

전이금속촉매에 의한 2-프로핀-1-올의 중합

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Polymerization of 2-Propyn-1-ol by Transition Metal Catalysts

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요 약 : Mo- 및 W-계 촉매를 사용하여 히드록기 관능기가 있는 프로파길유도체인 2-프로핀-1-올의 중합에 대해서 연구하였다. MoCl₅계 촉매의 활성이 WCl₆계의 그것보다 훨씬 큰 것으로 밝혀졌으며, MoCl₅-EtAlCl₂ 촉매 System의 경우 거의 정량적인 수율을 보였다. 본 중합은 클로로벤젠, 사염화탄소, 1,1,2-트리클로로에틸렌과 같은 방향족 및 할로겐화 탄화수소용매에서 잘 진행되었으며 중합수율은 중합온도가 증가할수록 현저히 증가하였다. 전이금속알콕사이드인 Mo(OEt)₅ 및 Mo(OEt)₅-EtAlCl₂ 촉매계를 본 중합에 사용해 본 결과 약 50% 내외의 중합수율을 보여주었다. 합성한 폴리(2-프로핀-1-올)의 적외선분광스펙트럼에서는 아세틸렌의 ≡C-H 및 C≡C 신축파를 보여주지 않는 대신 1650cm⁻¹ 부근에서의 탄소-탄소 이중결합의 특성 피크가 관찰되었다. 폴리(2-프로핀-1-올)은 사용한 촉매나 조건에 관계없이 유기용매에 녹지 않았으며 대부분 검은색의 분말상이었다.

Abstract : The polymerization of 2-propyn-1-ol, a propargyl derivative having hydroxy functional group was carried out by various Mo- and W-based catalysts. The catalytic activities of MoCl₅-based catalysts were found to be greater than those of WCl₆-based catalysts. MoCl₅-EtAlCl₂ catalyst system gave a quantitative yield of polymer. The polymerization was well proceeded in aromatic and halogenated hydrocarbon solvents such as chlorobenzene, CCl₄, 1,1,2-trichloroethylene etc. The polymer yield was increased as the polymerization temperature is increased. Mo(OEt)₅ and Mo(OEt)₅-EtAlCl₂ catalyst systems gave some moderate polymer yields. The infrared spectra of the resulting poly(2-propyn-1-ol) showed neither the acetylenic hydrogen stretching nor the carbon-carbon triple bond stretching frequency. Instead, a new carbon-carbon double bond stretching frequency at about 1650 cm⁻¹ appeared, which indicates that the highly conjugated polymer was formed. The resulting poly(2-propyn-1-ol)s were black powder and mostly insoluble in any organic solvents regardless of the catalysts and the polymerization conditions used.

INTRODUCTION

The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugated system, which can be used at present time as organic semiconductors.^{1,2} Polyacetylene has been the simplest organic conducting polymer, of which a rapidly increasing interest is being aroused in recent years, since the discovery of the high electrical conductivity of the doped polyacetylene was found in 1977.³ A number of studies for polyacetylene such as synthesis method, structure-properties correlation, electric and optical properties, and various cells for practical applications was carried out.⁴⁻⁶

However polyacetylenes were insoluble in any organic solvent and unstable to air oxidation. Thus various mono- and disubstituted polyacetylene derivatives were synthesized and characterized.⁷⁻⁸ In general, the study of substituted polyacetylenes involves many subjects as follows: ⁹ a) synthesis of new monomers and polymers, b) design and development of active catalyst systems,¹⁰⁻¹¹ c) polymer design (e. g., block and graft copolymers),¹² d) elucidation of polymer structure and properties,¹³⁻¹⁵ and e) development of polymer functions (e. g., electric and photoconductivities,¹⁶⁻¹⁷ gas permeations,¹⁸⁻¹⁹ liquid mixture separation²⁰ etc.).

The polymerization of propargyl derivatives, which are one of monosubstituted acetylenes was scarce and restricted to some cases such as propargyl halide,²¹ phenyl propargyl ether,²¹ dipropargyl ether,²² etc.

