Macromolecules 1993, *26*, 6267–6272

Polymerization of Monosubstituted Acetylenes Catalyzed by 2,6-Dimethylphenoxo Complexes of Group 5 and 6 Metals

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Received May 20, 1993; Revised Manuscript Received August 16, 1993[●]

ABSTRACT: Catalyst systems with bulky aryloxo ligands, e.g. $WCl_n(dmp)_{6-n}/EtMgBr$ (dmp = 2,6-dimethylphenoxo, $n = 1–4$), were examined for polymerization of 1-alkynes in toluene at −20 to 60 °C for 24 h. The system, $WCl_4(dmp)_2/Et_3Al$, was found to polymerize $t\text{-BuC}{\equiv}CH$ to a very high molecular weight polymer ($M_n > 2 \times 10^6$) with narrow PDI ($M_w/M_n \cong 1.2$). By increasing the number of aryloxo ligands on W(VI) species, less bulky 1-alkynes are polymerized to high molecular weight polymers. Thus, 1-butyne gave an orange polymer with $M_n = 9.4 \times 10^4$, $M_w/M_n = 3.5$.

Introduction

The polymerization of alkynes has attracted much interest in view of new organic materials, e.g., as conducting or gas permeable polymers.[1,2] In the case of the simplest alkyne, acetylene, Ziegler type catalysts such as $Ti(O\text{-}n\text{-}Bu)_4/Et_3Al$ are most useful as polymerization catalyst.[3] On the other hand, group 5 and 6 transition-metal halides have been reported as polymerization catalysts for bulky substituted acetylenes by Masuda *et al.*[4] However, high polymers of less bulky substituted acetylenes such as *n*-alkylacetylenes have not been obtained by the reported catalysts. Recently, the living polymerization of 1-chloro-1-alkynes has been achieved by the catalyst system based on a mixture of $MoOCl_4$, tetrabutyltin, and ethanol.[5] The ethanol might be a source of alkoxide ligand which is important for the activity and selectivity of catalyst.

Alkoxide and aryl oxide groups have been used as ligands stabilizing the carbene species, which has been regarded as the key intermediate of the polymerization of 1-alkyne.[6] Although various carbene complexes with aryloxo ligands have been prepared and were applied to the living ring-opening polymerization of cyclic olefins,[7–9] only a little examples of such complexes have been found useful for the polymerization of acetylenes.[10]

We have systematically prepared a series of 2,6-dimethylphenoxo complexes of group 5 and 6 transition metals (**1**, **2**, **3**, and **4**, dmp = 2,6-dimethylphenoxo) which have been revealed to have monomeric structures by crystallographic studies.[11,12] In the course of our research on the reactivity of these complexes, we found that they became effective catalyst precursors for polymerization of 1-alkynes upon treating them with a reducing agent such as Grignard reagents or alkyl aluminum.[13] The catalyst system based on well-characterized 2,6-dimethylphenoxo complexes (**1**–**4**) affords some important insights into the mechanism of alkyne polymerization, and thus we can tune the catalyst to be highly active and selective. The catalyst activity and selectivity for the polymerization of 1-alkynes were found to be delicately affected by the number of bulky aryloxo ligands and the geometry at the metal center. Thus, an extra high molecular weight polymer with narrow molecular weight distribution was obtained as the result of our investigation. Moreover, we report here that the tungsten complexes bearing three or four 2,6-dimethylphenoxo ligands catalyzed the polymerization of less bulky substituted acetylenes such as 1-butyne, 1-hexyne, and 1-octyne to give high molecular weight polymers for the first time.

Results and Discussion

Preparation of 2,6-Dimethylphenoxo Complexes of Tungsten, Molybdenum, Tantalum, and Niobium. A series of bulky aryloxo complexes of group 5 and 6 metals have already been reported.[14] Some of them have been prepared by the reaction of metal halides with phenol derivatives or alkali metal phenolate in suitable solvents or without solvent.[14a–c] However it is difficult to control the number of aryloxo ligands to be introduced on metal by such methods. It is especially difficult to prepare mono(aryloxo) complexes.

We have synthesized mono- and bis(2,6-dimethylphenoxo) complexes of group 5 and 6 metals by reaction of the corresponding metal halides with 2,6-dimethylphenyl trimethylsilyl ether.[11,12] This method was used to prepare complexes **1a**, **1b**, **2**, **3a**, **3b**, **4a**, and **4b**. Some of them have already been characterized by our crystallographic studies, which provide information on the catalytic mechanism (*vide infra*).

