

## 전이금속클로라이드와 유기알루미늄 화합물에 의한 2-에티닐피리딘의 중합

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## Polymerization of 2-Ethynylpyridine by Transition Metal Chloride and Organoaluminum Compounds

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요 약 : 전이금속클로라이드( $WCl_6$ ,  $MoCl_5$ ,  $TiCl_4$  등)와 유기알루미늄 화합물( $EtAlCl_2$ ,  $Et_2AlCl$  등)을 사용하여 여러 반응조건하에서 2-에티닐피리딘의 중합을 시도하였다. 중합에 있어서 촉매에 대한 몰비 효과, 조촉매 및 시간 효과등을 연구하였다. 가장 좋은 결과 (중합수율=78%,  $\eta_{inh}=0.16$ )는  $WCl_6$ 에 대한 2-에티닐피리딘 몰비와  $WCl_6$ 에 대한  $EtAlCl_2$ 의 몰비가 각각 50과 4였을때 나타났다.  $WCl_6$ -,  $MoCl_5$ -, 및  $TiCl_4$ -계 촉매 모두가 본 중합에 있어서는 유사한 촉매활성을 보였다. 특히  $EtAlCl_2$ ,  $Et_2AlCl$  같은 유기알루미늄 화합물이 매우 좋은 조촉매로 밝혀졌다.  $^1H$ -NMR, IR, UV-스펙트럼으로 확인한 결과 생성된 중합체는 피리딘 치환기를 갖는 공액 폴리엔구조임을 알 수 있었다. 폴리(2-에티닐피리딘)은 메탄올, 포름산, DMF 와 같은 극성용매에 완전히 용해하였다.

**Abstract:** The polymerization of 2-ethynylpyridine was carried out with transition metal chlorides ( $WCl_6$ ,  $MoCl_5$ ,  $TiCl_4$ , etc.) and organoaluminum compounds ( $EtAlCl_2$ ,  $Et_2AlCl$ , etc.) under various reaction conditions. The effects of monomer to catalyst mole ratio, cocatalyst, and time on the polymerization were studied. The best result (polymer yield=78%,  $\eta_{inh}=0.16$ ) were obtained when the mole ratios of 2-ethynylpyridine to  $WCl_6$  and  $EtAlCl_2$  to  $WCl_6$  are 50 and 4, respectively.  $WCl_6$ -,  $MoCl_5$ -, and  $TiCl_4$ -based catalysts exhibited a similar catalytic activities in this polymerization. Especially, organoaluminum compounds such as  $EtAlCl_2$  and  $Et_2AlCl$  were very effective cocatalysts. The  $^1H$ -NMR, IR, and UV spectra indicated that the resulting polymer has a linear conjugated polyene structure containing pyridine substituent. The poly(2-ethynylpyridine) was soluble in polar solvents such as methanol, formic acid, and DMF.

## INTRODUCTION

$WCl_6$  and  $MoCl_5$  are well known as catalyst components of the olefin metathesis reaction.<sup>1</sup> Usually these metal halides need organometallics such as alkylaluminum chlorides and alkylolithiums to catalyze the metathesis reaction.<sup>2</sup> In a previous paper, it was reported that  $WCl_6$  and  $MoCl_5$  work as effective catalysts for the polymerization of phenylacetylene.<sup>3</sup> In the course of the investigation on the effects of organometallics for the polymerization of phenylacetylene by  $WCl_6$  and  $MoCl_5$ ,  $Ph_4Sn$  was found to have a great activity. That is, the addition of  $Ph_4Sn$  increased the final conversion but also greatly increased the initial rate.<sup>4</sup> On the other hand, the polymerization was decelerated when  $Et_3Al$ ,  $Et_2AlCl$ , or  $EtAlCl_2$  were added to the  $WCl_6$  solution.<sup>5</sup>

The polymerization of 2-ethynylpyridine(2-EP) has been attempted so far by thermal methods.<sup>6,7</sup> However, there have no reports on the polymerization of 2-EP by transition metal catalysts such as  $WCl_6$  and  $MoCl_5$ . In the present work, we examined the catalytic activities of various transition metal catalysts, which are effective for the polymerization of phenylacetylene<sup>4</sup> and 2-ethynylthiophene,<sup>8</sup> in the polymerization of 2-EP. Further, the structure and properties of poly(2-ethynylpyridine) (P2EP) formed were studied.

