

Polymerization of *t*-Butylacetylene Catalyzed by MoCl₅ and WCl₆

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ABSTRACT: *t*-Butylacetylene was polymerized by MoCl₅ and WCl₆ as catalysts at 30°C or 0°C in hydrocarbon and halogenated hydrocarbon solvents. Poly(*t*-butylacetylene) was obtained in high yield especially with MoCl₅, and the highest polymer molecular weight exceeded 3×10^5 . The following relationship was obtained between the viscosity and molecular weight: $[\eta] = 10^{-5.12} M_n^{1.01}$. The polymer was soluble in nonpolar solvents, particularly in aliphatic hydrocarbons. The infrared (IR), ¹H nuclear magnetic resonance (NMR), and ¹³C NMR spectra supported the expected polymer structure, $\{CH=C(t-Bu)\}_n$. A pair of doublets were observed for the methyl carbon in the ¹³C NMR of polymer, making possible an evaluation of geometric structure.

KEY WORDS *t*-Butylacetylene / Coordination Polymerization / Molybdenum Pentachloride / Tungsten Hexachloride / Polyene / Geometric Structure / ¹³C Nuclear Magnetic Resonance /

Acetylenes substituted by a primary or secondary alkyl group have been polymerized by transition-metal catalysts to high-molecular-weight linear polymers: 1-Hexyne was first polymerized by Natta *et al.* by use of the TiCl₃-triethylaluminum (Et₃Al) catalyst.^{1,2} This polymer is a yellow "semisolid" which is gradually oxidized in the air.¹⁻³ The iron chelate-Et₃Al catalyst affords a similar high polymer,^{4,5} while C₆H₅CH₃·Mo(CO)₃ gives only an oligomer.⁶ Propyne was polymerized with Ziegler catalysts to an insoluble dark-brown polymer.⁷⁻⁹ During a study on the polymerization of optically-active alkylacetylenes, a *s*-alkylacetylene proved capable of being polymerized.¹⁰

On the other hand, it was reported that *t*-butylacetylene was not polymerized by several transition-metal catalysts which brought about the polymerization (including cyclotrimerization) of other acetylenes.¹¹⁻¹⁴ Very recently, Katz and Lee succeeded in obtaining high-molecular-weight poly(*t*-butylacetylene) by tungsten-carbene catalyzed polymerization;¹⁵ the catalysts used, however, were not very active. We found that a high polymer (molecular weight $MW \sim 3 \times 10^5$) is quantitatively obtained by polymerization induced by the ultra-

violet irradiation of Mo(CO)₆ in carbon tetrachloride solution.¹⁶ Thus, derivatives of VIA metal carbonyls effect the polymerization of *t*-butylacetylene to give high polymers. On the other hand, the polymerization of this monomer by MoCl₅, a halide of VIA metal, was reported only very briefly (polymer MW 8000),¹⁷ with neither detailed polymerization conditions nor polymer structure being described.

We reported earlier that MoCl₅ and WCl₆ were novel effective catalysts for the polymerization of aromatic acetylenes.¹⁸⁻²¹ It seems interesting to investigate the polymerization of aliphatic acetylenes by MoCl₅ and WCl₆ in comparison with that of aromatic acetylenes. In the present study, *t*-butylacetylene, which possesses a bulky substituent and no α hydrogen, was used as an aliphatic acetylene. This paper deals with the polymerization of *t*-butylacetylene with emphasis on the yield, molecular weight, and structure of the polymer.

EXPERIMENTAL

The monomer was prepared from pinacolone according to the literature method.^{22,23} bp 37—

39°C (lit. bp 36.5—38.5°C²³). The purity was over 99.5% according to gas chromatography. Polymerization was carried out under a dry nitrogen atmosphere at 30°C or 0°C, a monomer concentration of 1.0 mol l⁻¹, and a catalyst concentration of 20 mmol l⁻¹ for 24 h, unless otherwise stated. The polymer formed was isolated by pouring the reaction mixture into a large amount of methanol, filtered off, and dried under vacuum.

Number-average molecular weights, M_n , of polymers were determined in a toluene solution by osmotic-pressure measurements using a Mechrolab 502 osmometer. Intrinsic viscosities, $[\eta]$, were determined in a toluene solution at 30°C. Gel-permeation chromatograms were obtained on a JASCO TRIROTAR chromatograph (column: Shodex-A804, 805 polystyrene gel; eluent, tetrahydrofuran (THF)). IR spectra were recorded on a Shimadzu IR 27G spectrophotometer. ¹³C NMR spectra were observed in CDCl₃ solution (15 w/v%) on a JNM FX100 spectrometer.

