WCl₆ 및 MoCl₅계 촉매를 이용한 1-클로로-2-티에닐 아세틸렌의 중합에 관한 연구

갈 영 순 · 조 현 남 · 최 삼 권

한국과학기술원 화학과

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Polymerization of 1-Chloro—2-thienylacetylene by WCl₆-and MoCl₅-Based Catlysts

Yeong Soon Gal, Hyun Nam Cho, and Sam Kwon Choi

Department of Chemistry
Korea Advanced Institute of Science & Technology
P.O. Box 150, Chongangni, Seoul 131, Korea

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Abstract: 1-Chloro-2-thienylacetylene was prepared by the reaction of n-butyllithium with 2-(2,2-dichloro-1-fluorovinyl)thiophene which is the product of the reaction between lithiothiophene and 1,1-dichloro-2,2-difluoroethylene($CF_2=CCl_2$). The polymerization of 1-chloro-2-thienylacetylene was carried out by WCl_6 or $MoCl_5$ with cocatalysts such as organotin or organoaluminium compounds under various reaction conditions. An interesting result observed in this investigation is that WCl_6-organoaluminium and $MoCl_5$-organotin compounds are highly effective calalyst systems. The proton magnetic resonance, infrared, ultraviolet-visible, fluorescence spectra and elemental analysis indicated that the resulting polymer had a linear conjugated polyene structure containing thienyl and chloro substituents. This polymer was found to be stable up to 310°C by TGA and DSC analyses.

1. Introduction

The polymerization of acetylene and its derivatives in the presence of organometallic catalysts of Ziegler-Natta type, anionic, cationic, and radical initiators has been studied in detail[1-3].

The polymerization of disubstituted acetylenes, however, remains appreciably difficult, and virtually restricted to the following cases: diphenylacetylene[4-5], 1-phenylpropyne[6], dialkylacetylene[7], 1-chloro-2-phenylacetylene[8], 1-iodo-2-phenylacetylene[9], hexafluoro-2-butyne[10]. Recently, Katz et al. obtained mostly insoluble polymers from the polymerization of 2-butyne, 4-octyne and cyclooctyne by tungsten carbene complexes[7].

In particular, Masuda et al. reported that group (VI) metal-based catalysts were very active for the polymerization of acetylene derivatives[2-3,8,11]. We have also found that WCl_6 and $MoCl_5$-based catalyst systems are very effective for the polymerization of 2-ethynylthiophene[12] and 2-ethynylfuran[13] containing aromatic heterocycles.

This paper deals with the polymerization of 1-chloro-2-thienylacetylene by WCl_6 and $MoCl_5$-based catalysts and with the characterization of polymer formed.

2. Experimental

2-1 Materials

Thiophene was dried over calcium hydride and fractionally distilled. n-Buthyllithium (Aldrich Chemicals., 10-5 M solution in hexanes) was used as received. 1,1-Dichloro-2,2-difluoroethylene ($CF_2 = CCl_2$, PCR, bp 19°C) was used without purification. Tungsten (VI) chloride (Aldrich Chemicals., 99+%, mp 275°C) and molybdenum (V) chloride (Aldrich Chemicals., 99+%, mp 194°C) were used without further purification. Tetraphenyltin (Aldrich Chemicals., 97%, mp 270°C) was purified by recrystallizing twice from carbon tetrachloride. Tetra-n-Butyltin (Aldrich Chemical., 96%), tetramethyltin (Aldrich Chemicals., 99%),

triethylaluminium (Kanto Chemicals., 15% in hexane), tri-iso-buthylaluminium (Kanto Chemicals., 15% in hexane), and diethylaluminium chloride (Alfa Chemicals., 15% in hexane) were used without further purification.

All solvents were purified in the usual manner.

2-2. Preparation of 1-Chloro-2-thienylacetylene (CTA)

2-(2,2-Dichloro-1-fluorovinyl) thiophene was prepared by the reaction of lithiothiophene with 1,1-dichloro-2,2-difluoroethylene according to Okuhara method[14]. CTA was prepared by the reaction of 2-(2,2-dichloro-1-fluorovinyl) thiophene with 1 equiv. of n-buthyllithium at −40°C − −60°C for 2 h.