Complex **1c** was prepared according to the literature method.[14a] **1d** has already been reported by Schrock and co-workers.[14b] According to their paper, **1d** was prepared by the reaction of WCl_6 in melt 2,6-dimethylphenol at 80 °C. We modified the reaction condition for the ease of separation of **1d** from excess 2,6-dimethylphenol. Thus **1d** was obtained by refluxing a mixture of WCl_6 and 2,6-dimethylphenol in toluene. Only one of the pure above-mentioned complexes was used as catalyst precursors in the present investigation to limit the possible structure of active species.

$W(dmp)_nCl_{6-n}$ **1**
a: $n = 1$
b: $n = 2$
c: $n = 3$
d: $n = 4$

$Mo(dmp)_2Cl_3(thf)$ **2**

$Ta(dmp)_nCl_{5-n}(thf)$ **3**
a: $n = 1$
b: $n = 2$

$Nb(dmp)_nCl_{5-n}(thf)$ **4**
a: $n = 1$
b: $n = 2$

Polymerization of 3,3-Dimethyl-1-butyne. Bulky monosubstituted acetylene, e.g. 3,3-dimethyl-1-butyne, has been generally known to give higher polymers by catalysis of $MoCl_5$- and WCl_6-based catalysts.[4a,15] Since 3,3-

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[●] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

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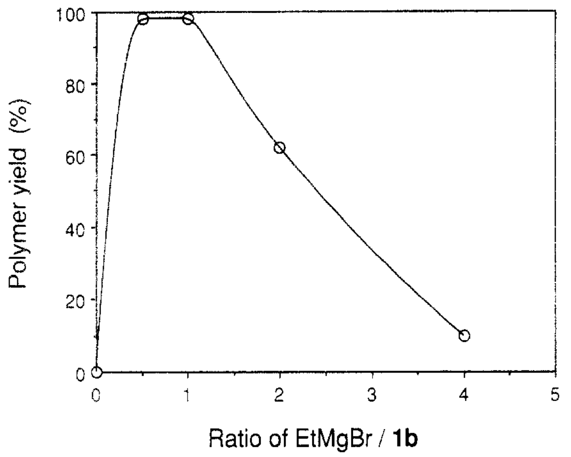


Figure 1. The yield of poly(3,3-dimethyl-1-butyne) depending on the molar ratio of complex **1b** and cocatalyst ethyl Grignard reagent. Polymerization was carried out in toluene at 30 °C for 24 h. $[monomer]_0$ = 1 M; [**1b**] = 10 mM.

dimethyl-1-butyne is reported to form stable high molecular weight polymers, we chose 3,3-dimethyl-1-butyne as a monomer to investigate the catalytic feature of complexes **1**–**4** for the polymerization. In general, the stepwise replacement of chloride by aryl oxide in $WCl_n(OAr)_{6-n}$ or $WOCl_n(OAr)_{4-n}$ complexes makes the species harder to be reduced.[16] Therefore, we selected a stronger reducing agent such as a Grignard agent or trialkylaluminum as a cocatalyst rather than alkyltin compounds which were usually used as a cocatalyst for WCl_6, $MoCl_5$, and $MoOCl_4$.[4]

The polymerization of 3,3-dimethyl-1-butyne was carried out in the presence of **1b** with various molar equivalents of EtMgBr. The results are shown in Figure 1, which shows clearly that the more reduced tungsten species are less active as the catalyst for polymerization. Thus, tungsten species in the high oxidation state may be a catalytic species because 0.5:1 and 1:1 ratios for the mixture of reducing reagent/**1b** gave the maximum yield of the polymerization. Such a tendency is consistent with the reported fact that a tungsten complex, $W(CHCMe_3)(NC_6H_3\text{-}2,6\text{-}{}^iPr_2)(O^tBu)_2$, is the catalyst for polymerization of C_2H_2.[10a] This carbene complex is in a formal oxidation state 6+, which is in accord with the formal oxidation states (5+ or 6+) estimated for the present catalyst species. Thus, the 1:1 ratio for catalyst/cocatalyst was used consistently for the following polymerization.