RESULTS AND DISCUSSION

Polymerization Conditions and Polymer Yield

Table I summarizes the results for the polymerization of *t*-butylacetylene by several catalysts in toluene solution. The MoCl₅ and WCl₆ catalysts polymerized *t*-butylacetylene very effectively, and

the polymer yield exceeded 90% in many cases. Generally, MoCl₅ was more active than WCl₆, in contrast to the polymerization of phenylacetylene where WCl₆ is more active than MoCl₅.¹⁸ Though most polymerizations were carried out for 24 h, polymer yields were high enough after only 10 min with MoCl₅ and after 2 h (86%) with WCl₆ at 30°C. Polymers were obtained in high yields even at 0°C; at temperatures lower than 0°C, however, not only polymerizability but also catalyst solubility disfavored polymer yield.

Small amounts of water and methanol as cocatalysts are known to appreciably increase polymer yields in the polymerizations of phenylacetylene¹⁸ and β -naphthylacetylene.²⁰ Table I also contains results for the polymerization of *t*-butylacetylene catalyzed by MoCl₅·(1/2)CH₃OH and WCl₆·(1/2)CH₃OH. As a consequence, methanol hardly affected the yields in the present polymerization. This seems due to the high activities of MoCl₅ and WCl₆ by themselves in the polymerization of *t*-butylacetylene.

Ziegler-type catalysts are capable of inducing the linear high polymerization of acetylenes: for example, Ti(*n*-BuO)₄·4Et₃Al for acetylene,²⁴ and iron chelates-3Et₃Al for alkylacetylenes,⁴ and for phenylacetylene.²⁵ In the present study, the polymerization of *t*-butylacetylene was attempted using three Ziegler-type catalysts: TiCl₄·3Et₃Al, iron(III)

Table I. Polymerization of *t*-butylacetylene by MoCl₅ and WCl₆ in toluene^a

No.	Catalyst	Temp	Time	Polymer yield	$[\eta]^b$	$M_n \times 10^{-3}^c$
		°C	h	%	dl g ⁻¹	
1	MoCl ₅	30	24	100	2.68	301*
2	"	30	1/6	95	—	—
3	"	0	24	96	3.42	383*
4	WCl ₆	30	24	92	0.52	54
5	"	30	1/6	10	—	—
6	"	0	24	88	0.85	89
7	MoCl ₅ ·(1/2)CH ₃ OH	30	24	100	2.03	190
8	"	0	24	100	2.27	255*
9	WCl ₆ ·(1/2)CH ₃ OH	30	24	90	0.27	35
10	"	0	24	58	0.68	78*
11	TiCl ₄ ·3Et ₃ Al	30	24	~0	—	—
12	Fe(acac) ₃ ·3Et ₃ Al	30	24	~0	—	—
13	Ti(<i>On</i> -Bu) ₄ ·4Et ₃ Al	30	24	~0	—	—

^a Polymerized at $[M]_0$, 1.0 mol l⁻¹; $[Cat]$, 20 mmol l⁻¹.

^b Measured in toluene at 30°C.

^c Determined by osmometry (the asterisked values from viscosities by eq 1).

Table II. Polymerization of *t*-butylacetylene by MoCl₅ and WCl₆ in various solvents^a

No.	Catalyst	Solvent	Polymer yield		$M_n \times 10^{-3c}$
			%	$[\eta]^b$ dl g ⁻¹	
1	MoCl ₅	CCl ₄	95	0.97	110*
2	"	CHCl ₃	91	0.41	47*
3	"	(CH ₂ Cl) ₂	89	1.08	123*
4	"	THF	20	—	—
5	WCl ₆	CCl ₄	91	0.81	92*
6	"	CHCl ₃	57	0.20	23
7	"	(CH ₂ Cl) ₂	58	1.62	183*
8	MoCl ₅ ·(1/2)CH ₃ OH	CCl ₄	86	2.12	280
9	"	(CH ₂ Cl) ₂	83	0.61	77
10	WCl ₆ ·(1/2)CH ₃ OH	CCl ₄	85	0.38	44*
11	"	(CH ₂ Cl) ₂	57	0.58	67

^a Polymerized at $[M]_0$, 1.0 mol l⁻¹; [Cat], 20 mmol l⁻¹, at 30°C for 24 h.

^b Measured in toluene at 30°C.

^c Determined by osmometry (the asterisked values from viscosities by eq 1).

