

Polymerization of *t*-Butylacetylene by Group 6 Transition Metal Catalysts: Geometric Structure Control by Reaction Conditions*

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ABSTRACT: The geometric structure of poly(*t*-butylacetylene) could be controlled by the choice of suitable polymerization conditions (solvents and catalysts): *t*-Butylacetylene was polymerized in high yield by MoCl₅ and WCl₆ in oxygen- or nitrogen-containing solvents (*e.g.*, anisole, acetophenone, benzonitrile and nitrobenzene). The molecular weights of the polymers formed were as high as $5 \times 10^4 - 2 \times 10^5$. According to ¹³C NMR, polymers prepared in nonpolar solvents like toluene comprised comparable amounts of *cis* and *trans* structures. On the other hand, polymers obtained with MoCl₅ in oxygen- or nitrogen-containing solvents possessed the *cis* structure exclusively. The mechanism of geometric structure control was discussed.

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

Polymers obtained from acetylene and its derivatives possess conjugated double bonds along the main chain. The geometric isomerism of the main chain in these polymers is an important problem, since it will have great influence on polymer properties. Both all-*cis* and all-*trans* polyacetylenes have been successfully synthesized with a Ziegler catalyst, Ti(*On*Bu)₄-Et₃Al, by the choice of proper polymerization temperature and catalyst composition.²

On the other hand, only a few reports have appeared on the geometric structure control of other acetylenic polymers: Polymers from arylacetylenes like phenylacetylene have been obtained under various polymerization conditions and their geometric structure have been qualitatively estimated by several research groups.³⁻⁵ In contrast, the geometric isomerism of polymers from aliphatic acetylenes has hardly been elucidated.

The purpose of the present study is to control the geometric structure of polymer by choice of solvents and catalysts in the polymerization of an aliphatic acetylene. *t*-Butylacetylene was employed as a

monomer, since its bulky *t*-butyl group would contribute to the selective formation of a particular geometric structure. *t*-Butylacetylene can be polymerized by MoCl₅ and WCl₆ in hydrocarbons and halogenated hydrocarbons to afford a high-molecular-weight polymer in high yield, and the geometric structure of the main chain can be determined by ¹³C NMR spectroscopy.⁶ Quite recently, a ¹³C NMR spectrum of poly(*t*-butylacetylene) has also been reported by Katz *et al.*,⁷ but no discussion was made regarding its geometric structure on the basis of the spectrum. We thus studied extensively the geometric structure of poly(*t*-butylacetylene) prepared under a variety of reaction conditions. Consequently, perfectly *cis* poly(*t*-butylacetylene) was obtained in quantitative yield with MoCl₅ catalyst.

EXPERIMENTAL

t-Butylacetylene was prepared from pinacolone according to the literature method.^{8,9} MoCl₅, WCl₆,

* Polymerization of Aliphatic Acetylenes. Part V. For Part 4, see ref 1.

Mo(CO)₆, and W(CO)₆ were commercially obtained. Solvents for polymerization (reagent grade) were distilled twice before use from appropriate drying agents at atmospheric or reduced pressure under nitrogen.

Polymerization was carried out under a dry nitrogen atmosphere at 30°C for 24 h at a monomer concentration of 1.0 mol l⁻¹ and a catalyst concentration of 30 mmol l⁻¹ (MoCl₅, WCl₆) or 10 mmol l⁻¹ (Mo(CO)₆, W(CO)₆). When tetraphenyltin (Ph₄Sn) was employed as cocatalyst, catalyst solutions were aged at 30°C for 20 min before use. A solution of metal carbonyl in carbon tetrachloride was irradiated with UV light (200 W high pressure Hg lamp) at 30°C for 1 h (this catalyst expressed as M(CO)₆-CCl₄-hν (M=Mo, W)). To the irradiated catalyst solution was added a monomer solution in the dark, and polymerization was run at 30°C for 24 h. The polymer formed was precipitated into a large amount of methanol, filtered off, and dried under vacuum. Polymer yields were determined by gravimetry.

Intrinsic viscosities, [η], of polymers were measured in toluene at 30°C. Molecular weights (*M*) were calculated from viscosities using eq (1) obtained in our previous study⁶:

$$[\eta] = 10^{-5.12} \times M^{1.01} \quad (\text{dl g}^{-1}) \quad (1)$$

¹³C NMR spectra were recorded in CDCl₃ so-

lution (ca. 15 w/v %) at room temperature on a JNM FX90Q spectrometer operating at 22.50 MHz under complete proton noise-decoupling. Accumulation of 2000–4000 scans was made using approximately a 45° pulse repeated every 2.0 s. Overlapping methyl carbon signals were separated with a du Pont 310 curve resolver.

