

전이금속촉매에 의한 프로파길 유도체들의 중합

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Polymerization of Propargyl Derivatives by Transition Metal Catalysts

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요 약 : W-, Mo-, Ti-계 촉매에 의한 프로파길 브로마이드, 프로파길 클로라이드, 및 프로파길 알코올의 중합에 관해서 연구하였다. 전이금속클로라이드와 EtAlCl_2 로 구성된 촉매가 중합수율이나 분자량면에서 매우 효과적이었다. 폴리(프로파길 브로마이드)와 폴리(프로파길 클로라이드)의 수평균분자량(\overline{M}_n)은 사용한 촉매와 조건에 따라 8,700에서 19,500이었다. 합성한 중합체의 구조는 각 치환기(CH_2Br , CH_2Cl , CH_2OH)를 갖는 공액 폴리엔으로 밝혀졌다. 또한 합성한 중합체들의 용해성과 열적성질에 관해서도 연구하였다.

Abstract : The polymerization of propargyl bromide, propargyl chloride, and propargyl alcohol by W-, Mo-, and Ti-based catalysts was studied. Transition metal chloride- EtAlCl_2 catalyst systems were found to be very effective in the viewpoint of polymer yield and molecular weight. The number-average molecular weight (\overline{M}_n)s of poly(propargyl bromide) and poly(propargyl chloride) were in the range of 8,700 to 19,500 depending on the catalysts and polymerization conditions. The polymer structure was identified as the conjugated polyene containing each substituent (CH_2Br , CH_2Cl , CH_2OH). The solubility behaviors and thermal properties of the resulting polymers were also discussed.

INTRODUCTION

Acetylenic monomers are polymerized by Ziegler-Natta catalysts, by complexed nickel catalyst, and by anionic, free radical and cationic catalysts, among others.^{1,2} In general, Ziegler-Natta catalysts

give the best results with substituted acetylenes. For example, a mixture of iron(III) acetylacetonate and triethylaluminum(1:3) [$\text{Fe}(\text{acac})_3 \cdot 3\text{Et}_3\text{Al}$] polymerizes pri- or sec-alkylacetylenes and phenylacetylene to give high yields.^{3,4}

In 1974, it was found that the group VI metal-

based catalysts exhibit high catalytic activity for the polymerization of phenylacetylene.⁵ Since then various acetylene derivatives have been polymerized to give high polymer yield and high molecular weight polymer.⁶⁻¹⁰ We have also found that WCl_6 - and $MoCl_5$ -based catalyst systems are very effective for the polymerization of mono- and di-substituted acetylenes containing heteroatom¹¹⁻¹⁴ and the cyclopolymerization of dipropargyl derivatives.¹⁵⁻¹⁸ To date, the polymerization of propargyl bromide (PB) and propargyl chloride (PC) was attempted using catalysts such as $PdCl_2 \gamma$ -ray,²⁰ $NiI_2(Ph_3P)_2$,²¹ $W(CO)_6-CCl_4-h\nu$,²² $MoCl_5$,²³ $MoCl_5$ -polymer.²⁴ However, these catalysts gave only insoluble and intractable polymers.

In our previous communication,²⁵ we shortly reported the polymerization of PB and PC by transition metal-based catalyst to give high molecular weight soluble poly(propargyl bromide) (PPB) and poly(propargyl chloride) (PPC). This article reports the full accounts for the polymerization of PB, PC, and propargyl alcohol (PA) by various transition metal based catalysts, and the characterization and physical properties of the resulting polymers.

EXPERIMENTAL

Materials

Propargyl bromide, propargyl chloride, and propargyl alcohol (Aldrich Chemicals) were dried and fractionally distilled by the recommended procedures. Tungsten (W) and molybdenum (V) chlorides (Aldrich Chemicals, resublimed, 99+%), Titanium (IV) chloride (Hayashi Pure Chemicals, EP grade), Tetraalkyltin and organoaluminum compounds (Aldrich Chemicals) were used as received. Solvents used were all analytical grade materials. They were dried and fractionally distilled.