## EXPERIMENTAL

### Materials

2-Vinylpyridine(Aldrich Chemicals., 97%) was used after distillation. Sodium amide(Aldrich Chemicals., 95%) was used as received.  $WCl_6$  and  $MoCl_5$ (Aldrich Chemicals., 99+%, resublimed), and  $TiCl_4$ (Hayashi Pure Chemicals., Extra pure reagent) were used without further purification.

Tetraphenyltin was recrystallized from carbon tetrachloride. Other organometals were used as purchased. Solvents for polymerization were distilled twice from calcium hydride under nitrogen atmosphere before use.

### Preparation of 2-EP

The monomer(2-EP) was prepared by the following bromination-dehydrobromination method.<sup>9</sup> To a stirred solution of 1 mole of freshly distilled 2-vinylpyridine in 600 ml of dry ether were added with cooling between  $-60^\circ C$  and  $-30^\circ C$  165g of bromine(about 30 min.). After the addition, the cooling bath was removed and the temperature was allowed to rise to  $0^\circ C$ . In the same time, a suspension of 4 moles of sodium amide in 2.5 L of liquid ammonia was prepared in the 5 L three neck flask. The cold( $0^\circ C$ ) solution of the bromine adduct was poured in a number of portions into the sodium amide suspension (in about 30 min.). A vigorous reaction ensued. The viscous residue which remained in the first reaction flask was thoroughly rinsed with ether. The washings were added to the sodium amide suspension. Immediately after the addition of the adduct, the ammonia was evaporated by placing the flask in a water bath of  $60^\circ C$ . When the stream of ammonia had become very faint, 300ml of ether were added and subsequently, as quickly as possible, 1.5kg of finely crushed ice.

The upper layer was separated and was freed from resinous lumps by filtration through a thin wad of glass-wool. The aqueous layer was extracted 3 times with a small amount of ether. The resinous material was also extracted with ether. The ether layers were washed with a concentrated  $NH_4Cl$  solution and dried over anhydrous magnesium sulfate. After removal of ether, the residue was distilled from calcium hydride through a 30cm vigreux column. The boiling point was  $81^\circ C / 18mmHg$  (lit.<sup>10</sup>  $78^\circ C / 12mmHg$ ) and the yield was 45%.

The structure was identified by  $^1H$ -NMR and IR spectroscopy. The  $^1H$ -NMR spectrum of 2-EP shows the acetylenic protons and the aromatic protons at 3.2ppm and 6.85~8.38ppm, respectively. The IR spectrum(Figure 4, A) gives the acetylenic  $\equiv C-H$  stretching band at  $3300cm^{-1}$  and it also shows the acetylenic  $C\equiv C$  stretching band at  $2110cm^{-1}$ .

### Procedures and Instruments

Polymerization was carried out as described

earlier.<sup>8,10</sup> The resulting polymer was dissolved in methanol followed by precipitation with excess ether. The precipitated polymer was filtered from the solution and dried to a constant weight under vacuum at 40°C for 24hrs. The polymer yield was calculated by gravimetry.

<sup>1</sup>H-NMR spectra were recorded on a Varian T-60A spectrometer or a Varian FT-80A NMR spectrometer. Infrared spectra were taken on a Perkin-Elmer 283B spectrophotometer using a potassium bromide pellets. Ultraviolet spectra were obtained with a Carey 17 spectrophotometer. Thermal transitions were measured with a Perkin-Elmer DSC-1B at a heating rate of 10°C/min, under nitrogen atmosphere. Inherent viscosities were measured at a concentration of 0.5g/dl in dimethylformamide at 20°C.

## RESULTS AND DISCUSSION

### Polymerization

Table 1 shows the results for the polymerization of 2-EP by WCl<sub>6</sub> or WCl<sub>6</sub>-R<sub>4</sub>Sn catalyst systems. WCl<sub>6</sub> and WCl<sub>6</sub>-R<sub>4</sub>Sn were highly effective in the polymerization of 2-ethynylthiophene<sup>8</sup> and phenylacetylene.<sup>3,4</sup> However, in this polymerization

of 2-EP, the above catalyst systems were less effective to give only low yield of P2EP. The polymer yield(ether-insoluble P2EP) was ranged between 7 and 25%.

