Note

4-Methylene-1,3-dioxolane 유도체의 WCl₆에 의한 중합

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Polymerization of 4-Methylene-1,3-dioxolane
Derivatives by Tungsten Hexachloride

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INTRODUCTION

4-Methylene-1,3-dioxolane (4-MDO) derivatives can be polymerized with various initiators to form the polymers resulting from mixed mode of polymerization. The three polymerization routes are conceivable for the polymerization of 4-MDO derivatives with cationic catalysts. They are vinyl, ring-opening and coupled vinyl and ring-opening polymerization. The ring-opening content depends on the substituent which stabilizes the carbocation at 2-position of 1,3-dioxolane ring.[1,2]

The radical polymerization of 4-MDO derivatives resulted in polymer with another mixed mode of polymerization: vinyl, coupled vinyl and ring-opening and elimination polymerization.[3]

Recently, it was reported that 2-phenyl-4-methylene-1,3-dioxolane underwent photo-initiated free radical ring-opening polymerization to form poly(keto ether) at room temperature. The polymerization takes place in a manner that carbon-carbon double bond is coupled with a concurrent acetal ring arrangement in the propagation step to give 'keto ether' sequence.[4,5]

If the substituent with special functions at 2-position of 4-MDO underwent ring-opening polymerization, the resulting poly(keto ether) could show particular physical properties. It was also of interest to survey a special catalyst for ring-opening polymerization of 4-MDO derivatives.

The tungsten hexachloride have been used as a catalyst for the olefin metathesis reaction and the metathesis polymerization of cyclic olefins.[6] However, there have been no reports on the polymerization of 4-MDO derivatives by metal based catalyst such as WCl_6. This article reports on the results of ring-opening polymerization of 4-MDO derivatives with tungsten hexachloride and the polymerizabilities are compared.

EXPERIMENTAL

4-Methylene-1,3-dioxolane derivatives were prepared by the method previously reported.[4,5] Dichloromethane was purified by distillation

after drying with sodium metal and calcium hydride. Tungsten hexachloride (Aldrich Chem. Co., 99+ %) was used without further purification. A catalyst was prepared by dissolving 0.2g of tungsten hexachloride in 30ml of methylene chloride under nitrogen.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Am-300 spectrometer. FT-IR spectra were obtained by Midac spectrophotometer. GPC data were obtained by Waters HPLC using three columns(μ-Styragel 10^2, 10^3 and 10^4 Å) in chloroform. Elemental analysis was obtained with a Yanaco MT-3 CHN-Analyzer.

Representative Polymerization of 4-methylene-1,3-dioxolane (4-MDO) with tungsten hexachloride. A solution of $\underline{4}$(1g, 5.7m mol) in 2ml of methylene chloride was introduced in a septum rubber capped glass ampoule under dry nitrogen. The ampoule was placed in a cooler at -50℃ and 2ml of tungsten hexachloride solution was added. After 6h, the polymerization mixture was quenched with triethyl amine and poured into a large volume of petroleum ether. The white precipitate was collected and purified by reprecipitation from methylene chloride into petroleum ether. White powdery polymer $\underline{\textbf{P4}}$(0.85g) was obtained after drying under vacuum at 50℃ for 6h. Other monomers, $\underline{1}$, $\underline{2}$, $\underline{3}$ and $\underline{5}$ were polymerized by similar procedures and obtained polymers **P1**, **P2**, **P3** and **P5**, respectively.

$\underline{\textbf{P1}}$: ^{1}H NMR(CDCl$_3$): δ=7.2(m, 5H, phenyl), 4.7(m, 1H, -O-CH(ϕ)-), 3.8(m, 2H, -CO-CH$_2$-O-), 2.8 and 2.6(2m, 2H, -CH$_2$-CO-CH$_2$-O-). ^{13}C NMR(CDCl$_3$): δ = 205.0(-CO-), 139.6, 128.6, 126.6(aromatic C's), 77.9(-CO--CH$_2$-O-), 74.3(-O-CH(ϕ)-), 47.1(-CH$_2$-CO-CH$_2$-O-). IR(KBr): 3060, 3020, 2880, 1735, 1350, 1110, 760, 710cm^{-1}. Elemental Anal, for (C$_{10}$H$_{10}$O$_2$)n: Calcd: C, 74.08%, H, 6.17% Found: C, 74.04%, H, 6.12%

