MoCl₅에 의한 폐닐아세틸렌의 중합에서 2-프로판-1-올의 영향

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The Effect of 2-Propyn-1-ol on the Polymerization of Phenylacetylene by MoCl₅

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요 약: MoCl₅-HC=CCH₂OH 촉매 시스템을 사용한 폐닐아세틸렌의 중합을 여러가지 반응조건하에
서 시도하였다. MoCl₅에 대한 HC=CCH₂OH의 용비, 활성화 온도 및 중합온도의 영향을 연구하였
다. MoCl₅에 대한 HC=CCH₂OH 용비가 5일 경우에는 가장 좋은 결과(증합수율=58%, M₅₀=7,200)을
얻었다. HC=CCH₂OH에 대한 MoCl₅의 활성화 온도에 관계없이 넓은 온도범위에서 중합이 잘 진
행되어 비교적 높은 수율을 보였다. HC=CCH₂OH가 MoCl₅의 염소원소를 침식시켜 중합시에 활성
촉매중으로 작용하는 몬드리에른의 알코올중합수를 만드는 것으로 판단되었다. MoCl₅-HC=CCH₂OH
촉매 시스템에 의해 형성된 폐닐아세틸렌의 구조를 NMR(¹H-, ¹³C-), IR, UV-visible 등과 같은
분석장비로 규명하였으며 형성한 폐닐아세틸렌의 열특성에 관해서도 연구하였다.

Abstract: The polymerization of phenylacetylene using MoCl₅-HC=CCH₂OH catalyst system was carri
ed out at various reaction conditions. The effects of the mole ratio of HC=CCH₂OH to MoCl₅, the
activation and polymerization temperatures, etc. were studied. The best result(polymer yield=58%,
M₅₀=7200) was obtained when the mole ratio of HC=CCH₂OH to MoCl₅ was 5. In a wide temperatur
es range(20~90°C), the polymerizations were well proceeded to give a relatively good yield, regardle
ss of the activation temperature of MoCl₅ by HC=CCH₂OH. It was concluded that the hydroxyl
group of HC=CCH₂OH substituted the chlorine atom of MoCl₅ to make an alkoxide derivative of moly
bdenum, which plays a role as an active catalytic species. The polymer structure of poly(phenylacet
ylene) prepared by MoCl₅-HC=CCH₂OH catalyst system was also characterized by various instrumen
tal methods such as NMR(¹H-, ¹³C-), IR, UV-visible spectroscopies. The thermal properties were a
iso studied.

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INTRODUCTION

The Mo- and W-based catalysts have been used as the catalyst for the olefin metathesis reaction and the metathesis polymerization of cyclic olefins. In 1974, it was found that phenylacetylene was polymerized with WCl₆ and MoCl₅. In this case, the MoCl₅-based catalysts were found to be less effective than WCl₆-based catalysts and to give a low yield of polymer (conversion: <20%).

Mo-based catalysts are of three main types: support oxides, generated in various ways: MoCl₅ activated with a suitable cocatalyst; Mo complexes also activated by a cocatalyst. It was known that the cocatalyst used in most homogeneous systems plays essential part in the whole process of metathesis. Besides its first action as alkylating and reducing agent for the transition metal compound, the cocatalyst may interact with active centers during propagation and may act upon metal ligands, labilizing and then creating vacant sites for coordination. In general, the metathesis catalysts have Lewis acid properties. They interact with the transition metal complex or are converted into more active species which are involved in the process. This interaction depends upon the nature of the transition metal and its ligands, the nature of cocatalyst metal, the solvent and the reaction conditions.

The Mo-based catalyst systems used in the olefin metathesis reaction and the polymerization of acetylenes are as follows: MoCl₅/Et₂Al for cyclopentene, MoCl₅(NO)₂(PPh₃)₂/ EtAlCl₂ for tetradec-1-ene/4-methylpent-1-ene, Mo(CO)₆/4-bromophenol for BuC≡CPh, MoCl₅/NaBH₄/DMF for C₆H₂ and C₆H₄, MoO(OPh)₃/ Et₂Al/PhOH for non-4-ylene, MoCl₅/Ph₃Sn for alk-2-yenes(C₆-C₆₁), etc.

The living polymerizations of some acetylene derivatives such as 1-chloro-2-alkynes and o-(trifluoromethyl)phenylacetylene using MoOCl₅/n-Bu₃Sn/ EtOH catalyst system, were carried out.