Table 2 shows the results for the polymerization of 2-EP by the catalyst systems consisted with WCl<sub>6</sub> and organoaluminum compounds(Et<sub>3</sub>Al, (i-Bu)<sub>3</sub>Al, Et<sub>2</sub>AlCl, and EtAlCl<sub>2</sub>). Et<sub>2</sub>AlCl and EtAlCl<sub>2</sub> were found to be very effective cocatalyst in the polymerization of 2-EP by WCl<sub>6</sub>. To date, there have been no reports on the high cocatalytic activity of organoaluminum compounds for the polymerization of monosubstituted acetylenes by transition metal chlorides such as WCl<sub>6</sub> and MoCl<sub>5</sub>. In our another work, we have found that Et<sub>2</sub>AlCl and EtAlCl<sub>2</sub> are effective cocatalysts for the polymerization of 1-chloro-2-thienylacetylene<sup>11</sup> and the cyclopolymerization of dipropargyl ether<sup>12</sup> by transition metal chlorides. The polymer yield according to organoaluminum compounds was increased in the following order.

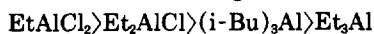


Figure 1 shows the mole ratio effect of EtAlCl<sub>2</sub> to WCl<sub>6</sub> for the polymerization of 2-EP by WCl<sub>6</sub>-EtAlCl<sub>2</sub>. As shown in this figure, the best result was obtained when the ratio is 4 and 5.

Table 1. Polymerization of 2-Ethynylpyridine by WCl<sub>6</sub> and WCl<sub>6</sub>-R<sub>4</sub>Sn Catalyst Systems<sup>a</sup>

Experiment Number	Catalyst System <sup>b</sup> (mole ratio)	Solvent	2-EP / Catalyst (mole ratio)	[M] <sub>0</sub> <sup>c</sup>	Temperature (°C)	Polymer Yield <sup>d</sup> (%)	$\eta_{inh}$ <sup>e</sup>
1	WCl <sub>6</sub>	Chlorobenzene	100	2	30	7	0.02
2	WCl <sub>6</sub>	Chlorobenzene	100	2	70	20	0.05
3	WCl <sub>6</sub>	Chlorobenzene	50	2	70	25	0.08
4	WCl <sub>6</sub>	Chlorobenzene	50	1	70	23	0.07
5	WCl <sub>6</sub>	Benzene	50	2	70	24	0.05
6	WCl <sub>6</sub>	Toluene	50	2	70	22	0.06
7	WCl <sub>6</sub> -Ph <sub>4</sub> Sn(1:1)	Chlorobenzene	50	2	70	26	0.10
8	WCl <sub>6</sub> -Me <sub>4</sub> Sn(1:2)	Chlorobenzene	50	2	70	24	0.09
9	WCl <sub>6</sub> -n-Bu <sub>4</sub> Sn(1:2)	Chlorobenzene	50	2	70	25	0.11
10	WCl <sub>6</sub> -n-Bu <sub>4</sub> Sn(1:4)	Chlorobenzene	50	2	70	21	0.10

<sup>a</sup>: Polymerization was carried out for 24hrs.

<sup>b</sup>: Mixture of WCl<sub>6</sub> and cocatalyst was aged at 30°C for 15 min. before use as catalyst.

<sup>c</sup>: Initial monomer concentration ([M]<sub>0</sub>).

<sup>d</sup>: Ethyl ether-insoluble polymer.

<sup>e</sup>: Measured at a concentration fo 0.5g/dl in DMF at 20°C.

Polymerization of 2-Ethynylpyridine

**Table 2.** Polymerization of 2-Ethynylpyridine by  $WCl_6$ -Organoaluminum Compounds<sup>a</sup>

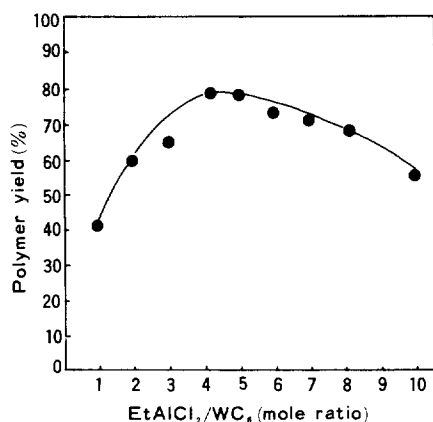
Experiment Number	Catalyst System <sup>b</sup> (mole ratio)	2-EP / Catalyst (mole ratio)	Polymer Yield <sup>c</sup> (%)	$\eta_{inh}^d$
1	$WCl_6-Et_3Al$	50	20	0.08
2	$WCl_6-(i-Bu)_3Al$	50	40	0.10
3	$WCl_6-(i-Bu)_3Al$	100	25	0.07
4	$WCl_6-Et_2AlCl$	50	62	0.13
5	$WCl_6-EtAlCl_2$	50	78	0.16
6	$WCl_6-EtAlCl_2$	100	62	0.15
7	$WCl_6-EtAlCl_2$	200	35	0.12

<sup>a</sup>: Polymerization was carried out for 24 hrs in chlorobenzene at 70°C. Initial monomer concentration([M]<sub>0</sub>) and  $WCl_6$  to cocatalyst mole ratio were 2M and 4, respectively.

