

전이금속 촉매에 의한 Indene 의 중합

조 현 남 · 최 삼 권

한국과학기술원 화학과
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Polymerization of Indene by Transition Metal Catalysts

Hyun-Nam Cho and Sam-Kwon Choi

*Department of Chemistry Korea Advanced Institute of Science and Technology
P.O. Box 150 Chongyangni, Seoul 131,*

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Abstract: The polymerization of indene was investigated in the presence of group V and VI transition metal halides such as WCl_6 , $MoCl_5$, $TaCl_5$, and $NbCl_5$ as catalysts under various reaction conditions. Indene was found to be easily polymerized with a high initial rate by these transition metal catalysts. Almost quantitative conversion and somewhat high molecular weight of polymer were obtained in chlorobenzene when the monomer to WCl_6 mole ratio 200. It was observed that the results of polymerization depended strongly on the monomer to catalyst mole ratio, and aromatic solvents generally gave better results in conversion and molecular weight of the polymers than aliphatic ones. The copolymerization of indene with acenaphthylene by WCl_6 in chlorobenzene also proceeded quantitatively. The structures of the resulting homo and copolymers were characterized by means of several spectroscopic analyses.

1. Introduction

Indene has been polymerized chemically with various catalysts¹⁻⁶. Electroinitiated polymerization of indene was also widely investigated by several workers⁷⁻¹⁰. However, it has not been reported that transition metal halides such as WCl_6 , $MoCl_5$, $TaCl_5$, and $NbCl_5$ were used as catalysts for the polymerization of indene.

On the other hand, WCl_6 -or $MoCl_5$ -based com-

ponents have been known as catalysts of the olefin metathesis reaction and polymerization¹¹. Moreover, a large number of publications on the polymerization of various acetylene derivatives by these transition metal catalysts have appeared in recent years¹²⁻¹⁵.

In our another study¹⁶, these transition metal catalysts were found to be effective in the polymerization of acenaphthylene and N-vinylcarbazole. Also, we have already reported the polymerization of 2-azabicyclo [2,2,1] hept-5-en-3-one¹⁷ and 2-

ethynylthiophene¹⁸ by using these catalyst systems.

This paper concerns the polymerization of indene using these transition metal catalysts under different conditions and the characterization of corresponding polymers. The copolymerization of indene with acenaphthylene is also described briefly.

2. Experiments

2-1. Materials

Indene (Aldrich) was washed several times with 6M HCl, water, and then 40% NaOH and water. After drying over CaH₂ for 12hr, the dried indene was fractionally distilled over CaH₂ under vacuo before use (bp. 40°C/4mmHg). Acenaphthylene (Aldrich) was purified by recrystallization from methanol followed by sublimation in vacuo; mp. 93°C.

Transition metal halides (Alfa, resublimed) were used without further purification and dissolved in chlorobenzene before use as 0.05M solution under nitrogen atmosphere.

All the solvents used were distilled before use from appropriate drying agents at atmospheric or reduced pressure under nitrogen.

2-2. Polymerization Procedures

The polymerization of indene with different transition metal catalysts was carried out under various reaction conditions in nitrogen atmosphere.

A typical procedure was as follows: in a 20mL ampoule equipped with rubber septum, 2.32g (20 mmol) of indene and 10mL of chlorobenzene were introduced at 20°C. To this mixture solution was added by hypodermic syringe 3.96×10^{-2} g (0.1 mmol) of WCl₆ dissolved in chlorobenzene as 0.05M solution. After standing at 20°C for 12hr, the polymerization was stopped by adding a small amount of methanol. The polymer was isolated by precipitation into a large excess of methanol followed by two subsequent precipitations from benzene into methanol. Almost quantitative conversion of white polymer was obtained gravimetrically

after drying under vacuum oven at 30°C for 24 hr. Copolymerization of indene with acenaphthylene was also performed by using a similar procedure applied to homopolymerization of indene.