Instruments and Measurements

¹H-NMR spectra were recorded on a Varian T-60A spectrophotometer. ¹³C-NMR spectra were taken on Bruker AM-200 spectrophotometer. Infrared (IR) spectra were taken on a Perkin-

Elmer, Model 267 grating spectrometer using a potassium bromide pellets. Ultraviolet-visible spectra were obtained with a Carey 17 spectro photometer in 1,2-dichloroethane. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C / min up to 600°C with Perkin-Elmer TGS-1 Thermobalance. Number-average molecular weight (\bar{M}_n)s were determined by gel permeation chromatography (Waters 150°C) equipped with μ -styragel columns using tetrahydrofuran as an eluent. Monodisperse polystyrene (PS) standard samples were employed for molecular weight calibration.

Polymerization Procedures

All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere because of the active species are sensitive to moisture or oxygen. Transition metal halides and organometallic compounds were dissolved in each solvents before use as 0.05, 0.1, 0.2 and 0.4 M solutions. A polymerization ampule equipped with rubber septum was flushed with purified nitrogen.

Injection of catalyst solution and monomer was done by means of hypodermic-syringes from which air and moisture were carefully excluded. Polymerization was terminated with a mixture of methanol and chloroform (volume ratio 1:5). Then, the polymerization mixture was diluted with chloroform, and the polymer formed was usually isolated by precipitation into a large excess of methanol. The precipitated polymer was filtered from the solution and dried to a constant under vacuum at 40°C for 24 hrs. The polymer yield (P.Y.) was calculated by gravimetry. Typical examples of the polymerization procedure described below.

Polymerization of PB by WCl_6

A solution of WCl_6 (1.7 ml 0.05M chlorobenzene solution, 0.084-mmol) and chlorobenzene (0.8ml, $[M]_0$ (initial monomer concentration)=1) is prepared. To this solution is added PB (0.5g, 4.2mmol) at room temperature and the polymerization was carried out at 40°C for 24 hrs, Polymer yield

35%.

Polymerization of PB by WCl₆-EtAlCl₂ (1:4)

A catalyst solution is prepared by mixing WCl₆ (1.7ml 0.05M chlorobenzene solution, 0.084mmol), EtAlCl₂ (1.7ml 0.2M chlorobenzene solution, 0.336mmol) and chlorobenzene (0.1 ml chlorobenzene, [M]₀=1) and aged by keeping at 30°C for 15min. To this solution is added PB (0.5g, 4.2mmol). Polymerization was carried out at 40°C for 24hrs. Polymer yield 78%.

Polymerization of PC by TiCl₄-EtAlCl₂(1:4)

A catalyst solution is prepared by mixing TiCl₄ (0.7ml 0.2M benzene solution, 0.134mmol), EtAlCl₂ (2.7ml 0.2M benzene, 0.536mmol) and benzene (0.7ml, [M]₀=1.5) and aged by keeping at 30°C for 15min. To this solution is added PC(0.5g, 6.7mmol). Polymweization was carried out at 40°C for 24hrs. Polymer yield 42%.

Polymerization of PA by MoCl₅-Ph₄Sn(1:1)

A catalyst solution is prepared by mixing MoCl₅ (3.7ml 0.05M chlorobenzene solution 0.187mmol), and Ph₄Sn(65mg, 0.187mmol) and chlorobenzene (0.2ml, [M]₀=2) and aged by keeping at 30°C for 15min is prepared. To this solution is added PA(0.5g, 9.33mmol) at room temperature, the polymerization was proceeded explosively at 65°C. Polymer yield 100%.

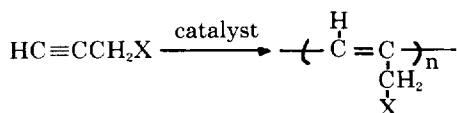
Polymerization of PA by MoCl₅ at 65°C

A solution of MoCl₅(3.7ml 0.05M chlorobenzene solution, 0.187mmol) and chlorobenzene(0.2ml, [M]₀=2) is prepared. To this solution is added PA(0.5g, 9.33mmol) at room temperature, the polymerization was proceeded explosively at 65°C. Polymer yield 100%.

RESULTS AND DISCUSSION

Polymerization

Propargyl halides and propargyl alcohol were polymerized by the aid of transition metal-based catalysts as following reaction Scheme I.



X=Br, Cl, OH.

Catalyst : WCl₆, MoCl₅, WCl₆-cocatalyst, MoCl₅-cocatalyst, TiCl₄-cocatalyst, etc.