The overall reaction scheme is as follows;
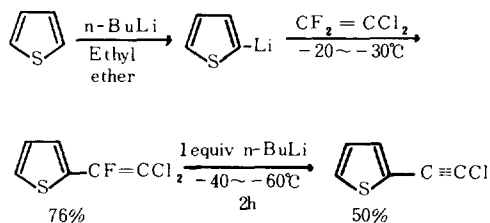
All reactions of n-buthyllithium and lithiothiophene were conducted under the nitrogen atmosphere using a T-tube for nitrogen inlet and outlet. Sodium-dried ethyl ether was exclusively used as reaction solvent.

CTA was identified by ^{1}H-NMR and IR spectroscopy.

^{1}H-NMR(CDCl$_3$); 6.8-7.0 ppm(2H), 6.6-6.7 ppm (1H).

IR (solution, NaCl); 3120 cm^{-1}, =C-H aromatic stretching band ; 2215 cm^{-1}, C ≡ C stretching band.

2-3. Polymerization Procedures

All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal halides and organometallic compounds were dissolved in chlorobenzene before use as 0.05 and 0.2 M solutions, respectively.

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The polymerization ampule was flushed with purified nitrogen and a septum was fitted to the neck. Injection of catalyst solution and monomer was done by hypodermic syringes from which air and moisture was carefully excluded. A typical procedure is as follows: In 15 ml ampule fitted with septum, solvent, catalyst solution, and cocatalyst solution (in case of need) are injected in these order. These catalyst systems were aged at 30°C for 15 min to reduce WCl$_6$ and MoCl$_5$. Finally, CTA was injected to the polymerization ampule. The polymerization was carried out at given conditions.

After a given period of polymerization, methanol containing a small amount of ammonia was added to stop further polymerization. The resulting polymer was dissolved in chloroform followed by precipitation with excess methanol. The precipitated polymer was filtered from the solution and dried to a constant weight under vacuum at 40°C for 24 h. The polymer yield was calculated by gravimetry.

2-4. Instruments and Measurements

^{1}H-NMR spectrum was recorded on a Varian T-60A spectrometer.

Infrared spectrum was taken on a Perkin-Elmer 283B spectrophotometer using potassium bromide pellet. Ultraviolet-visible and fluorescence spectra were obtained with a Carey 17 spectrophotometer and a Aminco-Bowmann spectrophofluometer with Aminco-XY recorder, respectively.

Elemental analysis was made on a Hewlett-pecked HP-185B analyzer.

Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere at heating rate of 10°C/min up to 600°C with a Perkin-Elmer TGS-1 thermobalance. Theremal transition was measured with a Perkin-Elmer DSC-1B at nitrogen atmosphere. Number-average molecular weight ($\overline{M}n$) was determinded in tetrahydrofuran solution by means of GPC-150C of Waters using a calibration curve for polystyrene.

3. Results and Discussion

3-1. Polymerization

WCl$_6$ and MoCl$_5$-based catalysts (typical metathesis catalyst) were used to synthesize poly (1-chloro-2-thienylacetylene) (PCTA), a disubstituted polyene containing thienyl and chloro substituents.
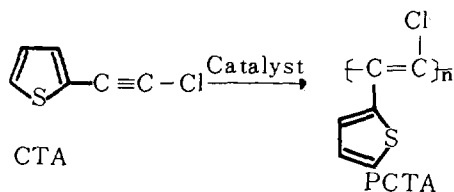
Catalyst WCl$_6$, MoCl$_5$

Cocatalst
Organotin Compounds
(Me$_4$Sn, n-Bu$_4$Sn, Ph$_4$Sn)
Organoaluminum Compounds
(Et$_3$Al. (i-Bu)$_3$Al, Et$_2$AlCl)

It was generally known that heteroatoms block the metathesis reaction because they interact with the catalyst system. However, it was found that sulfur atom of thienyl substituent does not hinder the polymerization of 2-ethynlthiophene in our previous work[12]. Thus, the same catalyst systems were also used in this polymerization.

Table 1 shows the results for the polymerization of CTA by using WCl$_6$ and organotin compounds which are highly effective cocatalysts in the polymerization of acetylene derivatives[12-13,15]. WCl$_6$ alone gives low polymer yield. WCl$_6$-R$_4$Sn catalyst systems polymerize CTA to yield a considerable amount of methanol-insoluble polymer.