2-3. Polymer Characterization

¹H- and ¹³C-NMR spectra were recorded on a Varian FT-80A NMR spectrometer using chloroform-d as solvent at room temperature. Infrared (IR) spectra were taken on a Perkin-Elmer 283B spectrophotometer as KBr pellets. Ultraviolet (UV) spectra were measured on a Cary 17 spectrophotometer. Fluorescence emission spectrum of copolymer was observed on an Aminco-Bowman spectrofluorometer with Amino XY-Recorder at room temperature. Solvent for the absorption and emission spectra was 1,2-dichloroethane. X-ray diffraction analyses were performed on a Rigaku Geiger-Flex X-ray diffractometer with copper target ($\lambda = 1.542$) at a scan speed 4°/min. Molecular weight (\bar{M}_w) were determined by gel permeation chromatography (Waters 150C) equipped with μ -styragel columns using tetrahydrofuran as an eluent.

3. Results and Discussion

Group V and VI transition metal halides such as WCl₆, MoCl₅, TaCl₅, and NbCl₅ were found to be effective catalysts for the polymerization of indene and its copolymerization with acenaphthylene (ACN). This is also found in the polymerization of ACN and N-vinylcarbazole by us.¹⁶

The results of polymerization of indene by different transition metal catalysts using chlorobenzene as a solvent are recorded in Table 1. As the polymerization conditions used, the monomer to catalyst mole ratio was 200 and the temperature was 20°C. Here, it is shown that the polymerization proceeds at a high initial rate and gives a polymer in a high conversion. The average molecular weight of the resulting polymer (polyindene) was in the range of 10,000-34,000 according to the kinds of catalysts used, which is somewhat higher than the molecular weight of

Table 1. Polymerization of Indene by Various Transition Metal Salts^a

Expt. No.	Catalyst	Time	Conversion (%)	$\bar{M}_w(\times 10^{-4})^b$
1	WCl ₆	1 min	90	1.8
2	WCl ₆	30 min	95	2.3
3	WCl ₆	1 hr	96	3.0
4	WCl ₆	12 hr	98	3.4
5	MoCl ₅	12 hr	93	1.2
6	TaCl ₅	12 hr	93	1.5
7	NbCl ₅	12 hr	91	1.0

a; Polymerizations were carried out in chlorobenzene at 20°C; the monomer to catalyst mole ratio was 200.

b; Determined by GPC in tetrahydrofuran (THF).

Table 2. Polymerization of Indene by WCl₆ under Different Conditions^a

Expt. No.	In/WCl ₆ (mole ratio)	Temperature (°C)	Conversion (%)	$\bar{M}_w(\times 10^{-4})^b$
1	100	20	88	3.0
2	200	0	95	2.3
3	500	20	86	1.6
4	1000	20	28	0.8
5	200	-20	93	3.0
6	200	60	88	2.2

a; Polymerizations were carried out in chlorobenzene for 12 hr.

b; Determined by GPC in tetrahydrofuran (THF).

polymer prepared by electronitiated cationic polymerization of indene in recent years⁹⁻¹⁰.

Table 2 shows the effects of the monomer to catalyst mole ratio and the temperature on the conversion and the molecular weight of polymer obtained by WCl₆ in chlorobenzene for 12hr. It is certain that the conversion and molecular weight of polymer are rather strongly affected by the monomer to catalyst mole ratio than by the temperature of polymerization. When the monomer to catalyst mole ratio was 1000, as an example, both the conversion and molecular weight of polymer were decreased.

The effects of solvent on the polymerization of indene by WCl₆ are summarized in Table 3. Max-

imum conversion and higher molecular weight of polymer were obtained in chlorobenzene at 20°C when the monomer to WCl₆ mole ratio was 200. Generally, aromatic solvents give the better results in the conversion and molecular weight of polymer than those in aliphatic solvents. In the case of using xylene as a solvent, however, the results of polymerization are markedly depressed. This is mainly attributed to the inhibition of polymerization as chain transfer agent of xylene, as shown in the cationic polymerization of styrene by WCl₆¹⁹. Therefore, it is suggested that the polymerization of indene by WCl₆ as well as other transition metal halides, which have been known as Friedel-Crafts catalysts²⁰, used in this in-

Table 3. Effect of Solvents on the Polymerization of Indene by WCl_6^a

Expt. No.	Solvent	Conversion (%)	$\bar{M}_w(x10^{-4})^b$
1	Benzene	90	1.4
2	Chlorobenzene	98	3.4
3	Toluene	85	1.2
4	Xylene	25	0.7
5	Nitrobenzene	91	2.2
6	$ClCH_2CH_2Cl$	35	0.8
7	CH_2Cl_2	60	1.0
8	CCl_4	78	1.1

a; Polymerizations were carried out at 20°C for 12hr; the monomer to catalyst mole ratio was 200.
b; Determined by GPC in tetrahydrofuran (THF).