The nature of cocatalyst sometimes caused difference in the catalyst activity. In the series of tungsten complexes when complex **1a** or **1b** was used above 30 °C as a catalyst for the polymerization, both of the cocatalysts, EtMgBr and Et_3Al, exhibit essentially the same activity. When complex **1b**/EtMgBr was used at −20 °C as a catalyst for the polymerization, the yield of the polymer is only 3%. When EtMgBr was replaced by $AlEt_3$, the polymer yield increased to 28% at the same condition. Such a tendency can speculatively be attributed to Lewis acidity of the metal center. Complex **1b** seems to interact with an anhydrous magnesium salt such as $MgCl_2$ to block the active site. On the other hand, system **1d**/EtMgBr is a good catalyst at 60 °C to give high polymer in 88% yield, while the low yield (5%) was observed for the catalyst system **1d**/$AlEt_3$. This probably resulted from the decreased reactivity of the polymerization-active chlorotungsten moiety from **1d** to $MgCl_2$ or $MgBr_2$.

Bis(2,6-dimethylphenoxo)–metal complexes with $AlEt_3$ were examined as catalyst for polymerization of 3,3-dimethyl-1-butyne and results are summarized in Table I. Generally, group 6 metals showed higher catalyst activity than group 5 metals. In the case of tantalum, the activity for the polymerization of 3,3-dimethyl-1-butyne is very low. It is interesting that the ligation of 2,6-dimethylphenoxo on niobium enabled polymerization of monosubstituted acetylenes instead of cyclotrimerization (*vide infra*). When mono- or bis(aryloxo)niobium complexes (**4a** and **4b**)/Grignard reagents or triethylaluminum systems were used as catalyst precursors for 3,3-dimethyl-1-butyne, high polymers formed in modest yields with M_n values of >2 × 10^6 and 3.7 × 10^5, respectively.

Table I. Polymerization of 3,3-Dimethyl-1-butyne by Various Catalysts[a]

run	catalyst	cocatalyst	temp (°C)	yield[b] (%)	$M_n/10^5$ [c]	M_w/M_n [c]
1	**1b**	$AlEt_3$	60	83	7.8	2.1
2		$AlEt_3$	−20	28	>20	1.2
3	**2**	$AlEt_3$	60	64	6.1	2.5
4		$AlEt_3$	−20	82	7.5	1.8
5	**3a**	$AlEt_3$	60	9	bimodal	
6	**3b**	$AlEt_3$	60	5		
7	**4a**	*t*-BuMgCl	60	92	>20	1.6
8	**4b**	$AlEt_3$	60	69	3.7	2.2

[a] Polymerization was carried out in toluene for 24 h; $[monomer]_0$ = 1 M, [catalyst] = [cocatalyst] = 10 mM. [b] Insoluble part in methanol. [c] Determined by GPC analysis.

This is in sharp contrast to the fact that most niobium complexes such as $NbCl_5$,[17] $[CpNb(diene)Cl]_2$,[18] $CpNbCl_4$/Mg,[19] $[NbCl_3(THT)]_2$ (THT = tetrahydrothiophene),[20] and $NbCl_3(DME)$ (DME = 1,2-dimethoxyethane)[21] have been used as catalysts for the cyclotrimerization of 1-alkynes. Generally niobium complexes catalyze polymerization of internal alkynes and cyclotrimerization of 1-alkynes.[4,17–21] The previous exception is the polymerization of $HC{\equiv}CCH(SiMe_3)R$ (R = n-C_5H_{11} and n-C_7H_{15})[22] and $HC{\equiv}CCH(SiMe_2R)$-n-Pr (R = n-C_6H_{13} and Ph),[23] which was catalyzed by $NbCl_5$-based catalysts. The bulkiness of the substituent on acetylene prevents the cyclotrimerization and linear oligomerization.

Activity of our catalyst system might be attributed to the presence of a bulky aryloxo group which has the same effect as the bulkiness on monomer. A catalyst system **4a**/*tert*-BuMgCl is also applied for the polymerization of phenylacetylene to find the polymer with M_n = 1.9 × 10^4, M_w/M_n = 2.7. In the case of less bulky acetylene 1-butyne, however, only cyclotrimers were produced by **4a**/EtMgBr and **4b**/EtMgBr (monitored by GLC).

