Cyclopolymerization of Dipropargyl Ether by Transition Metal Catalysts

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Abstract: The cyclopolymerization of dipropargyl ether was carried out by transition metal catalysts such as MoCl₅ or WCl₆–organoauminum compounds. The catalytic activity of MoCl₅ for this cyclopolymerization was greater than that of WCl₆. The polymerization of dipropargyl ether by MoCl₅ alone gives a quanitative yield of poly(dipropargyl ether) (PDPE). WCl₆ and organoauminum compounds such as Et₃Al, Et₃AlCl, and EtAlCl₂ were moderately effective in this polymerization. The PDPEs obtained were generally insoluble in common organic solvents. The IR spectrum of PDPE gives an aliphatic C–H stretching band and C–O–C stretching band at 2840–2940cm⁻¹ and 1070cm⁻¹, respectively. And it shows a new absorption band at about 1600cm⁻¹ owing to the conjugated double bond stretching. The thermal properties and oxidative stability of PDPE were also studied.

INTRODUCTION
Cyclopolymerization is any type of chain-growth addition polymerization that leads to introduce cyclic structures into the main chain of polymer via an alternating intramolecular-intermolecular
chain propagation. During the past three decades, studies on the cyclopolymerization of nonconjugated dienes have been made extensively.\textsuperscript{1,2}

In particular, the cyclopolymerization of diallyl derivatives, such as diallyl sulfide,\textsuperscript{3} diallyl silanes,\textsuperscript{4,5} and diallyl ammonium salts\textsuperscript{6,7} have been widely investigated. However, the cyclopolymerizations of nonconjugated diynes giving conjugated double bonds in the polymer backbone were virtually restricted to a few cases.

Polymerization initiators in the cyclopolymerization include Ziegler–Natta catalysts such as TiCl\textsubscript{4} – Et\textsubscript{3}Al\textsuperscript{8} and Ti(OR)\textsubscript{4} – R\textsubscript{3}Al(R = alkyl),\textsuperscript{9,10} PdCl\textsubscript{2},\textsuperscript{11} and anionic species such as \( \Gamma^\cdot \), Br\(^{-} \), CN\(^{-} \), of and CNS\textsuperscript{12}.

The cyclopolymerization of dipropargyl ether was attempted in the presence of PdCl\textsubscript{2} in DMF.\textsuperscript{11} However, the systematic study on the cyclopolymerization of dipropargyl ether by W, Mo- and Ti-based catalysts has not been studied. In recent years, it was known that group VI metal-based catalysts exhibit high catalytic activities for the polymerization of acetylene derivatives.\textsuperscript{13,14} We have also found that WCl\textsubscript{6}– and MoCl\textsubscript{5}– based catalyst systems are very effective for the polymerization of mono- and disubstituted acetylenes containing heteroatom.\textsuperscript{15–18} The present authors have investigated the reactivity of dipropargyl ether in the polymerization by MoCl\textsubscript{5}– and WCl\textsubscript{6}– based catalysts. The characterization and physical properties of the resulting poly(dipropargyl ether) (PDPE) will be discussed.

**EXPERIMENTAL**

**Materials**

Propargyl bromide (Aldrich Chemicals, 80 wt % solution in toluene) was dried over calcium hydride and fractionally distilled. Propargyl alcohol (Aldrich Chemicals, 97 %) was dried over magnesium sulfate and distilled under reduced pressure. Sodium hydroxide (Tedla Comp., Inc.) was used as received. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemicals, resublimed, 99 + %) were used without further purification.

Tetraphenyltin (Aldrich Chemicals, 97 %) was purified by recrystallizing twice from carbon tetrachloride. Tetra-n-butyltin, tetramethyltin and organoaluminum compounds such as triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride, were used without further purification. All the polymerization solvents (reagent grade) were fractionally distilled before use under nitrogen atmosphere.

**Preparation of Dipropargyl Ether (DPE)\textsuperscript{20}**

In the 11 four-neck flask equipped with a mechanical stirrer, thermometer, reflux condenser, and solid injection apparatus, were placed 119 g (1 mole) propargyl bromide and 73 g (1.3 moles) of propargyl alcohol.

Sodium hydroxide powder (60 g, 1.5 moles) was added in 30 min to the vigorously stirred mixture. The temperature rose gradually but was kept below 70°C by occasional cooling. Stirring and warming at 70°C were continued for an additional hour after the exothermic reaction had subsided. The mixture was then cooled to 30°C and 500 ml of ice water were added. The organic layers were separated and the aqueous layer was extracted with a very small amount of ethyl ether.

