Polymerization of 1-butyne and isopropyl-acetylene by transition metal catalysts and geometric structure of polymers*

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Polymerization of 1-butyne and isopropylacetylene was studied using $MoCl_5$, WCl_6, and two Ziegler catalysts [$Fe(acac)_3$-Et_3Al, $Ti(On$-$Bu)_4$-Et_3Al]. 1-Butyne was polymerized in high yields with WCl_6 and $Fe(acac)_3$-Et_3Al to give a yellow, air-sensitive polymer. The *cis* content of poly(1-butyne), evaluated by ^{13}C n.m.r., was about 80% irrespective of polymerization conditions. Isopropylacetylene was polymerized well by any of $MoCl_5$, WCl_6, and $Fe(acac)_3$-Et_3Al; the polymer formed was a light yellow air-sensitive powder. The *cis* content of poly(isopropylacetylene) varied from 65% to 90% according to polymerization conditions. Substituent effects on polymerization and polymer structure are discussed.
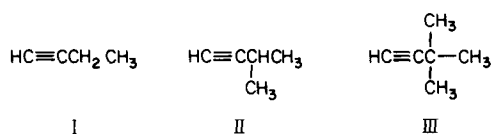
INTRODUCTION

The unsubstituted acetylene provides an insoluble polymer in the presence of Ti-based Ziegler catalysts such as a mixture of titanium(IV) *n*-butoxide and triethylaluminum [$Ti(On$-$Bu)_4$-Et_3Al][2]. On the other hand, 1-hexyne, a linear terminal alkyne, is best polymerized by Fe-based Ziegler catalysts (e.g., a mixture of Fe(III) naphthenate and triisobutylaluminum) to a high molecular weight polymer ($[\eta] = 2$–6 dL g^{-1})[3]. We have found that *tert*-butylacetylene, which is a fairly sterically hindered mono-substituted acetylene is polymerized to a high molecular weight polymer in high yields by $MoCl_5$ and WCl_6, but not by the above-mentioned Ziegler catalysts[4]. Thus the kind of suitable catalysts varies depending on the structure of the acetylenic monomer. We have also compared the polymerizability and polymer properties of all seven isomers of 1-hexyne to find large influences of both position of triple bond and the branching of substituents[5]. There have, however, been few other systematic studies on the relationship between monomer structure and catalyst activity.

Only a few reports have appeared on the quantitative evaluation of the geometric structure of acetylenic polymers: e.g., polyacetylene (i.r.[6] etc.), poly(phenylacetylene) (^1H n.m.r.[7] etc.) and poly(*tert*-butylacetylene) (^{13}C n.m.r.[8]). In general, polymer structure has great influence on polymer properties. It is, therefore, interesting and important to elucidate the effect of monomer structure and polymerization conditions on the geometric structure of acetylenic polymers.

This paper deals with the polymerization of 1-butyne(I) and isopropylacetylene (3-methyl-1-butyne; II), which are terminal alkynes bearing primary and secondary alkyl

groups, respectively. The geometric structure of polymers formed has also been studied by means of ^{13}C n.m.r. These results were compared with those for *tert*-butylacetylene (3,3-dimethyl-1-butyne; III)[4,8].

HC≡CCH₂CH₃   HC≡CCHCH₃   HC≡CC—CH₃
(structures I, II, III shown with CH₃ substituents)

  I   II   III

EXPERIMENTAL

1-Butyne (Tokyo Chemical Industry Co., Ltd.) was dried before use by passing through columns packed with sodium hydroxide and calcium chloride. Isopropylacetylene (Farchan Labs) was distilled from calcium hydride at the atmospheric pressure. Catalysts {$MoCl_5$, WCl_6, Iron(III) acetylacetonate [$Fe(acac)_3$], $Ti(On$-$Bu)_4$} and cocatalysts (Ph_4Sn, Et_3At) were commercially obtained and used without further purification. Solvents for polymerization were distilled from appropriate drying agents.

Two-component catalysts [$MoCl_5$-Ph_4Sn (1:1), WCl_6-Ph_4Sn (1:1), $Fe(acac)_3$-Et_3Al (1:3), $Ti(On$-$Bu)_4$-Et_3Al (1:4)] were aged in solution at 30°C for 20 min before use. The polymerization procedure is the same as described previously[4]. Polymer yields were determined by gravimetry.

