The elemental composition of the polymer agreed well with that calculated for the structure of $-(CCH_3=CFC)_n-$ [Calcd for $(C_{13}H_{12}Fe)_n$: C, 69.68%; H, 5.46%. Found: C, 68.94%; H, 5.40%]. Figure 1 shows the IR spectrum of the polymer. A broad absorption band due to C=C stretching is observed around 1600 cm^{-1} . Absorptions due to the CH_3 group are seen at 2900, 1460, and 1380 cm^{-1} . Further, a band due to the vibration of Fe-cyclopentadienyl ring appears at about 500 cm^{-1} , and those due to the C-H in-plane and out-of-plane bendings of ferrocenyl ring at 800 cm^{-1} and 1000–1100 cm^{-1} , respectively. The ¹H and ¹³C NMR spectra of polymer are shown in Figure 2, along with the assignment of each peak. These analytical and spectral data indicate the present polymer to have the following structure:



The polymer formed was a reddish brown to brown powdery solid, and soluble in aromatic hydrocarbons, cyclic ethers and halogenated hydrocarbons. The UV-visible spectrum (Shimadzu UV-190; in tetrahydrofuran) show-

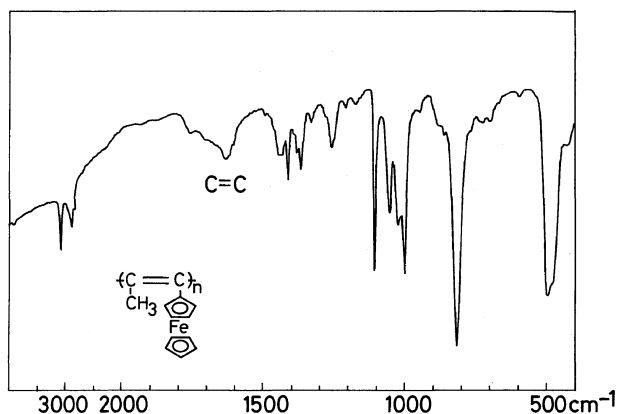


Figure 1. IR spectrum of poly(1-ferrocenyl-1-propyne) (Shimadzu IR-435; KBr disc).

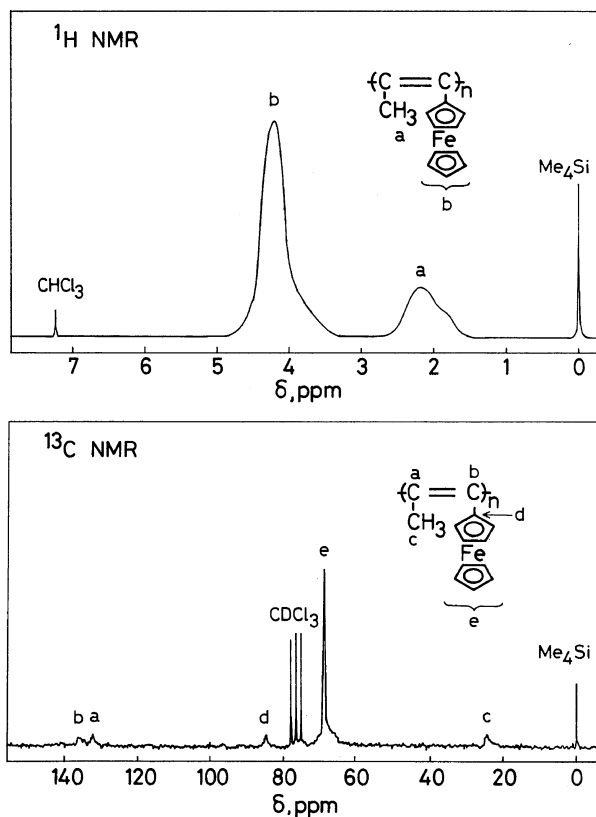


Figure 2. ^1H and ^{13}C NMR spectra of poly(1-ferrocenyl-1-propyne) (JEOL FX-90Q; CDCl_3 solution, 25°C).

ed absorption maxima at 300 nm (ϵ_{max} 2100) and 470 nm (ϵ_{max} 300). The absorption band continued up to about 570 nm.

According to the results of thermal gravimetric analysis (Shimadzu DT-20B, TG-20; heating rate $10^\circ\text{C}/\text{min}$), the polymer completely retained its original weight below $\sim 380^\circ\text{C}$ in nitrogen and below $\sim 350^\circ\text{C}$ in air. The weight loss at 500°C was 45% in nitrogen, and 50% in air. Thus this polymer is thermally fairly stable.

The electrical conductivity of the polymer at room temperature was about $5 \times 10^{-11} \text{ S cm}^{-1}$, lying in the insulator region. Electrical conductivities of most polymers from substituted acetylenes are smaller than $10^{-15} \text{ S cm}^{-1}$.⁹ In consideration of this, the conductivity of poly(1-ferrocenyl-1-propyne) is

considerably high among various polyacetylenes carrying substituents.

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