

전이금속촉매에 의한 카르바졸을 포함하는 아세틸렌 유도체의 중합

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Polymerization of Carbazole-Containing Acetylene Derivatives by Transition Metal Catalysts

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요 약 : 전이금속촉매를 사용하여 여러반응조건하에서 *N*-메틸-3-에티닐카르바졸과 *N*-프로파길카르바졸의 중합을 시도하였다. *N*-메틸-3-에티닐카르바졸의 중합에서는 WCl_6 가 $MoCl_5$ 보다 효과적이었고 *N*-프로파길카르바졸의 중합에서는 $MoCl_5$ 가 WCl_6 보다 더 효과적이었다. Ziegler-Natta 촉매도 중합에 사용하였다. 합성한 고분자의 구조는 1H -NMR, IR, UV스펙트럼으로 확인하였다. 폴리(*N*-메틸-3-에티닐카르바졸)은 클로로포름, 클로로벤젠, 1,2-디클로로에탄에는 완전히 용해되고 메탄올, 에틸에테르에는 녹지않았다. 폴리(*N*-프로파길카르바졸)은 유기용매에 녹지 않았다. 폴리(*N*-메틸-3-에티닐카르바졸)과 폴리(*N*-프로파길카르바졸)은 열중량분석 결과 각각 220°C와 300°C까지 무게감소가 없었다. 요오드로 도핑한 폴리(*N*-메틸-3-에티닐카르바졸)과 폴리(*N*-3-프로파길카르바졸)의 전기전도도는 $8.0 \times 10^{-3} \Omega^{-1}cm^{-1}$ 로 나타났다.

Abstract : The polymerization of *N*-methyl-3-ethynylcarbazole(NMEC) and *N*-propargylcarbazole(NPC) was attempted by transition-metal catalysts under various reaction condition. In the polymerization of NMEC, the catalytic activity of WCl_6 was greater than that of $MoCl_5$, but $MoCl_5$ was more effective than WCl_6 for the polymerization of NPC. Ziegler-Natta catalysts were also used. The polymer structures were characterized by various spectroscopic methods(1H -NMR, IR, and UV-Visible Spectroscopy). Poly(NMEC) was soluble in polar aromatic and halogenated solvents such as chloroform, chlorobenzene, 1,2-dichloroethane but insoluble in methanol and ethyl ether. On the other hand, Poly(NPC) was insoluble in any organic solvents. Poly(NMEC) and poly(NPC) did not show weight loss up to 220°C and 300°C under nitrogen atmosphere, respectively. The electrical conductivities of I_2 -doped poly(NMEC) and poly(NPC) were $8.0 \times 10^{-3} \Omega^{-1}cm^{-1}$ and $1.2 \times 10^{-5} \Omega^{-1}cm^{-1}$, respectively.

INTRODUCTION

The polymerization of substituted acetylenes has been attempted by various method : thermal,¹ light, radiation, radical,²⁻⁴ /ionic,^{5,6} and transition-metal catalysts.⁷⁻⁹ In most cases, however, the products are not polymers but linear oligomers and / or cyclotrimers. In general, Ziegler-Natta catalysts, which are widely used in the polymerization of olefins, have also found applications in the polymerization of acetylene derivatives, but Ziegler-Natta catalysts do not yield high polymers for sterically hindered acetylene such as *tert*-butylacetylene and disubstituted acetylenes.

Recently, it was known that the Group VI metal based catalysts exhibit high catalytic activity for the polymerization of mono- and disubstituted acetylenes such as phenylacetylene,¹⁰ β -naphthylacetylene,¹¹ diphenylacetylene,¹² etc. We have also found that WCl_6 and $MoCl_5$ based catalysts are very effective for the polymerization of acetylene derivatives containing aromatic heterocycles such as 2-ethynylthiophene,¹³ 2-ethynylfuran,¹⁴ and 1-chloro-2-thienylacetylene.¹⁵

In this paper, we describe the polymerization of a carbazole-containing acetylenic monomers by various transition-metal catalysts and the characterization of resulting polymers.