Molybdenum complex **2** in the presence of $AlEt_3$ is the most active catalyst precursor, and high polymers were obtained. As the number of aryloxo ligands coordinated to tungsten can easily be controlled, we investigated the tungsten system more precisely. Results are shown in Table II. Tungsten complexes such as WCl_6, **1a**, and **1b** became the catalyst precursor for polymerization of 3,3-dimethyl-1-butyne, but higher temperature (60 °C) was required for **1a** and **1b**. Although WCl_6 could be used as a catalyst even at 0 °C without cocatalysts, complex **1** showed no catalyst activity below 30 °C. On the other hand, the addition of cocatalyst activated the catalyst. At 60 °C, catalyst activity of complex **1** in the presence of cocatalyst increased considerably, and higher number-average molecular weight M_n values (5.4 × 10^5 to >20 × 10^5) are obtained for the resulting polymers. The M_n values of the obtained polymers are increased with increasing number of the aryloxo ligands. Thus, active species seem to be stabilized by the increasing number of bulky aryloxo ligands.

At lower temperature (0 °C or −20 °C), complexes **1d** showed low catalyst activity with or without cocatalyst.

Table II. Polymerization of 3,3-Dimethyl-1-butyne Catalyzed by Tungsten Complexes[a]

run	catalyst	cocatalyst	temp (°C)	yield[b] (%)	$M_n/10^5$ [c]	M_w/M_n[c]
1	WCl_6		60	76	1.4	2.0
2			0	55	2.3	2.6
3	**1a**		60	76	2.6	1.7
4			30	<1		
5		$AlEt_3$	60	86	5.4	2.5
6		$AlEt_3$	0	99	14	1.7
7		$AlEt_3$	−20	72	>20	1.5
8	**1b**		60	82	4.3	2.3
9			30	<1		
10		$AlEt_3$	60	83	7.8	2.1
11		$AlEt_3$	0	79	6.1	2.0
12		$AlEt_3$	−20	28	>20	1.2
13	**1c**		60	<1		
14		$AlEt_3$	60	80	18	1.5
15		$AlEt_3$	0	66	>20	1.2
16	**1d**		60	7	15	1.5
17		EtMgBr	60	88	>20	1.4
18		EtMgBr	0	<1		

[a] Polymerization was carried out in toluene for 24 h; $[monomer]_0$ = 1 M, [catalyst] = [cocatalyst] = 10 mM. [b] Insoluble part in methanol. [c] Determined by GPC analysis.

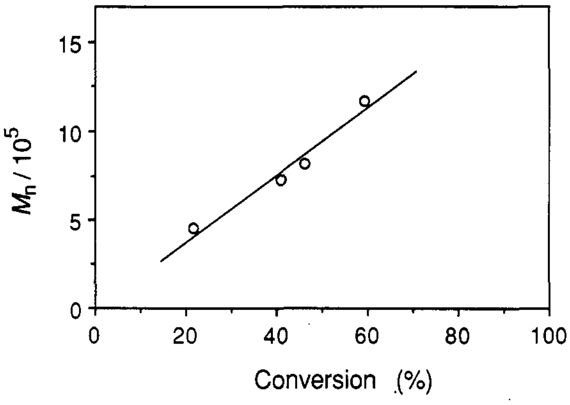


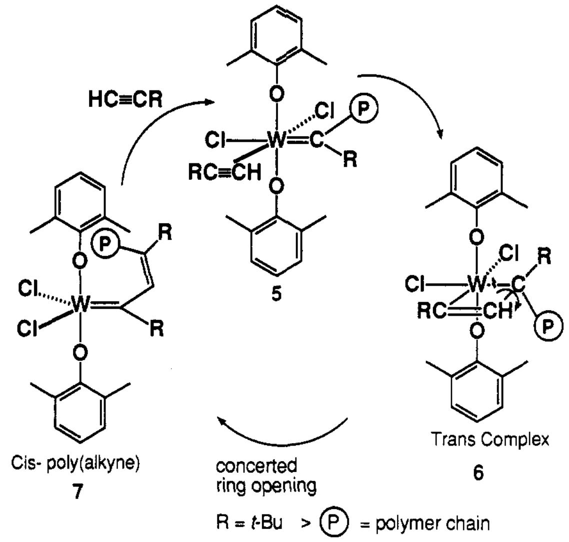
Figure 2. A plot for the averaged number molecular weight M_n vs consumption of monomer for the polymerization of 3,3-dimethyl-1-butyne. Polymerization was carried out in toluene at 0 °C by using catalyst system **1a**/$AlEt_3$.