Number-average molecular weights ($\bar{M}_n$) of polymers were measured by vapour pressure osmometry (v.p.o.) with a Hitachi 117 molecular weight apparatus. Intrinsic viscosities, $[\eta]$, of polymers were measured in toluene solution at 30°C. Some number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were also estimated by gel permeation chromatography (g.p.c.) on a Jasco Trirotar chromatograph (column: Shodex 802, 804, 806 poly-

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* Part 7 of 'Polymerization of Aliphatic Acetylenes'. For part 6, see Ref. 1

styrene gel; eluent chloroform; calibrated with monodisperse polystyrenes). Softening points of polymers were determined on a Yanaco MP-300 micro-melting point apparatus. ^{13}C n.m.r. spectra were recorded in CDCl$_3$ solution (~15% w/v) at room temperature on a JEOL FX90Q spectrometer operating at 22.50 MHz. I.r. spectra were observed on a Shimazu IR27G spectrophotometer.

RESULTS

Polymerization of 1-butyne

Table 1 shows results for the polymerization of 1-butyne by various catalysts. MoCl$_5$, a very effective catalyst for the polymerization of *tert*-butylacetylene[4,8], was not very active toward 1-butyne. WCl$_6$ afforded a methanol-insoluble poly(1-butyne) in high yield. Though a cocatalyst like Ph$_4$Sn is essential in the polymerization of disubstituted acetylenes[9], it is unnecessary for 1-butyne polymerization. Among Ziegler catalysts, a Fe(acac)$_3$–Et$_3$Al catalyst (molar ratio 1:3) provided poly(1-butyne) quantitatively. The number-average molecular weights of the polymers obtained with MoCl$_5$ and WCl$_6$ were only about 2000. Though the number-average molecular weights of the polymers obtained with Ziegler catalysts were not determined because of their partial insolubility, the viscosities of the soluble fractions indicated that they should be fairly higher than 2000. These polymer samples showed different broad softening points between 60° and 110°C, probably owing to variations in both molecular weight and geometric structure.

Table 2 lists polymer yields for the polymerization of 1-butyne in various solvents. Practically no polymer was formed with MoCl$_5$ in cyclohexane and carbon tetrachloride owing to the low solubility of MoCl$_5$ in these solvents at 0°C. WCl$_6$ produced favourable amounts of polymer in every solvent with low polarity. The Fe(acac)$_3$–Et$_3$Al catalyst is active enough not only in

hydrocarbons but in oxygen-containing solvents, though deactivated in halogenated hydrocarbons.

Temperature effect on the polymerization of 1-butyne was examined in a range of 0°C to −78°C (*Table 3*). No polymer was formed below −40°C with MoCl$_5$ and WCl$_6$. In contrast, Fe(acac)$_3$–Et$_3$Al produced poly(1-butyne) in fair yield at −78°C. The above results lead to the following two conclusions: (i) WCl$_6$ and Fe(acac)$_3$–Et$_3$Al are active catalysts for 1-butyne polymerization, while either MoCl$_5$ or Ti(O*n*–Bu)$_4$–Et$_3$Al is not so effective and, (ii) the molecular weights of the polymers obtained with MoCl$_5$ and WCl$_6$ are no more than 1000–2000.

Properties and structure of poly(1-butyne)

Poly(1-butyne) had a form of yellow powder. It dissolved readily in nonpolar solvents such as *n*-hexane, carbon tetrachloride and toluene, whereas solvents such as dimethyl sulphoxide and acetonitrile were nonsolvents. This polymer was unstable in air at room temperature, that is, gradually oxidized (the C=O band appeared in the i.r. spectrum).

Figure 1 shows the i.r. and ^{13}C n.m.r. spectra of poly(1-butyne) (sample: the WCl$_6$ polymer in *Table 1*). In the i.r. spectrum, a broad band due to the stretching of conjugated C=C is observed around 1600 cm^{-1}. Signals of two olefinic and two alkyl carbons appear in the ^{13}C n.m.r. spectrum. It seems reasonable to conclude from these spectra that this polymer has a conjugated polyene structure, (CH=CEt)$_n$.