In recent years, we found that the MoCl₅ alone is very active catalyst for the polymerization of HC=C.CH₂OH to give a quantitative yield of polymer. There have been some viewpoints that HC=C.CH₂OH activates the MoCl₅.

In our previous communication, we briefly reported on the cocatalytic activity of HC=C.CH₂OH for the polymerization of phenylacetylene by MoCl₅. This paper deals with the full accounts for the polymerization of phenylacetylene by MoCl₅—HC=C.CH₂OH catalyst system, and the characterization and physical properties of the resulting polymers.

EXPERIMENTAL

Materials. Phenylacetylene (PA, Aldrich Chemicals, 98%, bp 142~144°C) was dried with calcium hydride and fractionally distilled. 2-Propyn-1-ol (Aldrich Chemicals, 99%) was used after simple distillation. Molybdenum pentachloride (Aldrich Chemicals, resublimed, 99 + %) and ethylaluminum dichloride (Aldrich Chemicals, 25 wt% solution in toluene) were used as received. Solvents used were all analytical grade materials. They were dried and fractionally distilled.

Instruments and Measurement. NMR (¹H-, ¹³C-) spectra were recorded on a Bruker AM 200 spectrophotometer using CDCl₃. Infrared (IR) spectra were taken on a Bio-Rad Digilab FTS-60 spectrometer using KBr pellets. UV-visible spectra were recorded on a Beckman DU-6 Spectrometer in THF. The average molecular weights (Mₙ) of the resulting polymers were measured by means of GPC-150C of Waters using a calibration curves for polystyrene. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min with Dupont 951 Thermogravimetric Analyzer. Thermal transitions were measured with Dupont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/min.

Preparation of Catalyst Systems. Catalyst system preparations were carried out under nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal chlorides, organometallic compounds, and 2-propyn-1-
Polymerization of Phenylacetylene

ol were dissolved in as 0.05 M, 0.2 M, and 0.4 M chlorobenzene solutions before use.

**Polymerization Procedures.** Typical examples of the polymerization are described below. The obtained polymers were dissolved in chloroform followed by the precipitation into excess methanol. The precipitated polymers were filtered from the solution and dried to constant weight under vacuum at 40°C for 24 hr. The polymer yield was calculated by gravimetry.

**Polymerization of PA by MoCl<sub>5</sub>.** A solution of MoCl<sub>5</sub>(1.96 mol 0.05 M chlorobenzene solution, 0.0979 mmol) and chlorobenzene (2.39 ml, [M]<sub>0</sub> = 1 M) was prepared. To this solution was added PA (0.5 g, 4.9 mmol) at room temperature and the polymerization was carried out at 60°C for 24 hr. Polymer yield was 34%.

**Polymerization of PA by MoCl<sub>5</sub>/HC=CCH<sub>2</sub>OH (1/5).** A catalyst solution was prepared by mixing MoCl<sub>5</sub>(1.96 ml 0.05 M chlorobenzene solution, 0.0979 mmol), HC=CCH<sub>2</sub>OH (1.225 ml 0.4 M chlorobenzene solution, 0.490 mmol), and chlorobenzene (1.17 ml, [M]<sub>0</sub> = 1 M) and aged at 30°C for 15 min. To this solution was added PA (0.5 g, 4.9 mmol). Polymerization was carried out at 60°C for 24 hr. Polymer yield was 58%.

**Polymerization of PA by MoCl<sub>5</sub>/HC=CCH<sub>2</sub>OH/ EtAlCl<sub>2</sub> (1/5/2).** A catalyst solution was prepared by mixing MoCl<sub>5</sub>(1.225 ml 0.05 M chlorobenzene solution, 0.0979 mmol), HC=CCH<sub>2</sub>OH (0.98 ml 0.4 M chlorobenzene solution, 0.392 mmol), EtAlCl<sub>2</sub> (0.98 ml 0.2 M chlorobenzene solution, 0.196 mmol), and chlorobenzene (0.19 ml, [M]<sub>0</sub> = 1 M) in this order and aged at 30°C for 15 min. To this solution was added PA (0.5 g, 4.9 mmol). Polymerization was carried at 60°C for 24 hr. Polymer yield was 33%.