EXPERIMENTAL

Materials

Carbazole was recrystallized from ethyl alcohol. *n*-BuLi (Aldrich Chemical CO. 10.5 or 2.7 M solution in hexane) was used without calibration. Carbon tetrabromide, dimethyl sulfate, potassium hydroxide, triphenyl phosphine, phosphorus oxychloride and propargyl bromide were used without further purification. All reaction solvents were distilled before use from appropriate drying agents at atmospheric or reduced pressure and stored under nitrogen by rubber septum.

$W(CO)_6$, $Mo(CO)_6$, WCl_6 , $MoCl_5$ and Ziegler-Natta catalysts were used without further purification. All polymerization solvents(reagent

grade) were distilled before use from appropriate drying agents at atmospheric or reduced pressure under nitrogen.

Instruments and Measurements

¹H-NMR and Infrared(IR) spectra were recorded on a Varian T-60A spectrometer and Perkin-Elmer, Model 267 grating spectrometer, respectively. Ultraviolet- visible spectrum was obtained a Carey 17 spectrometer. Thermogravimetric analysis(TGA) was performed in nitrogen atmosphere at a heating rate of 20°C/min up to 800°C with a Perkin-Elmer TGS-1 Thermobalance.

Resistivity(Rs) was measured by hp 3435A Digital multimeter (Hewlett Packard). The electrical conductivity of the sample was determined using a standard four-point probe measurement. The polymer powder was pressed under 1500psi into compaction pellets. The sample pellets were doped with iodine vapor in vacuum desiccator(initial vacuum: 10⁻¹mmHg) at 15°C for 24 hrs. Inherent viscosities were determined with 0.5% solution of the polymers in chloroform at 30°C.

Preparation of *N*-methyl-3-ethynylcarbazole¹⁶

N-methyl-3-ethynylcarbazole, monomer, was synthesized by the reaction of *n*-BuLi with *N*-methyl-3-(2,2-dibromovinyl) carbazole which was obtained from the Witting reaction of *N*-methyl-3-formylcarbazole : To a stirred, ice-cooled solution of *N*-methyl-3-(2,2-dibromovinyl) carbazole(25 g, 0.0683 mol) in THF (200 ml) was added *n*-BuLi(8.75 g, 0.1366 mol) over a period of 2 hrs at -50~-60 °C and then 50 ml of distilled water was added dropwise. The reaction mixture was stirred for 2 hrs at room temperature, and then extracted with ethyl ether.

After removing the solvent, the residue was crystallized twice from mixed solvent(EtOH+Petroleum ether to give 9.1 g(65 %) of *N*-methyl-3-ethynylcarbazole : mp : 82 °C.

¹H-NMR(δ ppm) 3.1(1 H), 3.8(3 H), 7.1-8.3(7 H) (Fig. 1) IR(wave number, cm⁻¹, KBr pellet) 3300 cm⁻¹ : \equiv C-H stretching, 2100 cm⁻¹ : \equiv C stretching(Fig. 1).

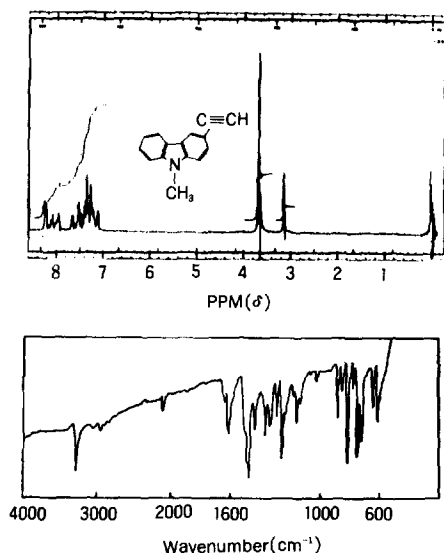


Fig. 1. ^1H -NMR and IR spectra of NMEC.