As seen in *Figure 1*, both signals due to methyl and methylene carbons are composed of a few overlapping peaks. This splitting should be attributed to the geometric isomerism of double bonds along the main chain. *Figure 2* shows the alkyl region of ^{13}C n.m.r. spectra of poly(1-butyne)s obtained with four catalysts. The methyl-carbon signal in every spectrum can be approximately regarded as consisting of two peaks. We attribute the larger peak appearing at lower field (δ 10.5–15.0 ppm) to *cis* structure and the smaller peak (δ 6.5–10.5 ppm) to *trans* in analogy with polyacetylene[6] and poly(phenylacetylene)[10] for which Ziegler catalysts usually afford *cis*-rich structures at 0°C or below. *Cis* contents, determined from the peak

Table 1 Polymerization of 1-butyne by various catalysts[a]

Catalyst	Polymer yield (%)	$\overline{M}_n$	Softening point (°C)
MoCl$_5$	23	1500[b]	86–112
MoCl$_5$–Ph$_4$Sn (1:1)	4	–	–
WCl$_6$	92	1600	80–98
WCl$_6$–Ph$_4$Sn (1:1)	81	2200[c]	77–94
Fe(acac)$_3$–Et$_3$Al (1:3)	100	–[d]	64–88
Ti(O*n*–Bu)$_4$–Et$_3$Al (1:4)	36	–[d]	62–84

[a]Polymerized in toluene at 0°C for 24 h : [M]$_0$ = 1.2 M, [Cat] = 20 mM
[b]$\overline{M}_n$ = 1900, $\overline{M}_w$ = 4000 by g.p.c.
[c]$\overline{M}_n$ = 2800, $\overline{M}_w$ = 5800 by g.p.c.
[d]Partly insoluble

Table 3 Temperature effect on the polymerization of 1-butyne[a]

Catalyst	Polymer yield (%)		
	0°C	−40°C	−78°C
MoCl$_5$	23	0	0
WCl$_6$	92	0	0
Fe(acac)$_3$–Et$_3$Al (1:3)	100	98	65
Ti(O*n*–Bu)$_4$–Et$_3$Al (1:4)	36	27	8

[a]Polymerized in toluene for 24 h: [M]$_0$ = 1.0 M, [Cat] = 20 mM

Table 2 Polymerization of 1-butyne in various solvents[a]

Catalyst	Polymer yield (%)				
	(CH$_2$)$_6$	CCl$_4$	(CH$_2$Cl)$_2$	PhOCH$_3$	PhCOOCH$_3$
MoCl$_5$	~0	~0	6	22	19
WCl$_6$	64	88	10	73	0
Fe(acac)$_3$–Et$_3$Al (1:3)	75	0	0	92	91
Ti(O*n*–Bu)$_4$–Et$_3$Al (1:4)	37	~0	~0	25	0

