

전이금속촉매에 의한 디프로파길 에테르의 고리화 중합

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(1987년 6월 30일 접수)

Cyclopolymerization of Dipropargyl Ether by Transition Metal Catalysts

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(Received June 30, 1987)*

요 약 : MoCl_5 및 WCl_6 -유기알루미늄 화합물과 같은 전이금속촉매를 사용하여 디프로파길 에테르를 고리화 중합시켰다. 디프로파길 에테르의 고리화중합에서는 MoCl_5 의 촉매활성이 WCl_6 의 촉매활성보다 높았다. 즉, MoCl_5 만으로도 거의 정량적인 수율로 폴리(디프로파길 에테르) (PDPE)를 합성할 수 있었다. WCl_6 와 유기알루미늄 화합물(Et_3Al , Et_2AlCl , EtAlCl_2)로 구성된 이성분계 촉매를 사용하였을 때는 적당한 수율로 중합체를 합성하였다. 합성한 PDPE는 일반적으로 유기용매에 녹지 않았다. PDPE의 IR스펙트럼에서 aliphatic C-H 신축띠와 C-O-C 신축띠를 각각 $2840\text{--}2940\text{cm}^{-1}$ 및 1070cm^{-1} 에서 볼 수 있었고 고분자 주쇄의 공액 이중결합에 해당하는 새로운 흡수띠를 1600cm^{-1} 부근에서 관찰할 수 있었다. 합성한 PDPE의 열적 특성 및 산화안정성에 관해서도 연구하였다.

Abstract : The cyclopolymerization of dipropargyl ether was carried out by transition metal catalysts such as MoCl_5 or WCl_6 -organoaluminum compounds. The catalytic activity of MoCl_5 for this cyclopolymerization was greater than that of WCl_6 . The polymerization of dipropargyl ether by MoCl_5 alone gives a quantitative yield of poly(dipropargyl ether) (PDPE). WCl_6 and organoaluminum compounds such as Et_3Al , Et_2AlCl , and EtAlCl_2 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 $2840\text{--}2940\text{cm}^{-1}$ 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.^{1,2}

In particular, the cyclopolymerization of diallyl derivatives, such as diallyl sulfide,³ diallyl silanes,^{4,5} and diallyl ammonium salts^{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 $\text{TiCl}_4\text{-Et}_3\text{Al}$ ⁸ and $\text{Ti(OR)}_4\text{-R}_3\text{Al(R=alkyl)}$,^{9,10} PdCl_2 ,¹¹ and anionic species such as I^- , Br^- , CN^- , of and CNS^- .¹²

The cyclopolymerization of dipropargyl ether was attempted in the presence of PdCl_2 in DMF.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 a high catalytic activities for the polymerization of acetylene derivatives.^{13,14} We have also found that $\text{WCl}_6\text{-}$ and $\text{MoCl}_5\text{-}$ based catalyst systems are very effective for the polymerization of mono- and di-substituted acetylenes containing heteroatom.¹⁵⁻¹⁹ The present authors have investigated the reactivity of dipropargyl ether in the polymerization by $\text{MoCl}_5\text{-}$ and $\text{WCl}_6\text{-}$ 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 (Tedia 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)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_2 and fractionally distilled twice under partial vacuum. (bp : 67°C / 85 mmHg, yield : 85 %)

¹H-NMR (CDCl_3) : 4.2 ppm (4H, doublet), 2.5 ppm (2H, triplet)

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

Polymerization Procedure

All polymerization procedures were carried out under dry nitrogen atmosphere. Catalyst solutions consisting of two components (e. g., WCl_6 and EtAlCl_2) 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^{-4} moles) of MoCl_5 (0.05 M solution in chlorobenzene), and 1 g (1.06×10^{-2} moles) of DPE were injected by hypodermic syringes. After standing at 60°C for 24 hrs, the

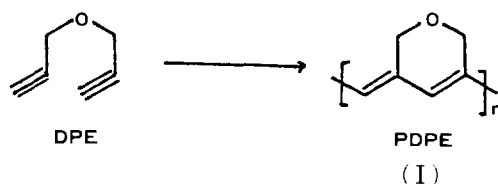
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polymerization was terminated with a small amount of methanol. Then, 10 ml of chloroform were added, and the polymer was isolated by precipitation into a large excess of methanol. The precipitated polymer was filtered from the solution and dried to a constant weight under vacuum at 40°C for 24 hrs. The polymer yield was calculated by gravimetry.