Table III. Cis Content of Poly(3,3-dimethyl-1-butyne) Catalyzed by Various Catalysts[a]

run	catalyst	cocatalyst	$M_n/10^3$ [b]	cis content[c] (%)
1	**4a**	*t*-BuMgCl	>2000	50
2	**4b**	*t*-BuMgCl	>2000	47
3	WCl_6		140	63
4	**2**		590	70
5	**1a**		260	71
6	**1b**		430	80
7	**1b**	$AlEt_3$[d]	>2000	88

[a] Polymerization was carried out in toluene at 60 °C for 24 h unless otherwise noted; $[monomer]_0$ = 1 M, [catalyst] = [cocatalyst] = 10 mM. [b] Determined by GPC analysis. [c] Determined by ^{13}C NMR spectra.[23] [d] Polymerization was carried out at −20 °C.

Scheme I



Complexes **1a**, **1b**, and **1c** still have catalyst activity for the polymerization to afford extra high molecular weight polymers (M_n = >2 × 10^6) with narrow molecular weight distribution. The best system is the combination of **1b** with $AlEt_3$ at −20 °C and **1c** with $AlEt_3$ at 0 °C. In the case of these catalyst systems, the polydispersity index (M_w/M_n) reached to 1.2. It is very interesting that such an extra-high polymer can be a result of a kind of living polymerization.

Conversion of 3,3-dimethyl-1-butyne was monitored by GLC analysis and the molecular weight M_n of polymer at each stage was quantitatively estimated by GPC analysis. The results are shown in Figure 2. The obtained good linear relationship indicates that the reaction is considered to be almost living polymerization (M_w/M_n = 1.5–1.8) and thus the active species are rather stable and long living. Although the initiator efficiency is very low (<1%), it is interesting that such extra-high polymers can be obtained in a somewhat living fashion. This is attributed to the stabilization effect of bulky aryl oxide ligand on active species.

Cis content of poly(3,3-dimethyl-1-butyne) can be estimated by ^{13}C NMR spectroscopy[24] and is shown in Table III. The increase of the bulkiness around tungsten increased the content of cis geometry of the polyene chain. As shown in Scheme I, alkylating reagents produce carbene species and there must be an open site available for the following alkyne coordination.[25,6b] Thus, carbene–alkyne species **5** is assumed as one of the intermediates, where trans geometry for two aryloxo groups are based on the structure of **1b** determined by X-ray crystallography.[12] In the next stage, the propagation reaction is the cleavage of W–C(sp^3) bond in the key intermediate, metallacyclobutene **6**, with rotating C(sp^3)–C(sp^2) bonds around its axis to form a double bond. During this rotation the steric repulsion between the aryloxo ligands on tungsten and *tert*-butyl group on C(sp^3) can drive the *tert*-butyl group away. The resulting polymer chain may predominantly have cis geometry. Thus, the bulkiness both on monomer and on catalyst are essentially important factors to produce high polymers with high cis content.

The cis contents of polymers obtained by using niobium complexes **4a** and **4b** are 50 and 47%, respectively. These values can be rationalized by assuming the intermediate **8**, whose stereochemistry is based on the crystal structure of **4b**[11] as shown in Figure 3. The intermediate **6** has two aryloxo ligands at trans position and catalyzes formation of *cis*-polyene as described above. On the other hand, niobium in **8** has two aryloxo ligands in cis-fashion and one coordination site is open to be coordinated by a solvent molecule. Therefore, the propagation step through **8** is not effectively restricted and no selection was observed.

Polymerization of 1-Alkynes with Less Bulky Substituents. We investigated steric influence in the polymerization by a systematic variation of substituent R on acetylene; thus, ethyl-, *i*-propyl-, and *tert*-butylacetylenes were examined for polymerization. The polymerization of 3-methyl-1-butyne was carried out by using tungsten complexes. As shown in Table IV, the catalyst

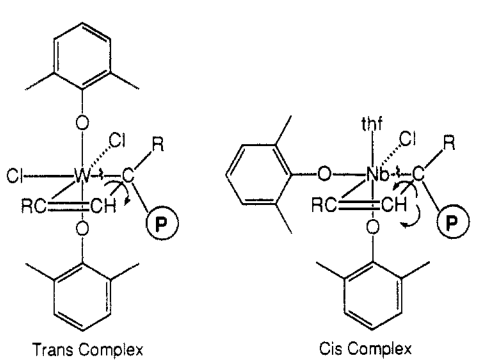


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Figure 3. Schematic drawings for the metallacyclic intermediates responsible for the stereoselectivity of polymerization catalyzed by **1b** and **4b**.