Extract and main portion were combined, washed with water and dried with magnesium sulfate. The crude DPE was dried with CaH\textsubscript{2} and fractionally distilled twice under partial vacuum (bp: 67°C / 85 mmHg, yield: 85 %)

\[ \text{^1H-NMR(CDCI}_3) : 4.2 \text{ ppm (4H, doublet), 2.5 ppm (2H, triplet)} \]

\[ \text{IR(KBr, wavenumber): 3300 cm}^{-1}(\text{C-H stretching}), 2120 \text{cm}^{-1}(\text{C=C stretching}). \]

**Polymerization Procedure**

All polymerization procedures were carried out under dry nitrogen atmosphere. Catalyst solutions consisting of two components (e.g., WCl\textsubscript{6} and EtAlCl\textsubscript{3}) were aged at 30°C for 15 min before use. A typical polymerization procedure is as follows:

In a 20 ml ampule equipped with rubber septum, solvent, 0.058 g (2.13 × 10\textsuperscript{2} moles) of MoCl\textsubscript{5} (0.05 M solution in chlorobenzene), and 1 g (1.06 × 10\textsuperscript{2} moles) of DPE were injected by hypodermic syringes. After standing at 60°C for 24 hrs, the
polymerization was terminated with a small amount of methanol. Then, 10 ml of chloroform were added, and the polymer was isolated by precipitation into a large excess of methanol. The precipitated polymer was filtered from the solution and dried to a constant weight under vacuum at 40°C for 24 hrs. The polymer yield was calculated by gravimetry.

**Instruments**

'$^1$H-NMR spectra were recorded on a Varian T-60A spectrometer, IR spectra were taken on a Perkin-Elmer 283B spectrophotometer using KBr pellet. Elemental analyses (C, H) were taken with 240C Elemental Analyzer. Tungsten and molybdenum residues in polymer were detected by Beckman DU-7 UV-VIS spectrophotometer. Aluminum residue in polymer was detected by energy dispersive X-ray analysis. X-ray diffraction analyses were performed on JEOL X-ray diffractometer with Cu-Kα radiation at a scan speed of 4°C/min. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min up to 600°C with Perkin-Elmer TGS-1 thermobalance.

**RESULTS AND DISCUSSION**

**Table 1. Polymerization of Dipropargyl Ether by MoCl₅-Based Catalysts**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Catalyst System (mole ratio)</th>
<th>Solvent</th>
<th>M / C (mole ratio)</th>
<th>[M]</th>
<th>Temp. (°C)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoCl₅</td>
<td>Chlorobenzene</td>
<td>50</td>
<td>1.5</td>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>MoCl₅</td>
<td>Chlorobenzene</td>
<td>50</td>
<td>1.5</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>MoCl₅</td>
<td>Chlorobenzene</td>
<td>100</td>
<td>1</td>
<td>60</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>MoCl₅</td>
<td>Chlorobenzene</td>
<td>100</td>
<td>2</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>MoCl₅</td>
<td>Chlorobenzene</td>
<td>50</td>
<td>1.5</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>MoCl₅</td>
<td>Benzene</td>
<td>50</td>
<td>1.5</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>MoCl₅</td>
<td>Toluene</td>
<td>30</td>
<td>1.5</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>MoCl₅</td>
<td>p-Dioxane</td>
<td>50</td>
<td>1.5</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>MoCl₅</td>
<td>Chloroform</td>
<td>50</td>
<td>1.5</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>MoCl₅</td>
<td>CH₂Cl₂</td>
<td>50</td>
<td>1.5</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>11</td>
<td>MoCl₅</td>
<td>Nitrobenzene</td>
<td>50</td>
<td>1.5</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>MoCl₅·Ph₅Sn(1 : 2)*</td>
<td>Chlorobenzene</td>
<td>50</td>
<td>2</td>
<td>60</td>
<td>91</td>
</tr>
<tr>
<td>13</td>
<td>MoCl₅·EtAlCl₃(1 : 2)*</td>
<td>Chlorobenzene</td>
<td>50</td>
<td>2</td>
<td>60</td>
<td>71</td>
</tr>
</tbody>
</table>

*: Polymerization was carried out for 24 hrs.

*: Mixture of MoCl₅ and cocatalyst in chlorobenzene was aged at 30°C for 15 min before use as catalyst.
polymerization in less polar solvents such as chlorobenzene, benzene, p-dioxane, etc.

The polymer yield in the more polar α,α,α-trichloroethane was lower than that in the less polar solvents. The use of much more polar nitrobenzene as solvent prohibited the formation of polymer, regardless of the polymerization conditions. On the other hand, the cationic polymerization ofacenaphthylene and N-vinylcarbazole by MoCl₅ was accelerated in more polar solvents such as nitrobenzene.