RESULTS AND DISCUSSION

Polymerization under Various Conditions—Yield and Molecular Weight of Polymer

Table I shows the results for the polymerization of *t*-butylacetylene by MoCl₅ and WCl₆ in oxygen-containing solvents such as ethers, esters, and ketones. These solvents are seemingly unfavorable, because they may coordinate to catalyst metals to reduce catalytic activity and also because they are nonsolvents of poly(*t*-butylacetylene). Contrary to such expectation, *t*-butylacetylene was polymerized in high yields in these solvents. In general, the polymer yield was higher with MoCl₅ than with WCl₆, and in aromatic solvents than in aliphatic solvents. The molecular weights of the polymers reached 5 × 10⁴–2 × 10⁵, which are comparable to those attained in hydrocarbons and halogenated hydrocarbons.⁶ Generally, MoCl₅ provided higher molecular weights than did WCl₆.

The polymerization by MoCl₅ took place even in

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

No.	Catalyst	Solvent	Polymer yield	[η] ^b	$\bar{M} \times 10^{-3}$	¹³ C NMR, δ
			%	dl g ⁻¹		32.4: 31.2
1	MoCl ₅	1,2-Dimethoxyethane	100	1.63	190	0: 100
2	MoCl ₅	Anisole	100	1.69	197	0: 100
3	MoCl ₅	Ethyl acetate	55	1.78	208	0: 100
4	MoCl ₅	Methyl benzoate	100	1.60	186	0: 100
5	MoCl ₅	Acetone	21	0.98	115	0: 100
6	MoCl ₅	Acetophenone	100	1.47	171	0: 100
7	WCl ₆	1,2-Dimethoxyethane	54	0.85	100	3: 97
8	WCl ₆	Anisole	82	0.48	57	21: 79
9	WCl ₆	Ethyl acetate	70	1.04	122	2: 98
10	WCl ₆	Methyl benzoate	42	0.92	108	3: 97
11	WCl ₆	Acetone	30	0.40	47	5: 95
12	WCl ₆	Acetophenone	53	0.41	48	9: 91

^a Polymerized at 30°C for 24 h; [M]₀ = 1.0 mol l⁻¹, [Cat] = 30 mmol l⁻¹.

^b Measured in toluene at 30°C.

Polymerization of *t*-Butylacetylene

Table II. Polymerization of *t*-butylacetylene by MoCl₅ in nitrogen-containing solvents^a

No.	Catalyst	Solvent	Polymer yield		[η] ^b dl g ⁻¹	$\bar{M} \times 10^{-3}$	¹³ C NMR, δ
			%				32.4: 31.2
1	MoCl ₅	Acetonitrile	7		—	—	0:100
2	MoCl ₅	Benzonitrile	90		1.60	186	0:100
3	MoCl ₅	Nitroethane	2		—	—	—
4	MoCl ₅	Nitrobenzene	36		0.84	98	3: 97
5	MoCl ₅ ·Ph ₄ Sn	Acetonitrile	48		—	—	0:100
6	MoCl ₅ ·Ph ₄ Sn	Benzonitrile	100		1.76	205	0:100
7	MoCl ₅ ·Ph ₄ Sn	Nitroethane	43		—	—	0:100
8	MoCl ₅ ·Ph ₄ Sn	Nitrobenzene	63		1.27	148	0:100

^a Polymerized at 30°C for 24 h; [M]₀ = 1.0 mol l⁻¹, [Cat] = 30 mmol l⁻¹.

^b Measured in toluene at 30°C.

Table III. Polymerization of *t*-butylacetylene by M(CO)₆-CCl₄-*hw* (M=Mo, W)^a

No.	Metal carbonyl	Temp	Polymer yield		[η] ^b dl g ⁻¹	$\bar{M} \times 10^{-3}$	¹³ C NMR, δ
		°C	%				32.4: 31.2
1	Mo(CO) ₆	30	100		2.60	292	14: 86
2	Mo(CO) ₆	0	95		2.26	263	12: 88
3	W(CO) ₆	30	92		1.54	180	20: 80

^a Polymerized in CCl₄ at 30°C for 24 h; [M]₀ = 1.0 mol l⁻¹, [M(CO)₆] = 10 mmol l⁻¹.