Table 4. Copolymerization of Indene with Acenaphthylene by WCl_6^a

Expt. No.	IN/ACN ^b Mole Ratio	Conversion (%)	$\bar{M}_w^c(x10^{-4})$
1	3:7	97	1.8
2	5:5	97	1.9
3	7:3	98	2.4

a; Copolymerizations were carried out in chlorobenzene at 20°C for 12hr; catalyst mole ratio was 200.
b; IN: Indene, ACN: Acenaphthylene
c; Determined by GPC in tetrahydrofuran (THF).

vestigation should proceed by a cationic mechanism.

Copolymerization of indene with ACN was also carried out in chlorobenzene with WCl_6 as a catalyst at 20°C. The results are given in Table 4. Like as the homopolymerization of indene, almost quantitative conversion and high molecular weight of copolymers were obtained.

The structure of the resulting homo and copolymers was characterized by several spectroscopic analyses. 1H - and ^{13}C -NMR spectra of polyindene obtained are shown in Figure 1 and 2. These spectra are similar to those of polymer prepared by conventional polymerization. Figure 3 shows the IR spectra of the homo and copolymer (1:1). IR spectrum of polyindene gives characteristic absorption bands at 1480 and

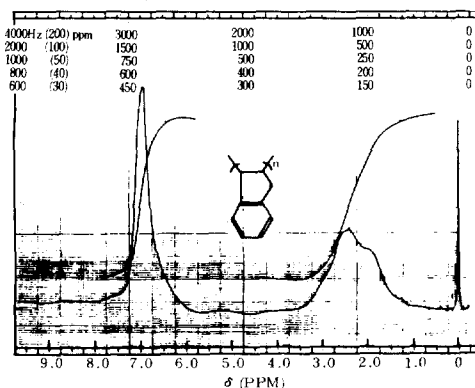


Fig. 1. 1H -NMR spectrum of polyindene obtained by WCl_6 .

$750cm^{-1}$, which is practically identical with those reported in the literature^{9,21}. In the case of

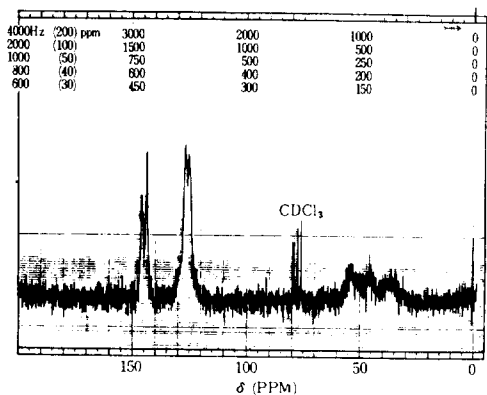


Fig. 2. ¹³C-NMR spectrum of polyindene obtained by WCl₆.

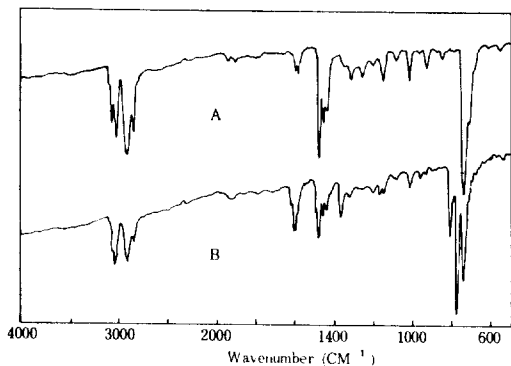


Fig. 3. IR spectra of polyindene (A) and 1:1 copolymer with ACN (B) obtained by WCl₆.

copolymer with ACN, however, new bands at 820 and 780 cm⁻¹ which are characteristic bands of ACN polymer (PACN)^{9,16} are observed. The intensity of these two bands increased gradually as the mole ratio of ACN in the copolymerization was increased. The UV spectra (Fig. 4) unequivocally support the formation of homo and copolymers.