The polymerization of CTA by WCl$_6$ and organoaluminium compounds is shown in Table 2. In general, organoaluminium compounds were known to be highly effective cocatalyst in the olefin metathesis reaction[16] and metathesis polymerization of cycloolefin[17]. To date, however, it has been known that the polymerization is decelerated when organoaluminium compounds

Table 1. Polymerization of 1-Chloro-2-thienylacetylene by WCl₆ and Organotin Compounds[a]

Exp. No.	Catalyst System[b] (mole ratio)	Solvent	M/C (mole ratio)	Temp. (°C)	P.Y[c] (%)	$\overline{M}_n$[d]
1	WCl$_6$	Chlorobenzene	100	60	30	6,000
2	WCl$_6$	Benzene	100	60	25	5,600
3	WCl$_6$-Me$_4$Sn(1:2)	Chlorobenzene	100	60	50	9,200
4	WCl$_6$-Ph$_4$Sn(1:1)	Chlorobenzene	100	60	45	8,400
5	WCl$_6$-n-Bu$_4$Sn(1:2)	Chlorobenzene	100	30	20	7,900
6	WCl$_6$-n-Bu$_4$Sn(1:2)	Chlorobenzene	50	60	54	7,000
7	WCl$_6$-n-Bu$_4$Sn(1:2)	Chlorobenzene	100	60	49	10,500
8	WCl$_6$-n-Bu$_4$Sn(1:3)	Chlorobenzene	100	60	40	9,900
9	WCl$_6$-n-Bu$_4$Sn(1:4)	Chlorobenzene	100	60	38	9,700

a : Polymerizations were carried for 24 h; Initial monomer concentration ([M]$_0$) was 2 M.

b : Mixtures of WCl$_6$ and organotin compound in solution were aged at 30°C for 15 min before use as catalyst.

c : Methanol-insoluble polymer.

d : Number-average molecular weight of soluble PCTA.

Table 2. Polymerization of 1-Chloro-2-thienylacetylene by WCl₆ and Organoaluminum Compounds[a]

| Exp. No.	Catalyst System[b] (mole ratio)	M/C (mole ratio)	[M]$_0$	Temp. (°C)	P.Y[c] (%)	$\overline{M}_n$[d]
1	WCl$_6$-Et$_3$Al(1:2)	100	2	60	67	6,300
2	WCl$_6$-(i-Bu)$_3$Al(1:2)	100	2	60	75	7,200
3	WCl$_6$-Et$_2$AlCl(1:2)	100	2	60	83	17,000
4	WCl$_6$-Et$_2$AlCl(1:2)	50	2	60	90	13,200
5	WCl$_6$-Et$_2$AlCl(1:2)	200	2	60	66	18,200
6	WCl$_6$-Et$_2$AlCl(1:2)	500	2	60	19	—
7	WCl$_6$-Et$_2$AlCl(1:2)	100	1	60	72	15,000
8	WCl$_6$-Et$_2$AlCl(1:2)	100	2	30	59	8,800

a : Polymerization for 24 h in chlorobenzene.

b : Mixture of WCl$_6$ and organoaluminum compounds in chlorobenzene were aged at 30°C for 15 min before use as catalyst.

c : Methanol-insoluble polymer.

d : Number-average molecular weight of soluble PCTA.

are used as cocatalyst in the polymerization of acetylene derivatives[12-13,17]. But, to our surprise, organoaluminium compounds exhibited high cocatalytic activity in this polymerization.

The polymer yield according to organoaluminium compounds was increased in the following order;

$$Et_2AlCl > (i-Bu)_3Al > Et_3Al$$
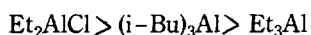
The polymer yield and molecular weight of the resulting PCTA were found to be strongly depen-

dent on the mole ratio of CTA to catalyst (Exp. No; 3,4,5,6). This result is consistent with the polymerization of 2-ethynylthiophene[12]. The time dependence curve of the polymerization of CTA by WCl$_6$-Et$_2$AlCl (1:2) catalyst system is shown in Fig 1. The polymerization proceeded rapidly within 1 h to the extent of 50% and then increased slowly.

The PCTAs obtained by WCl$_6$-based catalyst were black or dark-brown colored powder and

partially soluble in organic solvents. The number-average molecular weights (Mn) of this soluble PCTA were in a range of 5,600-18,200.

