WCl$_6$ 및 MoCl$_5$계 촉매에 의한 2-에티닐푸란의 중합과 2-에티닐티오펜과의 공중합

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Polymerization of 2-Ethynylfuran and Its Copolymerization with 2-Ethynylthiophene by WCl$_6$- and MoCl$_5$- Based Catalysts

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Abstract: The polymerization of 2-ethynylfuran was carried out by WCl$_6$ or MoCl$_5$ associated with cocatalysts such as organotin and oranoaluminum.compounds under various reaction conditions. The effects of monomer to catalyst mole ratio, solvent, cocatalyst, and temperature on the polymerization were studied. The highest yield (43%) and the highest molecular weight ($\overline{\text{Mn}}$: 12,000) were obtained when the mole ratios of 2-ethynylfuran to WCl$_6$ as a catalyst and WCl$_6$ to n-Bu$_4$Sn as a cocatalyst are 100 and 4, respectively. WCl$_6$-based catalysts were more effective than MoCl$_5$-based catalysts. Poly(2-ethynylfuran) (PEF)s obtained were partially soluble in organic solvents such as chloroform, toluene and 1,2-dichloroethane. The nuclear magnetic resonance, infrared, and ultraviolet-visible spectra indicated that the resulting soluble polymer has a linear conjugated polyene structure containing furyl substituents. Copolymerization of 2-ethynylfuran with 2-ethynylthiophene exhibited lower reactivity of 2-ethynylfuran in comparison with 2-ethynylthiophene.

INTRODUCTION

The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of linear conjugated polymers. The simplest of the conjugated polymers, polyacetylene, has been synthesized with a wide variety of catalysts[1-2], of which the procedure described by Shirakawa et al.[3-5] has received the most attention. On the other hand, substituted polyenes such as poly(methylacetylene)[6], poly(t-butylacetylene)[7], poly(N-ethynylcarbazole)[8], poly(5-ethynylacenaphthene)[9], poly(phenylacetylene)[10-11], and poly(α-

ethynylnaphthalene)[12] have been prepared and subsequently characterized. So far, however, there have been no reports on the preparation of poly(2-ethynylfuran) (PEF), a polyene containing furyl substituents.

Various catalysts have been used for the polymerization of acetylene derivatives. Especially, the polymerization of phenylacetylene has been carried out by the catalyst SnCl$_4$,[13] CCl$_3$COOH,[14] ArCr-(CO)$_3$,[15] Co(NO$_3$)$_2$-NaBH$_4$,[16] AlEt$_3$-Ti(OBu)$_4$,[17] BF$_3$-OEt$_2$,[18] CF$_3$COOH,[18] and as well as heat.[19] The average molecular weights obtained from these catalysts were generally low, mostly in the range of 300-

10,000. In recent years, it was reported that group VI transition metal-based catalysts are very effective for the polymerization of phenylacetylene.[20-22] We have also found that WCl_6 and $MoCl_5$-based catalyst systems are very effective for the polymerizations of 2-ethynylthiophene[23] and 1-chloro-2-thienylacetylene.[24] This paper deals with the polymerization of 2-ethynylfuran and its copolymerization with 2-ethynylthiophene by WCl_6-and $MoCl_5$-based catalysts and with the characterization and physical properties of polymer formed.

EXPERIMENTAL

Materials

Furan (Aldrich Chemicals, 99 + %) was dried over sodium and fractionally distilled. n-Butyllithium (Aldrich Chemicals, 10.5M in hexane) and 1,1-dichloro-2,2-difluoroethylene ($CF_2 = CCl_2$, P.C.R., b.p. 19°C) were used as received. WCl_6 and $MoCl_5$(Aldrich Chemicals, 99 + %, resublimed) were used without further purification. Tetraphenyltin was purified by recrystallizing twice from carbon tetrachloride. Tetra-n-butyltin (Aldrich Chemicals, 98%), tetramethyltin(Aldrich Chemicals, 99%), triethylaluminum (Kanto Chemicals, 25% in hexane) and triisobutylaluminum (Kanto Chemicals, 25% in hexane) were used without further purification. All the polymerization solvents (reagent grade) were fractionally distilled before use under nitrogen atmosphere.