[a]Polymerized at 0°C for 24 h: [M]$_0$ = 1.2 M, [Cat] = 20 mM
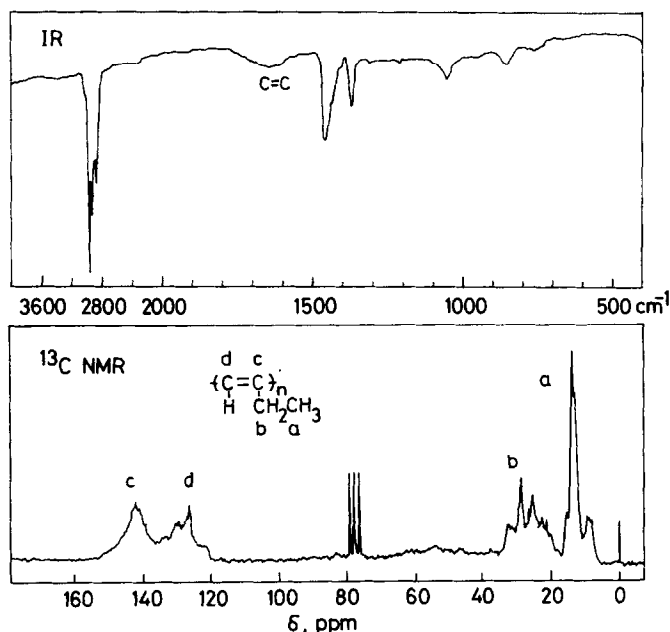
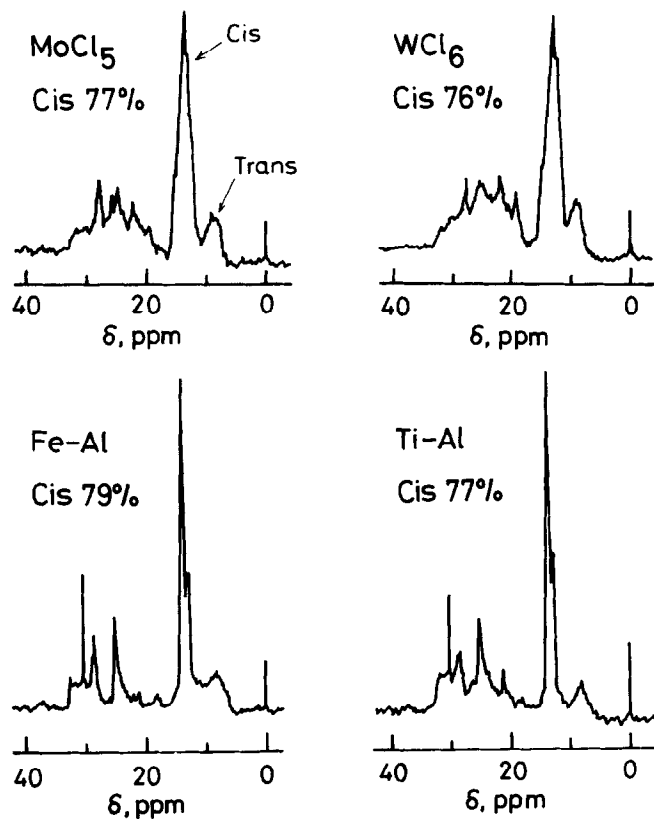**Figure 1** I.r. and ^{13}C n.m.r. spectra of poly(1-butyne) (WCl$_6$, toluene, 0°C, 24 h)

Figure 2 Methyl- and methylene-carbon signals in ^{13}C n.m.r. of poly(1-butyne) (toluene, 0°C, 24 h)

ratios of methyl carbon are shown in *Figure 2*. The *cis* content of polymers is about 80% irrespective of the kind of catalysts, indicating that the geometric structure of poly(1-butyne) is hardly affected by catalyst. Solvent effect on the geometric structure of polymer was also negligible. It is, however, noted in *Figure 2* that the polymers obtained with MoCl$_5$ and WCl$_6$ show different peak patterns (groups of less sharp peaks) from those of the polymers formed with Ziegler catalysts. It is reported that

poly(*N*-ethynylcarbazole) having stereoblock structure is obtained by Ziegler catalysts[11]. The difference in peak pattern of poly(1-butyne), therefore, might be due to a difference in sequence distribution of *cis* and *trans* structures.

Polymerization of isopropylacetylene

Isopropylacetylene is an acetylene having a substituent of intermediate bulkiness as compared with 1-butyne and *tert*-butylacetylene, and it is interesting to compare their polymerization behaviour with one another. As shown in *Table 4*, this monomer was polymerized in good yields by any of MoCl$_5$, WCl$_6$ and Fe(acac)$_3$-Et$_3$Al. This contrasts with the result of 1-butyne for which MoCl$_5$ is not so effective. Owing to the instability of poly(isopropylacetylene), its $\bar{M}_n$ could not be measured by v.p.o. The intrinsic viscosities, $[\eta]$, of the polymers formed with MoCl$_5$ and WCl$_6$ were only 0.1 to 0.2 dL g^{-1}, and their $\bar{M}_n$ estimated by g.p.c. were no more than several thousand. It is worth noting that Fe(acac)$_3$-Et$_3$Al affords a polymer with $\bar{M}_n$ up to $\sim 5 \times 10^5$. Softening points of poly(isopropylacetylene)s are 80°C–140°C, somewhat higher than those of poly(1-butyne).

Table 5 gives yields of poly(isopropylacetylene) in various solvents. Both MoCl$_5$ and WCl$_6$ gave a methanol-insoluble polymer in good yields in all the solvents examined. Fe(acac)$_3$-Et$_3$Al also achieved high polymer yields in solvents other than halogenated hydrocarbons. All of the MoCl$_5$, WCl$_6$ and Fe(acac)$_3$-Et$_3$Al catalysts are active enough at 25°C and 0°C (*Table 6*). MoCl$_5$ and WCl$_6$ are, however, inactive at −40°C.