Table 1 shows the results for the polymerization of PB by W, Mo, and Ti-based catalysts. WCl₆ and MoCl₅ alone give relatively low yield of polymer. In order to investigate the cocatalytic effect, various organotin and organoaluminum compounds were tested. The maximum polymer yield was obtained when EtAlCl₂ was used as cocatalyst. In recent year, it was found that organoaluminum compounds such as EtAlCl₂ were very effective cocatalyst for the polymerization of some mono- and di-substituted acetylenes by WCl₆ and MoCl₅ in our previous works.¹⁵⁻¹⁸ The polymer yields were found to be strongly dependent on the mole ratio of PB to catalyst. When the monomer to catalyst mole ratio(M/C) was 200 or 500, the polymer yield was very low. This low activity may be due to the interaction of a heteroatom (ie, Br of substituent) with the catalyst, thus hindering triple bond coordination by catalyst. Similar experimental results were reported in the polymerization of 2-ethynylthiophene by the similar catalyst system.¹¹

The effect of initial monomer concentration ([M]₀) on the polymer yield were also investigated (Exp. No 8, 13-15). When the values were 1 and 2, the highest polymer yields (78-80%) were obtained. MoCl₅-EtAlCl₂ catalyst system was as effective as WCl₆-EtAlCl₂ catalyst system. When TiCl₄ alone was used as catalyst, no methanol-insoluble polymer was obtained. However, TiCl₄-EtAlCl₂ catalyst system gave a moderate yield of completely soluble PPB.

Table 2 shows the results for the polymerization of propargyl chloride (PC) by various transition metal catalyst. As with the polymerization of PB, WCl₆ and MoCl₅ alone and WCl₆-organotin compound give a moderate yield of poly (propargyl chloride) (PPC). Organoaluminum compounds such as Et₂AlCl and EtAlCl₂ were also very effective cocatalyst for the polymerization of PC by WCl₆,

Polymerization of Propargyl Derivatives by Transition Metal Catalysts

Table 1. Polymerization of Propargyl Bromide by Transition Metal Catalysts.^a

Exp. No.	Catalyst System ^b (mole ratio)	M / C (mole ratio)	(M) ₀	P.Y. ^c (%)
1	WCl ₆	100	1	28
2	WCl ₆	50	1	35
3	WCl ₆ -n-Bu ₄ Sn(1:2)	50	1	51
4	WCl ₆ -Et ₃ Al(1:4)	50	1	57
5	WCl ₆ -(i-Bu) ₃ Al(1:4)	50	1	60
6	WCl ₆ -Et ₂ AlCl ₂ (1:4)	50	1	63
7	WCl ₆ -EtAlCl ₂ (1:2)	50	1	73
8	WCl ₆ -EtAlCl ₂ (1:4)	50	1	78
9	WCl ₆ -EtAlCl ₂ (1:4)	100	1	43
10	WCl ₆ -EtAlCl ₂ (1:4)	200	1	10
11	WCl ₆ -EtAlCl ₂ (1:4)	500	1	5
12	WCl ₆ -EtAlCl ₂ (1:4)	1000	1	~0
13	WCl ₆ -EtAlCl ₂ (1:4)	50	0.25	20
14	WCl ₆ -EtAlCl ₂ (1:4)	50	0.5	62
15	WCl ₆ -EtAlCl ₂ (1:4)	50	2	80
16	MoCl ₅	50	1	20
17	MoCl ₅ -n-Bu ₄ Sn(1:2)	50	1	22
18	MoCl ₅ -EtAlCl ₂ (1:4)	50	1	75
19 ^d	TiCl ₄	50	1	0
20 ^d	TiCl ₄ -EtAlCl ₂ (1:4)	50	1	52

^a Polymerization was carried out in chlorobenzene at 40°C for 24 hrs. Initial monomer concentration ((M)₀) was 1M.

^b Mixture of catalyst and cocatalyst was aged at 30°C for 15min before use.

^c Methanol-insoluble polymer.

^d Polymerization solvent was benzene.

MoCl₅, and TiCl₄. The polymer yield was 91% when the mole ratios of PB to WCl₆ as a catalyst and EtAlCl₂ to WCl₆ as cocatalyst are 50 and 4, respectively. TiCl₄ alone gave no polymer. However, TiCl₄-EtAlCl₂ and Ti(O-n-Bu)₄-EtAlCl₂ resulted in 42% and 9% yields of polymer, respectively.