$\underline{\textbf{P2}}$: ^{1}H NMR(CDCl$_3$): δ=3.8(m, -CO-CH$_2$-O- and -O-CH$_2$-C(CH$_2$-)-O-), 2.6(m, 2H, -CH$_2$-CO-), 1.8(m, -CH$_2$ CH$_2$ CH$_2$ CH$_2$ CH$_3$,

-OCH$_2$-C(CH$_2$-)-O-)1.5(m,-CH$_2$ CH$_2$ CH$_2$ CH ^{2}CH$_3$ and -O-C(CH$_3$) (C$_5$H$_{11}$)-). ^{13}C NMR (CDCl$_3$): δ=206(-CO-), 108(O-C-O), 78(-CO-CH$_2$-O-),67(-CO-CH$_2$-O-C(CH$_3$)(C$_2$H$_5$),52 (-CH$_2$-CO-), 43, 42, 41, 30, 26, 23(-C$_5$H$_{11}$, -CH$_3$). IR(KBr): 2936, 1730, 1462, 1375, 1250 -1070, 893cm^{-1}

$\underline{\textbf{P3}}$: ^{1}H NMR(CDCl$_3$): δ=4(m, -O-CH$_2$-C (CH$_2$-)-O- and -CH$_2$-CO-CH$_2$-O-), 2.4(m, -CH$_2$-CO-CH$_2$-O-), 1.5(m, -OCH$_2$-C(CH$_2$-) -O-, CH$_2$ CH$_2$ CH$_2$ CH$_2$ CH$_2$-). IR(KBr): 2951, 2890, 1725, 1268, 1098.5, 912cm^{-1}.

$\underline{\textbf{P4}}$: ^{1}H NMR(CDCl$_3$): δ=7.2(m, phenyl), 5.8 (s, -O-CH(CH$_2$$\phi$)-O-), 4.2~3.8(m, -CO-CH$_2$-O- and -O-CH$_2$-C(CH$_2$-)-O-), 2.7(m, -CH$_2$-CO-), 2.2(d, -CH$_2$-$\phi$), 1.8(m, -CH$_2$-C(CH$_2$-)-O-). ^{13}C NMR(CDCl$_3$): δ=207(-CO-), 132, 131, 131.5, 130, 129, 128(aromatic C's), 108(-O-CH(CH$_2$$\phi$)-O-), 78(-CO-CH$_2$-O-), 72(-CH$_2$-C(CH$_2$-)-O-), 69(-O-CH$_2$-C(CH$_2$-)-O-), 67(-CO-CH$_2$-O-CH(CH$_2$$\phi$)-), 43(-CH$_2$-CO-), 32, 34(-CH$_2$-$\phi$), and 24(-CH$_2$-C(CH$_2$-)-O-). IR(KBr): 3120, 2954, 1735, 1350, 1268, 1098, 872, 768cm^{-1}.

$\underline{\textbf{P5}}$: ^{1}H NMR(CDCl$_3$): δ=4.8(m, -O-CH$_2$-O-),3.8(-O-CH$_2$-C(CH$_2$-)-O-,-CH$_2$-CO-CH^2-O-CH$_2$- and -CO-CH$_2$-O-)), 2.4(-CH$_2$-CO-CH$_2$-O-CH$_2$-) and 1.5(-O-CH$_2$-C(CH$_2$-)-). IR (KBr): 2973, 1726, 1383, 1259, 1088, 1016, 798cm^{-1}.

RESULTS AND DISCUSSION

4-Methylene-2-phenyl-1,3-dioxolane $\underline{(1)}$, 2-methyl-2-pentyl-4-methylene-1,3-dioxolane $\underline{(2)}$, cyclohexanespro-2'-(4-methylene-1,3-dioxolane$\underline{(3)}$, 2-benzyl-4-methylene-1,3-dioxolane$\underline{(4)}$ and 4-methylene-1,3-dioxolane$\underline{(5)}$ were synthesized by acetallization of benzaldehyde, 2-heptanone, cyclohexanone, phenylacetaldehyde and trioxane with 3-chloro-1,2-propanediol, respectively, followed by dehydro-chlorination of the resulting chloromethyl-1,3-dioxolane derivatives.