Instruments

¹H-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



Polymerization

Mo- and W-based catalysts were used to prepare poly(dipropargyl ether)(PDPE) via cyclopolymerization of DPE.

Table 1 lists results for the polymerization of DPE by MoCl₅-based catalysts. MoCl₅ alone polymerized DPE very effectively: i.e., the polymer yield was almost quantitative when the polymerization temperature and DPE to MoCl₅ mole ratio were 60°C or 90°C and 50°C respectively. In some cases, the polymerizations were proceeded explosively. This finding is interesting as compared with those for other acetylenic monomers: WCl₆ alone was more active than MoCl₅ alone in the polymerization of phenylacetylene,¹³ 2-ethynylthiophene,¹⁵ and 2-ethynylfuran.¹⁶

The solvent effect on the polymerization of DPE was also investigated. DPE was easily

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

Exp. No.	Catalyst System (mole ratio)	Solvent	M / C (mole ratio)	[M]	Temp. (°C)	Conversion (%)
1	MoCl ₅	Chlorobenzene	50	1.5	30	52
2	MoCl ₅	Chlorobenzene	50	1.5	60	100
3	MoCl ₅	Chlorobenzene	100	1	60	98
4	MoCl ₅	Chlorobenzene	100	2	60	100
5	MoCl ₅	Chlorobenzene	50	1.5	90	100
6	MoCl ₅	Benzene	50	1.5	60	100
7	MoCl ₅	Toluene	50	1.5	60	100
8	MoCl ₅	p-Dioxane	50	1.5	60	100
9	MoCl ₅	Chloroform	50	1.5	60	100
10	MoCl ₅	CH ₂ Cl ₂	50	1.5	60	65
11	MoCl ₅	Nitrobenzene	50	1.5	60	0
12	MoCl ₅ · Ph ₃ Sn(1 : 2) ^b	Chlorobenzene	50	2	60	91
13	MoCl ₅ · EtAlCl ₂ (1 : 2) ^b	Chlorobenzene	50	2	60	71

^a : Polymerization was carried out for 24 hrs.

^b : 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 of acenaphthylene²¹ and *N*-vinylcarbazole²² by MoCl_5 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 Ph_4Sn and *n*- Bu_4Sn increases the polymer yield and molecular weight in the MoCl_5 -catalyzed polymerization of 2-ethynylthiophene¹⁵ and 2-ethynylfuran¹⁶ and also, the organoaluminum compounds such as Et_2AlCl and EtAlCl_2 were very effective cocatalyst in the polymerization of 2-ethynylpyridine by MoCl_5 .²³ However, Ph_4Sn or EtAlCl_2 exhibit no cocatalytic activity in this MoCl_5 -catalyzed polymerization of DPE.

Table 2 shows the results for the polymerization of DPE by WCl_6 -based catalysts. As compared with Table 1, WCl_6 alone was less effective than MoCl_5 . This lower catalytic activity of WCl_6 than that of MoCl_5 is consistent with the results of the cyclopolymerization of dipropargyl sulfide²⁴

and the polymerization of *N*-propargylcarbazole.²⁵

When organotin compounds were used as cocatalyst, a slight increase of polymer yield was observed. On the other hand, when organoaluminum compounds which exhibited high cocatalytic activity in the metathesis reaction²⁶ and metathesis polymerization of cycloolefin²⁷ were used, the polymer yield was increased from 8% to 52%. This high cocatalytic activity of EtAlCl_2 in WCl_6 -catalyzed polymerization of DPE is consistent with the results of the cyclopolymerization of dipropargyl sulfide.²⁴