Table III. Effects of monomer and catalyst concentrations on the polymerization of *t*-butylacetylene by MoCl₅^a

No.	[M]	[MoCl ₅]	Polymer yield		$M_n \times 10^{-3c}$
	mol l ⁻¹	mmol l ⁻¹	%	$[\eta]^b$ dl g ⁻¹	
1	0.25	20	54	0.41	46
2	0.50	20	40	1.02	116*
3	1.0	20	100	2.68	301*
4	1.0	10	100	2.95	331*
5	1.0	5	100	2.88	323*

^a Polymerized in toluene at 30°C for 24 h.

^b Measured in toluene at 30°C.

^c Determined by osmometry (the asterisked values from viscosities by eq 1).

acetylacetonate-3Et₃Al, and Ti(*n*-BuO)₄·4Et₃Al. These catalysts, however, afforded no or but negligible amounts of methanol-insoluble polymer (see Table I). This led to the conclusion that Ziegler-type catalysts, being mostly heterogenous, are unsuitable for the polymerization of sterically-hindered acetylenes like *t*-butylacetylene. But the activities of MoCl₅ and WCl₆ are less influenced by steric factors, since these catalysts work in a homogeneous state. This might account for the effective polymerization of not only *t*-butylacetylene but also disubstituted acetylenes such as 1-phenylpropyne¹⁹ and diphenylacetylene²¹ by Mo- and W-based catalysts.

The polymerization of *t*-butylacetylene by MoCl₅

and WCl₆ proceeded in high yields not only in hydrocarbons such as toluene, benzene, and cyclohexane but also in halogenated hydrocarbons such as carbon tetrachloride and ethylene dichloride (see Table II). It is interesting to note that ethylene dichloride is suitable enough as a polymerization solvent, although its dielectric constant is fairly larger than those of hydrocarbons and it is a nonsolvent of poly(*t*-butylacetylene). A polymer was obtained even in THF solution.

The effects of monomer and catalyst concentrations on polymer yield were examined (Table III). Polymer yield tended to increase with increasing monomer concentration, while the yield was always quantitative at catalyst concentrations from

5 to 20 mmol l⁻¹.

Viscosity and Molecular Weight of Polymer

Tables I—III list intrinsic viscosities of polymers. The viscosities ranged from 0.20 to 3.42 dl g⁻¹. The number-average molecular weights of some ten polymers were measured by the osmotic-pressure method; they are shown in Tables I—III without asterisks. As is obvious from Figure 1, the plots of intrinsic viscosity *versus* molecular weight obeyed a linear relationship. Application of the least-squares method to these plots provided the following equation.

$$[\eta] = KM_n^a$$

$$K = 10^{-5.12 \pm 0.24} \text{ dl g}^{-1}, a = 1.01 \pm 0.05 \quad (1)$$

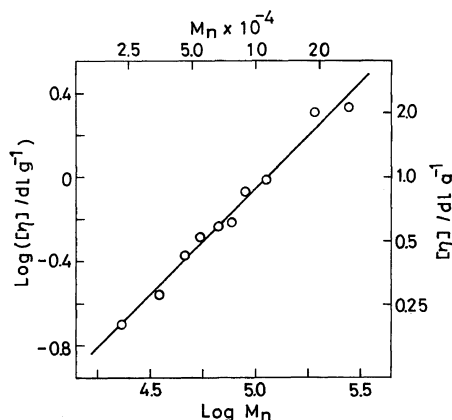


Figure 1. Relationship between the intrinsic viscosity and molecular weight of poly(*t*-butylacetylene)s.

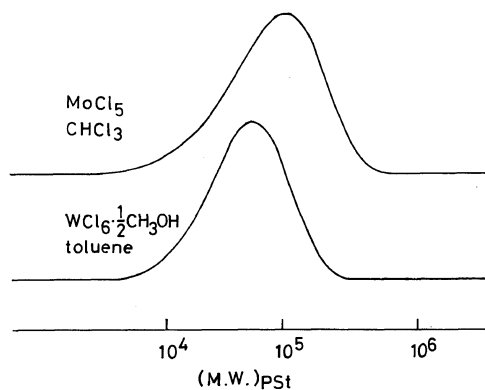


Figure 2. Gel-permeation chromatograms of poly(*t*-butylacetylene)s: *MW* calibrated for polystyrene is tentatively shown.

It is worth noting that the exponent of 1.01 is appreciably larger than those (0.5—0.8) usually observed for vinyl polymers. Poly(*t*-butyl crotonate), which has a fairly stiff backbone owing to the two substituents, has been reported to show an exponent of 0.96.²⁶ The asterisked molecular weights in Tables I—III were obtained from intrinsic viscosities by use of eq 1.