Table 3 shows the results for the polymerization of CTA by MoCl$_5$ in the presence of organotin and organoaluminium compounds. The polymerization was carried out in chlorobenzene at 60°C for 24 h. When Me$_4$Sn and n-Bu$_4$Sn were used as cocatalyst, the reaction proceeded quantitatively
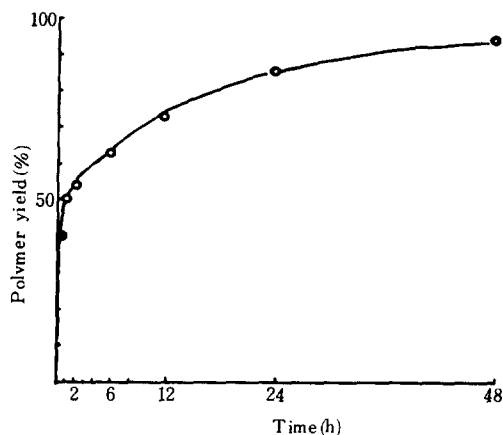

Fig. 1. Time dependence curve of the polymerization of 1-chloro-2-thienylacetylene by WCl$_6$-ET$_2$AlCl(1:2); in chlorobenzene, 60°C, [M]$_o$ = 2M, M/C = 100.

to give methanol-insoluble polymers having high molecular weights (Mn = 13,200-20,900). Ph$_4$Sn also produces a moderate yield of methanol-insoluble polymer.

On the other hand, organoaluminium compounds which are highly active cocatalyst in the polymerization of CTA by WCl$_6$-based catalysts exhibit no cocatalytic activity. The PCTA's obtained by MoCl$_5$-based catalysts were generally soluble in aromatic and halogenated hydrocarbon solvents (ie; chloroform, chlorobenzene, DMSO, diglyme, and THF etc).

3-2. Structure of PCTA

The values of elemental analysis for PCTA agreed well with the theoretical values (Calcd. for (C$_6$H$_3$ClS)$_n$: C, 50.5%; H, 2.1%; Cl, 24.9%; S, 22.5%. Found: C, 50.7%; H, 2.2%; Cl, 24.6%; S, 22.5%).

The ^{1}H-NMR spectrum of PCTA is shown in Fig 2. A broad peak appeared at 6.5-7.8 ppm in the ^{1}H-NMR spectrum is assignable to the protons on the thienyl substituent. The IR spectrum (Fig. 3) gives the aromatic =C-H stretching band at 3120 cm^{-1} and it shows an absorption band at 1600 cm^{-1} owing to the conjugated double bonds. The band at 800 cm^{-1} is due to the =C-Cl stretching

Table 3. Polymerization of 1-Chloro-2-thienylacetylene by MoCl$_5$-Based Catalysts[a]

Exp. No.	Catalyst System[b] (mole ratio)	M/C (mole ratio)	Temp. (°C)	P.Y[c] (%)	Mn[d]
1	MoCl$_5$	100	60	60	10,200
2	MoCl$_5$-n-Bu$_4$Sn(1:2)	100	60	93	16,100
3	MoCl$_5$-n-Bu$_4$Sn(1:4)	100	60	75	13,200
4	MoCl$_5$-Me$_4$Sn(1:2)	100	60	95	20,900
5	MoCl$_5$-Me$_4$Sn(1:2)	50	30	70	15,000
6	MoCl$_5$-Ph$_4$Sn(1:2)	100	60	81	15,700
7	MoCl$_5$-Et$_3$Al(1:2)	100	60	49	6,100
8	MoCl$_5$-(i-Bu)$_3$Al(1:2)	100	60	55	6,400
9	MoCl$_5$-Et$_2$AlCl(1:2)	100	60	67	8,700

a : Polymerization for 24 h in chlorobenzene; [M]$_o$ = 2 M

b : Mixture of MoCl$_5$ and cocatalyst in chlorobenzene was aged at 30°C for 15 min before use as catalyst.
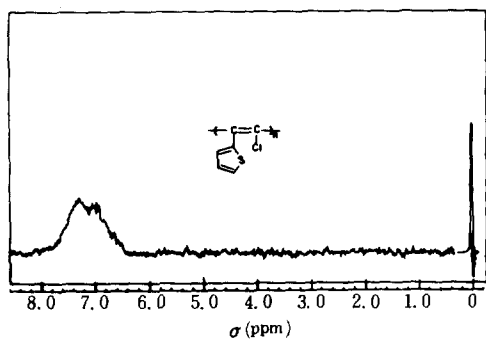
c : Methanol-insoluble polymer.

