NOTE

**Polymerization of Symmetrical Dialkylacetylenes
(3-Hexyne, 4-Octyne, and 5-Decyne) by $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$
and $\text{MoCl}_5 \cdot \text{Ph}_4\text{Sn}$**

Toshio MASUDA, Yoshinori KUWANE,
and Toshinobu HIGASHIMURA

*Department of Polymer Chemistry, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606, Japan.*

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Fairly many studies have appeared on the polymerization of acetylene and monosubstituted acetylenes, and several transition-metal catalysts are now known to provide high polymers.¹ The polymerization of disubstituted acetylenes, however, remains appreciably difficult, and virtually restricted to the following cases: hexafluoro-2-butyne (anionic catalyst; insoluble polymer),² dicyanoacetylene (anionic catalysts; polymer molecular weight, MW 500),³ 1-phenylpropyne ($\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$; polymer MW 6000),⁴ diphenylacetylene (anionic catalysts; polymer MW ≤ 1800)⁵ ($\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$; insoluble polymer),⁶ 1-chloro-2-phenylacetylene ($\text{Mo}(\text{CO})_6\text{-}h\nu$; polymer MW 4×10^5),⁷ and dialkylacetylenes^{8–10} (*vide infra*).

Mauret *et al.* obtained a mixture of linear polymer and cyclic trimer in the reaction of 3-hexyne catalyzed by diarylcobalts.^{8,9} The polymer was insoluble in organic solvents and susceptible to air oxidation. Very recently, Katz and Lee obtained mostly insoluble polymers in the polymerization of 2-butyne, 4-octyne, and cyclooctyne by tungsten-carbene complexes.¹⁰

We have reported that WCl_6 - and MoCl_5 -based catalysts are very effective for the polymerization of aromatic acetylenes including disubstituted acetylenes.^{4,6,7,11} Now it seems appropriate to study whether these catalysts can polymerize aliphatic disubstituted acetylenes as well. This paper deals with the polymerization of symmetrical dialkyl-

acetylenes (3-hexyne, 4-octyne, and 5-decyne) by use of WCl_6 - and MoCl_5 -based catalysts and with the characterization of polymers formed.

EXPERIMENTAL

Dialkylacetylenes (3-hexyne, 4-octyne, and 5-decyne; Tokyo Chemical Industry Co.) were used without further purification (purities > 99%). Unless otherwise stated, polymerizations were carried out at 30°C in toluene for 24 h under a dry nitrogen atmosphere; $[\text{M}]_0 = 1.0 \text{ mol dm}^{-3}$, $[\text{Cat}] = 30 \text{ mmol dm}^{-3}$. The 1:1 mixtures of tetraphenyltin and either WCl_6 or MoCl_5 in solution were aged at 30°C for 15 min before use as catalysts.¹² Monomer consumptions and polymer yields were determined by gas chromatography and gravimetry, respectively.

RESULTS AND DISCUSSION

Polymerization of Dialkylacetylenes

The $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$ catalyst is known to effect the polymerization of phenylacetylene,¹² 1-phenylpropyne,⁴ and cyclopentene.¹³ This catalyst polymerized 3-hexyne to afford a methanol-insoluble polymer in high yield in toluene solution within several hours (Table I). The polymerization proceeded almost quantitatively in halogenated hydrocarbons. Thus, $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$ is much more

Table I. Polymerization of 3-hexyne^a

No.	Catalyst	Solvent	Polymer yield/% ^b
1	WCl ₆ ·Ph ₄ Sn	Toluene	87
2 ^c	WCl ₆ ·Ph ₄ Sn	Toluene	71
3	WCl ₆ ·Ph ₄ Sn	CCl ₄	95
4	WCl ₆ ·Ph ₄ Sn	(CH ₂ Cl) ₂	96
5	MoCl ₅ ·Ph ₄ Sn	Toluene	16
6	WCl ₆	Toluene	0
7	MoCl ₅	Toluene	3
8	WCl ₆ ·(1/2)CH ₃ OH	Toluene	0
9	MoCl ₅ ·(1/2)CH ₃ OH	Toluene	8
10	Fe(acac) ₃ ·3Et ₃ Al	Toluene	~0
11	Ti(On-Bu) ₄ ·4Et ₃ Al	Toluene	~0
12	TiCl ₄ ·3Et ₃ Al	Toluene	~0

^a Polymerized at 30°C for 24 h: [M]₀ = 1.0 mol dm⁻³, [Cat] = 30 mmol dm⁻³.

^b Methanol-insoluble polymer.

^c Polymerized for 1 h.

active than any other catalysts ever used for the polymerization of dialkylacetylenes.⁸⁻¹⁰ The MoCl₅·Ph₄Sn catalyst was less active, but it also gave a methanol-insoluble polymer.

The polymerization of 3-hexyne by WCl₆·Ph₄Sn and MoCl₅·Ph₄Sn produced small amounts of methanol-soluble oligomer (2–10% of the whole products) in addition to the methanol-insoluble polymer. Hexaethylbenzene (cyclic trimer) was not found in the oligomeric product.

On the other hand, WCl₆ and MoCl₅ were, by themselves, practically inactive for the polymerization of 3-hexyne (see Table I). Certain oxygen-containing compounds, such as water and methanol, serve as cocatalysts for the WCl₆- and MoCl₅-catalyzed polymerization of phenylacetylene.¹¹ Methanol, however, was hardly effective as a cocatalyst in the present polymerization.

