

## 전이금속 촉매에 의한 디프로파길 에테르와 페닐아세틸렌의 공중합

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## Copolymerization of Dipropargyl Ether and Phenylacetylene by Transition Metal Catalysts

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**요 약 :** 본 논문은 디프로파길 에테르를 페닐아세틸렌과 공중합시킴으로서 용해하는 폴리아세틸렌 유도체의 합성과 그 특성을 다루었다.  $WCl_6$  및  $MoCl_5$ -계 촉매가 효과적이었으며 특히  $PdCl_2$ 를 사용할 경우 중합수율은 낮지만(43%) 합성된 공중합체는 대부분의 용매에 용해하였다. NMR( $^1H$ -,  $^{13}C$ -), IR 등의 분석을 통해 생성된 공중합체의 구조와 조성비를 파악하였으며 열분석(TGA)을 통하여 공중합체의 열안정성을 연구하였다.

**Abstract :** This paper deals with the synthesis and properties of soluble polyacetylene derivatives by copolymerizing of dipropargyl ether and phenylacetylene. The  $WCl_6$ - and  $MoCl_5$ -based catalysts were effective for this copolymerization. The copolymers prepared by  $PdCl_2$  were mostly soluble in organic solvents although the polymer yield was low(43%). The copolymer structure and the composition ratio of each component were identified by NMR( $^1H$ - and  $^{13}C$ -) and IR spectroscopies. The thermal properties (TGA) of resulting copolymers were also studied.

### INTRODUCTION

The copolymerization of acetylene monomers with another one is an interesting subject to improve some properties of acetylenic homopolymers.<sup>1~5</sup> We reported that dipropargyl ether(DPE), a 1,

6-heptadiyne homologue, was polymerized with  $MoCl_5$  and  $WCl_6$ -based catalysts to provide a new conjugated polymer in high yield<sup>6</sup> and the resulting poly(dipropargyl ether)[Poly(DPE)] shows extremely high electrical conductivity(iodine-doped,  $\sigma_{max} = 1.2 \times 10^{-2} \Omega^{-1} cm^{-1}$ ).<sup>7</sup> However the PD-

PEs were insoluble in any organic solvents and very unstable to air oxidation.

The polymerization of phenylacetylene(PA) by various catalysts was carried out to obtain soluble high molecular weight poly(phenylacetylene)[Poly (PA)].<sup>8,9</sup> From these viewpoints, it is reasonable to assume that DPE will be copolymerize with PA to provide some soluble, thus castable polymers.

The present authors have investigated the copolymerization of DPE and PA by various transition metal catalysts. The characterization and physical properties of the resulting copolymers will be also discussed.

## EXPERIMENTAL

### Materials

Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemicals, resublimed, 99+ %) and palladium(II) chloride (Aldrich Chemicals, 99.995%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried with calcium hydride and fractionally distilled. Propargyl alcohol (Aldrich Chemicals, 99%) were used without further purification. Phenylacetylene (Aldrich Chemicals, 98%) was dried with calcium hydride and fractionally distilled. Ethyl aluminum dichloride (Kanto Chemicals, 25 wt% in hexanes) was used as received. Tetraphenyltin (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. All polymerization solvents were dried with appropriate drying agent and fractionally distilled under nitrogen atmosphere.

### Preparation of DPE

DPE was prepared by the reaction of propargyl alcohol and propargyl bromide with sodium hydroxide according to the literature<sup>10</sup> (yield 85%, bp : 67°C/85 mmHg).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ , ppm) : 4.2 (4H, doublet), 2.5 (2H, triplet)

IR (KBr, wavenumber, cm<sup>-1</sup>) : 3300 ( $\equiv$  C-H stretching), 2120 (C  $\equiv$  C stretching)

### Preparation of Catalyst Systems

All procedures for catalyst system preparation were carried out under dry nitrogen atmosphere. Tungsten(VI) and molybdenum(V) chlorides, and ethylaluminum dichloride were dissolved in chlorobenzene to make 0.2 M and 0.05 M solutions before use. Palladium(II) chloride was added as powder in a polymerization ampule.

### Polymerization

To a 20 ml ampule equipped with a rubber septum, solvent, DPE and PA calculated by comonomer feed ratio were added and degassed. Then, catalyst solution was injected in the polymerization ampule. When the cocatalyst was used, these catalyst systems were added after shaking for 15 min at 30°C to reduce transition metal chlorides. After a given period of polymerization, the polymerization was stopped with 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 under vacuum at 40°C for 24 hr. The polymer yield was calculated by gravimetry.

### Instruments

NMR (<sup>1</sup>H- and <sup>13</sup>C-) spectra were recorded on a Bruker AM-200 spectrometer. Infrared spectra were taken on a Bio-Rad Digilab FTS-60 spectrometer using potassium bromide pellets. Thermogravimetric analysis(TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min with Perkin-Elmer TGS-1 thermobalance. Number-average molecular weights( $\bar{M}_n$ ) were determined in tetrahydrofuran solution by a Waters GPC-150C using a calibration curve for polystyrene.

## RESULTS AND DISCUSSION

The copolymerization of dipropargyl ether (DPE) and phenylacetylene(PA) was carried out by various transition metal catalysts.