Fig. 1 shows the time dependence of polymer yield in the polymerization of DPE by MoCl_5 or $\text{WCl}_6 \cdot \text{EtAlCl}_2$ (1 : 2). The polymerization by MoCl_5 alone proceeded rapidly within 1 hr

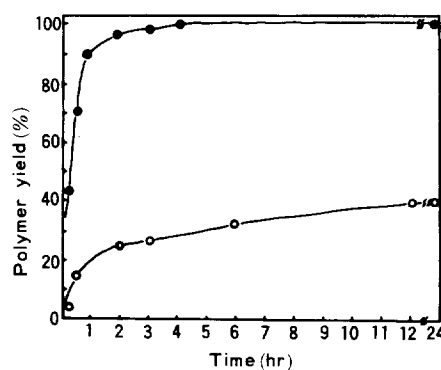


Fig. 1. Time dependence curves of the polymerization of dipropargyl ether (catalyst system: ● = MoCl_5 , ○ = $\text{WCl}_6 \cdot \text{EtAlCl}_2$ (1 : 2), polymerization conditions : temperature = 60°C, $[\text{M}]_0 = 2$, $\text{M} / \text{C} = 50$)

Table 2. Polymerization of Dipropargyl Ether by WCl_6 -Based Catalysts^a

Exp. No.	Catalyst System ^b (mole ratio)	Polymer Yield (%)
1	WCl_6	8
2	$\text{WCl}_6 \cdot \text{EtAlCl}_2$ (1:2)	40
3	$\text{WCl}_6 \cdot \text{Et}_2\text{AlCl}$ (1:2)	52
4	$\text{WCl}_6 \cdot \text{Et}_3\text{Al}$ (1:2)	42
5	$\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$ (1:1)	12
6	$\text{WCl}_6 \cdot \text{Bu}_4\text{Sn}$ (1:2)	15
7	$\text{WCl}_6 \cdot \text{Me}_4\text{Sn}$ (1:2)	14

^a : Polymerization was carried out at 60°C for 24 hrs in chlorobenzene. Initial monomer concentration ($[\text{M}]$) and catalyst to monomer mole ratio (M / C) were 1.5 and 50, respectively.

^b : Mixture of WCl_6 and cocatalyst was aged at 30°C for 15 min. before use as catalyst.

Table 3. Polymerization of Dipropargyl Ether by $\text{M}(\text{CO})_6\text{-CCl}_4/\text{h}\nu$ Catalyst Systems^a

Exp. No.	Catalyst	Polymer Yield
1	$\text{Mo}(\text{CO})_6$	15
2	$\text{W}(\text{CO})_6$	7
3	$\text{Cr}(\text{CO})_6$	trace

^a : Ultraviolet irradiation of $\text{M}(\text{CO})_6$ in CCl_4 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.

Table 4. Elemental Analysis of Poly(dipropargyl ether)s

Catalyst		Element			Catalyst residues in polymer
		C	H	O ^a	
WCl ₆ · Et ₂ AlCl	Calcd.	76.59	6.38	17.39	1.25(W and Al)
	Found	72.60	6.15	20.00	
MoCl ₅	-	73.50	6.23	19.75	0.52(Mo)
MoCl ₅ ^b	-	52.30	4.45	42.94	0.31(Mo)

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 · Et₂AlCl₂(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 phenylacetylene²⁸ 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 MoCl₅ or WCl₆-Et₂AlCl, which rigorously excluded oxygen and immediately analyzed after drying under vacuum 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 MoCl₅), (B)PDPE(by WCl₆ · Et₂AlCl₂), (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 2840~2940cm⁻¹. And they also show an absorption band at about 1600cm⁻¹ and 1070cm⁻¹ owing to the conjugated double bond stretching and C-O-C stretching, respectively.