Table 3 shows the solvent effect for the polymerization of PB by WCl₆-EtAlCl₂ (1:4) catalyst system. PB was polymerized in less polar solvents such as chlorobenzene, toluene, benzene, carbon tetrachloride, chloroform, cyclohexane, and 1,2-dichloroethane. The use of much more polar solvents such as nitrobenzene and DMF prohibited the formation of the polymer, regardless of the polymerization conditions.

Table 4 shows the temperature effect for the polymerization of PB and PC by MoCl₅ or WCl₆-EtAlCl₂ catalyst system. The polymerization of PB and PC by MoCl₅ alone at -78°C gives no methanol insoluble polymer. As the polymerization temperature is increased, the polymer yield was gradually increased. Above 40°C, the polymer yields were nearly constant.

Fig. 1 shows the time dependence of polymer yield in the polymerization of PC by WCl₆-EtAlCl₂ (1:4) and WCl₆. The polymerization by WCl₆ alone proceeded slowly. On the other hand, the polymerization by WCl₆-EtAlCl₂ proceeded rapidly within 1hr to the extent of 70%, and exhibited nearly constant yield after 6hrs.

Table 5 shows the results for the polymerization

Table 2. Polymerization of Propargyl Chloride by Transition Metal Catalysts.^a

Exp. No.	Catalyst System ^b (mole ratio)	M / C (mole ratio)	P.Y. ^c (%)
1	WCl ₆	50	40
2	WCl ₆	100	27
3	WCl ₆ -Me ₄ Sn(1:2)	50	43
4	WCl ₆ -n-Bu ₄ Sn(1:2)	50	46
5	WCl ₆ -Et ₂ AlCl ₂ (1:4)	50	76
6	WCl ₆ -EtAlCl ₂ (1:2)	50	85
7	WCl ₆ -EtAlCl ₂ (1:4)	50	91
8	MoCl ₅	50	30
9	MoCl ₅	100	20
10	MoCl ₅ -EtAlCl ₂ (1:2)	50	67
11	MoCl ₅ -EtAlCl ₂ (1:4)	50	75
12	MoCl ₅ -n-Bu ₄ Sn(1:2)	50	33
13 ^d	TiCl ₄	50	0
14 ^d	TiCl ₄ -EtAlCl ₂ (1:4)	50	42
15 ^d	Ti(O-n-Bu) ₄ -EtAlCl ₂ (1:4)	50	9

^a Polymerization was carried out in chlorobenzene at 40°C for 24 hrs. Initial monomer concentration ((M)₀) was 1.5M.

^b Mixture of catalyst and cocatalyst was aged at 30°C for 15min before use.

^c Methanol-insoluble polymer.

^d Polymerization solvent was benzene.

Table 3. Solvent Effect on the Polymerization of Propargyl Bromide by WCl₆-EtAlCl₂ (1:4).^a

Exp. No.	Solvent	P.Y. ^b (%)
1	Chlorobenzene	78
2	Toluene	75
3	Benzene	60
4	Carbon tetrachloride	74
5	Chloroform	70
6	Cyclohexane	73
7	1,2-Dichloroethane	45
8	Nitrobenzene	0
9	DMF	0

^a Polymerization was carried out at 40°C for 24 hrs. Monomer to catalyst mole ratio(M / C) and initial monomer concentration were 50 and 1M, respectively.

^b Methanol-insoluble polymer.

of propargyl alcohol(PA) by various transition metal catalysts. WCl₆ and WCl₆-cocatalyst give a low yield of polymer. TiCl₄ and TiCl₄-EtAlCl₂ catalyst system give no polymer. However,

MoCl₅-based catalysts were very effective for this polymerization. In the polymerization of PA by MoCl₅ alone at 40°C, the polymer yield was 82%. When Ph₄Sn and EtAlCl₂ were used as cocatalyst, the polymer yield were 94% and 88%, respectively. Especially, the polymerization of PA by MoCl₅ at 65°C proceeded explosively to exhibit a quantitative yield. This high catalytic activity of MoCl₅-based catalyst than WCl₆-based catalyst consistent with the results for the polymerization of dipropargyl ether.¹⁶