The highest number-average molecular weight of poly(*t*-butylacetylene) in the present study reached 380 000, which was attained with MoCl₅ as a catalyst (Table I, No 3). To our knowledge, this value is one of the highest among those ever reported not only for poly(*t*-butylacetylene) but also for any acetylenic polymers.¹⁶ In general, MoCl₅ provided poly(*t*-butylacetylene) having a higher molecular weight than WCl₆ did.

The effects of polymerization conditions on polymer molecular weight are as follows: A decrease in temperature from 30°C to 0°C brought about an increase in the molecular weight in every case. The addition of methanol as a cocatalyst resulted in a decrease in the molecular weight (Table I). Chloroform produced rather low-molecular-weight polymers as compared with other polymerization solvents (Table II). Further, polymer molecular weight increased with increasing monomer concentration, whereas it was unaffected by catalyst concentration (Table III).

Figure 2 shows a couple of gel-permeation chromatograms of poly(*t*-butylacetylene)s. Number- and weight-average molecular weights were tentatively calculated from the chromatograms by using a calibration curve for polystyrene. The number-average molecular weights from chromatography were similar to those from osmometry or viscosity. The values of M_w/M_n ranged from 2.0 to 2.5, which is reasonable for a homogeneous polymerization.

Properties and Structure of Polymer

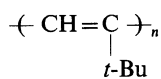
The elemental composition of all polymers agreed well with the theoretical one: *e.g.*, *Anal.* Calcd for (C₆H₁₀)_n: C, 87.73%; H, 12.27%. Found: C, 87.78%; H, 12.22% (sample: Table I, No 1; MoCl₅/toluene polymer). Poly(*t*-butylacetylene) had the form of white powder. A film could be easily prepared from the polymer solution. The polymer was stable enough, as demonstrated by the fact that no change could be observed in the IR spectrum of

polymer after standing for several months at room temperature in the air. In contrast to this, poly(1-hexyne), which has an identical elemental composition, was gradually oxidized in the air and the carbonyl group appeared in the IR spectrum.²⁷

No gel fraction was formed at all in the present polymerization. Poly(*t*-butylacetylene) dissolved very readily in aliphatic hydrocarbons such as hexane and cyclohexane. It also dissolved in aromatic hydrocarbons, carbon tetrachloride, chloroform, and THF, whereas polar solvents such as ethylene dichloride, ethyl acetate, acetonitrile, acetone, nitrobenzene, dimethyl sulfoxide, and ethanol were nonsolvents.

Poly(*t*-butylacetylene) showed a sharp softening point (within 2°C) between 245°C and 265°C depending on polymerization conditions. In the differential thermal analysis of polymers under a stream of nitrogen, a few exothermic peaks were observed above 200°C, but no endothermic peak appeared between room temperature and 500°C. The present polymers turned out to be amorphous according to X-ray diffraction analysis of powder samples: *e.g.*, MoCl₅-toluene polymer 2θ (Δ2θ/2θ), 9.2° (0.33) and 18.4° (0.22).

Figure 3 shows the IR spectra of polymers produced under several conditions. The absorptions are assigned as follows: 2950—2850 (=CH, CH₃), 1650—1550 (C=C), 1475, 1385, 1355, 1230—1190 (CH₃), 870 (=CH) cm⁻¹. The IR spectra support polymer structure I. The absorptions at 1260, 1100, and 800 cm⁻¹ varied with polymerization con-



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ditions, and were the largest in the MoCl₅-THF polymer. These absorptions seem to depend on the geometric structure of the polymer, and this will be made clearer below by ¹³C NMR spectra.

The ¹H NMR spectrum of polymer measured in a

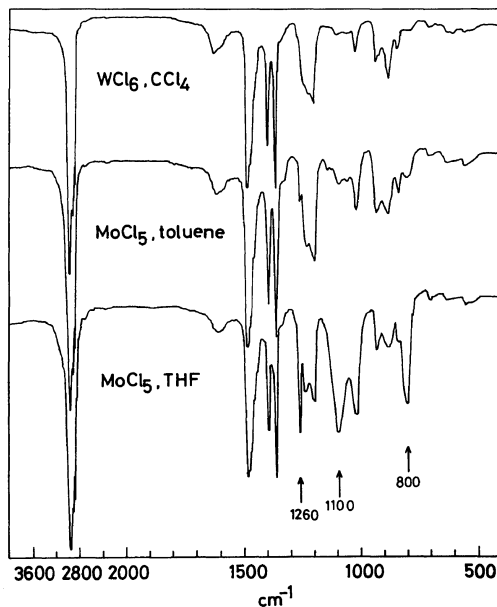


Figure 3. IR spectra of poly(*t*-butylacetylene)s.