Preparation of *N*-propargylcarbazole

A mixture of 83.6 g (0.5 mol) of carbazole dissolved in 300 ml of DMSO, 42.1 g (0.75 mol) of potassium hydroxide dissolved in 60 ml of water, and 200 ml of benzene was refluxed for 24 hrs at 90 °C. And then 83g(0.7mol) of propargyl bromide was added dropwise at -20°C. The reaction mixture was stirred for 2 hrs at 30 °C and poured into 1.5ℓ of water and then extracted with CH_2Cl_2 . After the solvent(CH_2Cl_2) was removed by a rotatory evaporator, the residue was crystallized twice from ethyl ether to give 56g(55%) of pure *N*-propargylcarbazole : mp : 110°C.

^1H -NMR(δ ppm)

2.2(1 H), 5.0(2 H), 7.2~7.6 (6 H), 8.2(2 H). (Fig. 2)

IR(wave number, cm^{-1} , KBr pellet)

3300 cm^{-1} : $\equiv\text{C}-\text{H}$ stretching, 2110 cm^{-1} : $\text{C}\equiv\text{C}$ stretching (Fig. 2).

Polymerization

All procedures for catalyst system preparation and polymerization were carried out under 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 tungsten hexachloride(WCl_6) and molybdenum pentachloride(MoCl_5) in various

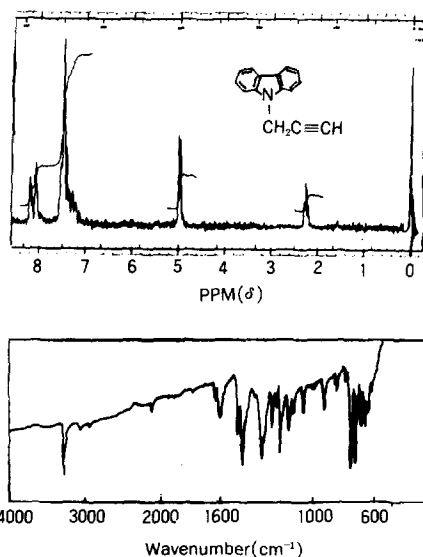


Fig. 2. ^1H -NMR and IR spectra of NPC.

solvents.

(b) 0.2 M solution of TiCl_4 , $\text{Ti}(\text{OBu})_4$, Et_3Al , Et_2AlCl , and EtAlCl_2 , in benzene.

(c) 0.2 M solution of *n*- Bu_4Sn , (*i*- Bu) $_3\text{Al}$ and Et_3Al in chlorobenzene.

The polymerization ampoule(15ml) was flushed with purified nitrogen and a septum was fitted to the neck. Injection of catalyst and monomer solution was done by means of hypodermic syringes from which air and moisture were carefully excluded. (a) polymerization of *N*-methyl-3-ethynylcarbazole by WCl_6 or MoCl_5 alone. A typical procedure is as follows : In a 15 ml ampoule fitted with septum, 0.5 g(2.4 mmol) of NMEC was dissolved in 2 ml of chlorobenzene. Then, 0.024 mmol of WCl_6 was introduced into the reactor. Polymerization was performed at 60°C for 24 hrs.

(b) Polymerization of *N*-methyl-3-ethynylcarbazole by Ziegler-Natta catalysts. In a 15 ml ampoule fitted with septum, 0.5 g(2.4 mmol) of NMEC was dissolved in 2 ml of benzene. Then, the mixed catalysts solution of TiCl_4 (0.048 mmol) and Et_3Al (0.19 mmol) was introduced into the reactor. (The mixed solution of TiCl_4 and Et_3Al was aged performed at 60°C for 24 hrs. The polymerization of *N*-propargylcarbazole was also proceeded as

described above.

RESULTS AND DISCUSSION

Polymerization

Table 1 shows the results for the polymerization of NMEC by WCl_6 and MoCl_5 in various reaction solvents. The catalytic activity of WCl_6 was greater than that of MoCl_5 . Aromatic solvents such as benzene and toluene were the most favorable solvents. On the other hand, low conversion was

obtained in halogenated hydrocarbons and no polymerization was observed in oxygen-containing solvent.