Preparation of 2-Ethynylfuran(2-EF)

2-EF was prepared by new synthetic method of arylacetylenes using 1,1-dichloro-2,2-difluoroethylene reported by Okuhara.[25]

Preparation of 2-(2,2-Dichloro-1-fluorovinyl)furan

To a stirred, ice-cooled solution of furan (100g, 1.47 mol) in ethyl ether (Na-dried, 600 ml) was added n-butyllithium (10.5 M in hexane, 143ml), for 30 min. The resulting solution was refluxed for 1 hr. and $CF_2=CCl_2$ (200g, 1.5 mol) in 100ml ice-cooled ether was added to the lithiofuran solution over a period of 1 hr. at –20––40°C. After 4 hrs. of refluxing 162g of 2-(2,2-dichloro-1-fluorovinyl)furan (b.p: 80°C/32mmHg), were obtained as the sole product.

Preparation of 2-EF

To a stirred, cooled solution of 2-(2,2-dichloro-1-fluorovinyl)furan (85g, 0.47 mol) in ethyl ether(Na-dried, 400 ml) was added n-butyllithium (10.5 M in hexane, 89.5 ml), over a period of 2 hrs. at -50°C — -60°C.

Work-up procedure was performed by conventional methods of hydrolysis by ice plus hydrochloric acid followed by extraction with ether. In this case, phase separation was considerably difficult because the reaction mixtures contain lithium fluoride, and lithium fluoride should be removed by suction filtration. After washing with 10% sodium bicarbonate solution two times, the ether solution was dried with anhydrous magnesium sulfate for overnight.

After the solvent was removed by simple distillation, the residue was fractionally distilled. The pure 2-EF of 32g (0.35 mol, 74%) was obtained; b.p. 40-42°C/80 mmHg. 2-EF was identified by ^{1}H-NMR and IR spectroscopy.

^{1}H-NMR(CDCl$_3$); 3.25 ppm(1H), 6.2 ppm(1H), 6.5 ppm(1H), 7.2 ppm(1H).

IR(Solution, NaCl); 3300 cm^{-1}: $\equiv$ C–H stretching, 3155 cm^{-1}: C–H(aromatic) stretching, 2120 cm^{-1}: C $\equiv$ C stretching.

This compound has a characteristic lachrymatory odor and exhibits yellow-reddish color when it contacts with air at room temperature, and it was stored at –20°C under nitrogen before use.

Preparation of 2-Ethynylthiophene (2-ET)

2-ET was prepared by reaction of n-butyllithium with 2-(2,2-dichloro-1-fluorovinyl)thiophene which was obtained from the reaction of lithiophene with 1,1-dichloro-2,2-difluoroethylene according to the Okuhara method.[25]

Polymerization

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. The catalyst solutions were prepared as follows: (a) 0.05 M solution of WCl_6 or $MoCl_5$ in various solvents, (b) 0.2 M solutions of n-Bu$_4$Sn, (i-Bu)$_3$Al, and Et$_3$Al in chlorobenzene(contain residual hexane from master solution in case of organoaluminum compounds).

A polymerization ampule equipped with rubber septum was flushed with purified nitrogen. Injection of monomer and catalyst solutions was done by means of hypodermic syringes. Typical polymerization procedures are as follows.

Polymerization of 2-EF by WCl₆ or MoCl₅ alone
Injection order of reactants is as follows. A calculated amount of solvent and catalyst solution according to the initial monomer concentration ($[M]_0$) and mole ratio of 2-EF to catalyst are injected through septum. Finally, 2-EF was injected to the catalyst solution.

Polymerization of 2-EF by Binary Catalyst Systems
The calculated amount of chlorobenzene, catalyst solution (WCl₆ or MoCl₅ in chlorobenzene) and cocatalyst solution(organotin or organoaluminum compounds in chlorobenzene) are injected in that order. These catalyst systems were aged at 30°C for 15 min. Finally, 2-EF are injected to the catalyst solution.