Table IV. Polymerization of 1-Alkynes by Tungsten Catalysts[a]

run	monomer	catalyst	cocatalyst	yield[b] (%)	$M_n/10^3$ [c]	M_w/M_n [c]
1	3-methyl-1-butyne	WCl_6		71	45	1.6
2		**1a**	$AlEt_3$	88	130	1.5
3		**1b**	$AlEt_3$	7	110	1.8
4		**1c**	EtMgBr	7	730	1.7
5	1-butyne	WCl_6		41	5	1.6
6		**1a**	$AlEt_3$	89	bimodal[d]	
7		**1b**	$AlEt_3$	59	4	1.3
8		**1c**	EtMgBr	69	94	3.5
9		**1d**	EtMgBr	92	50	2.0
10	1-hexyne	WCl_6		50	8	1.7
11		**1c**	EtMgBr	63	92	2.7
12		**1d**	EtMgBr	92	170	2.9
13	1-octyne	WCl_6		67	10	1.7
14		**1c**	EtMgBr	98	220	2.6
15		**1d**	EtMgBr	17	350	2.2

[a] Polymerization was carried out in toluene at 0 °C for 24 h; $[\text{monomer}]_0 = 1$ M, [catalyst] = [cocatalyst] = 10 mM. [b] Insoluble part in methanol. [c] Determined by GPC analysis. [d] $M_n = 2.4 \times 10^4$ and 2.2×10^3.

system based on **1c** gave a polymer with higher M_n value (7.3×10^5) than that (4.5×10^4) obtained by using WCl_6. Bulkiness on tungsten also increased the value of M_n.

We have also examined polymerization of *n*-alkyl substituted acetylenes. Previous reports on the polymers from *n*-alkylacetylene have shown that the molecular weight is rather low ($M_n = \sim 10^4$).[6b,26] 1-Butyne was reported to be polymerized by catalysis of WCl_6, but the molecular weight of the obtained polymer is rather low ($M_n = 5 \times 10^3$). The catalyst systems based on **1a** or **1b** exhibited comparable activity with WCl_6. On the other hand, the system **1c**/EtMgBr is the best catalyst precursor of polymerization of 1-butyne to give high polymer, $M_n = 9.4 \times 10^4$. The obtained polymer is an orange elastomer.

Similarly, the polymerization of 1-hexyne and 1-octyne by using WCl_6 as a catalyst afforded a yellow viscous oil, while the catalyst system **1d**/EtMgBr afforded red elastomers ($M_n = 1.7 \times 10^5$ and 3.5×10^5, respectively). These values of M_n were about 10 times larger than those previously reported.[6b,26a,26c] This remarkable feature can presumably be attributed to the bulkiness around the active metal center in these catalyst systems. The bulky phenoxo group may prevent the side reactions such as chain transfer reaction[27] or cyclotrimerization.[26a]

UV–vis spectra (Figure 4) of the high polymer of 1-hexyne show a new peak at λ_{max} of 305 nm. Compared with the low molecular weight conjugated polyenes,[28] the λ_{max} values of the poly(*n*-alkylacetylene)s obtained by $WCl_2(dmp)_4$/EtMgBr were close to those of H(–CH═CH–)$_n$H whose *n* values are 4 to 5 as shown in Table V. Considering that the λ_{max} values of the polymers obtained by WCl_6 were as close to those of H(–CH═CH–)$_n$H whose *n* value is 3, the present result indicates the extension of conjugated segments in the polymers produced by aryloxo complex-based catalysts.