Table I. The Results of the Polymerization of Various Monomers

Polymer	Monomer	Initiator (mole %)	Temp (°C)	Yield (%)	M_n	M_n	RO (%)	RI (%)
P1	1	WCl_6	25	64	1200	6400	85	15
		2	0	80	1100	4500	95	5
			-50	76	1300	4200	100	0
P2	2	WCl_6 2	-50	–	4200	1300	70	30
P3	3	WCl_6 2	-50	94	4800	1200	32	68
P4	4	WCl_6 2	-50	72	7900	23800	30	70
P5	5	WCl_6 2	-50	85	–	–	33	67

*Ring-opening, **Ring-intact

R : Ph , CH_3 , [cyclohexyl] , CH_2Ph , H

R' : H , C_5H_{11} , H , H

1   2   3   4   5
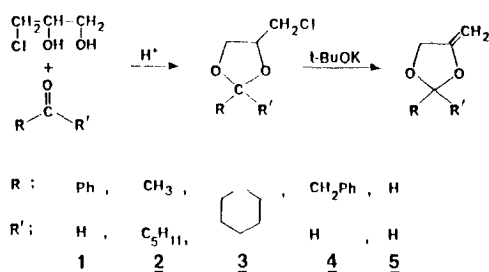
The substituted monomers were polymerized and the results and conditions were summarized in Table 1. When the monomer **1** was polymerized at -50°C for 4h with 2 mole% of WCl_6 as an initiator, a white powdery polymer was isolated after purification.

The presence of a signal in ^{13}C NMR spectrum at 204ppm corresponding to the carbonyl carbon and the absence of a peak around 103 ppm corresponding to acetal carbon indicated that **1** had undergone almost quantitative ring-opening to form poly(keto ether) as exhibited in Fig. 1 (a) and 1(b). This observation is consistent with its ^1H NMR spectrum in Fig. 2 ; a signal at 4.7ppm corresponding to the methine proton attached to oxygen formed by ring opening and no signal at 5.8 ppm assignable to the acetal proton of unopened ring.

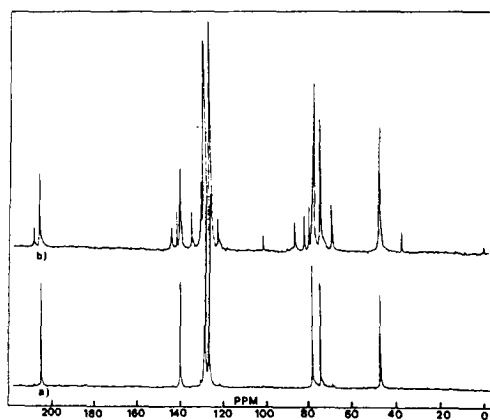In order to elucidate the effect of temperature on the extent of ring-opening, monomer **1** was

Fig. 1. ^{13}C NMR spectra of polymer obtained from monomer 1 (a) at -50 and (b) 25 with tungsten hexachloride in $CDCl_3$.

polymerized at 0°C and 25°C. In the ^1H NMR spectum, the polymer obtained at 25°C showed somewhat different from that obtained at -50°C as shown in Fig. 2(a) and 2(b). It was of interest to calculate the amounts of ring-opened and the ring-unopened units from the integration in NMR spectrum.

The ring-opening content of polymers obtained at 0°C and 25°C is 85% and 95%, repectively, by the integration ratio of the methine proton of unopened ring appeared at
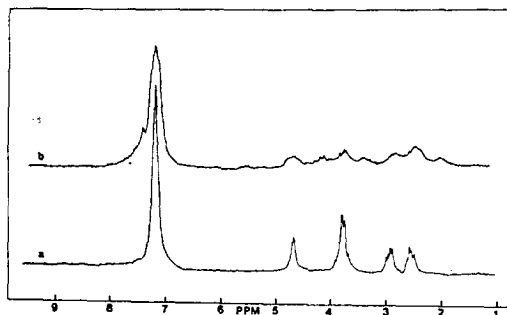
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Fig. 2. ^{1}H NMR spectra of polymer obtained from monomer **1** (a) at -50℃ and (b) 25℃ with tungsten hexachloride in $CDCl_3$.

5.8ppm and phenyl proton at 7.2ppm. When the polymerization **P2** is carried out at 50℃ with tungsten hexachloride as an initiator, the polymer of **2** was isolated by reprecipita-ting methylene chloride solution of the polymer-ization mixture into hexane or methanol. Finally the polymers were obtained as a viscous liquid. At -50℃, 70% of ring opened and 30% of ring intact copolymer was obtained.