In recent years we have reported the polymerization of propargyl halides,^{23,24} propargyl ethers,²⁵ and propargyl amines²⁶ and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether,²⁷ dipropargyl diphenylmethane,²⁸ dipropargylsilanes,²⁹ dipropargylgermaniums,³⁰ etc. The polymerization of 2-propyn-1-ol, having a hydroxy functional group, have been carried out by PdCl₂,²¹ NiI₂(Ph₃P)₂,³¹ Ni(NCS)(C≡CR)(Ph₃P)₂,³¹ γ -rays,³² plasma,³³ etc.

The MoCl₅-catalyzed polymerization of 2-pro-

pyn-1-ol briefly reported.³⁴ However there have been no reports for the systematic polymerizations of 2-propyn-1-ol by various transition metal catalyst systems.

The present paper deals with the full accounts for the polymerization of 2-propyn-1-ol, a propargyl derivative containing hydroxy functional group, and the characterization of the resulting poly(2-propyn-1-ol).

EXPERIMENTAL

Materials

2-Propyn-1-ol (Aldrich Chemicals., 99%) was dried and fractionally distilled by the recommended procedure. MoCl₅ and WCl₆ (Aldrich Chemicals, resublimed, 99+%), and organoaluminum compounds (Et₃Al, (i-Bu)₃Al, Et₂AlCl, EtAlCl₂, Aldrich chemicals., 1.8M solution in toluene) were used as received. Tetraphenyltin (Aldrich Chemicals., 97%) was purified by recrystallizing twice from carbon tetrachloride. Tetrabutyltin (Aldrich Chemicals., 99%) and n-butyllithium (Aldrich Chemicals., 2.5M solution in hexanes) were used without further purification. Transition metal alkoxides [Mo(OEt)₅, W(OEt)₆, High Purity Chemicals.] were used as received. All polymerization solvents were analytical grade materials. They were dried with appropriate drying agent and fractionally distilled.

Instruments

Infrared spectra were recorded on a Bio-Rad Digilab FTS-60 spectrometer using KBr pellet. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 °C/min up to 750°C with Dupont 951 Thermogravimetric Analyzer.

Polymerization Procedures

All procedures for catalyst solution preparation and polymerization were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal catalysts and organoaluminum compounds were dissolved in each solvent before use as 0.05, 0.1,

0.2 and 0.4M solutions. A polymerization ampule equipped with rubber septum was flushed with nitrogen.

Injections of catalyst solution and monomer were done by means of hypodermic syringes from which air and moisture were carefully excluded. After a given polymerization time, the polymer solution was diluted with chloroform, and the polymer was purified by pouring into a large excess of methanol. The polymer was filtered from the solution and dried to a constant weight under vacuum at 40°C for 24hr. The polymer yield was calculated by gravimetry.

Polymerization of 2-Propyn-1-ol by MoCl₅

A solution of MoCl₅(1.78ml 0.05M chlorobenzene solution, 0.0892mmol) and chlorobenzene(2.18ml, [M]₀=2) is prepared. To this solution is added 2-propyn-1-ol(0.5g, 9.33mmol) at room temperature, the polymerization was proceeded at 60°C for 24hr. Polymer yield 87%.

Polymerization of 2-Propyn-1-ol by MoCl₅-EtAlCl₂

A catalyst solution is prepared by mixing MoCl₅(1.78ml 0.05M chlorobenzene solution, 0.0892 mmol), EtAlCl₂(0.892ml 0.2M chlorobenzene solution, 0.178mmol), and chlorobenzene(1.29ml, [M]₀=2) and aged by keeping at 30°C for 15min. Polymerization was carried out at 60°C for 24hr. Polymer yield 99%.