Table 6 shows the results for the polymerization of propargyl derivatives by a novel catalyst systems, ie., transition metal alkoxides. To date, these transition metal alkoxides such as Mo(OEt)₅, Ta(O-t-Bu)₅, and Nb(OEt)₅ were not used for the polymerization of any vinyl and acetylenic monomers. Mo(OEt)₅ was found to be effective for the polymerization of PC, PB, and PA. EtAlCl₂ shows some cocatalytic activity though Ph₃Bi shows no cocatalytic activity in the polymerization

Polymerization of Propargyl Derivatives by Transition Metal Catalysts

Table 4. Temperature Effect on the Polymerization of Propargyl Bromide and Propargyl Chloride by Transition Metal Catalysts.^a

Exp. No.	Monomer	Catalyst System ^b (mole ratio)	Temperature (°C)	P. Y. ^c (%)
1 ^d	PB	MoCl ₅	-78	0
2	PB	MoCl ₅	-20	5
3	PB	MoCl ₅	40	20
4 ^d	PB	WCl ₆ -EtAlCl ₂ (1:4)	-78	10
5	PB	WCl ₆ -EtAlCl ₂ (1:4)	-20	18
6	PB	WCl ₆ -EtAlCl ₂ (1:4)	40	78
7 ^d	PC	MoCl ₅	-78	0
8	PC	MoCl ₅	-20	8
9	PC	WCl ₆ -EtAlCl ₂ (1:4)	-20	21
10	PC	WCl ₆ -EtAlCl ₂ (1:4)	0	70
11	PC	WCl ₆ -EtAlCl ₂ (1:4)	20	85
12	PC	WCl ₆ -EtAlCl ₂ (1:4)	40	91
13	PC	WCl ₆ -EtAlCl ₂ (1:4)	60	92

^a Polymerization was carried out in chlorobenzene for 24 hrs. Monomer to catalyst mole ratio(M/C) was 50. Initial monomer concentrations of PB and PC were 1 and 1.5M, respectively.

^b Mixture of WCl₆ and EtAlCl₂ was aged at 30°C for 15min before use.

^c Methanol-insoluble polymer.

^d Polymerization solvent was toluene.

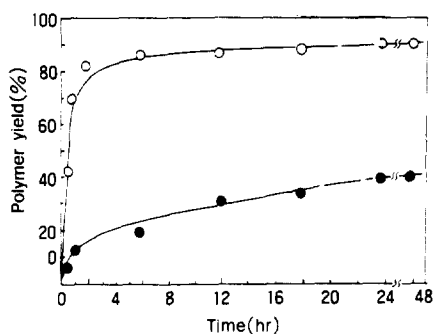


Fig. 1. Time dependence curves in the polymerization of propargyl chloride(catalyst system:○=WCl₆-EtAlCl₂ (1:4), ●=MoCl₅, Polymerization conditions : temperature=40°C, [M]₀=1.5, M/C=50).

of PC by Mo(OEt)₃. However, other transition metal alkoxides such as Ti(O-t-Bu)₃, and Nb(OEt)₅ gives no methanol insoluble polymer. The polymer yields of PB and PA by Mo(OEt)₃ were 20 and 42%, respectively.

Table 7 shows the methanol-insoluble polymer yields and the chloroform soluble(methanol-in-

soluble) polymer yields of some representative polymers. It was found that the amount of soluble polymer depends on the catalyst system and the polymerization conditions, WCl₆-EtAlCl₂ and MoCl₅-EtAlCl₂ gives much more soluble polymer than transition metal chloride does. And also, MoCl₅-based catalyst gives much more soluble polymer in organic solvents than WCl₆-based catalyst. Especially, the polymers obtained by TiCl₄-EtAlCl₂ were completely soluble in organic solvents though the polymer yield are relatively low. The number average molecular weight(\bar{M}_n)s of PPB and PPC were in the range of 8,700 and 19,500 depending on the catalyst and polymerization conditions.