Thus it has been revealed that MoCl$_5$, WCl$_6$ and Fe(acac)$_3$-Et$_3$Al are all active for the polymerization of isopropylacetylene. The molecular weights of the polymers formed with Mo and W catalysts were only several thousand.

Properties and structure of poly(isopropylacetylene)

Poly(isopropylacetylene) was a light yellow powder having solubility similar to that of poly(1-butyne). This polymer readily oxidized in air at room temperature (the C=O band appeared in the i.r. spectrum). In addition, high molecular weight polymer formed with Fe(acac)$_3$–Et$_3$Al rapidly degraded in air (the intrinsic viscosity decreased from 2.78 to 0.10 dL g^{-1} when left in air at room temperature for one day).

Figure 3 shows the i.r. and ^{13}C n.m.r. spectra of poly(isopropylacetylene) (sample: the WCl$_6$ polymer in

Table 4 Polymerization of isopropylacetylene by various catalysts[a]

Catalyst	Polymer yield (%)	$[\eta]$ [b] (dL g^{-1})	Softening point (°C)
MoCl$_5$	77	0.14	105–110
MoCl$_5$–Ph$_4$Sn (1:1)	51	0.21[c]	92–98
WCl$_6$	66	0.13	131–136
WCl$_6$–Ph$_4$Sn (1:1)	88	0.13[d]	126–132
Fe(acac)$_3$–Et$_3$Al (1:3)	86	2.78[e]	84–105
Ti(O*n*–Bu)$_4$–Et$_3$Al (1:4)	23	–[f]	95–100

[a] Polymerized in toluene at 25°C for 24 h: [M]$_0$ = 1.0 M, [Cat] = 20 mM
[b] Measured in toluene at 30°C
[c] $\bar{M}_n$ = 6600, $\bar{M}_w$ = 21600 by g.p.c.
[d] $\bar{M}_n$ = 4000, $\bar{M}_w$ = 9700 by g.p.c.
[e] $\bar{M}_n$ = 4.7 $\times$ 10^5, $\bar{M}_w$ = 1.0 $\times$ 10^6 by g.p.c.
[f] Partly insoluble

Table 5 Polymerization of isopropylacetylene in various solvents[a]

Catalyst	Polymer yield (%)				
	$\{CH_2\}_6$	CCl_4	$(CH_2Cl)_2$	$PhOCH_3$	$PhCOOCH_3$
$MoCl_5$	40	81	33	89	57
WCl_6	86	80	31	58	23
Fe(acac)$_3$—Et$_3$Al (1:3)	78	0	0	78	81
Ti(On—Bu)$_4$—Et$_3$Al (1:4)	10	0	0	38	0

[a]Polymerized at 25°C for 24 h: [M]$_0$ = 1.0 M, [Cat] = 20 mM

Table 6 Temperature effect on the polymerization of isopropyl-acetylene[a]