It has been known that the addition of a small amount of reducing agents such as Ph₃Sn and n-Bu₃Sn increases the polymer yield and molecular weight in the MoCl₅-catalyzed polymerization of 2-ethylthiophene and 2-ethylfurran and also, the organoaluminum compounds such as Et₂AlCl and EtAlCl₃ were very effective cocatalyst in the polymerization of 2-ethylpyridine by MoCl₅. However, Ph₃Sn or EtAlCl₃ exhibit no cocatalytic activity in this MoCl₅-catalyzed polymerization of DPE.

Table 2 shows the results for the polymerization of DPE by WCl₆-based catalysts. As compared with Table 1, WCl₆ alone was less effective than MoCl₅ This lower catalytic activity of WCl₆ than that of MoCl₅ is consistent with the results of the cyclopolymerization of dipropargyl sulfide.

![Graph of polymer yield vs. time](image)

**Fig. 1.** Time dependence curves of the polymerization of dipropargyl ether (catalyst system: ○=MoCl₅
○=WCl₆⋅EtAlCl₃ (1:2), polymerization conditions: temperature =60°C, [M]₀=2, M/C=50)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Catalyst System</th>
<th>Polymer Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WCl₆</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>WCl₆⋅EtAlCl₃(1:2)</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>WCl₆⋅EtAlCl₃(1:2)</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>WCl₆⋅EtAlCl₃(1:2)</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>WCl₆⋅Ph₃Sn(1:1)</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>WCl₆⋅Bu₃Sn(1:2)</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>WCl₆⋅Me₃Sn(1:2)</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 3. Polymerization of Dipropargyl Ether by M(CO)₆-CCL₆ Catalyst Systems

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Catalyst</th>
<th>Polymer Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mo(CO)₆</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>W(CO)₆</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Cr(CO)₆</td>
<td>trace</td>
</tr>
</tbody>
</table>

* : Polymerization was carried out at 60°C for 24 hrs in chlorobenzene. Initial monomer concentration ([M]₀) and catalyst to monomer mole ratio (M/C) were 1.5 and 50, respectively. Mixture of WCl₆ and cocatalyst was aged at 30°C for 15 min, before use as catalyst.

: Ultraviolet irradiation of M(CO)₆ in CCL₆ was performed with 200 W a high-pressure mercury lamp (Model 440 W absorbance detector fixed at 350 nm). Polymerization was carried out at 30°C for 24 hrs. Monomer to catalyst mole ratio (M/C) was 30.
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Table 4. Elemental Analysis of Poly(dipropargyl ether)s

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Element</th>
<th>Catalyst residues in polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>WCl₆·EtAlCl₂</td>
<td>Calc.</td>
<td>76.59</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>72.60</td>
</tr>
<tr>
<td>MoCl₆</td>
<td>-</td>
<td>73.50</td>
</tr>
<tr>
<td>MoCl₆⁺</td>
<td>-</td>
<td>52.30</td>
</tr>
</tbody>
</table>

a: Oxygen Content(%) = 100% - other element (C, H, and cat. residues) content(%)
b: PDPE exposed to air at room temperature for 1 month.

to the extent of 90%, and exhibited a quantitative yield at 4 hrs. On the other hand, the polymerization of DPE by WCl₆·EtAlCl₂(1:2) proceeded more slowly.

Table 3 shows the results for the polymerization of DPE by M(CO)₆·CCl₄·hv catalyst systems. These catalyst systems were known to be very effective for the polymerization of phenylacetylene to give a high molecular weight polymer. However, in this cyclopolymerization, only low yield of PDPE was obtained.

Polymer Structure

The elemental analysis data of PDPEs are listed in Table 4. The values of elemental analysis for PDPE prepared with MoCl₆ or WCl₆·EtAlCl₂, which rigorously excluded oxygen and immediately analyzed after drying under vacuum and agreed with the calculated ones with a small deviation. However, as the PDPE was exposed to air at room temperature for 1 month, the absolute values for percent oxygen was increased from 19.75% to 42.17%. We believe that this increase of oxygen content is primarily due to the sensitivity of PDPE to oxidation.

Fig. 2 shows the infrared spectra of PDPEs: (A) PDPE(by MoCl₆), (B)PDPE(by WCl₆·EtAlCl₂), (C)PDPE which was exposed to air at room temperature for 1 month. The IR spectra of (A), (B), and (C) give an aliphatic C-H stretching band at 2840~2940 cm⁻¹. And they also show an absorption band at about 1740 cm⁻¹ attributable to the air oxidation was observed. In (C), however, the absorption

Fig. 2. IR spectra of poly(dipropargyl ether)s: A (PDPE by MoCl₆), B(PDPE by WCl₆·EtAlCl₂), C(PDPE which was exposed to air at room temperature for 1 month.