The results of polymerization of NMEC by Ziegler-Natta catalysts are summarized in Table 2. The maximum polymer yield (85 %) was obtained when $\text{Me}_3\text{Al}-\text{TiCl}_4$ (4 : 1) was used. In the polymerization of NMEC by Ziegler-Natta catalysts, it was found that the activity of catalysts, containing $\text{Ti}(\text{OBu})_4$ was very low.

Fig.3 shows the time effect on the polymerization

Table 1. Polymerization of *N*-Methyl-3-ethynylcarbazole in Various Reaction Solvents.^a

Expt. No.	Catalyst	Solvents	M / C. (mole ratio)	P.Y(%) ^b	η_{inh}^c
1	WCl_6	Chlorobenzene	50	73	0.078
2	WCl_6	Chlorobenzene	100	55	0.078
3	WCl_6	Chlorobenzene	200	24	0.083
4	WCl_6	Toluene	50	67	0.077
5	WCl_6	Benzene	50	74	0.077
6	WCl_6	CCl_4	50	40	0.083
7	WCl_6	CHCl_3	50	4	—
8	WCl_6	p-Dioxane	50	trace	—
9	MoCl_5	Chlorobenzene	50	trace	—
10	MoCl_5	Chlorobenzene	100	trace	—

^a Polymerization was carried out at 60 °C for 24 hrs.

^b Methanol-insoluble polymer

^c Concentration of 0.5 g / dl in chloroform at 30 °C

Table 2. Polymerization of *N*-Methyl-3-ethynylcarbazole by Ziegler-Natta Catalysts.^a

Exp. No.	Catalyst () : (mole ratio)	P.Y(%) ^b	η_{inh}^c
1	$\text{AlEt}_3 / \text{TiCl}_4$ (4 : 1)	60	0.051
2	$\text{AlEt}_3 / \text{Ti}(\text{OBu})_4$ (4 : 1)	5	—
3	$\text{Et}_2\text{AlCl} / \text{TiCl}_4$ (1 : 1)	6	—
4	$\text{Et}_2\text{AlCl} / \text{TiCl}_4$ (2 : 1)	13	0.064
5	$\text{Et}_2\text{AlCl} / \text{TiCl}_4$ (3 : 1)	22	0.076
6	$\text{Et}_2\text{AlCl} / \text{TiCl}_4$ (4 : 1)	75	0.076
7	$\text{EtAlCl}_2 / \text{TiCl}_4$ (4 : 1)	68	0.051
8	$\text{Me}_3\text{Al} / \text{Ti}(\text{OBu})_4$ (4 : 1)	trace	—
9	$\text{Me}_3\text{Al} / \text{TiCl}_4$ (4 : 1)	85	0.064
10	$\text{Et}_2\text{AlCl} / \text{Ti}(\text{OBu})_4$ (4 : 1)	trace	—

^a Polymerization was carried out at 60 °C for 24 hrs in benzene. M / Cat=50

^b Methanol-insoluble polymer.

^c Concentration of 0.5 g / dl in chloroform at 30 °C.

of NMEC. The polymer yield and inherent viscosity were found to be dependent on the polymerization time.

Table 3 shows the results for the polymerization of NPC by various catalysts under different reaction conditions. The polymerization was accelerated when organo tin compounds were used as cocatalysts. As shown in Table 3, MoCl_5 catalyst is generally more effective than WCl_6 . $\text{W}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$ and $\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$ catalysts systems were less effective. In the polymerization of NPC by Ziegler-Natta catalysts, the maximum polymer yield (75%) was obtained when $\text{Me}_3\text{Al-TiCl}_4$ (4 : 1) was used.

Identification of Poly(NMEC) and Poly(NPC)

Figure 4 shows the IR, $^1\text{H-NMR}$ and UV-VIS spectra of poly(NMEC).

The IR spectra show the vinyl $=\text{C-H}$ stretching band at 3080 cm^{-1} and they shows absorption bands at about 1620 cm^{-1} owing to conjugated double bonds.

In the $^1\text{H-NMR}$ spectrum a broad aliphatic proton peak of N-CH_3 appeared at around 3.8 ppm and the proton on conjugated chain and aromatic proton of carbazole appeared at 5.8-8.2 ppm. The characteristic peak of NMEC at 3.1 ppm (acetylenic proton) was disappeared and a new broad peak was observed in the aromatic region.