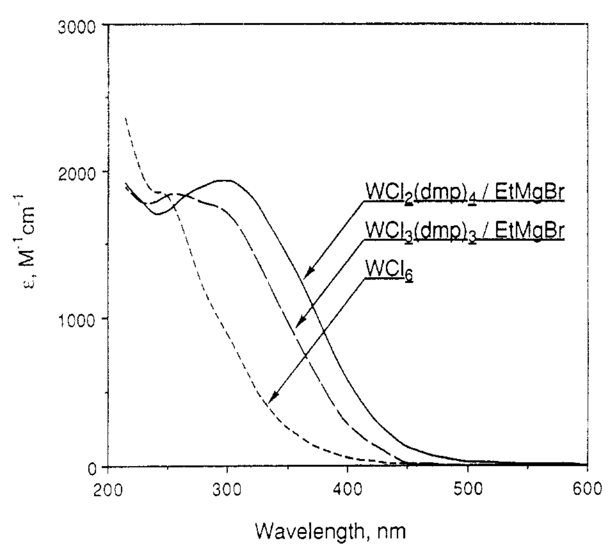

Figure 4. UV–visible spectra of poly(1-hexyne) in hexane. ϵ_{max} values of the polymers were calculated per monomer unit.

Table V. UV-Visible Spectral Data of Low Molecular Weight Conjugated Polyenes and Poly(1-alkyne)s

compounds	λ_{max} (nm)	ϵ_{max}[a] ($M^{-1}\,cm^{-1}$)
H(–CH═CH–)$_n$H[b]		
$n = 2$	217	11000
3	268	11000
4	304	16000
5	334	24000
6	364	23000
poly(1-butyne)[c]		
catalyzed by WCl_6	240	2100
$WCl_2(dmp)_4$/EtMgBr	291	1900
poly(1-hexyne)[c]		
catalyzed by WCl_6	248	1900
$WCl_2(dmp)_4$/EtMgBr	305	1900
poly(1-octyne)[c]		
catalyzed by WCl_6	255	1200
$WCl_2(dmp)_4$/EtMgBr	330	1900

[a] Calculated per one double bond. [b] Measured in isooctane.[28] [c] Measured in hexane.

Structural regularity of poly(1-butyne) can be estimated by ^{13}C NMR spectroscopy.[26b] Cis content of the poly(1-butyne) obtained by WCl_6 and **1d**/EtMgBr was similar, i.e. 84% and 86%, respectively. Thus the extension of conjugated segments is mainly due to the increase of the molecular weight. Preparation of high polymers of 1-butyne enabled us to prepare a firm pellet. The specific conductivity of poly(1-butyne) measured with the two-probe method was less than 10^{-9} S/cm. After doping with iodine vapor, the iodine uptake was 66 wt % and the specific conductivity increased to 3.3×10^{-4} S/cm. The iodine-doped poly(1-butyne) was a black brittle solid. The conductivities of poly(1-hexyne) and poly(1-octyne) were also less than 10^{-9} S/cm, while iodine-doped poly(1-hexyne) (including 62 wt % iodine) showed conductivities of 3.1×10^{-5} and 8.9×10^{-5} S/cm, respectively, and both were black gummy materials. These values were comparable to the conductivites of iodine-doped poly(phenylacetylene) (10^{-4}–10^{-3} S/cm)[29] or polypropyne (10^{-3} S/cm).[30]

Thus, we have found that the ligation of the bulky aryloxo group on the active metal center dramatically enhances the molecular weight of the resulting polymer with higher conjugated structure.

Experimental Section

General Procedures. Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were measured on JEOL JNM-FX90Q and JEOL GX-270 spectrometers. UV–visible spectra were recorded on a JASCO Ubest-30 spectrometer. Mass spectra were measured on a JEOL SX-102 spectrometer. Elemental analyses were performed at the Elemental Analysis Center of Osaka University. All melting points were measured in sealed tubes and were not corrected. The conductivity of the polymer sample pellets was measured by the two-probe method with a FLUKE 37 multimeter.

All manipulations involving air- and moisture-sensitive compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl. Phenylacetylene 1-butyne, 1-hexyne, and 1-octyne were purchased from Tokyo Kasei. 3-Methyl-1-butyne and 3,3-dimethyl-1-butyne were obtained from Lancaster. These monomers were dried by calcium hydride and distilled under argon atomosphere before use.

Complexes **1a** and **1b** were prepared by our previously published method.[12] Complexes **1c**,[14a] **3a**,[14e] and **3b**[14e] were prepared according to the reference method, but THF was used instead of ether for **3a** and **3b**.

Preparation of 1d. To a solution of WCl_6 (1.61 g, 4.06 mmol) in toluene (40 mL) at 0 °C was added a solution of HOC_6H_3-2,6-Me_2 (2.64 g, 21.61 mmol) in toluene. The color of the solution immediately changed from deep blue to deep purple. The reaction mixture was refluxed for 5 h and then this solution was cooled to 0 °C to afford the titled complex as deep purple microcrystals (2.45 g, 82%). Spectral data were superimposable to those in ref 14b.