Polymerization of 2-Propyn-1-ol Mo(OEt)₅-EtAlCl₂

A catalyst solution is prepared by mixing Mo(OEt)₅(0.446ml 0.2M chlorobenzene solution, 0.0892mmol), EtAlCl₂(0.892ml 0.2M chlorobenzene solution, 0.178mmol), and chlorobenzene(2.622ml, [M]₀=2) and aged by keeping at 30°C for 15min. Polymerization was carried out at 60°C for 24hr. Polymer yield 53%.

RESULTS AND DISCUSSION

The polymerization of 2-propyn-1-ol containing hydroxy functional group, was carried out by various transition metal-based catalysts.

Table 1 shows the results for the polymerization of 2-propyn-1-ol by WCl₆-, MoCl₅-, and TiCl₄-based catalysts. WCl₆ and WCl₆-cocatalyst(Cocatalyst : Ph₄Sn, n-Bu₄Sn, EtAlCl₂) systems show only a low yield of polymer. However MoCl₅ and MoCl₅-Ph₄Sn catalyst systems showed a high catalytic activity for this polymerization of 2-propyn-1-ol. TiCl₄-TiCl₄-EtAlCl₂ catalyst systems, which gave some moderate yied of polymer in the polymerization of propargyl halides such as propargyl bromide and propargyl chloride, give no polymer.

Table 2 shows the results for polymerization of 2-propyn-1-ol by MoCl₅-based catalysts. Organotin and organoaluminum compounds, typical cocatalysts for the polymerizatio of substituted acetylenes and cycloolefins, were used. And also n-BuLi and ethanol were used as cocatalyst(reducing agent). In present polymerization of 2-propyn-1-ol, MoCl₅ alone shows a high catalytic activity. Ph₄Sn and n-Bu₄Sn did not show a enhanced cocatalytic activity. Four organoaluminum compounds such as Et₃Al, Et₂AlCl, EtAlCl₂, and (i-Bu)₃Al were used as cocatalyst. Then the polymer yields were somewhat increased when Et₂AlCl and EtAlCl₂ are used

Table 1. Polymerization of 2-Propyn-1-ol by Transition Metal Catalysts^a

Exp. No.	Catalyst System ^b (mole ratio)	Solvent	Polymer Yield(%)
1	WCl ₆	Chlorobenzene	7
2	WCl ₆ -Ph ₄ Sn(1 : 1)	Chlorobenzene	10
3	WCl ₆ -n-Bu ₄ Sn(1 : 2)	Chlorobenzene	7
4	WCl ₆ -EtAlCl ₂ (1 : 2)	Chlorobenzene	5
5	MoCl ₅	Chlorobenzene	87
6	MoCl ₅ -Ph ₄ Sn(1 : 1)	Chlorobenzene	90
7	TiCl ₄	Benzene	0
8	TiCl ₄ -EtAlCl ₂ (1 : 2)	Benzene	0

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

Monomer to catalyst mole ratio(M/C) and initial monomer concentration([M]₀) were 100 and 2M, respectively.

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

Table 2. Polymerization of 2-Propyn-1-ol by MoCl₅-Based Catalysts^a

Exp. No.	Catalyst System ^b (mole ratio)	Polymer Yield ^c (%)
1	MoCl ₅	87
2	MoCl ₅ -Ph ₃ Sn(1 : 1)	90
3	MoCl ₅ -n-Bu ₄ Sn(1 : 2)	85
4	MoCl ₅ -Et ₃ Al(1 : 2)	84
5	MoCl ₅ -Et ₂ AlCl(1 : 2)	95
6	MoCl ₅ -EtAlCl ₂ (1 : 2)	99
7	MoCl ₅ -(i-Bu) ₃ Al(1 : 2)	86
8	MoCl ₅ -n-BuLi(1 : 1)	73
9	MoCl ₅ -n-BuLi(1 : 3)	50
10	MoCl ₅ -n-BuLi(1 : 5)	44
11	MoCl ₅ -EtOH(1 : 2)	84

^a Polymerization was carried out for 24hr in chlorobenzene at 60°C. Monomer to catalyst mole ratio(M/C) and initial monomer concentration([M]₀) were 100 and 2, respectively.

