

NOTE

**$\alpha$ -히드록시 아세틸렌의 중합 : (II) 팔라듐 및 플라티늄  
클로라이드에 의한 에티스테론의 중합<sup>1</sup>**

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**Polymerization of  $\alpha$ -Hydroxyacetylene : (II) Polymerization of Ethisterone  
by Palladium and Platinum Chlorides<sup>1</sup>**

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INTRODUCTION

As a propargyl derivative, 2-propyn-1-ol has been polymerized by many catalysts or polymerization methods, such as  $\text{PdCl}_2$ ,<sup>2</sup>  $\text{MoCl}_5$ ,<sup>1,3</sup>  $\text{NiI}_2(\text{Ph}_3\text{P})_2$ ,<sup>4</sup>  $\text{Ni}(\text{NCS})(\text{C}\equiv\text{CR})(\text{Ph}_3\text{P})_2$ ,<sup>4</sup>  $\gamma$ -rays,<sup>5</sup> plasma,<sup>6</sup> etc. However, the resulting poly(2-propyn-1-ol) was not soluble in any organic solvents. For example, the solid-state polymerization of 1-ethynyl-1-cyclohexanol was carried out recently by the irradiation of a Co-60  $\gamma$ -ray source at a dose rate of 0.06 Mrad/hour in benzene solution or in solid state.<sup>7</sup> The polymerization proceeded in solution to give almost 80~90% of the polymer yield, whereas in the solid state it is limited to about 50% conversion. Moreover, needed polymerization time was very long for both cases and the products at lower conversions were mixtures of trimer, oligo-

mers, and polymer. On the other hand, palladium-based catalysts effectively polymerized 1-ethynyl-1-cyclohexanol to give poly(1-ethynyl-1-cyclohexanol) in high yields.<sup>8</sup>

In this report, we polymerized an  $\alpha$ -hydroxyacetylene having a bulky substituent, ethisterone (ETHI), with palladium and platinum-based catalysts and characterized the resulting poly(ETHI).

EXPERIMENTAL

ETHI(Aldrich Chemicals, 98%) was used after drying under vacuum at 40°C for 24 hours.  $\text{PdCl}_2$  (Aldrich Chemicals, 99.995%) and  $\text{PtCl}_2$  (Strem) were used without further purification.  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  was prepared by the reported method.<sup>9</sup> All polymerization solvents were analytical grade. They were dried with appropriate drying agents

followed by fractional distillation.  $\text{PdCl}_2$ ,  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ , and  $\text{PtCl}_2$ , were added as powder in the polymerization ampule.

A typical polymerization procedure is as follows :  $\text{PdCl}_2$  [0.095 g, 0.053 mmol, monomer to catalyst mole ratio(M/C)=30] was dissolved in DMF(2.702 ml,  $[\text{M}]_0=0.5 \text{ M}$ ) at  $90^\circ\text{C}$ . To this catalyst solution, ETHI(0.5 g, 1.6 mmol) was added and flushed with dry nitrogen. The polymerization was carried out at  $90^\circ\text{C}$  for 48 hours. Then 10 ml of co-solvent(DMF/ethanol, vol. ratio=3/1) was added and the polymer solution was precipitated into a large excess of distilled water. The polymer was filtered from the solution and dried under vacuum at  $40^\circ\text{C}$  for 24 hours.

$^1\text{H}$ -NMR spectra of polymers were obtained by using a Bruker AM-200 spectrometer in  $\text{CDCl}_3$  and the chemical shifts were assigned in ppm units compared with tetramethylsilane as internal standard. Infrared spectra were obtained with a Bio-Rad Digilab FTS-60 spectrometer using potassium bromide pellets. Ultraviolet(UV)-visible spectra were obtained using a Shimadzu UV-3100s spectrophotometer in chloroform. Number average molecular weights of polymers were measured using Waters GPC-510 after a calibration with polystyrene standards. Thermogravimetric analyses (TGA) were performed under nitrogen atmos-

phere at a heating rate of  $10^\circ\text{C}/\text{min.}$  up to  $700^\circ\text{C}$  with a DuPont 1090 Analyzer.

## RESULTS AND DISCUSSION

The polymerization of  $\alpha$ -hydroxyacetylene having a bulky substituent, ETHI, was carried out by palladium and platinum chlorides.