^b Measured in toluene at 30°C.

nitrogen-containing solvents such as nitriles and nitro compounds (Table II), although they should coordinate to the catalyst more strongly than oxygen-containing solvents. Polymer yields increased considerably in the presence of Ph₄Sn co-catalyst (equimolar to MoCl₅), as observed in the polymerization of phenylacetylene.¹⁰ In contrast, WCl₆ afforded hardly any polymers either in the presence or absence of Ph₄Sn in the nitrogen-containing solvents.

No polymerization occurred when such solvents were used as dimethyl sulfoxide, *N,N*-dimethylformamide, pyridine, and acetic acid, probably because these solvents coordinate strongly to catalysts to form inactive complexes or react with catalysts to decompose them.

The kind of ligands on a catalyst is expected to have a large influence, both sterically and electroni-

cally, on the behavior of the catalyst. Thus, polymerization of *t*-butylacetylene was carried out in carbon tetrachloride using the M(CO)₆-CCl₄-*hw* catalysts (M=Mo, W). These catalysts have been used for olefin metathesis¹¹ and the polymerization of certain acetylenic monomers.¹² As shown in Table III, the metal carbonyl catalysts polymerized *t*-butylacetylene almost quantitatively. The polymer molecular weights were higher than those obtained with the corresponding metal chlorides in the same solvent (*cf.* $M = 11 \times 10^4$ with MoCl₅, 9.2×10^4 with WCl₆).⁶

Poly(*t*-butylacetylene)s obtained in hydrocarbons and halogenated hydrocarbons dissolve readily in nonpolar solvents such as hexane and toluene.⁶ Transparent films can be prepared from these polymer solutions. On the other hand, some of the polymers obtained in oxygen- or nitrogen-

containing solvents were partly insoluble and gave translucent films. This might be due to partial crystallinity of the polymers, although no sharp crystalline X-ray diffraction patterns were observed.

Geometric Structure of Polymer

^{13}C NMR Analysis. Figure 1 shows the ^{13}C NMR

spectrum of poly(*t*-butylacetylene) obtained with WCl_6 in toluene. Two well-resolved methyl signals are seen at 31.2 (a_1) and 32.4 (a_2) ppm, as previously reported.⁶ The areas of signals a_1 and a_2 are comparable. On the other hand, the polymer formed with MoCl_5 in anisole shows only a_1 (Figure 2). It should also be noted that all the signals of the latter

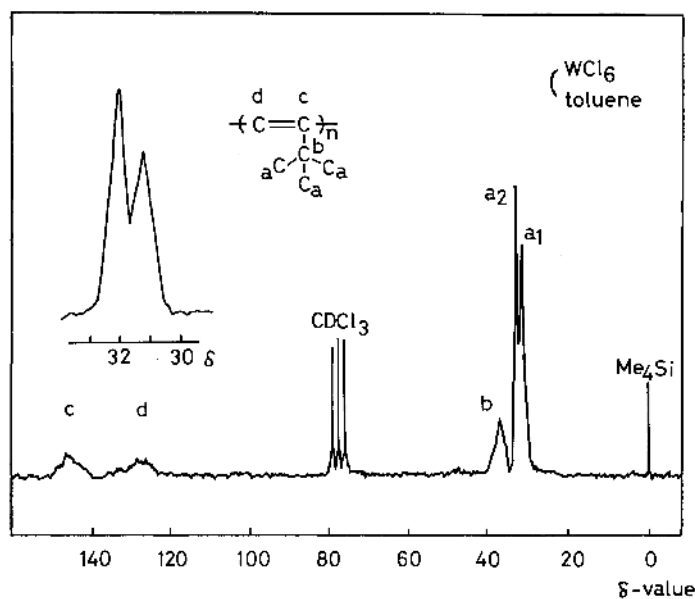


Figure 1. ^{13}C NMR spectrum of poly(*t*-butylacetylene). (sample from Table IV, No. 1, WCl_6)