The UV and Visible spectra were obtained in 1,2-dichloroethane. The poly(NMEC) showed

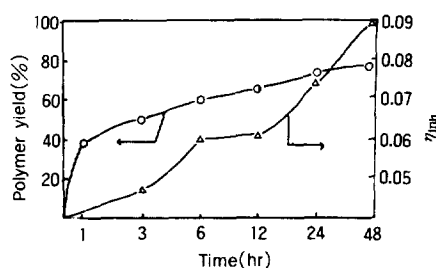


Fig. 3. Time effect on the polymerization of NMEC.

Table 3. Polymerization of *N*-Propargylcarbazole by Various Catalysts.^a

Exp. No.	Catalyst system () : mole ratio	Solvent	M / Cat (mole ratio)	P.Y (%) ^b
1	MoCl_5	Chlorobenzene	50	92
2	MoCl_5	Chlorobenzene	100	60
3	MoCl_5	Chlorobenzene	200	45
4	WCl_6	Chlorobenzene	50	72
5	WCl_6	Chlorobenzene	100	32
6	$\text{MoCl}_5 / \text{Bu}_4\text{Sn} (1 : 1)^c$	Chlorobenzene	100	70
7	$\text{MoCl}_5 / \text{Bu}_4\text{Sn} (1 : 2)^c$	Chlorobenzene	100	86
8	$\text{MoCl}_5 / \text{Bu}_4\text{Sn} (1 : 4)^c$	Chlorobenzene	100	66
9	$\text{W}(\text{CO})_6\text{-CCl}_4\text{-UV}^d$	CCl_4	50	8
10	$\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-UV}^d$	CCl_4	50	6
11	$\text{AlEt}_3 / \text{TiCl}_4 (4 : 1)$	Benzene	50	59
12	$\text{AlEt}_3 / \text{Ti}(\text{OBu})_4 (4 : 1)$	Benzene	50	5
13	$\text{Et}_2\text{AlCl} / \text{TiCl}_4 (4 : 1)$	Benzene	50	trace
14	$\text{Et}_2\text{AlCl} / \text{Ti}(\text{OBu})_4 (4 : 1)$	Benzene	50	trace
15	$\text{AlMe}_3 / \text{TiCl}_4 (4 : 1)$	Benzene	50	75
16	$\text{EtAlCl}_2 / \text{TiCl}_4 (4 : 1)$	Benzene	50	trace

a Polymerization was carried out 60°C for 24 hrs.

b Methanol-insoluble polymer.

c Mixture of MoCl_5 and cocatalyst was aged at 30°C for 15 minutes before use as catalyst.

d Ultraviolet irradiation of $\text{M}(\text{CO})_6$ in CCl_4 was performed with 200 a high pressure mercury lamp (Model 440 W absorbance detector fixed at 350 nm).

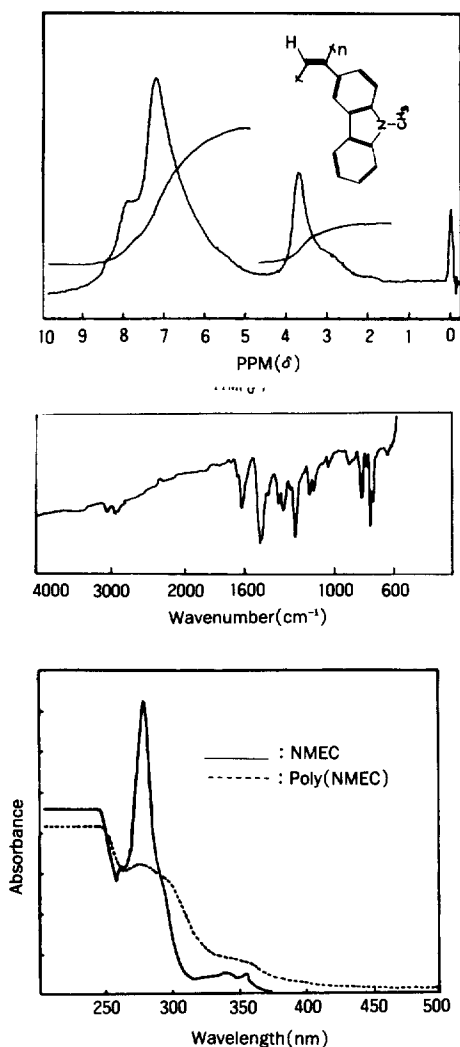
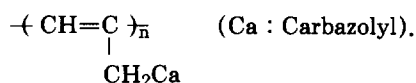