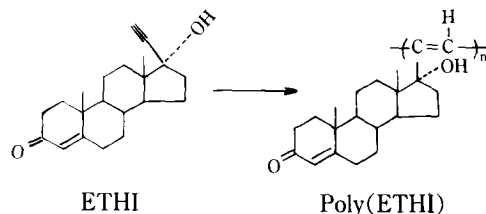


Table 1 shows the results for the polymerization of ETHI by palladium and platinum-based chlorides. In most cases,  $\text{PdCl}_2$  was found to be very effective catalyst for this polymerization. DMF, formic acid, and nitrobenzene were found to be good solvents for the present polymerization. The polymer yield at  $\text{M/C}=30$  was greater than that at  $\text{M/C}=50$ . The effects of initial monomer concentration( $[\text{M}]_0$ ) for the polymerization were also investigated(Exp. No. : 2, 3, 4, 5). As the  $[\text{M}]_0$  is increased, the polymer yield and the number average molecular weight( $\bar{M}_n$ ) were also gradually increased.

**Table 1.** Polymerization of Ethisterone by Palladium and Platinum Chlorides<sup>a</sup>

Experiment No.	Catalyst	M/C <sup>b</sup>	$[\text{M}]_0^c$	Solvent	P. Y. <sup>d</sup> (%)	$\bar{M}_n^e$
1	$\text{PdCl}_2$	50	0.25	DMF	64	2643
2	$\text{PdCl}_2$	30	0.25	DMF	83	3678
3	$\text{PdCl}_2$	30	0.15	DMF	72	2689
4	$\text{PdCl}_2$	30	0.50	DMF	86	3743
5	$\text{PdCl}_2$	30	1.00	DMF	88	3814
6	$\text{PdCl}_2$	30	0.25	$\text{HCO}_2\text{H}$	80	1257
7	$\text{PdCl}_2$	30	0.25	nitrobenzene	77	1072
8	$(\text{Ph}_3\text{P})_2\text{PdCl}_2$	30	0.25	DMF	0	—
9	$\text{PtCl}_2$	30	0.25	DMF	61	2072

<sup>a</sup> Polymerization was carried out for 48 hours at  $90^\circ\text{C}$ .

<sup>b</sup> Monomer-to-catalyst ratio.

<sup>c</sup> Initial monomer concentration, M.

<sup>d</sup> Polymer yield.

<sup>e</sup> Measured by means of GPC-510C of Waters using calibration curves for polystyrene.

While  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  provides some catalytic activities for the polymerization of 1-ethynyl-1-cyclohexanol,<sup>8</sup> it shows no catalytic activity in the polymerization of ETHI.  $\text{PtCl}_2$  was found to be effective for this polymerization of ETHI to give 61% of the polymer yield. Mo- and W- based catalysts, which showed a catalytic activity for the polymerization of 2-propyn-1-ol and 1-ethynyl-1-cyclohexanol, gave no polymers. These behaviors of Mo- and W- based catalysts are thought presumably to be due to the poisoning by  $\alpha,\beta$ -unsaturated ketone of ETHI and/or high steric hinderance of the bulky substituent.

Fig. 1 shows the  $^1\text{H}$ -NMR spectrum of poly(ETHI) prepared by  $\text{PdCl}_2$ . It shows the vinyl protons in the polymer backbone and  $\alpha,\beta$ -unsaturated ketone of the substituent at about 5.8 ppm and the hydroxyl protons at 2.9 ppm. The saturated aliphatic protons of the substituent were observed in the range of 0.5 and 2.7 ppm. A direct comparison with ETHI was impossible due to insolubility of the ETHI in the NMR solvent.

Fig. 2 shows the IR spectra of ETHI and poly(ETHI) in KBr pellet. The IR spectrum of poly(ETHI) showed neither the acetylenic  $\equiv\text{C-H}$  stretching band ( $3259\text{ cm}^{-1}$ ) nor the carbon-carbon triple bond stretching band ( $2108\text{ cm}^{-1}$ ) presented at the IR spectrum of ETHI. Instead the carbon-carbon double bond stretching band of the polymer backbone and substituent were observed at  $1616\text{ cm}^{-1}$ . The carbonyl stretching band was observed at  $1674\text{ cm}^{-1}$ .