**RESULTS AND DISCUSSION**

The polymerization of PA by transition metal chloride-HC=CCH<sub>2</sub>OH catalyst systems. MoCl<sub>5</sub> alone gave 34% yield of polymer. When HC=CCH<sub>2</sub>OH, a new activator, was used with MoCl<sub>5</sub> in the polymerization of PA, the polymer yield was increased from 34% to 58%. Organoauminum compounds, which have been used in the metathesis of cis-2-pentene by MoCl<sub>5</sub>/2,6-diisopropylphenol and MoCl<sub>5</sub>/PhCH<sub>2</sub>CHOHCH=Ph<sup>16</sup> were used as a third component. Thus in the present study, EtAlCl<sub>2</sub> which have been found to be an effective cocatalyst for the polymerization of 1-chloro-2-thienylacetylene<sup>17</sup> 2-ethylnylpyridine<sup>18</sup> and dipropargyl sulfide<sup>19</sup> by WCl<sub>6</sub> and MoCl<sub>5</sub> was also used. But, the polymer yield was slightly increased in comparison to that of MoCl<sub>5</sub> alone used. Mo(OEt)<sub>5</sub> and Mo(OEt)<sub>5</sub>/HC=CCH<sub>2</sub>OH catalyst systems were also used for the present polymerization. However these catalyst systems gave no polymers. In WCl<sub>6</sub>-based catalysts, WCl<sub>6</sub> alone gave a good yield of polymer (84%) as reported in 1974 by Masuda et al.<sup>20</sup> However, in the WCl<sub>6</sub>-catalyzed polymerization of PA using HC=CCH<sub>2</sub>OH, HC=CCH<sub>2</sub>OH deactivated WCl<sub>6</sub> to give only low

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Catalyst System&lt;sup&gt;b&lt;/sup&gt; (mole ratio)</th>
<th>Polymer Yield&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoCl&lt;sub&gt;5&lt;/sub&gt;</td>
<td>34</td>
<td>6850</td>
</tr>
<tr>
<td>2</td>
<td>MoCl&lt;sub&gt;5&lt;/sub&gt;/HC=CCH&lt;sub&gt;2&lt;/sub&gt;OH (1/5)</td>
<td>58</td>
<td>7200</td>
</tr>
<tr>
<td>3</td>
<td>MoCl&lt;sub&gt;5&lt;/sub&gt;/HC=CCH&lt;sub&gt;2&lt;/sub&gt;OH/ EtAlCl&lt;sub&gt;2&lt;/sub&gt; (1/5/2)</td>
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<td>Mo(OEt)&lt;sub&gt;5&lt;/sub&gt;/HC=CCH&lt;sub&gt;2&lt;/sub&gt;OH (1/4)</td>
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<td>-</td>
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<td>7</td>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;/HC=CCH&lt;sub&gt;2&lt;/sub&gt;OH (1/4)</td>
<td>8</td>
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<tr>
<td>8</td>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;/HC=CCH&lt;sub&gt;2&lt;/sub&gt;OH/ EtAlCl&lt;sub&gt;2&lt;/sub&gt; (1/4/2)</td>
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<td>9</td>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;/EtAlCl&lt;sub&gt;2&lt;/sub&gt; (1/2)</td>
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<sup>a</sup> Polymerization was carried at 60°C for 24 hr in chlorobenzene. Initial monomer concentration ([M]<sub>0</sub>) and monomer to catalyst mole ratio (M/C) were 1 M and 50, respectively.

<sup>b</sup> Mixture of MoCl<sub>5</sub> and cocatalyst was aged at 30°C for 15 min before use.

<sup>c</sup> Methanol-insoluble polymer.
Fig. 1. The effect of HC≡CCH₂OH to MoCl₅ mole ratio on the polymerization of phenylacetylene.

yield of polymer.

Fig. 1 shows the effect of HC≡CCH₂OH to MoCl₅ mole ratio on the polymerization of PA. The polymer yields were gradually increased as the mole ratio of HC≡CCH₂OH to MoCl₅ was increased. And then above [MoCl₅]/[HC≡CCH₂OH] = 5, the polymer yield was somewhat decreased. The best results (polymer yield = 58%) was obtained when the mole ratio of HC≡CCH₂OH to MoCl₅ was 5. The role of HC≡CCH₂OH in the activation of MoCl₅ was deduced to be due to the substitution of the chlorine atom of molybdenum by HC≡CCH₂OH to some extents although the exact molecular structure of molybdenum complex activated by HC≡CCH₂OH was not elucidated. In the preparation of catalyst solution, the initial purple color of MoCl₅ solution was disappeared as soon as the HC≡CCH₂OH solution was added.