On the other hand, the fluorescence emission properties of polymers with pendant aromatic groups has received considerable attention²². Thus, the emission spectra of copolymers with ACN were investigated (Fig. 5). The resulting copolymers show two broad emissions at about 350 and 410 nm when it was excited at 300 nm. The low-energy bands at 410 nm can be assigned to excimer emission of ACN, occurred as a conse-

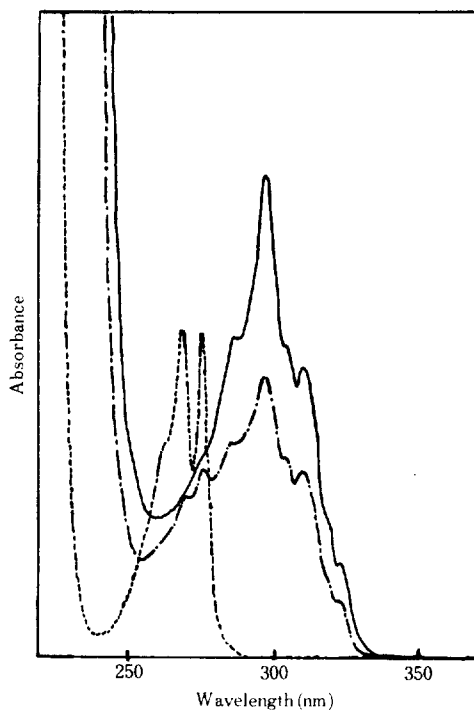


Fig. 4. UV spectra of polyindene (---), PACN (—), and 1:1 copolymer (-·-) obtained by WCl₆.

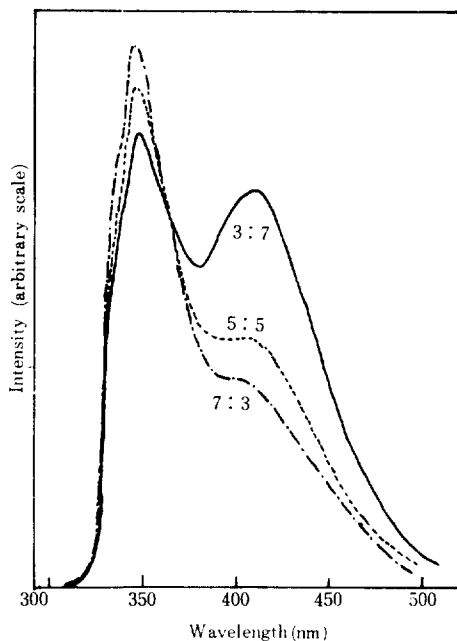


Fig. 5. Fluorescence emission spectra of copolymers obtained by WCl₆. See Table 4 as to copolymerization conditions.

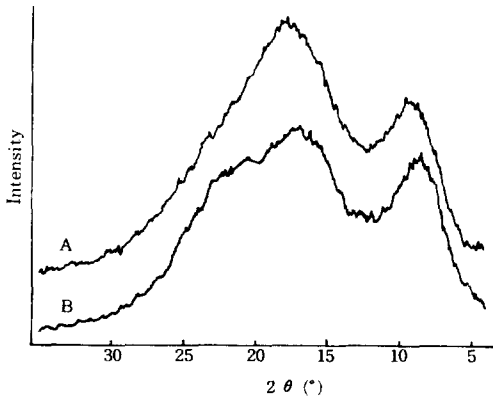


Fig. 6. X-ray diffractograms of polyindene (A) and 1:1 copolymer (B) obtained by WCl_6 .

quence of next-to-nearest neighbors²³. As shown in Figure 5, it was observed that the intensity of excimer emission of copolymers increased with an increase in the content of the ACN in the copolymer. This excimer formation was also found in the ACN copolymers with maleic anhydride, methacrylonitrile, and methyl methacrylate reported by Wang and Morawetz²⁴.

X-ray diffractograms of the resulting homo and copolymer powder samples obtained by WCl_6 are shown in Figure 6. These powder samples give the Bragg spacings: $d = 9.6\text{Å}$, $d = 5.0\text{Å}$ in the polyindene and $d = 11.8\text{Å}$, 5.2Å , 4.3Å in the copolymer. It is shown that both the homo and copolymer have low crystallinity, which is also found in the PACN prepared by Ziegler-Natta catalyst²⁵.

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