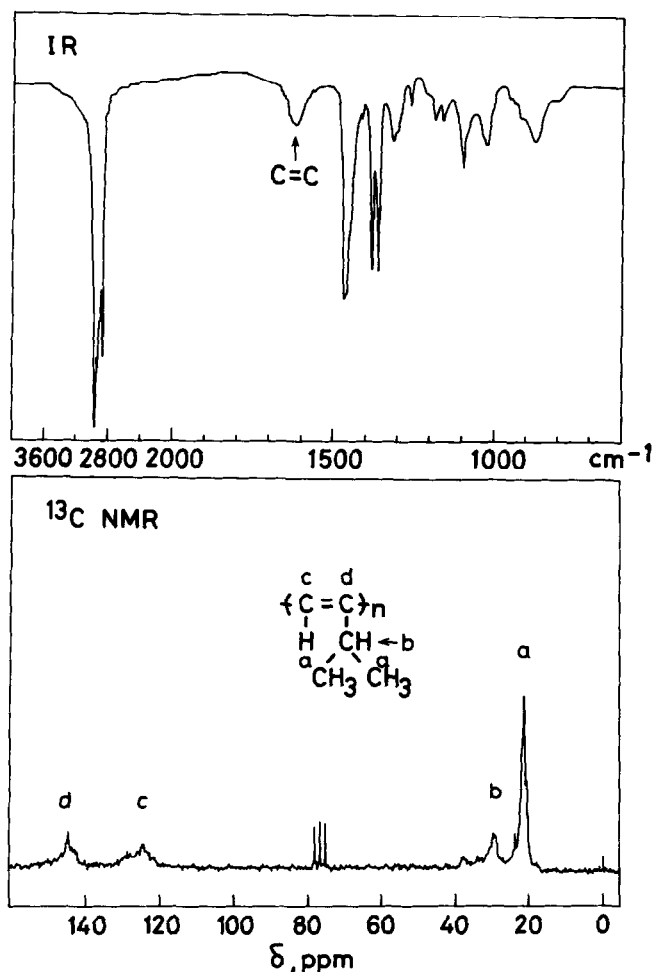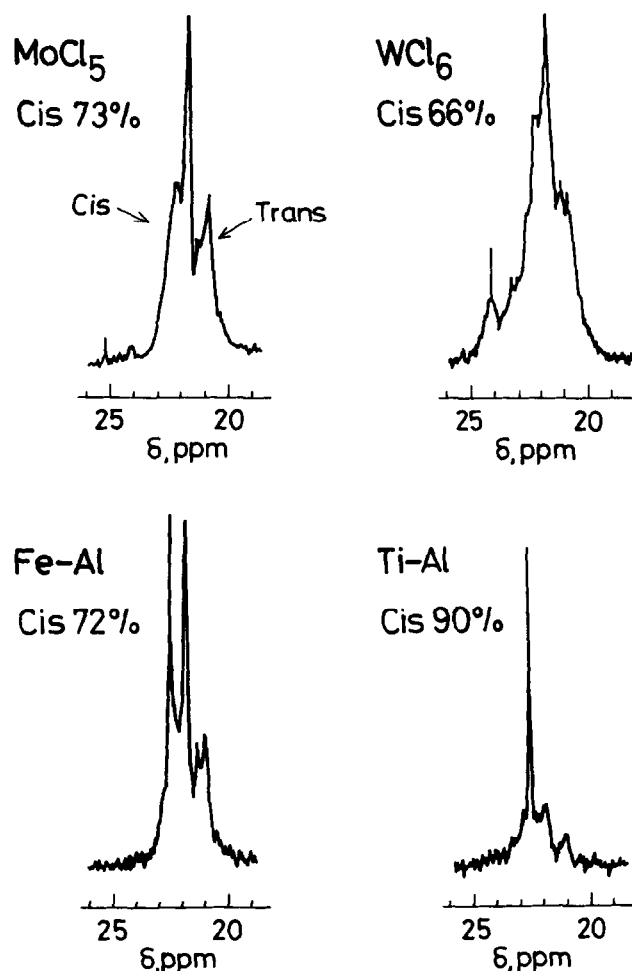| Catalyst	Polymer yield (%)			
	25°C	0°C	−40°C	−78°C
$MoCl_5$	77	68	0	0
WCl_6	66	47	0	0
Fe(acac)—Et$_3$Al (1:3)	86	88	85	0
Ti(On-Bu)—Et$_3$Al (1:4)	23	15	12	0

[a]Polymerized in toluene for 24 h: [M]$_0$ = 1.0 M, [Cat] = 20 mM

Figure 3 I.r. and ^{13}C n.m.r. spectra of poly(isopropylacetylene) (WCl$_6$, toluene, 25°C, 24 h)

Figure 4 Methyl-carbon signals in ^{13}C n.m.r. of poly(isopropylacetylene) (toluene, 25°C, 24 h)

Table 4). In the i.r. spectrum, a broad band due to the stretching of conjugated C=C is observed at 1550–1650 cm^{-1}. Each signal in the ^{13}C n.m.r. is assigned as shown in the Figure. These spectral data indicate that the polymer has the expected polyene structure,-$\{CH=Ci-Pr\}_n$.