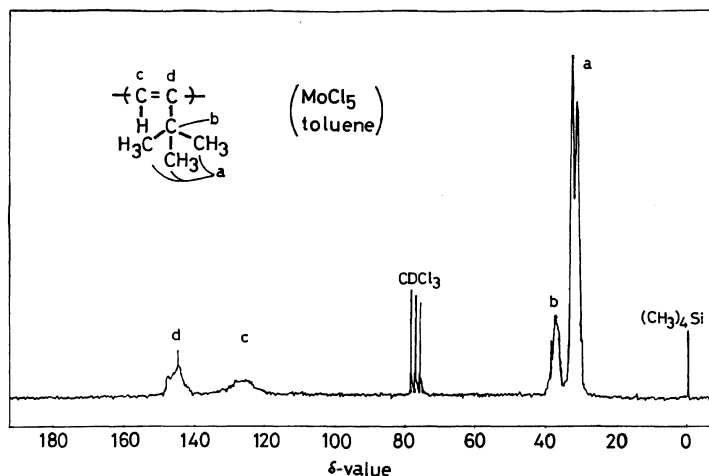


Figure 4. ¹³C NMR spectrum of poly(*t*-butylacetylene).

carbon tetrachloride solution simply showed a singlet peak (9H) at 1.0 ppm due to the *t*-butyl protons and a broad peak (1H) centered at 5.7 ppm due to the olefinic proton. The ^{13}C NMR spectrum of the MoCl_5 -toluene polymer is shown in Figure 4. Both ^1H and ^{13}C NMR spectra support the expected polymer structure, **I**, again.

In the ^{13}C NMR spectrum of poly(*t*-butylacetylene), a pair of doublets were observed at 32.4 and 31.2 ppm for the three equivalent methyl carbons. As is seen in Figure 5, the relative intensities of the two peaks greatly changed according to the kinds of catalyst and solvent. It seems reasonable to attribute this splitting to the geometric structure of the double bonds along the main chain. In the case of phenylacetylene, MoCl_5 generally produced a polymer containing more *cis* structure than did WCl_6 .²⁸ If this holds also for *t*-butylacetylene, the peak at 31.2 ppm may be attributed to the *cis* structure and the one at 32.4 ppm to the *trans* by comparing Figure 5a with 5c. Thus, the *cis* contents of polymer samples a, b, c, and d in Figure 5 are evaluated as 54, 55, 71, and 78%, respectively. The three absorptions at 1260, 1100, and 800 cm^{-1} in the IR spectrum increased as the peak at 31.2 ppm in the ^{13}C NMR spectrum increased.

Poly(*t*-butylacetylene) showed only an absorption ($\epsilon_{\text{max}} \sim 1480$) at 283 nm and no absorption in the visible region, although it possessed many conjugated double bonds. This suggests that the main chain has a twisted structure owing to the bulky substituent.

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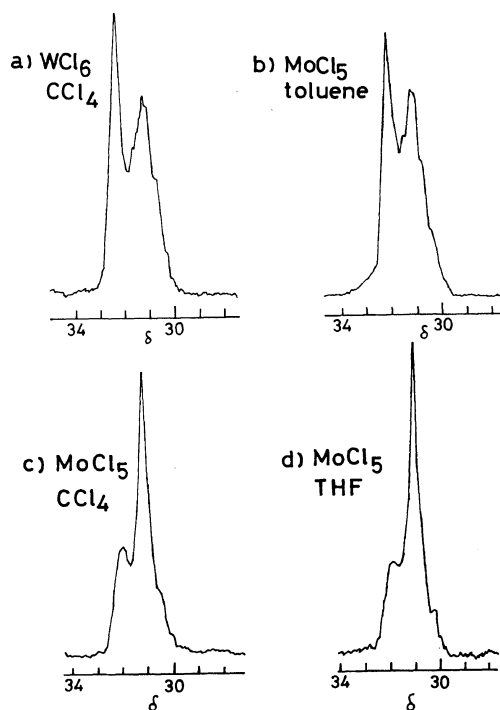


Figure 5. Methyl carbon peaks in ^{13}C NMR spectra of poly(*t*-butylacetylene)s.

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