Fig. 4. ^1H -NMR, IR and UV-VIS spectra of poly(NMEC).

a broad and weak absorption at 300-500 nm which is characteristic feature of conjugated polymers.

Figure 5 shows the IR spectrum of poly(NPC). It support the expected polymer structure,



Solubility

Solubility test of poly(NMEC) prepared by

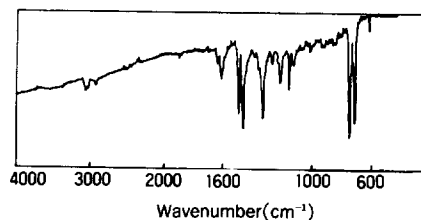
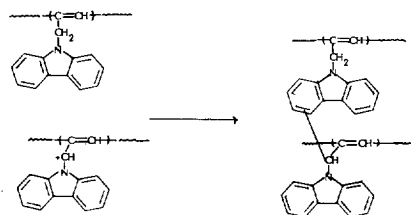


Fig. 5. IR spectrum of poly(NPC).

Table 4. Solubility of Poly(*N*-Methyl-3-ethynyl-carbazole).

Soluble	Chloroform, Chlorobenzene, 1,2-Dichloroethane, Dichloromethane, DMF, DMSO, Nitrobenzene
Partially Soluble	Acetone, CS_2 , <i>p</i> -Dioxane, Xylene, Toluene
Insoluble	Benzene, Monoglyme, Methanol, Ethyl Ether, Formic Acid, CCl_4 , Petroleum Ether



WCl_6 in chlorobenzene was performed for powdery samples in excess solvents. The solubility data of poly(NMEC) are summarized in Table 4.

Poly(NMEC) was soluble in polar aromatic and halogenated solvents such as chloroform, chlorobenzene, 1,2-dichloroethane, but insoluble in methanol and ethyl ether, and partially soluble in monoglyme, carbon disulfide, etc. Poly(NPC) was insoluble in any organic solvents, which is probable due to the cross-linking between polymer chains.

Thermal and Electrical Properties

According to thermogravimetric analysis, poly(NMEC) and poly(NPC) did not show weight loss up to 220 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ under nitrogen, respectively (Fig. 6). These polymers were stable enough, as demonstrated by the fact that no change could be in the IR spectra of polymers after standing in air at room temperature for several months.

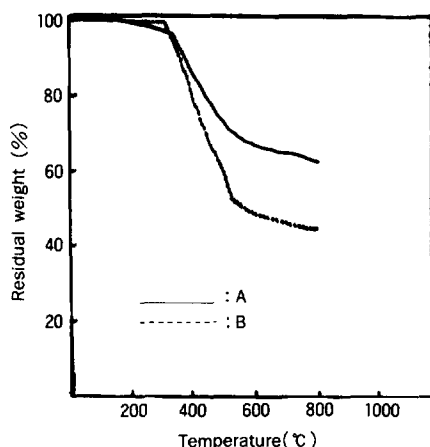


Fig. 6. TGA curves of poly(NMEC) (A) and poly (NPC) (B).

The electrical conductivities (composition of doped polymer) of iodine doped poly(NMEC) and poly(NPC) were $8.0 \times 10^{-3} \Omega^{-1} \text{cm}^{-1} [(C_{15}H_{11}N)_1(I_2)0.95]$ and $1.2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1} [(C_{15}H_{11}N)_1(I_2)0.2]$, respectively.

More detailed studies on the microstructures and electronic properties of the resulting polymers are in progress.

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