Copolymerization of 2-EF with 2-ET The calcualted amount of 2-EF and 2-EF according to comonomer feed ratios (2-EF: 2-ET = 7:3, 5:5, 3:7) and chlorobenzene are injected. After mixing two monomer exclusively, WCl₆ and n-Bu₄Sn solution (in chlorobenzene) were injected to the polymerization ampule. The polymerization was carried out at 60°C for 12hrs..

Work-up Procedure After a given period of polymerization, polymerization was terminated by adding a small amount of methanol. 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 hrs. The polymer yield (methanol-insoluble) was calculated by gravimetry.

Instruments
¹H-NMR spectra were recorded on a Varian T-60A Spectrometer. Infrared spectra were taken on a Perkin-Elmer 283B Spectrophotometer using potassium bromide pellets. Ultraviolet-visible spectra were obtained with a Carey 17 Spectrophotometer. Thermogravimetric analyses(TGA) were performed in a nitrogen atmosphere at a heating

rate of 10°C/min up to 600°C with a Perkin-Elmer TGS-1 thermobalance. Thermal transitions were measured with a Perkin-Elmer DSC-1B at a heating rate of 10°C/min under nitrogen atmosphere.

Number-average molecular weights (M̄n) were determined by means of GPC 150C of Waters using a calibration curve for polystyrene.

RESULTS AND DISCUSSION

Polymerization
The polymerization of 2-EF was carried out by transition metal catalysts such as WCl₆ or MoCl₅ with various cocatalysts

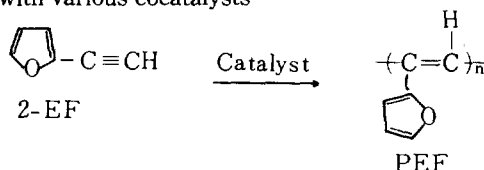
Table 1 shows the results for the polymerization of 2-EF by WCl₆ under various reaction conditions. It is generally known that heteroatoms hinder metathesis reaction because they interact with the catalyst system. In order to understand the effect of furyl substituent, the effect of 2-EF to catalyst mole ratio was investigated (Exp. No., 1, 2 and 3). The polymer yields were found to be strongly dependent on the mole ratio of 2-EF to catalyst. The dependence of polymer yield on the mole ratio of monomer to catalyst was greater than that for the polymeriza-

Table 1. Polymerization of 2-Ethynylfuran by WCl₆[a]

Exp. No.	2-EF/WCl₆ (mole ratio)	$[M]_0$	Temp. (°C)	Time (hr.)	P.Y[b](sol[c]) (%)
1	100	1	60	1	33 (20)
2	200	1	60	1	10 (30)
3	500	1	60	1	trace
4	100	2	60	1	34 (18)
5	100	1	30	1	19 (15)
6	100	1	30	12	25 (15)
7	100	1	0	12	trace

[a]; Polymerization solvent: chlorobenzene.
[b]; Methanol-insoluble polymer.
[c]; Soluble portion in chloroform.

Table 2. Polymerization of 2-Ethynylfuran by WCl_6—Based Catalysts[a]

Exp. No.	Catalyst system[b] (mole ratio)	P.Y[c](sol[d]) (%)
1	$WCl_6(1).Me_4Sn(4)$	36(60)
2	$WCl_6(1).n\text{-}Bu_4Sn(4)$	43 (55)
3	$WCl_6(1).Ph_4Sn(4)$	35 (20)
4	$WCl_6(1).Et_3Al(4)$	10 (—)
5	$WCl_6(1).(i\text{-}Bu)_3Al(4)$	15 (—)

[a]; Polymerization was carried out at 60°C for 12 hrs. in chlorobenzene. Initial monomer concentration ($[M]_0$) and 2-EF/Cat. mole ratio were 2M and 100, respectively.
[b]; Mixture of WCl_6 and cocatalyst in chlorobenzene was aged for 15 min. at 30°C before use as catalyst.
[c]; Methanol-insoluble polymer.
[d]; Soluble portion in chloroform.