**Table 1.** Copolymerization of DPE and PA by Various Transition Metal Catalysts<sup>a</sup>

Exp. No	Catalysts(mole ratio) <sup>b</sup>	Solvent	[M] <sub>0</sub> <sup>c</sup>	P. Y. <sup>d</sup>	$\bar{M}_n$
1	WCl <sub>6</sub>	Chlorobenzene	1	47	6200
2	WCl <sub>6</sub> -Ph <sub>4</sub> Sn(1 : 1)	⋈	1.5	52	9000
3	WCl <sub>6</sub> -EtAlCl <sub>2</sub> (1 : 2)	⋈	1.5	40	10200
4	MoCl <sub>5</sub>	⋈	1.5	98	insol
5	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	⋈	1.5	50	7200
6	PdCl <sub>2</sub>	DMF	1	43	5600

<sup>a</sup> Polymerization was carried out for 12 hrs at 90°C. The mole ratios of monomer to catalyst and DPE to PA were 50 and 1, respectively.

<sup>b</sup> Mixtures of catalyst and cocatalyst were aged for 15 min at 30°C before use.

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

<sup>d</sup> Methanol-insoluble polymer.

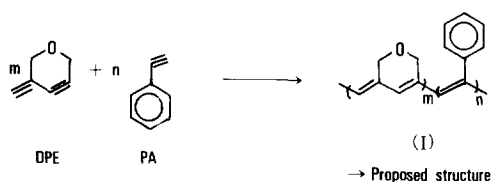


Table 1 shows the results for the copolymerization of DPE with PA by various transition metal catalysts. WCl<sub>6</sub>, WCl<sub>6</sub>-Ph<sub>4</sub>Sn, and WCl<sub>6</sub>-EtAlCl<sub>2</sub> copolymerize DPE and PA to some moderate yield. Especially, MoCl<sub>5</sub> explosively copolymerizes DPE and PA to quantitative yield. In general, the copolymers obtained by W- and Mo-based catalysts were partially soluble (soluble part < 50%) in common organic solvents such as chloroform, chlorobenzene, and tetrahydrofuran. However the copolymers obtained by PdCl<sub>2</sub> were completely soluble in common organic solvents although the polymer yield was low (43%).

As previously described in the introduction, the poly(DPE) homopolymer is insoluble in organic solvents though the poly(PA) homopolymer is completely soluble in benzene, chloroform, tetrahydrofuran, etc. In general the solubility of the resulting copolymers is increased as the feed ratio of PA is increased. And it is assumed that the insoluble(cross-linked) polymers are produced by the interaction of the allyl protons of poly(DPE) in co-

polymers and the W- and Mo-moiety. However, in the copolymerization by PdCl<sub>2</sub>, the polymerization rate and initial monomer concentration([M]<sub>0</sub>) is relatively low. And the allyl protons of copolymers are less affected by Pd-moiety. Thus the copolymers prepared by PdCl<sub>2</sub> were soluble. From these observations, it was concluded that the solubility of acetylenic polymers depends on the molecular structure of polymers and the catalyst systems used.

Table 2 shows the results for the copolymerization of DPE with PA by PdCl<sub>2</sub> according to comonomer feed ratio. As the mole fraction of DPE was increased, the polymer yield was also increased. The mole fraction of DPE in resulting copolymer and number-average molecular weight were linearly increased as the feed ratio of DPE was increased.

The <sup>1</sup>H-NMR spectra of copolymers from DPE and PA shows the proton peaks of the phenyl substituent and the conjugated vinyl protons of the main chain at 6.5-8.2 ppm. The methylene protons adjacent to the oxygen atom are shown in the range of 3.0-5.2 ppm. The <sup>13</sup>C-NMR spectrum of copolymer from DPE and PA shows the peaks at 136-150 ppm due to the carbons on the conjugated double bond. The peaks of methylene carbons adjacent to oxygen atom are observed at 70-85 ppm.

The IR spectrum of copolymer from DPE and

**Table 2.** Copolymerization of DPE and PA by PdCl<sub>2</sub> According to Comonomer Feed Ratio<sup>a</sup>

Exp. No.	DPE/PA (mole ratio)	P. Y. <sup>b</sup> (%)	Mole fraction of DPE in copolymer <sup>c</sup>	$\bar{M}_n$
1	1/0	58	1	9800
2	7/3	54	0.81	7000
3	5/5	43	0.60	5600
4	3/7	35	0.35	4200
5	0/1	27	0	3500

<sup>a</sup> Polymerizations were carried out at 90°C for 12 hrs in DMF. Initial monomer concentration was 1 M.

<sup>b</sup> Methanol-insoluble polymer.

<sup>c</sup> Calculated from <sup>1</sup>H-NMR integration.

PA shows the characteristic peaks of poly(DPE) at 2840–2940, 1600, and 1070 cm<sup>-1</sup> and it also shows the characteristic peaks of poly(PA) at 1550–1600, 755, and 693 cm<sup>-1</sup>.

In our another work,<sup>6</sup> it was proposed a number of possible structures for poly(DPE) besides ideal six-membered cyclic structure. The present copolymer has also a possibility of other polymer structures besides structure I. The present copolymer is assumed to be of more random sequence than the alternating one.

The copolymers prepared by WCl<sub>6</sub>- and MoCl<sub>5</sub>-based catalysts were yellow. The color of copolymers prepared by PdCl<sub>2</sub> according to comonomer feed ratio was changed from brown to orange as the feed ratio of PA is increased. The ability of film formation was increased as the feed ratio of PA in copolymers is increased.

The TGA thermogram of the copolymer from

DPE and PA[comonomer feed ratio, DPE/PA (5/5)] shows that it retains 95% of its original weight at 260°C, 90% at 320°C, 70% at 487°C, 58% at 750°C. As the feed ratio of PA in copolymers is increased, the thermal stability at low temperature (to 200°C) was increased, but the char yield at 750°C was decreased.

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