Identification of Polymer Structure

Polymer structure was identified by NMR (¹H-and ¹³C-), IR, UV-visible spectroscopy. Figure 2 shows the ¹H-NMR spectra of poly(propargyl bromide) (PPB) and poly(propargyl chloride) (PPC) prepared by TiCl₄-EtAlCl₂. A broad peaks at 6-8ppm and at 0.5-4 ppm are due to the vinylic protons in the polymer backbone

Table 5. Polymerization of Propargyl Alcohol by Transition Metal Catalysts.^a

Exp. No.	Catalyst System ^b (mole ratio)	Solvent	Temperature (°C)	P. Y. ^c (%)
1	WCl ₆	Chlorobenzene	40	5
2	WCl ₆ -Me ₄ Sn(1:2)	Chlorobenzene	40	6
3	WCl ₆ -EtAlCl ₂ (1:2)	Chlorobenzene	40	3
4	MoCl ₅	Chlorobenzene	40	82
5	MoCl ₅ -Ph ₄ Sn(1:1)	Chlorobenzene	40	94
6	MoCl ₅ -EtAlCl ₂ (1:2)	Chlorobenzene	40	88
7	MoCl ₅	Chlorobenzene	65	~100 ^d
8	TiCl ₄	Benzene	40	0
9	TiCl ₄ -EtAlCl ₂ (1:2)	Benzene	40	0
10 ^e	PdCl ₂	DMF	90	43

^a Polymerization was carried out for 24 hrs. Monomer to catalyst mole ratio(M/C) and initial monomer concentration ((M)₀) were 50 and 2.5M, respectively.

^b Mixture of catalyst and cocatalyst was aged at 30°C for 15 min before use.

^c Petroleum ether-insoluble polymer.

^d Explosively polymerized.

^e Monomer to catalyst mole ratio (M/C) and initial monomer concentration ((M)₀) were 30 and 1, respectively.

Table 6. Polymerization of Propargyl Derivatives by Transition Metal Alkoxides.^a

Exp. No.	Monomer	Catalyst System ^b (mole ratio)	P.Y. ^c (%)
1	PC	Mo(OEt) ₅	51
2	PC	Mo(OEt) ₅	5
3	PC	-Ph ₃ Bi(1:2)	64
4	PC	Mo(OEt) ₅	0
5	PC	-EtAlCl ₂ (1:4)	0
6	PC	Ta(O-t-Bu) ₅	0
7	PC	Ta(O-t-Bu) ₅	0
8	PC	-Et ₂ Al(1:4)	0
9	PC	Ta(O-t-Bu) ₅	0
10	PB	-EtAlCl ₂ (1:4)	0
11	PA	Nb(OEt) ₅	0
		Mo(OEt) ₅	20
		Mo(OEt) ₅	42

^a Polymerization was carried out at 60°C for 24 hrs. Monomer to catalyst mole ratio(M/C) was 50. Initial monomer concentration((M)₀) for the PC and PA and the PB were 1 and 1.5M, respectively.

^b Mixture of catalyst and cocatalyst in toluene was aged at 30°C for 5 min before use.

^c Methanol-insoluble polymer (mostly insoluble).

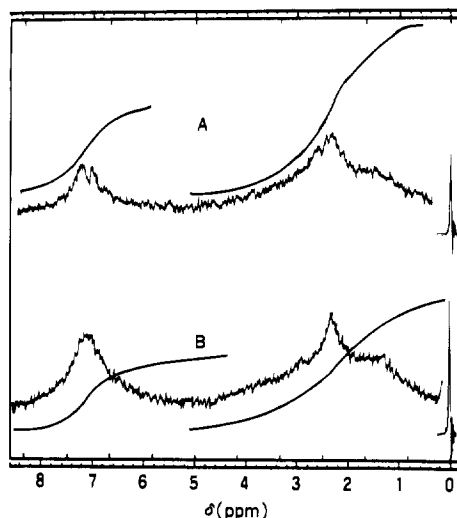


Fig. 2. ¹H-NMR spectrum of poly(propargyl bromide) (A) and poly(propargyl chloride) (B) prepared by TiCl₄-EtAlCl₂ (solvent : CDCl₃).

and the methylene protons, respectively.