Preparation of 2. The 1:2 reaction of anhydrous $MoCl_5$ (0.56 g, 2.06 mmol) with $Me_3Si(OC_6H_3$-2,6-$Me_2)$ (0.81 g, 4.19 mmol) in toluene (30 mL) under reflux for 7 h is followed by recrystallization from a mixture of THF and hexane to give $MoCl_3(OC_6H_3$-2,6-$Me_2)_2$(thf) (0.16 g, 15%) as purple black microcrystalline powder. Anal. Calcd for $C_{20}H_{26}Cl_3MoO_3$: C, 46.49; H, 5.07. Found: C, 46.39; H, 5.27.

Preparation of 4a. To a suspension of $NbCl_5$ (350 mg, 1.30 mmol) in toluene (40 mL) at −78 °C was added $Me_3Si(OC_6H_3$-2,6-$Me_2)$ (250 mg, 1.30 mmol). The reaction mixture was stirred at ambient temperature for 12 h. After the solvent was removed, the resulting powdery product was recrystallized from a mixture of THF and hexane to give $NbCl_4(OC_6H_3$-2,6-$Me_2)$(thf) (369 mg, 66%) as red crystals, mp 141–145 °C. Anal. Calcd for $C_{12}H_{17}Cl_4NbO_2$: C, 33.68; H, 4.00. Found: C, 34.00; H, 4.05. ^1H NMR ($CDCl_3$, 30 °C): δ 6.9–7.1 (m, 3H, aromatic protons), 4.92 (m, 4H, thf), 2.83 (s, 6H, CH_3), 2.24 (m, 4H, thf). Mass spectrum for ^{93}Nb m/z, 354 (M^+ − thf).

Preparation of 4b. The 1:2 reaction of anhydrous $NbCl_5$ (3.34 g, 12.4 mmol) with $Me_3Si(OC_6H_3$-2,6-$Me_2)$ (4.93 g, 25.4 mmol) in toluene (100 mL) at 80 °C for 2 h is followed by recrystallization from a mixture of THF and hexane. $NbCl_3(OC_6H_3$-2,6-$Me_2)_2$(thf) (4.17 g, 66%) was obtained as red crystals, mp 173–176 °C. Anal. Calcd for $C_{20}H_{26}Cl_3NbO_3$: C, 46.76; H, 5.10. Found: C, 46.43; H, 5.29. ^1H NMR ($CDCl_3$, 30 °C): δ 6.7–7.0 (m, 6H, aromatic protons), 4.66 (m, 4H, thf), 2.54 (s, 6H, CH_3), 2.45 (s, 6H, CH_3), 2.14 (m, 4H, thf). Mass spectrum for ^{93}Nb m/z, 440 (M^+ − thf).

Polymerization of 1-Butyne. General Procedures. To a suspension of $WCl_2(dmp)_4$ (15 mg, 0.02 mmol) in toluene (0.9 mL) was added a 0.2 M ethereal solution of EtMgBr (0.1 mL, 0.02 mmol) at 0 °C. The color of the suspension scarcely changed from deep purple. After stirring for 10 min at room temperature, the reaction mixture was cooled to −78 °C and then a solution of 1-butyne (0.24 mL, 0.16 g, 2 mmol) in toluene (0.76 mL) was added to the mixture. The reaction tube was sealed in argon and kept for 24 h at 0 °C with stirring. A large excess (ca. 20 mL) of methanol was added to the reaction mixture under argon atmosphere to precipitate the polymer. The resulting orange rubbery solid polymer was collected by centrifugation and dried *in vacuo*. The yield was 92%.

GPC Analyses. Gel permeation chromatographic (GPC) analyses were carried out using Tosoh TSKgel HXL-H and L columns connected to a Tosoh RI-8021 differential refractometer and a Tosoh UV-8010 absorbance detector. Samples were prepared in THF (0.1–0.3% (w/v)) and were filtered through a Advantec DISMIC-25_{JP} filter in order to remove particulates before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) which ranged from 500 to 1.11 × 10^6 MW.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area Organic Unusual Valency (No. 04217102) from the Ministry of Education, Science and Culture, Japan, and also by the Ciba-Geigy Foundation (Japan) for the promotion of science.

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