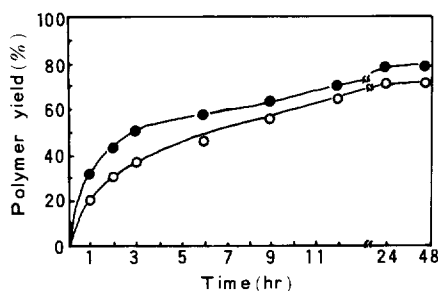
<sup>b</sup>: Mixture of  $WCl_6$  and organoaluminum compound in chlorobenzene was aged at 30°C for 15 min. before use as catalyst. use as catalyst.

<sup>c</sup>: Ethyl ether-insoluble polymer.

<sup>d</sup>: Measured at a concentration fo 0.5g / dl in DMF at 20°C.



**Fig. 1.** The mole ratio effect of  $EtAlCl_2$  to  $WCl_6$  for the polymerization of 2-EP by  $WCl_6-EtAlCl_2$ .



**Fig. 2.** Time dependence curves for the polymerization of 2-EP by  $WCl_6-EtAlCl_2$  (●) and  $MoCl_5-EtAlCl_2$  (○).

Figure 2 shows the time dependence curves for the polymerization of 2-EP by  $WCl_6-EtAlCl_2$  and  $MoCl_5-EtAlCl_2$ . The polymerization proceeded rapidly within 3hrs to the extent of 50% and 37%, respectively. Then, the polymerization proceeded slowly.

Table 4 shows the results for the polymerization of 2-EP by  $TiCl_4$ -based catalysts. As with  $WCl_6$ - and  $MoCl_5$ -based catalyst systems, the catalyst systems, which consisted with  $TiCl_4$  and organoaluminum compounds (especially,  $Et_2AlCl$  and  $EtAlCl_2$ ), were also effective. The inherent viscosities of P2EP prepared by  $TiCl_4$ -based catalysts were in the range of 0.07~0.15.

Table 5 shows the results for the polymerization

Table 3 shows the results for the polymerization of 2-EP by  $MoCl_5$ -based catalysts. As with  $WCl_6$ -based catalysts,  $MoCl_5$  alone and  $MoCl_5-R_4Sn$  catalyst systems were found to be less effective. Organoaluminum compounds were also effective cocatalysts for the polymerization of 2-EP by  $MoCl_5$ . Unlike the case of the polymerization of 2-ethynylthiophene<sup>8</sup> and 2-ethynylfuran,<sup>10</sup>  $MoCl_5$ -based catalysts exhibit a similar reactivity with  $WCl_6$ -based catalysts. The inherent viscosities of P2EP prepared by  $WCl_6$ - and  $MoCl_5$ -based catalysts were in the range of 0.02~0.16.

**Table 3.** Polymerization of 2-Ethynylpyridine by  $WCl_5$ -Based Catalysts<sup>a</sup>

Experiment Number	Catalyst System <sup>b</sup> (mole ratio)	Polymer Yield <sup>c</sup> (%)	$\eta_{inh}^d$
1	$MoCl_5$	15	0.04
2	$MoCl_5$ - $Me_3Sn$ (1:2)	8	0.04
3	$MoCl_5$ - <i>n</i> - $Bu_3Sn$ (1:2)	10	0.05
4	$MoCl_5$ - $Et_3Al$ (1:4)	17	0.08
5	$MoCl_5$ -( <i>i</i> - $Bu$ ) <sub>3</sub> $Al$ (1:4)	30	0.10
6	$MoCl_5$ - $Et_2AlCl$ (1:4)	53	0.11
7	$MoCl_5$ - $EtAlCl_2$ (1:2)	64	0.13
8	$MoCl_5$ - $EtAlCl_2$ (1:4)	70	0.14

a : Polymerization was carried out for 24 hrs in chlorobenzene at 70°C. Initial monomer concentration( $[M]_0$ ) and 2-EP to catalyst mole ratio were 2 M and 50, respectively.

b : Mixture of  $WCl_5$  and cocatalyst in chlorobenzene was aged at 30°C for 15 min. before use as catalyst.

c : Ethyl ether-insoluble polymer.

d : Measured at a concentration fo 0.5g / dl in DMF at 20°C.