The IR spectra (Figure 3) of PPB, PPC, and PPA gives the aliphatic C-H stretching band at 2940cm⁻¹ and also show an absorption band at 1600cm⁻¹ owing to C=C stretching band

Table 7. Number Average Molecular Weights of Soluble Poly(propargyl derivatives).^a

Sample (A-B) ^b	Polymer	Catalyst System (mole ratio)	Polymer Yield ^c (Soluble, %) ^d	\bar{M}_n
1 - 2	PPB	WCl ₆	35 (10)	8,700
1 - 8	PPB	WCl ₆ -EtAlCl ₂ (1:4)	78 (46)	18,200
2 - 1	PPC	WCl ₆	40 (11)	9,400
2 - 4	PPC	WCl ₆ -n-Bu ₃ Sn(1:2)	46 (20)	11,000
2 - 7	PPC	WCl ₆ -EtAlCl ₂ (1:4)	91 (61)	19,500
2 - 11	PPC	MoCl ₅ -EtAlCl ₂ (1:4)	75 (64)	17,600
1 - 20	PPB	TiCl ₄ -EtAlCl ₂ (1:4)	52 (52)	10,100
2 - 14	PPC	TiCl ₄ -EtAlCl ₂ (1:4)	42 (42)	9,700
6 - 1	PPC	Mo(OEt) ₃	51 (0)	-
5 - 4	PPA	MoCl ₅	82 (0)	-

^a Determined by GPC in tetrahydrofuran using a calibration curve for polystyrene.

^b A=table number, B=Experiment number.

^c Methanol-insoluble polymer.

^d Chloroform-soluble (methanol insoluble) polymer.

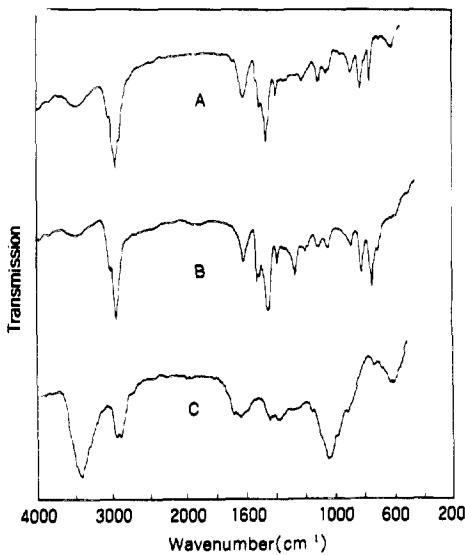


Fig. 3. IR spectra of poly(propargyl bromide) (A), poly(propargyl chloride) (B), and poly(propargyl alcohol) in KBr pellet.

of the conjugated polymer backbone.

Figure 4 show the ¹³C-NMR spectrum of PPB prepared by MoCl₅-EtAlCl₂ catalyst system. The chemical shifts of the carbon on the polymer backbone were 129 and 135 ppm, whereas that of the methylene carbons was 40 ppm.

Figure 5 show the UV-visible spectra of PC,

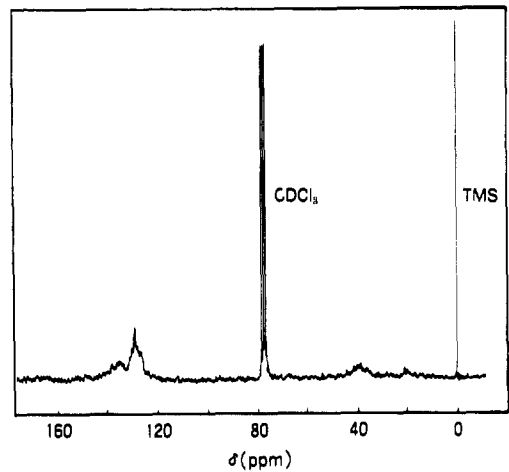


Fig. 4. ¹³C-NMR spectrum of poly(propargyl bromide) (PPB) prepared by MoCl₅-EtAlCl₂ (50.32MHz on a Bruker AM-200 spectrometer).

PPB, and PPC in 1,2-dichloroethane. A broad and weak $\pi \rightarrow \pi^*$ absorption peak of conjugated double bonds in the polymer main chain, which are absent in monomer, appeared at longer wavelengths (280-550nm) in the UV-visible spectra of the resulting PPB and PPC.