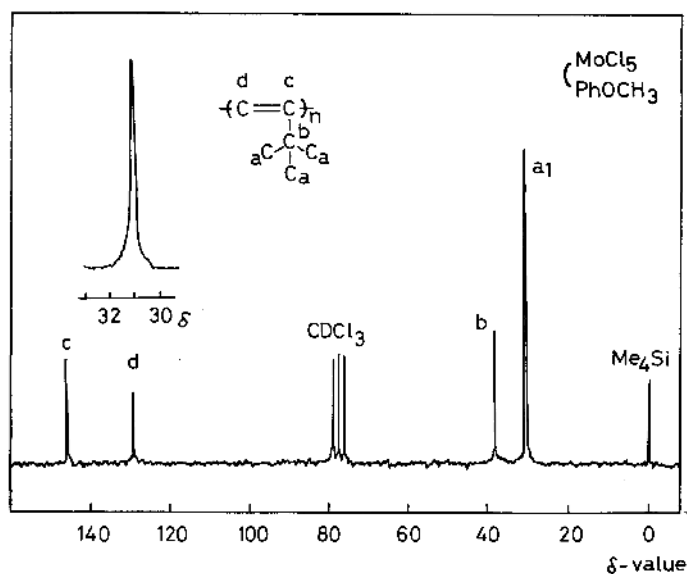


Figure 2. ^{13}C NMR spectrum of poly(*t*-butylacetylene). (sample from Table I, No. 2)

polymer are very sharp.

It seems reasonable to attribute a_1 to *cis* and a_2 to the *trans* structure of the polymer backbone for the following reasons: i) The relative intensity of peak a_1 to a_2 is greater with MoCl_5 than with WCl_6 for polymers prepared otherwise under the same conditions. Provided that, as for poly(arylacetylenes),^{5,13} MoCl_5 gives poly(*t*-butylacetylene) having higher *cis* content than does WCl_6 , then a_1 can be attributed to the *cis* structure. ii) Polymers whose a_1 and a_2 are similar in magnitude show a broad α carbon signal (b) centered at 37.1 ppm (see Figure 1), whereas polymers having only a_1 exhibit a sharp α carbon signal at 38.2 ppm (see Figure 2). In the case of retinal and its congeners, which have conjugated double bonds, the *cis* isomers show a signal due to α carbon at lower field than do the corresponding *trans* isomers.¹⁴ In this analogy, a_1 is attributed to *cis* structure. iii) The above assignment of a_1 and a_2 is supported by CNDO molecular orbital calculation.¹⁵

Effect of Solvents and Catalysts. Tables I—III include relative areas of a_2 and a_1 signals. These relative areas directly indicate the *trans*-to-*cis* ratios according to the above peak assignment. For comparison, ratios for the polymers prepared in hydrocarbons and halogenated hydrocarbons⁶ are given in Table IV.

Polymers formed in nonpolar solvents such as toluene consist of both *trans* and *cis* structures; in particular, the *trans* and *cis* contents are about the same when WCl_6 is used as the catalyst. Thus, the polymerization in nonpolar solvents lacks the selec-

tivity for geometric structure. On the other hand, the polymers produced with MoCl_5 in oxygen-containing solvents possess exclusively the *cis* structure (see Table I). Similarly, the use of oxygen-containing solvents increases the *cis* content appreciably in the WCl_6 -catalyzed polymerization. All-*cis* polymers are also formed with $\text{MoCl}_5 \cdot (\text{Ph}_4\text{Sn})$ in nitrogen-containing solvents (see Table II). The poly(*t*-butylacetylene) prepared with a tungsten carbene, $\text{Ph}(\text{CH}_3\text{O})\text{C}=\text{W}(\text{CO})_5$ by Katz *et al.* appears to comprise mostly *cis* structure according to the reported ^{13}C NMR spectrum.⁷

Effects of the amount of oxygen-containing solvent on the geometric structure were examined using mixtures of anisole and toluene (Figure 3). When anisole was less than 50 vol%, the *cis* content varied only slightly, and even an amount of anisole as high as 75 vol% was not enough to provide all-*cis* polymer.

The *cis* contents of polymers obtained with the $\text{M}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$ catalysts were somewhat higher than those with the corresponding metal chlorides in carbon tetrachloride (Table III, No. 1 and 3; Table IV, No. 3). Increases in *cis* content remained within 10% even though, in place of carbon tetrachloride, its 1:1 mixtures with oxygen-containing solvents were used for the $\text{M}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$ system.

In a previous paper,⁶ we reported that some bands in the IR spectrum of poly(*t*-butylacetylene) changed in accordance with the *cis* content evaluated by ^{13}C NMR. In subsequent studies, however, no such absorptions could be found. These bands might have been due to impurities present in the polymer samples.