The polymer structure was determined by the relative rates of ring-opening isomerization and propagation. The relative rate is dependent on the substituents, which stabilize the carbon atom at 2-position.

This substitution effect has been demonstrated by the exclusive isolation of essentially poly (keto ether)s[7] from the 2-phenyl-, 2-phenyl-2-methyl- and 2-(β-phenylvinyl)-derivatives since the benzyl and ally cation formed by ring opening is considerably more stable than tertiary, secondary and primary cation theoretically formed by ring opening of **2**, **3**, **4**, and **5**.

In the case of polymerization of **3**, the ring-opening content is lower than that of **2** under same conditions. The extent of ring opening is determined by the ratio of the rate of ring opening to the rate of addition of the unopened ring to the monomer. The formation of the relatively stable ketone group is a strong driving force for the ring opening and relative stability of the resulting ring opened species is also a factor.

Since the tertiary carbocation formed from monomer **3** is as stable as the one formed from **2**. However, the six-membered cyclohexane ring produces more steric hindrance to the direct polymerization of monomer **3** than in the monomer **2**. When monomer **3** was polymerized at -50℃ for 6h with 2 mole% of tungsten hexachloride as a initiator, the white powdery polymer were obtained in 94% yield after precipitation into methanol.

In the IR spectrum, the band at $1730cm^{-1}$ corresponding to carbonyl stretching is somewhat weak. And the peak at 3.8ppm corresponding to ring opened $-CH_2-CO-CH_2-O-$ in ^{1}H NMR spectrum is also weak. These indicate that the monomer **3** undergoes not only ring-opening but also vinyl polymerization. The ring opening content is 32%.

Also in the related study, 2-benzyl derivative was prepared and polymerized with tungsten hexachloride at -50℃. Since the resulting secondary cation at 2-position is apparently higher in energy than the foregoing polymerization of **1**, **2** and **3**, the extent of ring opening is lowered. Even at -50℃, only 30% of the rings were opened.

As expected in the polymerization of **1**, **2**, **3** and **4** with different substituent at 2-position of 1,3-dioxolane ring, monmer **5** underwent 30% ring-opening polymerization. Goodman and co-workers reported that 4-MDO derivatives were polymerized by Lewis acids such as $AlCl_3$ and $BF_3 \cdot Et_2O$ to give polymers with the mixed modes of polymerization: vinyl, ring-opening and coupled vinyl and ring opening.[1]

In the case of cationic polymerization of 2,2-dimethyl-, 2-methyl-4-methylene-1,3-dioxolane, ring-opening content is estimated to be between 40~90% which varied appreciably depending upon the catalyst system and temperature employed.[2] It can be expected in terms of stability of formed carbonium ion, which was produced during polymerization by acetal ring rearrangement. In this experiment, the ring

opening content is about 30%.

For further information of the ring-opening only of ·1,3-dioxolane ring, a model reactions using 1,3-dioxolane and 2-phenyl-1,3-dioxolane were performed with WCl_6 as an initiator. No polymer was formed with tungsten hexachloride, but the viscous liquid polymer was formed with $BF_3 \cdot Et_2 O$.

At this point, it is difficult to suggest the mechanism of polymerization. The substituent at 2-position has related with ring-opening. This indicates that the polymerization does not proceed in concerted mechanism for the polymerization of 4-MDO derivatives by tungsten hexachloride. The mode of polymerization and the structual feature of polymers obtained from WCl_6 were similar to those obtained from $BF_3 \cdot Et_2 O$ catalyst. On the basis of these results, the polymerization mechanism is suggested as follows:
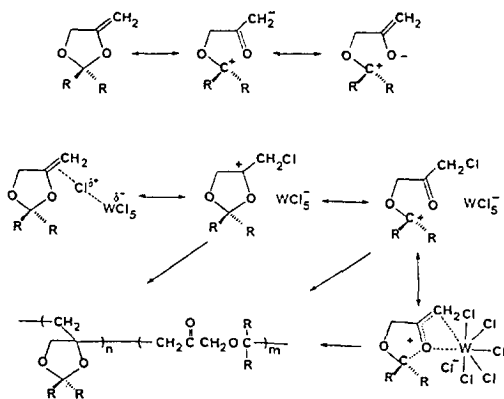
Further works on the model studies for polymerization mechanism and other derivatives are now in progress and will be presented in the future.

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