Physical Properties

The solubility test was performed for powderly samples in excess solvent. The solubility behavior

Table 8. Solubility Behaviors of Poly(propargyl bromide) (PPB), Poly(propargyl chloride) (PPC), and Poly(propargyl alcohol) (PPA).^a

Polymer	Solvent									
	Chlorobenzene	Toluene	Benzene	Chloroform	THF	CCl ₄	DMF	HCO ₂ H	MeOH	Ethyl ether
PPB ^b	+	+	+	+	+	+	±	-	-	-
PPC ^b	+	+	+	+	+	+	±	-	-	-
PPA ^c	-	-	-	-	-	-	-	-	-	-

^a Solubility test was performed for powdery samples in excess solvent, (+=soluble, ±=partially soluble, -=insoluble).

^b PPB and PPC by TiCl₄-EtAlCl₂ or the soluble portion in chloroform of PPB and PPC obtained by WCl₆-EtAlCl₂.

^c PPA by MoCl₅.

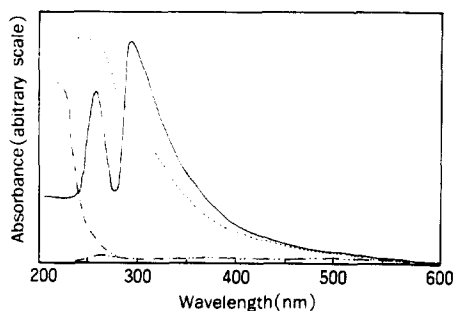


Fig. 5. Ultraviolet-visible spectra of poly(propargyl bromide) (—), poly(propargyl chloride) (·····), and propargyl chloride(- · - · -) in 1,2-dichloroethane(- - - - -).

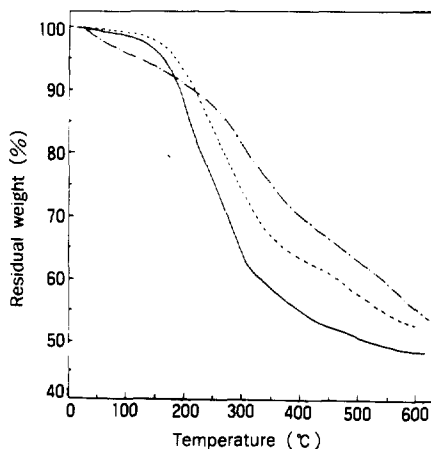


Fig. 6. TGA, thermograms of poly(propargyl bromide) (—), poly(propargyl chloride) (·····), and poly(propargyl alcohol) (- - - - -).

of PPB, PPC and PPA are listed in Table 8. PPB and PPC prepared by TiCl₄-EtAlCl₂ are completely soluble in aromatic and halogenated hydrocarbons such as toluene, benzene, chloroform, and CCl₄, and partially soluble in DMF, but insoluble in formic acid, methanol, and ethyl ether. PPB and PPC prepared by other transition metal catalysts are partially soluble in organic solvents. The solubility behavior of the soluble polymer in chloroform of PPB and PPC is similar to those of PPB and PPC prepared by TiCl₄-EtAlCl₂. However, PPA was not soluble in any organic solvents regardless of the polymerization conditions. This insolubility of PPA is assumed to be internal cross-linking of polymer chain by reactive hydroxy group.

It was reported that polyacetylene was insoluble in any organic solvents. And also, the polymers from symmetrically disubstituted acetylenes are

usually insoluble owing to the small free volumes in these polymers and, in turn, little interaction with solvents (e.g., -CMe=CMe-_n , $\text{-C(n-Bu)=C(n-Bu)-}_n$, $\text{-C(CF}_3\text{)=C(CF}_3\text{)-}_n$, -C(Ph)=C(Ph)-_n , etc.). Poly(phenylacetylene) was soluble in aromatic and halogenated hydrocarbons but insoluble in polar protic solvents such as methanol and formic acid.⁵ However, poly(2-ethynylpyridine) containing pyridine substituent was completely soluble in methanol and formic acid.²⁶

From these results, it can be concluded that the solubility behaviors of acetylenic polymers depend on the nature (aromaticity, bulkiness, polarity, etc.), and the number (no substituent (ie, polyacetylene, mono-, di-substituted and symmetrically disubstituted ones)) of the substituent

and the extent of cross-linking (depending on the polymerization catalyst and conditions).

Figure 6 show the TGA thermograms of PPB, PPC, and PPA. PPB, PPC and PPA show 5% weight losses at 190°C, 170°C, and 115°C, respectively. The residual weights of PPB, PPC, and PPA at 600°C were 48%, 52.5%, and 55%, respectively.

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