Table 2 shows the temperature effect for the polymerization of PA by MoCl₅/HC≡CCH₂OH(1/5) catalyst system. The polymerization at 5℃ did not yield any polymer. However, in the wide temperature ranges between 20℃ and 90℃, the polymerization was well proceeded to give a similar polymer yield. The average molecular weights (Mₐ) of poly(PA) according to the polymerization temperature, were ranged between 5210 and 11700.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Temperature (℃)</th>
<th>Polymer Yield (%)</th>
<th>Mₐ</th>
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<tr>
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<td>40</td>
<td>51</td>
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<td>60</td>
<td>58</td>
<td>7200</td>
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<tr>
<td>5</td>
<td>90</td>
<td>49</td>
<td>5210</td>
</tr>
</tbody>
</table>

*Polymization was carried out for 24 hr in chlorobenzene. Initial monomer concentration ([Mₐ]) and monomer to catalyst mole ratio (M/C) were 1 M and 50, respectively. Mixture of MoCl₅ and cocatalyst was aged for 15 min at 30℃ before use.

Table 3 shows the activation temperature effect of MoCl₅ /HC≡CCH₂OH(1/5) Catalyst System for the Polymerization of Phenylacetylene

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Activation Temperature (℃)</th>
<th>Polymer Yield (%)</th>
<th>Mₐ</th>
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<td>55</td>
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<tr>
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<tr>
<td>5</td>
<td>90</td>
<td>57</td>
<td>6450</td>
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</table>

*Polymization was carried out at 60℃ for 24 hr in chlorobenzene. Initial monomer concentration ([Mₐ]) and monomer to catalyst mole ratio (M/C) were 1 M and 50, respectively. Mixture of MoCl₅ and cocatalyst was aged for 15 min at 30℃ before use.

In the polymerization of PA catalyzed by MoCl₅ /HC≡CCH₂OH system, the effect of temperature on the activation of MoCl₅ and HC≡CCH₂OH solution was also tested. (Table 3) Similar polymerization results were observed in most activation temperature ranges. From these observations, it was known that the activation temperature of MoCl₅ by HC≡CCH₂OH is not an important variable for the present polymerization.

In the polymerization of PA, it can be deduced that the HC≡CCH₂OH have two functional groups, which activate the molybdenum chloride, i.e., the acetylenic hydrogen and the hydroxy group. These
Polymerization of Phenylacetylene

two functional groups are thought to act as an activator of molybdenum chloride. It was also reported that the catalytic activity of Mo-based catalysts was greater than that of W-based catalysts when the organic compounds containing oxygen atom are used as monomer or solvent. From these viewpoints, it may be deduced that the contribution of hydroxy functional group is greater than that of acetylenic hydrogen functional group for the activation of molybdenum chloride.

The polymer structure of poly(PA) prepared by MoCl₅/HC=CCH₂OH catalyst system was characterized by NMR(¹H-, ¹³C-), IR, UV-visible spectroscopies, and elemental analysis. The elemental analysis agreed well with the calculated value(e. g., poly(PA) prepared by MoCl₅/HC=CCH₂OH(1/5), calculated for(C₆H₅)₉ : C, 94.08% ; H, 5.92% ; found : C, 93.21% ; H, 5.83%).

Fig. 2 shows the ¹H-NMR spectrum of poly(PA) prepared by MoCl₅/HC=CCH₂OH catalyst system. A broad peak at 5.0~8.0 ppm is due to the vinyl protons on the conjugated chain and phenyl substituents. This spectrum was similar to that of poly (PA) prepared by WCl₆.²³

The differences in chemical shifts of aromatic protons were qualitatively estimated by theoretical calculations according to Johnson and Bovey and Haigh and Mallion.²⁵ The conformation of macromolecular chains was reproduced by using atomic model. Taking into account the distance from the center of the phenyl ring to the hydrogen atom in question and the distance between the planes of these rings, the chemical shifts were estimated.