Table 3. Solvent Effect on the Polymerization of 2-Ethynylfuran[a]

Exp. No.	Solvent	P.Y[b](Sol[c]) (%)
1	Chlorobenzene	43 (55)
2	Benzene	35 (60)
3	Toluene	42 (50)
4	CCl_4	39 (40)
5	$CHCl_3$	30 (45)
6	CH_2Cl_2	20 (47)

[a]; Polymerization was carried out at 60°C for 12 hrs. by $WCl_6(1).n\text{-}Bu_4Sn(4)$. Initial monomer concentration ($[M]_0$) and 2-EF/Cat. mole ratio were 2M and 100, respectively.
[b]; Methanol-insoluble polymer.
[c]; Soluble portion in chloroform.

Table 4. Polymerization of 2-Ethynylfuran by $MoCl_5$—Based Catalysts[a]

Exp. No.	Catalyst System[b] (mole ratio)	Temperature (°C)	P.Y[c](Sol[d]) (%)
1	$MoCl_5$	60	19 (68)
2	$MoCl_5$	30	15 (70)
3	$MoCl_5(1).n\text{-}Bu_4Sn(4)$	60	33 (52)
4	$MoCl_5(1).Me_4Sn(4)$	60	25 (87)
5	$MoCl_5(1).Ph_4Sn(4)$	60	8 (—)
6	$MoCl_5(1).Et_3Al(4)$	60	5 (—)

[a]; Polymerization for 12 hrs. in chlorobenzene. Initial monomer concentration ($[M]_0$) and 2-EF/Cat. mole ratio 2M and 100, respectively.
[b]; Mixture of $MoCl_5$ and cocatalyst in chlorobenzene were aged at 30°C for 15 min. before use as catalyst.
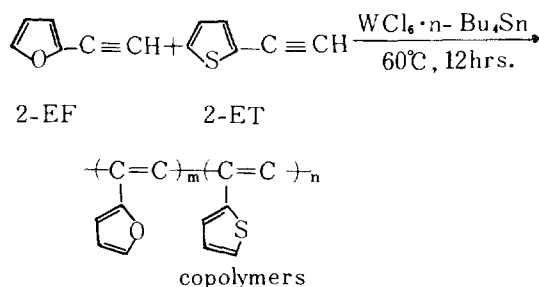[c]; Methanol-insoluble polymer.
[d]; Soluble portion in chloroform.

tion of phenylacetylene. When the mole ratios of 2-EF to WCl_6 were 200 and 500, the catalytic activities were shown to be low. Similar result was observed in the polymerization of 2-ethynylthiophene in our previous work.[23]

This low activity may be due to the interaction of the heteroatom (oxygen of furyl substituent) with the catalyst, which hinders the coordination of the triple bond. In general, poly(2-ethynylfuran) (PEF)'s obtained were partially soluble in chloroform. The portion soluble in chloroform is less than 30% of polymer yield.

Table 2 shows the results for the polymerization of 2-EF by WCl_6 associated with cocatalysts such as organotin- and organoaluminum compounds. When organotin compounds were used as cocatalysts, considerable cocatalytic effect was observed.

The maximum polymer yield (43%) was obtained when $n\text{-}Bu_4Sn$ was used as cocatalyst. Organoaluminum compounds such as Et_3Al and $(i\text{-}Bu)_3Al$ which are highly effective cocatalyst in the olefin metathesis reaction[26] and metathesis polymerization of cycloolefin[27] exhibit no cocatalytic activity.

The solvent effect on polymer yield was also investigated (Table 3). 2-EF was easily polymerized in various solvents. The polymer yield decreased in the following order;

Chlorobenzene ≒ Toluene > CCl_4 > Benzene > $CHCl_3$ > CH_2Cl_2.

Table 4 shows the results for the polymerization of 2-EF by $MoCl_5$-based catalysts. The catalytic activities of $MoCl_5$-based catalysts were less effective than those of WCl_6-based catalysts. This result is in agreement with the polymerization of phenylacetylene.[20] $n\text{-}Bu_4Sn$ was also found to be the most effective cocatalyst among $MoCl_5$-based catalyst systems. In the polymerization of 2-EF by $MoCl_5$—

based catalysts, the polymer yield is generally low. However, the portion soluble in organic solvent was greater than that of PEF obtained by WCl_6-based catalysts. Et_3Al did not also show any cocatalytic activity. The number average molecular weights ($\overline{M}n$) of the resulting soluble polymer(PEF) were in the range of 5,800-12,000 according to the polymerization conditions used (Table 5).