[Diagram of IR spectra]

[Structural formulas (II), (III), (IV), (V)]
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\[
\text{O} \quad + \quad \text{O} \quad \xrightarrow{\text{cyclization}} \quad \text{IV}
\]

\[
\text{polymerization} \quad \rightarrow \quad \text{IV}
\]

band at about 1740 cm\(^{-1}\) was much larger than that in (A) and (B). These results are consistent with the elemental data of PDPE. This unstability of PDPE to air oxidation is same with that of poly(1,6-heptadiyne)\(^{10}\) having a similar structure with PDPE.

In the present time, we may propose the structure of PDPE prepared by transition metal catalysts. In addition to structure I, structures II and III are also possible for PDPE via different cyclopolymerization pathways.

Structure IV can arise from the following pathway. This product was expected to be soluble in organic solvents. However, PDPE obtained in this polymerization was insoluble and there are no characteristic peaks of 1,2,4-trisubstituted benzene rings (885-870 cm\(^{-1}\)(s), 825-805 cm\(^{-1}\)(s), and 1900-1700 cm\(^{-1}\)(w)\(^{31}\) in the IR spectra of PDPEs. From these fact, structure IV can be excluded from possible structures.

The exo-endo double bond rearrangements of I to A and II to B and /or C are likely.\(^{29,30}\)

For I this would bring about loss of conjugation along the polymer backbone; in the case of II, C would result in such a loss, but B might be more stable than C because structure B retains conjugation along the polymer backbone. This fact was identified by IR spectrum of PDPE treated with heat(150°C, 20 hrs, under vacuum) : no furan moieties are seen in the IR spectrum.\(^{16,31}\) II is presumably more stable than its isomer D and in either case, backbone conjugation is maintained. On these basis, structure I is most favorable in the view point of its stability and probability associated with the transition state in cyclopolymerization.\(^{32}\)

**Physical Properties**

The PDPE obtained was insoluble in any organic solvents and was red or orange colored powder. Though the reasons for this insolubility are not necessarily clear, we assume the insolubility of PDPE to the rigidity similar to trans-polyacetylene structure, or some cross-linking by the moieties such as structure V and the active allyl proton. Such cross-linking, of course, do not interrupt the backbone conjugation of the polymer. The polymer color changed from dark red to light orange when the PDPE is exposed to air at room temperature. Presumably, this transformation involves the double bond rearrangement and the air oxidation of conjugated double bond, which eliminate the conjugation of the polymer backbone.

The notable increase of oxygen content in elemental
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composition and the appearance of the carbonyl absorption peak in the IR spectrum (Fig. 2, C) are connected with the rapid oxidation of PDPE during treatment and exposing to air. It has been already reported that polyacetylene is easily oxidized in the presence of air yielding a polymer with a carbonyl group in its structure. These oxidation processes may be described as following scheme.

This process destroys the conjugation of polymer backbone and it was confirmed by the IR spectra and color change of PDPE.

X-ray diffraction (Fig. 3) of PDPE prepared by MoCl₅ in chlorobenzene did not show any evidence of crystallinity. TGA curve (Fig. 4) of PDPE prepared by MoCl₅ in chlorobenzene showed that it retained 95% of its original weight at 150°C, 90% at 225°C, 80% at 310°C and 20% at 600°C.

**Polymerization Mechanism**

In the metathesis polymerization of cycloolefin expressed eq. 1, it is now generally accepted that metal carbenes (VI) and metallacyclobutanes (VII) mediate the reaction as shown in eq. 2.

MoCl₅ and WCl₆ were known to be very effective conventional cationic catalysts for the vinyl polymerization of styrene, acenaphthylene, and N-vinylcarbazole. In the vinyl polymerization catalyzed by MoCl₅ or WCl₆, the high polymer yields were obtained not only in the nonpolar solvents such as benzene and chlorobenzene but

\[ \text{(eq. 1)} \]

\[ \text{(eq. 2)} \]
also in the polar solvent such as nitrobenzene. However, in this cyclopolymerization of DPE by MoCl₅, the use of polar nitrobenzene as solvent prohibited the formation of polymer to give only methanol-soluble oligomeric materials. The decreased polymerizability in more polar solvents is explained as well in terms of a stabilization of the propagating end due to the dissociation of the counter ion.

That is to say, the polymerization of DPE by MoCl₅ may proceed well when the interaction between the propagating end and the counter ion produced from MoCl₅ is strong: that is reminiscent of a coordination polymerization.⁴ According to the above discussion, the following propagation reaction involving metal carbene(VIII) and metallacyclobutenes (IX) can be depicted for the present polymerization.

![Chemical structures](image)

**REFERENCES**

Cycopolymerization of Dipropargyl Ether by Transition Metal Catalysts