Ziegler-type catalysts are known to bring about the polymerization of acetylenes: for example, iron (III) chelates-3Et₃Al for 1-alkynes¹⁴ and phenylacetylene,¹⁵ Ti(On-Bu)₄·4Et₃Al for acetylene,¹⁶ and TiCl₄·3Et₃Al for phenylacetylene (cyclotrimerization).¹⁷ For the sake of comparison, the polymerization of 3-hexyne was carried out using these catalysts. Almost no methanol-insoluble polymer, however, was formed. Consequently it is concluded that Ziegler-type catalysts, which are usually heterogeneous, are unsuitable for the polymerization of

Table II. Polymerization of 4-octyne and 5-decyne^a

No.	Monomer	Catalyst	Solvent	Polymer yield/% ^b
1	4-Octyne	WCl ₆ ·Ph ₄ Sn	Toluene	70
2	4-Octyne	MoCl ₅ ·Ph ₄ Sn	Toluene	13
3	5-Decyne	WCl ₆ ·Ph ₄ Sn	Toluene	61
4	5-Decyne	WCl ₆ ·Ph ₄ Sn	CCl ₄	57
5	5-Decyne	WCl ₆ ·Ph ₄ Sn	(CH ₂ Cl) ₂	65
6	5-Decyne	MoCl ₅ ·Ph ₄ Sn	Toluene	10

^a Polymerized at 30°C for 24 h: [M]₀ = 1.0 mol dm⁻³, [Cat] = 30 mmol dm⁻³.

^b Methanol-insoluble polymer.

sterically-hindered acetylenes like dialkylacetylenes.

The results for the polymerizations of 4-octyne and 5-decyne are shown in Table II. 4-Octyne and 5-decyne were also polymerized in fairly high yields by WCl₆·Ph₄Sn. As the alkyl group became longer, the polymer yield decreased (3-hexyne > 4-octyne > 5-decyne). The solvent effects on the polymerization of 5-decyne were similar to those for 3-hexyne. The chlorides of W and Mo by themselves and the Ziegler-type catalysts described above did not polymerize 5-decyne.

Properties and Structure of Polymers

The elemental compositions of polymers agreed well with the theoretical values: *e.g.*, Poly(3-hexyne) (Table I, No. 1) Calcd for (C₆H₁₀)_n: C, 87.73%; H, 12.27%. Found: C, 87.56%; H, 12.12%. Poly(4-octyne) (Table II, No. 1) Calcd for (C₈H₁₄)_n: C, 87.19%; H, 12.81%. Found: c, 87.18%; H, 12.83%. Poly(5-decyne) (Table II, No. 3) Calcd for (C₁₀H₁₈)_n: C, 86.88%; H, 13.12%. Found C, 86.29%; H, 13.20%.

The poly(dialkylacetylene)s obtained had the form of white powder. No softening point was observed below 300°C. In the differential thermal analysis, the polymers showed no endo- or exothermic peak below 200°C but complex exothermic peaks above 200°C. Even though the polymers were exposed to the air at room temperature for a month, no change occurred in the polymer color, elemental compositions or IR spectra. This indicates that the polymers are fairly stable against air oxidation.

The major portions of the polymers (70–90%) were insoluble (polymers were precipitated during

polymerization regardless of the reaction time), and even the soluble fractions became gradually insoluble after isolation. This seems due to cross-linking which occurs slightly and gradually.

The IR spectrum of poly(3-hexyne) showed the following absorptions: 2950—2850 (s), 1660—1580 (w), 1460 (m), 1370 (m), 1310 (m), 1260 (m), 1150—1000 (m), and 800 (m) cm^{-1} . The weak and broad absorption at 1660—1580 cm^{-1} is due to the C=C stretching of conjugated double bonds along the main chain. The spectra of poly(4-octyne) and poly(5-decyne) were also similar, though a little more complex. The intensities of absorptions at 1150—1000 cm^{-1} depended on the kind of catalysts used, ($\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$ and $\text{MoCl}_5 \cdot \text{Ph}_4\text{Sn}$), suggesting a difference in the geometric structure of polymers.

^1H nuclear magnetic resonance (NMR) and ultraviolet (UV)-visible spectra were measured using the soluble part of poly(5-decyne) which was more soluble than poly(3-hexyne) and poly(4-octyne): ^1H NMR (CCl_4) δ 2.5—0.5 ppm (broad singlet); UV_{max} (cyclohexane) 273 nm (ϵ 450). If the present polymerization is accompanied by isomerization to terminal acetylenes, the polymers formed should be colored and show olefinic-proton peaks around δ 5—6 ppm in the ^1H NMR spectra. Thus the expected polymer structure, $\{ \text{CR}=\text{CR} \}_n$ ($\text{R}=\text{Et}$, $n\text{-Pr}$, $n\text{-Bu}$) is supported.

CONCLUSIONS

The $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$ and $\text{MoCl}_5 \cdot \text{Ph}_4\text{Sn}$ catalysts effectively polymerized 3-hexyne, 4-octyne, and 5-decyne. The polymers produced were in the form of white powder, mostly insoluble and sufficiently stable. The polymer structure, $\{ \text{CR}=\text{CR} \}_n$ ($\text{R}=\text{Et}$,

$n\text{-Pr}$, $n\text{-Bu}$) was confirmed by IR and ^1H NMR spectra.

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