Table IV. Ratios of methyl carbon signals in the ^{13}C NMR spectra of poly(*t*-butylacetylene)^a

No.	Solvent	^{13}C NMR, δ	
		32.4:31.2	
		MoCl_5	WCl_6
1	Toluene	24:76	50:50
2	Cyclohexane	15:85	50:50
3	CCl_4	26:74	45:55
4	$(\text{CH}_2\text{Cl})_2$	14:86	23:77

^a Polymerization conditions: $[\text{M}]_0 = 1.0 \text{ mol l}^{-1}$, $[\text{Cat}] = 20 \text{ mmol l}^{-1}$, 30°C , 24 h. See ref 6 for polymer yields and molecular weights.

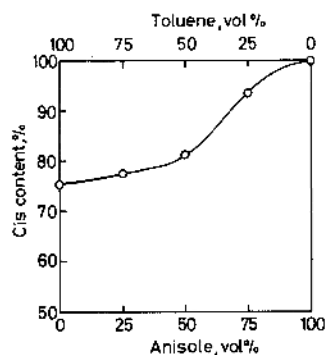
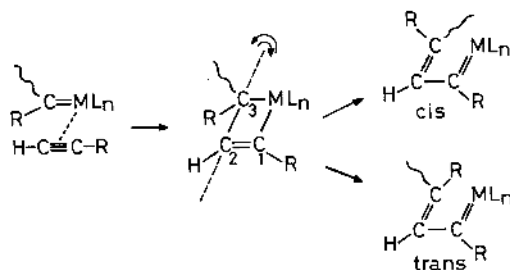


Figure 3. Dependence of the *cis* content of poly(*t*-butylacetylene) on solvent composition. (anisole and toluene; MoCl_5)

Cis-Trans Thermal Isomerization. To gain an understanding of the relative stability of *cis* and *trans* structures, the thermal isomerization of poly(*t*-butylacetylene) was examined. A polymer sample containing 50% *cis* was dissolved in decalin and heated at 160°C for 24h under nitrogen. Consequently, the *cis* content increased by about 10%, and the polymer molecular weight decreased slightly. This indicates that the *cis* structure is more stable than *trans*. This contrasts with the fact that polyacetylene¹⁶ and poly(phenylacetylene)³ thermally isomerize from *cis* to *trans*, the latter being more stable. The bulky *t*-butyl group seems responsible for the unusual relative stability (*cis* > *trans*) and, in turn, isomerization (*trans* to *cis*) of poly(*t*-butylacetylene). At temperatures above 180°C considerable polymer decomposition occurred besides isomerization. No observable isomerization took place below 100°C over long periods of time.

Mechanism of Geometric Structure Control. The extremely high *cis* contents of poly(*t*-butylacetylene)s obtained in oxygen- or nitrogen-containing solvents (Tables I and II) can be interpreted by using a model proposed by Katz *et al.*



Scheme I.

(Scheme I): The present polymerization is thought to proceed *via* metal carbene and a metallacyclobutene intermediate^{5,17} that forms from a polymeric metal carbene ($\sim\text{CR}=\text{ML}_n$). In the second step of Scheme I, the metallacyclobutene undergoes ring scission (cleavage of the C_3 -metal linkage), during which the C_3 - C_2 bond rotates around its axis to form a coplanar double bond. Katz *et al.*⁷ proposed that the geometric structure of polymer is determined by the direction of this rotation; the C_3 - C_2 bond should rotate in such a way as to minimize the steric interaction between the coordinated metal (ML_n) and substituent R or the polymer backbone.

When oxygen- or nitrogen-containing solvents are used, they coordinate to the catalyst metal (the coordination might be loose and reversible, since the catalyst is active enough). The coordinated active center should be bulky and susceptible to steric effect as compared with an uncoordinated one. The result of thermal isomerization (see above) suggests that the *t*-butyl group exerts a greater steric effect than does the polymer chain. For such a bulky substituent, the rotation by which the substituent recedes from the coordinated active center will be favorable to minimize steric hindrance. Eventually, a *cis* polymer tends to form in coordinating solvents.

MoCl_5 can give perfectly *cis* poly(*t*-butylacetylene), while WCl_6 cannot. A possible reason for this is that the atomic radius of molybdenum is shorter than that of tungsten, and therefore the interaction of the Mo-bearing active center with *t*-butyl groups is greater.

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