**Table 4.** Polymerization of 2-Ethynylpyridine by  $TiCl_4$ -Organoaluminum Compounds<sup>a</sup>

Experiment Number	Catalyst System <sup>b</sup> (mole ratio)	Polymer Yield <sup>c</sup> (%)	$\eta_{inh}^d$
1	$TiCl_4$	33	0.08
2	$TiCl_4$ - $Et_3Al$ (1:4)	27	0.07
3	$TiCl_4$ -( <i>i</i> - $Bu$ ) <sub>3</sub> $Al$ (1:4)	45	0.10
4	$TiCl_4$ - $Et_2AlCl$ (1:2)	52	0.11
5	$TiCl_4$ - $Et_2AlCl$ (1:4)	60	0.14
6	$TiCl_4$ - $EtAlCl_2$ (1:4)	76	0.15
7	$Ti$ ( <i>o</i> - $Bu$ ) <sub>4</sub> - $EtAlCl_2$ (1:4)	25	0.08

a : Polymerization was carried out for 24 hrs at 60°C in benzene. Initial monomer concentration( $[M]_0$ ) and monomer to catalyst mole ratio were 2 M and 50, respectively.

b : Mixture of  $TiCl_4$  and cocatalyst in benzene was aged at 30°C for 5 min. before use as catalyst.

c : Ethyl ether-insoluble polymer.

d : Measured at a concentration of 0.5g / dl in DMF at 20°C.

of 2-EP by other transition metal catalyst systems. Tantalum(V) and niobium(V) halides were known to be very effective catalysts for the cyclotrimerization of phenylacetylene<sup>13</sup> and polymerization of some disubstituted acetylenes.<sup>14,15</sup> In this polymerization, however, these catalysts were less effective to give low yield of P2EP. The polymerization of 2-EP by  $M(CO)_6-CCl_4-h\nu$  was carried out at 70°C.  $W(CO)_6-CCl_4-h\nu$  showed some activity, where as  $Mo(CO)-CCl_4-h\nu$  gives no catalytic activity.

We failed to polymerize 2-vinylpyridine by

these transition metal catalyst systems. But, as described above, the high polymer yields were obtained in the polymerization of 2-EP by transition metal chloride and organoaluminum compounds. These high polymerizability of 2-EP by transition metal chloride-based catalyst systems may be attributable to the higher coordination ability of the triple bond with catalyst than that of pyridine substituent with catalysts.

#### Structure of P2EP

Figure 3 shows the <sup>1</sup>H-NMR spectrum of P2EP in  $CD_3OD$ . A broad peak at 6~9ppm is owing

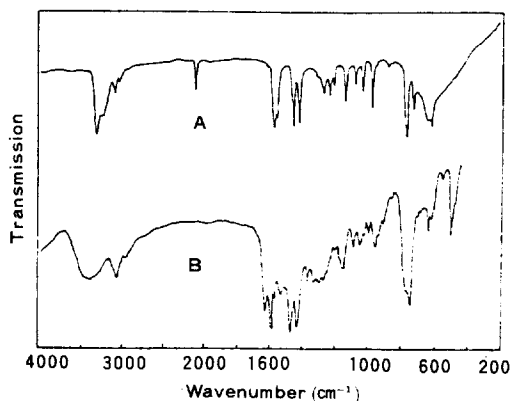
**Table 5.** Polymerization of 2-Ethynylpyridine by Other Transition Metal Catalysts<sup>a</sup>

Experiment Number	Catalyst System <sup>b</sup>	Polymer Yield <sup>b</sup> (%)
1	TaCl <sub>5</sub>	19
2	NbBr <sub>5</sub>	13
3	NbCl <sub>5</sub>	17
4	W(CO) <sub>6</sub> -CCl <sub>4</sub> -h <sup>v</sup> c	10
5	W(CO) <sub>6</sub> -CCl <sub>4</sub> -h <sup>v</sup> c	~0

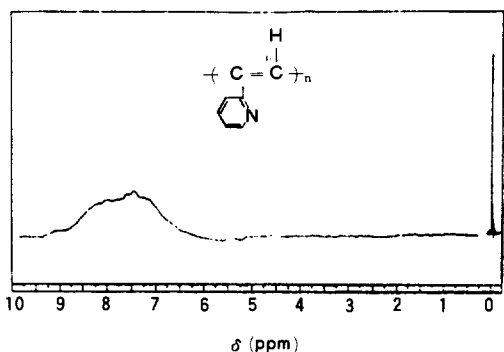
<sup>a</sup>: Polymerization was carried out for 24 hrs in chlorobenzene at 70°C. Initial monomer concentration ([M]<sub>0</sub>) and monomer to catalyst mole ratio were 2 M and 50, respectively.