The theoretical NMR studies of the four helicoidal structure models(cis-cisoidal, cis-transoidal, trans-cisoidal, and trans-transoidal) of poly(PA) indicated that for the trans-transoidal(12/1) structure, two aromatic protons must be shifted to the lower values of δ for the cis-cisoidal(3/1) structure, one aromatic proton must be shifted to lower value of δ, while in the case of the cis-transoidal(3/1) structure, two protons(one aromatic and one from the main chain) must be shifted to the lower values of δ. Only for the trans-cisoidal(3/1) structure all protons appear in the same field.²⁶²⁷

The present poly(PA) shows only one broad peak at 5~8 ppm. The shoulder peak at 5.82 ppm may be correlated with that of cis-transoidal structure. Moreover, the present NMR spectrum shows a weak, wide resonance peaks at 1.0~4.5 ppm. These signals may be due to a low content of aliphatic(methyl, ethyl) protons, which arise from the initiation step(migratory insertion of monomer into the metal-alkyl bond).²⁸

Fig. 3 shows the ¹³C-NMR spectrum of poly(PA) prepared by MoCl₅/HC=CCH₂OH. The chemical shifts of the carbons on the phenyl substituent were observed at 125~130 ppm, whereas those of the carbons on the conjugated double bond were observed at 138~144 ppm.

Fig. 4 shows the IR spectrum of poly(PA) prepared by MoCl₅/HC=CCH₂OH catalyst system. It shows the aromatic =C-H stretching frequencies of phenyl substituents at 3011~3045 cm⁻¹ and the vinyl C=C stretching frequencies at 1600 cm⁻¹. The absorption frequencies at 755 and 693 cm⁻¹ are due to the C-H out-of-plane deformation of mono-substituted benzene. Further, the polymer posses-

![Fig. 2. ¹H-NMR spectrum of poly(PA) prepared by MoCl₅/HC=CCH₂OH(1/5).](image)

![Fig. 3. ¹³C-NMR spectrum of poly(PA) prepared by MoCl₅/HC=CCH₂OH(1/5).](image)
sed three absorptions at 910, 880, and 840 cm⁻¹. It has been known that the absorption at 880 cm⁻¹ is a characteristic of cis structure in poly(PA).²⁹,³⁰ and a ratio \( D_{880}/D_{910} \) can be used as a measure of cis-structure content. The \( D_{880}/D_{910} \) ratio of present poly(PA) prepared by MoCl₅/HC=CC₂H₂OH was 0.72.

The UV-visible spectrum of poly(PA) prepared by MoCl₅/HC=CC₂H₂OH catalyst system is given in Fig. 5. A characteristic peak of conjugated polymer, a wide broad \( \pi \rightarrow \pi^* \) absorption of poly(PA) was observed as far as ca. 550 nm.

The poly(PA)s prepared by MoCl₅/HC=CC₂OH catalyst system were mostly soluble in aromatic and halogenated hydrocarbons such as benzene, chlorobenzene, chloroform, methylene chloride, but insoluble in methanol, ethyl ether, formic acid, etc. The color of poly(PA) prepared by MoCl₅/HC=CC₂H₂OH catalyst system was light brown or yellow.

Fig. 6 shows the TGA thermogram of poly(PA) prepared by MoCl₅/HC=CC₂H₂OH catalyst system. It showed that it retains 95% of its original weight at 278°C, 57% at 400°C, 36% at 500°C, and 30% at 700°C.

Fig. 7 shows the DSC thermogram of poly(PA) prepared by MoCl₅/HC=CC₂H₂OH catalyst system. The two exothermic peaks at 208 and 225°C were observed. In the case of poly(β-ethynylnaphtha-
line)³¹ and poly(N-ethynylcarbazole),³² it was also reported that the exothermic peak at similar temperature was due to the isomerization from cis-cisoidal structure to trans-cisoidal structure. And the present poly(PA) starts to fuse at about 295°C. This process involved the decomposition of the polymer to low molecular-weight oligomers and a cross-linked solid.³³
CONCLUSIONS

A new activator, 2-propyn-1-ol, for the polymerization of PA by MoCl₅ was tested and evaluated. The activator, HC=CH₂OH, increased the polymer yield from 34% to 58% in the polymerization of PA by MoCl₅. It was found that the catalytic activity of MoCl₅/HC=CH₂OH catalyst system was greater than that of WCl₆/HC=CH₂OH catalyst system. The activation temperature of MoCl₅ by HC=CH₂OH and the polymerization temperature was found to be not important factor for the present polymerization. The high catalytic activity of MoCl₅/HC=CH₂OH catalyst system was deduced that the partially substituted molybdenum compounds by HC=CH₂OH are active species though the mechanism is not fully understood. It was concluded that the contribution of the hydroxyl functional group of HC=CH₂OH was greater than that of acetylenic hydrogen functional group of HC=CH₂OH for the activation of molybdenum chlorides.

REFERENCES

23. Y. S. Gal, Unpublished data.