In (A) and (B), very weak carbonyl absorption

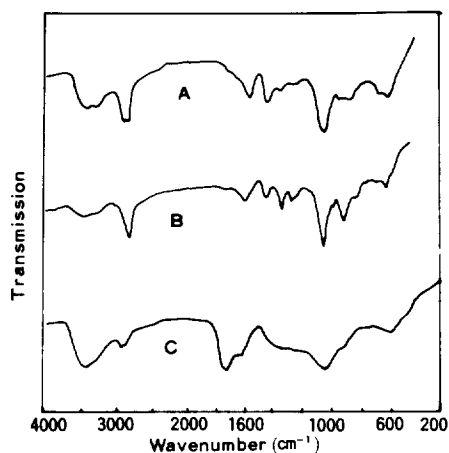
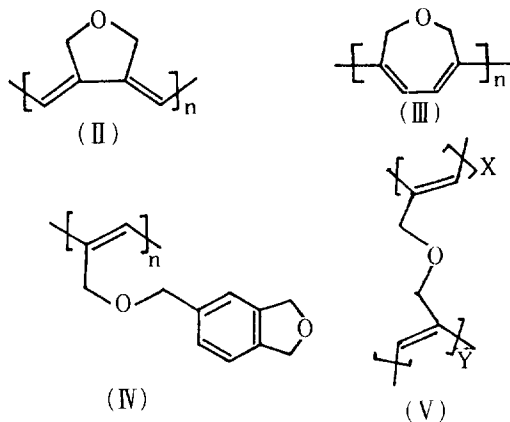
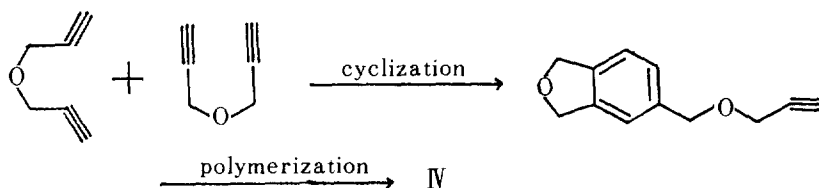


Fig. 2. IR spectra of poly(dipropargyl ether)s : A (PDPE by MoCl₅), B(PDPE by WCl₆ · Et₂AlCl₂), C(PDPE which was exposed to air at room temperature for 1 month.

at about 1740cm⁻¹ attributable to the air oxidation was observed. In (C), however, the absorption



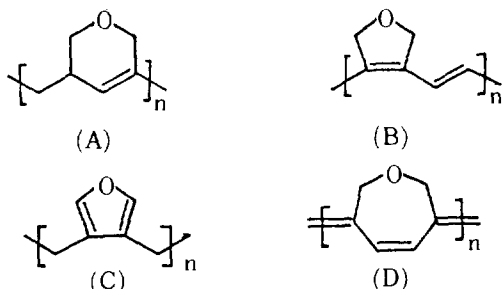


band at about 1740cm^{-1} was much larger than that in (A) and (B). These results are consistent with the elemental data of PDPE. This unstability of PDPE to air oxidation is same with that of poly(1,6-heptadiyne)¹⁰ having a similar structure with PDPE.

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 ($885\text{--}870\text{cm}^{-1}(\text{s})$, $825\text{--}805\text{cm}^{-1}(\text{s})$, and $1900\text{--}1700\text{cm}^{-1}(\text{w})$)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}



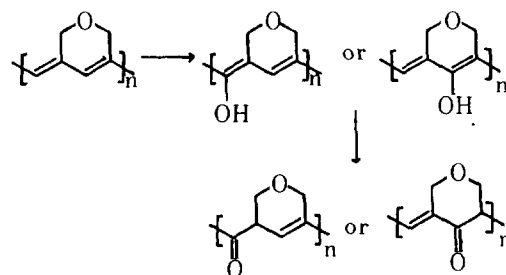
For I this would bring about loss of conjugation along the polymer backbone; in the case of II, C would result in such a loss, but B might be more stable than C because structure B retains

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



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 reported³³ 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 MoCl_5 in chlorobenzene did not show any evidence of crystallinity. TGA curve(Fig. 4) of PDPE prepared by MoCl_5 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 accepted¹⁴ that metal carbenes(VI) and metallacyclobutanes(VII) mediate this reaction as shown in eq.2.