<sup>b</sup>: Ethyl ether-insoluble polymer.

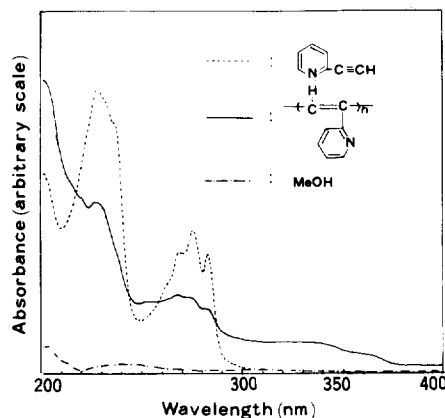
<sup>c</sup>: Ultraviolet irradiation of M(CO)<sub>6</sub> in CCl<sub>4</sub> was performed with 200W a high-pressure mercury lamp (Model 440 W absorbance detector fixed at 350 nm).



**Fig. 4.** IR spectra of 2-EP(A) and P2EP(B) in KBr pellet.



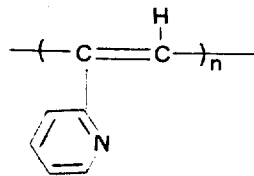
**Fig. 3.** <sup>1</sup>H-NMR spectrum of P2EP in CD<sub>3</sub>OD.



**Fig. 5.** UV spectra of 2-EP and P2EP in methanol.

to the protons of pyridine substituent and the vinyl protons of polymer backbone. The IR spectra of 2-EP and P2EP are shown in Figure 4. The IR spectrum of P2EP gives the aromatic=C-H stretching band at 3060cm<sup>-1</sup> and it shows no peak at 2110cm<sup>-1</sup> owing to the acetylenic C≡C stretching frequency. Instead, the carbon-carbon double bond (in the polymer backbone) stretching frequency at about 1630cm<sup>-1</sup> indicates a highly conjugated unsaturation.

The UV spectra of 2-EP and P2EP in methanol are shown in Figure 5. In the UV spectrum of P2EP, a new absorption absented in that of 2-EP was observed above 302nm. From these spectral data, it is concluded that this polymer has a conjugated polyene structure as follow.



**Physical Properties of P2EP**

P2EPs were black-colored powder. Solubility test of P2EP was performed for powderly samples in excess solvent. Poly(phenylacetylene)<sup>16</sup> and poly(2-ethynylthiophene)<sup>8</sup> were soluble in aromatic and halogenated hydrocarbons. However, P2EPs were soluble in polar solvents such as methanol, DMF, and water, but insoluble in aromatic and halogenated hydrocarbons. This very different solubility behaviors of P2EP were mainly attributable to the property of pyridyl substituent.

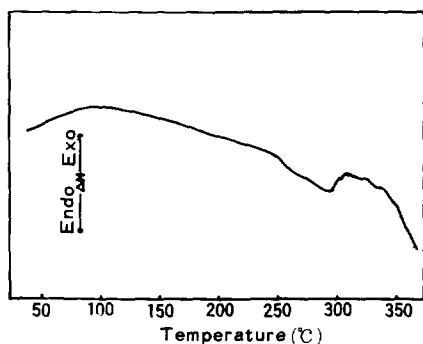


Fig. 6. DSC thermogram of P2EP prepared by  $WCl_6$ - $EtAlCl_2$  (1 : 4).

Figure 6 shows the DSC thermogram of P2EP prepared by  $WCl_6$ - $EtAlCl_2$ (1 : 4). It shows that the P2EP start to diffuse at about 297°C with a large exotherm. This behavior may be attributable to the decomposition of the polymer and to the formation of a cross-linked solid due to the double bonds in the polymer backbone. This process may be compared to the decomposition of poly(2-ethynylthiophene)<sup>8</sup> and poly(1-chloro-2-thienylacetylene)<sup>11</sup> at 250°C and 310°C, respectively.

Further work on the electronic properties of P2EP and doped P2EP is now in progress.

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