When the methyl-carbon region in the ^{13}C n.m.r. spectrum of *Figure 3* was expanded, four partially resolved peaks were observed. As *Figure 4* shows, the pattern of the methyl-carbon signal considerably changes depending on the kind of catalysts. Like poly(1-butyne), this splitting should be attributed to the geometric structure of the double bonds along the main chain. It is presumed that the signal is primarily split into two peaks by the geometric structure of the nearest double bond, and that each peak is further split probably because of the sequence distribution of double bonds. Assuming that two peaks at higher field (δ 19.5–21.4 ppm) are due to *trans* and those at lower field (δ 21.4–24.0 ppm) to *cis* structure, *cis* contents were evaluated. The values are shown in the Figure. Unlike poly(1-butyne) the *cis* content of poly(isopropylacetylene) appreciably changes with varying catalysts. The *cis* content increased slightly when

Table 7 Comparison of the polymerizations and polymers of 1-butyne, isopropylacetylene, and *tert*-butylacetylene

Monomer	$HC{\equiv}CCH_2CH_3$	$HC{\equiv}CCHCH_3$ $\vert$ CH_3	CH_3 $\vert$ $HC{\equiv}CC{-}CH_3$ $\vert$ CH_3
Catalyst activity	$MoCl_5 < WCl_6 < Fe{-}Al$	$MoCl_5 \fallingdotseq WCl \fallingdotseq Fe{-}Al$	$MoCl_5 > WCl_6$; $Fe{-}Al = 0$
MW (Mo, W)	10^3	$10^3{-}10^4$	10^5
Cis content			
percentage	75–85	65–90	50–100
catalyst effect	$W \fallingdotseq Mo \fallingdotseq Fe{-}Al$, $Ti{-}Al$	$W \leqslant Mo \leqslant Fe{-}Al$, $Ti{-}Al$	$W < Mo$
Colour	yellow	light yellow	white
Softening point (°C)	60–110	80–140	245–265
Stability in air	unstable	unstable	stable

oxygen-containing polymerization solvents were used in place of toluene.

CONCLUSIONS

Table 7 summarizes results for the polymerizations and polymers of the two monomers above and *tert*-butylacetylene[4,8]. These results enable the following discussions:

(i) The kind of suitable catalysts greatly depends on the bulkiness of substituents in the monomer: The Ti(O*n*–Bu)$_4$–Et$_3$Al catalyst, which is well known for the polymerization of acetylene, is not very effective for any substituted acetylenes. Fe(acac)$_3$–Et$_3$Al exhibits a high activity toward acetylenes with unbulky substituents such as 1-butyne and 1-hexyne[5]. However, *tert*-butylacetylene, which is a sterically fairly hindered monomer, is best polymerized by MoCl$_5$, and not at all by Fe(acac)$_3$–Et$_3$Al. Isopropylacetylene behaves in an intermediate manner, that is, it polymerizes well with every catalyst like 3-methyl-1-pentyne[5]. It is concluded that MoCl$_5$ and WCl$_6$ are especially effective for the polymerization of sterically hindered monomers.

(ii) The molecular weights of the polymers obtained with MoCl$_5$ and WCl$_6$ increase with increasing bulkiness of substituent. This can be explained as follows: A large steric hindrance will make the main chain twisted and less conjugated. This results in the destabilization and, therefore, activation of the propagating species to provide a high polymer. The twisting of main chain also prohibits the formation of biradicals to protect the formed polymer from degradation.

(iii) It has been assumed[8,12] that the geometric structure of these polyacetylenes is determined by the direction of the substituent rotation at the opening of metallacyclobutenes. The varience of *cis* content with polymerization conditions becomes greater as the substituent of the

monomer is bulkier, the transition state at which the geometric structure is determined becomes more sensitive to reaction conditions.

(iv) The colour of polymer becomes lighter with increasing bulkiness of the pendant group. This is just explained in terms of the extent of conjugation along the main chain.

(v) A bulkier substituent makes the polymer chain stiffer, which results in a higher softening point.

(iv) Poly(1-butyne) and poly(isopropylacetylene) are readily oxidized and degraded in air at room temperature, whereas poly(*tert*-butylacetylene) is stable enough in ambient conditions for a long period of time. This high stability of poly(*tert*-butylacetylene) is interpreted as follows: (a) a highly twisted structure of the main chain inhibits the formation of biradicals; (b) no active hydrogen exists on the carbon bonded to the main chain.

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