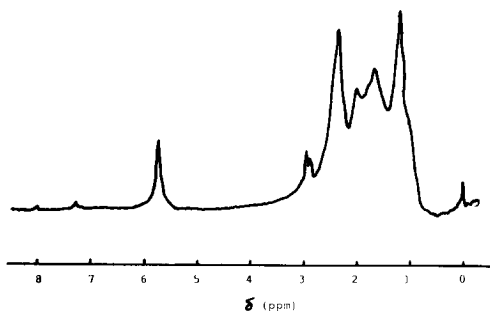


Fig. 1.  $^1\text{H}$ -NMR spectrum of poly(ETHI) prepared by  $\text{PdCl}_2$ .

The UV-visible spectrum (Fig. 3) of poly(ETHI) was recorded in chloroform. It shows a characteristic absorption peak of conjugated polymer,  $\pi \rightarrow \pi^*$  absorption at long wavelength (up to 600 nm).

From these spectral data, it can be concluded that the present poly(ETHI) have a conjugated backbone polymer structure having bulky  $\alpha$ -hydroxy substituent.

Fig. 4 shows the TGA thermogram of poly(ETHI) prepared by  $\text{PdCl}_2$ . The poly(ETHI) is thermally more stable than those of poly(2-propyn-

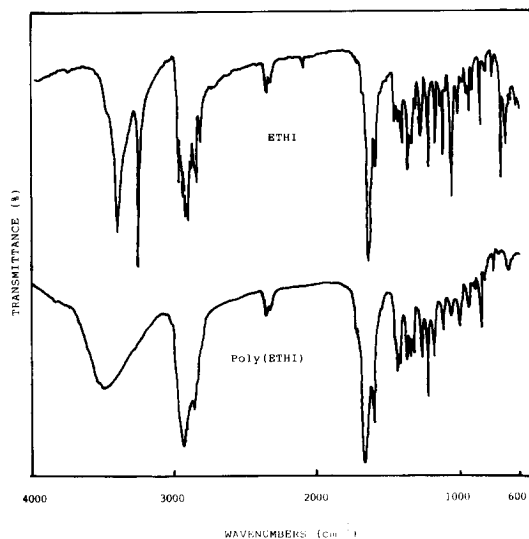


Fig. 2. IR spectrum of ETHI and poly(ETHI) prepared by  $\text{PdCl}_2$ .

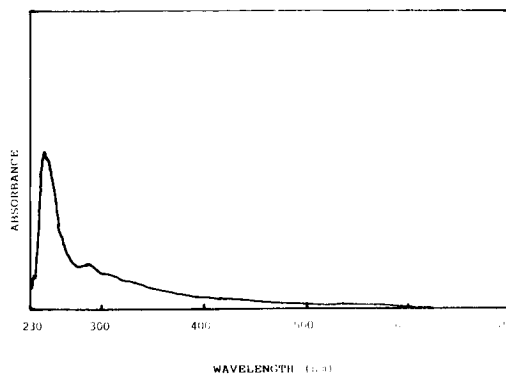


Fig. 3. UV-visible spectrum of poly(ETHI) prepared by  $\text{PdCl}_2$ .

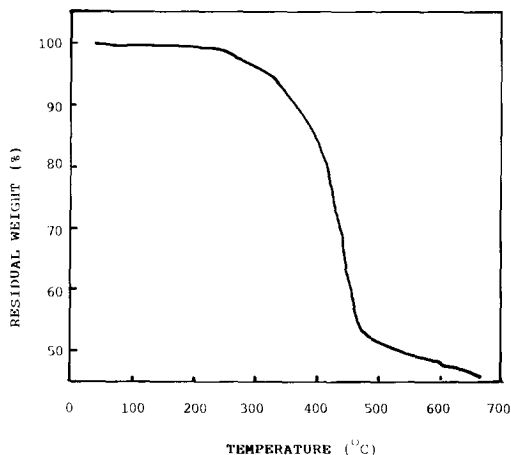


Fig. 4. TGA thermogram of poly(ETHI) prepared by  $\text{PdCl}_2$ .

1-ol)<sup>1</sup> and poly(1-ethynyl-1-cyclohexanol).<sup>8</sup> It showed that the poly(ETHI) retains 98% of its original weight at 270°C, 95% at 323°C, 83% at 400°C and 47% at 600°C. The resulting poly(ETHI)s were light-brown colored powder and completely soluble in aromatic and halogenated hydrocarbon solvents such as benzene, chlorobenzene, chloroform, and 1,1,1-trichloroethane, but insoluble in methanol and n-hexane.

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