Copolymerization of 2-EF with 2-Ethynylthiophene

In order to compare the reactivities of 2-EF and 2-ET in polymerization, the copolymerization with 2-ET at various monomer feed ratios was carried out at 60°C for 12 hrs. (solvent: chlorbenzene)

The results of copolymerization are shown in Table 6. The polymer yield and inherent viscosity of the resulting polymer were increased as the feed ratio of 2-ET was increased.

Poly(2-ethynylthiophene) was mostly soluble in organic solvents. On the other hand, as the feed ratio of 2-EF in copolymerization is increased, insoluble portion of copolymer was increased. Sulfur analyses of the three copolymers strongly suggested greater reactivity of 2-ET in comparison with 2-EF.

This low reactivity of 2-EF can be attributable to the more strong interaction of oxygen of furyl substituent with catalyst system than that of sulfur of thienyl substituent with catalyst system and low aromaticity(high vinyl character) of furyl substituent.

The formation of some cross-linked polymer (insoluble) is due to the high vinyl character of furyl substituent (low aromaticity[28] compared to phenyl or thienyl substituent).

Characterization of PEF and Its Copolymers

The ^{1}H-NMR spectra of PEF, PET and

Table 5. Number-Average Molecular Weights of Some Poly(2-ethynylfuran)

Sample (A-B)[a]	Catalyst	$\overline{M}n$ [b]
1-1	WCl_6	8,200
2-2	WCl_6.n-Bu_4Sn	12,000
3-1	$MoCl_5$	4,700
3-3	$MoCl_5$.n-Bu_4Sn	5,800

[a]; A = Table Number, B = Exp. Number.
[b]; Number average molecular weights of soluble poly(2-ethynylfuran).

Table 6. Copolymerization of 2-Ethynylfuran with 2-Ethynylthiophene[a]

Exp. No.	Weight ratio		P.Y(sol) (%)	η_{inn}[b]	Sulfur analysis(%)	
	2-EF	2-ET			Calcd.[c]	Found
1	1.0	0	43(55)	0.08	—	—
2	0.7	0.3	57(66)	0.09	9.9	14.5
3	0.5	0.5	70(81)	0.11	16.0	20.2
4	0.3	0.7	75(89)	0.13	21.7	25.3
5	0	1	92(97)	0.14	29.7	30.4

[a]; Polymerization at 60°C for 12 hrs. in chlorobenzene Catalyst: WCl_6.n-Bu_4Sn, M/C:100, $[M]_0$:2M.
[b]; Concentration of 0.5g/dl in chloroform at 30°C.
[c]; The value of sulfur analysis when it is supposed that the reactivities of 2-EF and 2-ET were equal.

copolymer (2-EF:2-ET = 5:5) are shown in Fig. 1. The ^{1}H-NMR spectrum of PEF soluble in $CHCl_3$ shows broad peak at 7~7.7 ppm owing to 5-position proton of furyl substituent and at 5.4~7 ppm due to the 3,4-position proton of furyl substituent and vinyl proton of conjugated backbone.