MoCl_5 and WCl_6 were known to be very effective conventional cationic catalysts for the vinyl polymerization of styrene,²¹ acenaphthylene,²¹ and N-vinylcarbazole.²² In the vinyl polymerization catalyzed by MoCl_5 or WCl_6 , the high polymer yields were obtained not only in the nonpolar solvents such as benzene and chlorobenzene but

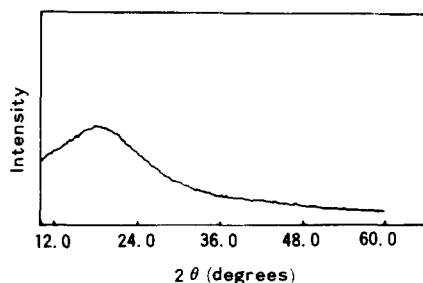


Fig. 3. Typical x-ray diffraction spectrum of poly(dipropargyl ether) prepared by MoCl_5 ($2\theta = 18.44^\circ$, $d = 4.8\text{\AA}$).

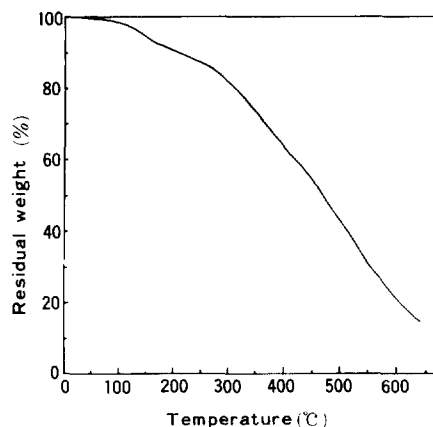
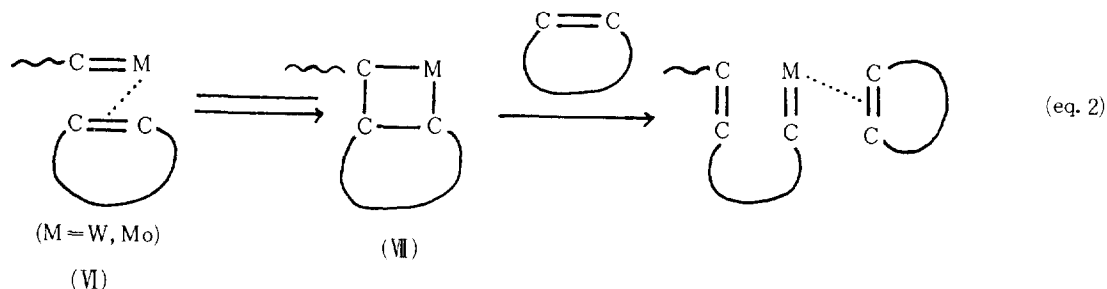
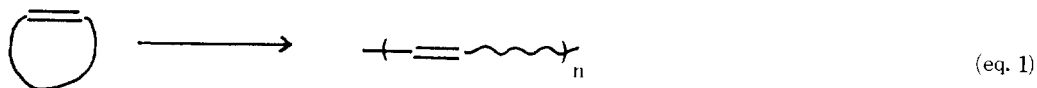
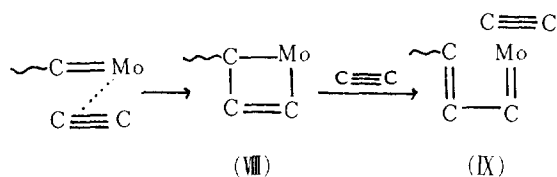


Fig. 4. TGA thermogram of poly(dipropargyl ether) prepared by MoCl_5 .



also in the polar solvent such as nitrobenzene. However, in this cyclopolymerization of DPE by MoCl_5 , 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 MoCl_5 may proceed well when the interaction between the propagating end and the counter ion produced from MoCl_5 is strong; that is reminiscent of a coordination polymerization.¹⁴ According to the above discussion, the following propagation reaction involving metal carbene(VIII) and metallacyclobutenes (IX) can be depicted for the present polymerization.



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