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

as cocatalyst. MoCl₅-EtAlCl₂ catalyst system showed a quantitative yield of polymer. n-Butyllithium and ethanol were also used as cocatalyst. However the polymer yield was rather decreased. The high catalytic activity of MoCl₅ alone in the polymerization of 2-propyn-1-ol may be explainable as the cocatalytic activity of 2-propyn-1-ol itself by reducing MoCl₅ although the mechanism is not fully understood. The similiar high catalytic activity of MoCl₅-based catalyst was also observed in the polymerization of propiolic acid containing polar carboxylic acid.³⁶

Table 3 shows the solvent effect for the polymerization of 2-propyn-1-ol by MoCl₅. It was found that aromatic and chlorinated hydrocarbon solvents are good solvents for this polymerization. Tetrahydrofuran and methyl ethyl ketone solvents gave relatively low yields of polymer. Nitrobenzene and hexane solvents give no polymers.

Table 4 shows the temperature effect for the polymerization of 2-propyn-1-ol by MoCl₅. In general,

Table 3. Solvent Effect for the Polymerization of 2-Propyn-1-ol by MoCl₅

Exp. No.	Solvent	Temperature (°C)	Polymer Yield ^b (%)
1	Chlorobenzene	60	87
2	Toluene	60	71
3	Benzene	60	65
4	CCl ₄	60	84
5	Chloroform	20	58
6	CH ₂ Cl ₂	20	25
7	CHCl=CCl ₂	60	82
8	THF	60	33
9	MEK	60	15
10	Hexane	60	0
11	Nitrobenzene	60	0

^a Polymerization was carried out for 24hr. Monomer to catalyst mole ratio(M/C) and initial monomer concentration([M]₀) were 100 and 2M, respectively.

Table 4. Temperature Effect for the Polymerization of 2-Propyn-1-ol by MoCl₅^a

Exp. No.	Temperature (°C)	Polymer Yield (%)
1	r. t	0
2	r. t(48hr) + 60	65
3	40	73
4	60	87
5	90	93
6	120	94

^a Polymerization was carried out in chlorobenzene for 24hr. The polymerization solvent was chlorobenzene. Monomer to catalyst mole ratio(M/C) and initial monomer concentration([M]₀) were 100 and 2M, respectively.

the polymer yield was increased as the polymerization temperature is increased. The polymerization did not proceed at room temperature(at about 20°C). The polymerization was proceeded at 60°C even after the polymerization solution(mixture of monomer, catalyst, and solvent) was stood for 48hr at room temperature. This phenomenon indicates that the catalyst(MoCl₅) did not deactivate though

Table 5. Polymerization of 2-Propyn-1-ol by Transition Metal Alkoxides^a

Exp. No.	Catalyst System ^b (mole ratio)	M/C ^c	[M] ₀ ^d	P. Y
1	Mo(OEt) ₅	50	1	42
2	Mo(OEt) ₅	100	2	21
3	Mo(OEt) ₅ -EtAlCl ₂ (1 : 2)	50	1	53
4	W(OEt) ₆	50	1	0
5	W(OEt) ₆ -EtAlCl ₂ (1 : 2)	50	1	10

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

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

^c Monomer to catalyst mole ratio.