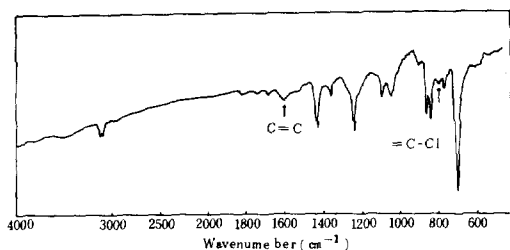**Fig. 2.** ¹H-NMR spectrum of poly (1-chloro-2-thieny-lacetylene) (in CDCl₃).

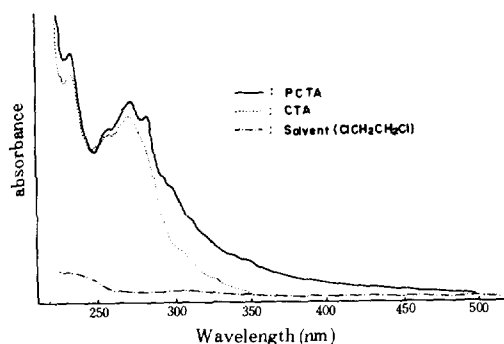**Fig. 3.** IR spectrum of poly (1-chloro-2-thienylacety-lene) in KBr pellet.

Fig. 4. UV and visible spectra of 1-chloro-2-thienylace-tylene and poly (1-chloro-2-thienylacetylene).

Fig. 5. The fluorescence spectra of 1-chloro-2-thienl-acetylene and poly (1-chloro-2-thienylace-tylene).
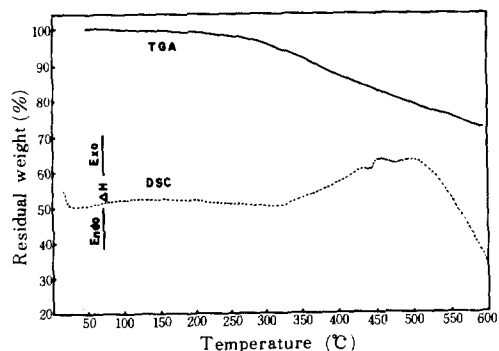
Fig. 6. TGA and DSC thermograms of poly (1-chloro-2-thienylacetylene) produced by MoCl₅-Me₄Sn (1:2).

band. The most strong band at 690 cm⁻¹ is at-tributed to the C-H out of plane deformation of thienyl substituent.

The UV spectra of CTA and PCTA were obtained in 1,2-dichloroethane (Fig. 4). A charac-teristic peak of conjugated polymer, broad and weak $\pi - \pi^*$ absorption, appeared in the visible region in the case of PCTA.
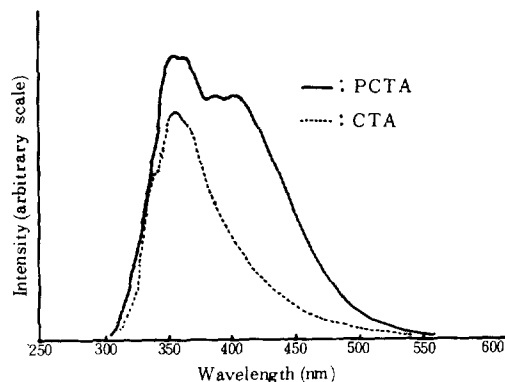
The emission spectra of CTA and PCTA were also obtained in 1,2-dichloroethane (Fig. 5). There emission spectra excited at wavelength of 320 nm shows a strong emission at 355 and 412 nm. The emission at 412 nm may be caused by the transi-tion from the excited singlet state to the ground state of conjugated double bonds.

3-3. Thermal Properties of PCTA

TGA and DSC thermograms of PCTA are shown in Fig 6. TGA curve of PCTA obtained by MoCl₅-n-Bu₄Sn (1:2) showed that this retained 95% of its original weight at 310°C, 90% at 373°C, and 72% at 600°C. The DSC curve show-ed that the resulting polymer started to fuse at

310°C with a large exotherm. This melting process involved the decomposition of the polymer to a cross-linked solid. This was confirmed by the small amount of dark solid left after heating up to 600°C.

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