The ^{1}H-NMR spectrum of copolymer shows a composite broad peak at 5.4~7.8 ppm owing to furyl, thienyl, and vinyl proton. The IR spectra of PEF, PET and copolymer (2-EF:2-ET = 5:5) are shown in Fig. 2. The IR spectrum of PEF gives the aromatic=C-H stretching band at 3155 cm^{-1} and it shows an absorption at 1600 cm^{-1} owing to the conjugated double bonds. The IR spectrum of copolymer (2-EF:2-ET = 5:5) shows the characteristic bands of both PEF and PET, ie. 1500-1560
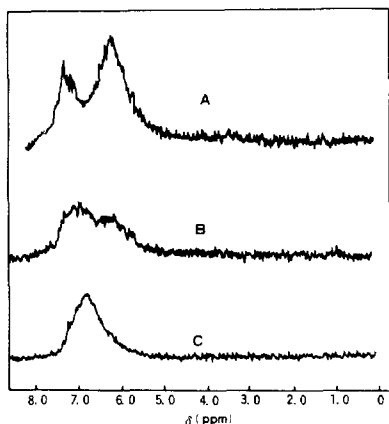
Fig. 1. ^{1}H-NMR spectra of poly(2-ethynylfuran) (A), copolymer(2-EF:2-ET = 5:5) (B) and poly(2-ethy-nylthiophene) (C) in CDCl$_3$.
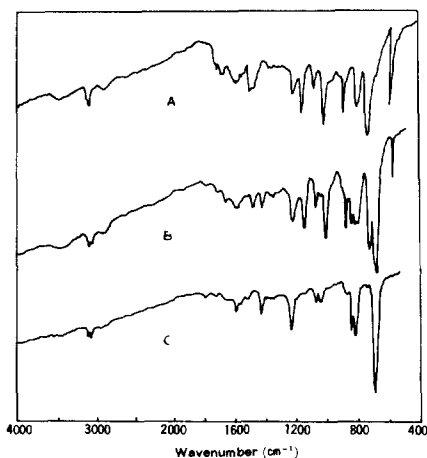

Fig. 2. IR spectra of poly(2-ethynylfuran) (A), copolymer (2-EF:2-ET = 5:5) (B) and poly(2-ethynylthio-phene) (C) in KBr pellet.

Fig. 3. UV and visible spectra of poly(2-ethynylfuran) and 2-ethynylfuran (solvent: 1,2-dichloroethane).

Fig. 4. TGA and DSC thermograms of poly(2-ethy-nylfuran) prepared by WCl$_6$.n-Bu$_4$Sn.

cm^{-1} and 1050 cm^{-1} of PEF, and 1235cm^{-1} and 824-850 cm^{-1} (two bands) of PET. The intensity of bands at 1500-1560 cm^{-1} and 1050 cm^{-1} decreases gradually as the feed ratio of 2-EF in the copolymerization is decreased.

The UV-visible spectrum of PEF was obtained in 1,2-dichloroethane (Fig. 3). The absorption of PEF continued as far as 500 nm indicating that the conjugated system is long. This absorption at long wavelength is attributed to the $\pi \rightarrow \pi^*$ absorption of conjugated backbone. These spectral data in-
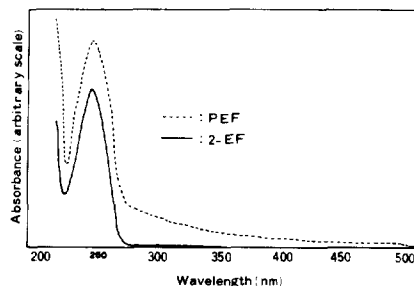
dicate the present soluble polymer to have con-jugated polyene structure containing aromatic heterocycles.

Physical Properties of Poly(2-ethynlfuran)

PEF was brown or black colored powder. It has been known that polyacetylene is insoluble in any solvent, regardless of its geometric structure. On the other hand, poly(phenylacetylene)[21] and poly(2-ethynylthiophene)[23] is soluble in aromatic and halogenated hydrocarbons. Poly(1-phenylpropyne), a polymer of disubstituted acetylene, was soluble but poly(diphenylacetylene)[29] was insoluble in any common solvents. This PEF was partially soluble in organic solvents. From these results, it can be deduced that the solubility of acetylenic polymers depends on the nature (aromaticity) and number of substituent.

The TGA curve (Fig. 4) of PEF prepared by WCl$_6$.n-Bu$_4$Sn showed that it retained 95% of its original weight at 320°C, 90% at 410°C and 52% at 600°C. The DSC thermogram shows that the PEF start to diffuse at about 250°C with a large ex-

otherm. This may be attributed to the decomposition of the polymer and to the formation of a cross-linked solid due to the furyl substituents and double bonds in the polymer backbone.

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