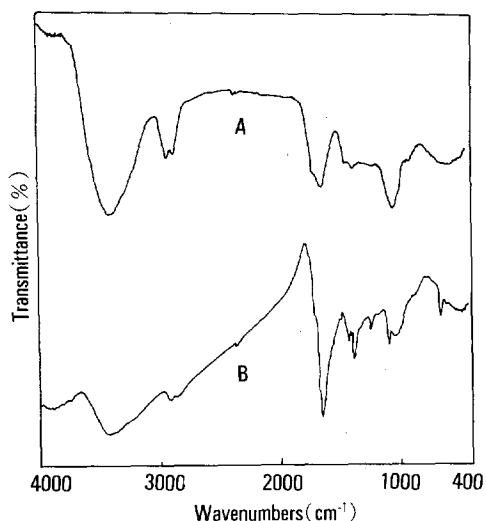
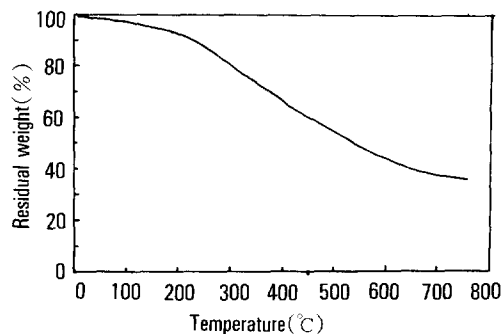
^d Initial monomer concentration ([M]₀).

the polymerization solution has been stood for 48 hr at room temperature.

Table 5 shows the results for the polymerization of 2-propyn-1-ol by transition metal alkoxides. Transition metal alkoxides such as Mo(OEt)₅ and W(OEt)₆, have not been used for the polymerization of acetylene derivatives. Mo(OEt)₅ alone gives some moderate yield of polymer(42%). EtAlCl₂ shows somewhat cocatalytic activity for this polymerization of 2-propyn-1-ol by Mo(OEt)₅. W(OEt)₅ alone gives no polymer. However W(OEt)₅-EtAlCl₂ catalyst system gives a lower yield of polymer(20%). In the polymerization of 2-propyn-1-ol by transition metal alkoxides, the catalytic activity of Mo(OEt)₅-based catalysts was also found to be greater than that of W(OEt)₆-based catalysts.

The resulting poly(2-propyn-1-ol)s were insoluble in any organic solvents regardless of the polymerization conditions and the catalysts used and were mostly black powder.

Fig. 1 shows the infrared spectra of poly(2-propyn-1-ol)s. The infrared spectrum of polymers showed neither the acetylenic hydrogen stretching nor the carbon-carbon triple bond stretching frequencies presented in the infrared spectrum of the monomer, 2-propyn-1-ol. Instead, new carbon-


Fig. 1. Infrared spectra of poly(2-propyn-1-ol) : A (MoCl₅), B[Mo(OEt)₅-EtAlCl₂].

Fig. 2. TGA thermogram of poly(2-propyn-1-ol) prepared by MoCl₅.

carbon double bond stretching frequency at about 1650cm⁻¹ appeared, which indicates that a highly conjugated polymer was formed. As the result of insolubility of present polymers, the identification of polymer by various instrumental methods [NMR(¹H-, ¹³C-), GPC, UV-visible] was not carried out. Although the spectral data is insufficient, it was thought that there is no any possibility of other structure besides ideal poly(2-propyn-1-ol) structure. Of course, the present polymer was seen to have some cross-linked part, which may be caused by activated allyl protons of resulting poly(2-

propyn-1-ol) and/or the hydroxy functional group.

Fig. 2 shows the TGA thermogram of poly(2-propyn-1-ol). It shows that the poly(2-propyn-1-ol) retained 92% of its original weight at 200°C, 80% at 300°C, 54% at 500°C, and 37% at 700°C.

CONCLUSIONS

In this study, poly(2-propyn-1-ol) containing polar hydroxy functional group, was synthesized by various transition metal catalysts. The catalytic activities of Mo-based catalysts were found to be greater than those of W-based catalysts. EtAlCl₂ were found to be effective cocatalysts for the polymerization of 2-propyn-1-ol by MoCl₅ and Mo(OEt)₅. The polymerization was well proceeded in various aromatic and halogenated hydrocarbon solvents except for nitrobenzene, hexanes. The resulting poly(2-propyn-1-ol)s were insoluble in any organic solvents regardless of the polymerization conditions and the catalysts used. This insolubility is assumed to be due to the crosslinking of resulting polymers by the active allyl protons and/or the hydroxy functional group during polymerization.

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Polymerization of 2-Propyn-1-ol by Transition Metal Catalysts

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