

Bulky Aryloxo Complexes of Tungsten and Niobium as Catalyst Precursors for High Polymerization of Alk-1-yne

Yuushou Nakayama, Kazushi Mashima and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Mixtures of reducing reagents and 2,6-dimethylphenoxo-tungsten(vi) or -niobium(v) complexes are catalyst precursors for the polymerizations of alk-1-yne; the number of aryloxo ligands on the metal has been found to control the activity of the polymerization of monoalkylsubstituted acetylenes resulting in the formation of high molecular mass polymers.

One of the goals for homogeneous catalysis is the achievement of high activity and selectivity for a target reaction. Recent development in this field has been based on the use of bulky ligands coordinated to the catalytically active metal centre. Pentamethylcyclopentadienyl and 2,6-dialkylphenoxo groups are typical bulky ligands used to achieve the highly active and selective reactions.¹ Metathesis polymerization of some alkynes has been studied in terms of the kind of metals at the catalytic centre,² but the variation of ligands attached to the metal has been little studied. In this contribution, we report that the tungsten and niobium complexes bearing bulky aryloxo ligands with a reducing reagent such as a Grignard

reagent or alkyl aluminum become effective catalysts for the polymerization of alk-1-yne.

2,6-Dimethylphenoxo complexes of tungsten **2a**,³ **b**^{3,4}, **c**⁴ and **d**⁵ were prepared by the literature method. Niobium complexes (**3a** and **b**)[†] were prepared using a similar procedure as for **2a** and **b**.

The polymerization of alkynes (**1a-e**) was initiated by tungsten and niobium complexes in the presence of a

[†] Satisfactory elemental analyses and spectral data for new compounds was obtained.

Table 1 Polymerization of alk-1-yne catalysed by 2,6-dimethylphenoxy complexes of niobium and tungsten^a

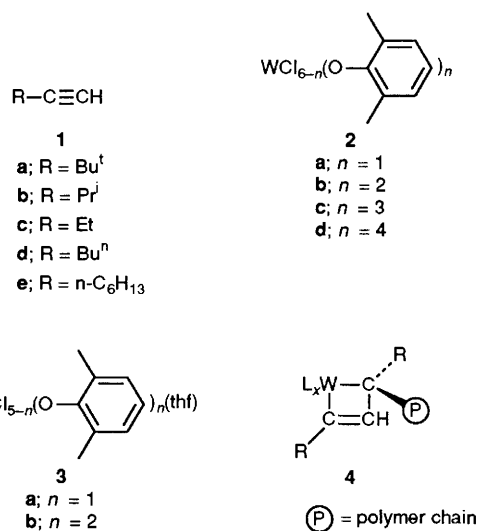
Monomer	Complex	Cocatalyst	T/°C	Polymer		
				Yield(%)	$M_n/10^{3b}$	M_w/M_n^b
1a	WCl ₆	—	0	55	230	2.6
	2a	Et ₃ Al	0	99	1400	1.7
	2b	Et ₃ Al	-20	28	>2000	1.2
	2c	Et ₃ Al	0	66	>2000	1.2
	2d	EtMgBr	0	< 1 ^c	—	—
	3a	Bu ^t MgBr	60	92	>2000	1.7
	3b	Bu ^t MgBr	60	94	790	2.4
1b	WCl ₆	—	0	71	45	1.6
	2a	Et ₃ Al	0	88	130	1.5
	2b	Et ₃ Al	0	7	110	1.8
	2c	EtMgBr	0	7	730	1.7
	2d	EtMgBr	0	50	370	1.7
1c	WCl ₆	—	0	41	5 ^d	1.6
	2a	Et ₃ Al	0	89	Bimodal	—
	2b	Et ₃ Al	0	59	4	1.3
	2c	EtMgBr	0	69	94	3.5
	2d	EtMgBr	0	92	50 ^e	2.0
1d	WCl ₆	—	0	50	8	1.7
	2d	EtMgBr	0	92	170	2.9
1e	WCl ₆	—	0	67	10	1.7
	2d	EtMgBr	0	17	350	2.2

^a Polymerized in toluene for 24 h; [monomer]₀ = 1.0 mol dm⁻³, [complex] = [cocat] = 10 mmol dm⁻³. ^b M_n and M_w determined by gel permeation chromatography using polystyrene samples for calibration. ^c Monomer was not consumed. ^d UV(hexane) λ_{\max} = 240 nm (ϵ = 2100 dm³ cm⁻¹ mol⁻¹) ^e UV(hexane) λ_{\max} = 291 nm (ϵ = 1900 dm³ mol⁻¹ cm⁻¹).

cocatalyst and the results are shown in Table 1.‡ Polymerization of 3,3-dimethylbut-1-yne **1a** was catalysed by tungsten complexes bearing 1–3 equiv. of 2,6-dimethylphenoxy ligand in the presence of cocatalyst. In the comparison of the three catalyst precursors WCl₆, **2a** and **b** the introduction of the aryloxy ligand made the molecular mass of the resulting polymer higher and the molecular mass distribution narrower. When a bis-aryloxy complex **2b**–Et₃Al was used as initiator, an extra high molecular mass polymer ($M_n > 2 \times 10^6$) with narrow molecular mass distribution ($M_w/M_n = 1.2$) was obtained.

The metallacyclobutene **4** can be regarded as the key intermediate in the polymerization of alk-1-yne.^{6a} In the formation of **4**, it is assumed that the total bulkiness on both monomer and ligand effectively prevented side reactions such as chain transfer reaction or cyclotrimerization. The ligation of aryloxy ligands progressively stabilizes the intermediates, and results in the increase in the molecular mass of poly(3,3-dimethylbut-1-yne). However, the catalytic system, **2d** in the presence of EtMgBr, seems to be too crowded to polymerize **1a**.

The polymerization of monosubstituted acetylenes with smaller substituents than **1a**, such as 3-methylbut-1-yne **1b** and but-1-yne **1c** in the catalyst system of **2a** and **b** afforded



‡ *Typical procedure*: Polymerization of but-1-yne was carried out by the following procedure. To a suspension of **2d** (15 mg, 0.02 mmol) in toluene (0.9 ml) was added an 0.2 mol dm⁻³ ethereal solution of EtMgBr (0.1 ml, 0.02 mmol) at 0°C. The colour of the suspension scarcely changed from deep-purple. After stirring for 10 min at room temp., the reaction mixture was cooled to -78°C and then a solution of but-1-yne (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%.

polymers of rather low molecular mass (e.g. for **1c**: $M_n = 4 \times 10^3$ – 10^4), which is comparable to the polymer obtained using WCl₆ as a catalyst. In the polymerization of these acetylenes it is important to achieve a suitable bulkiness around the metal centre by increasing the number of bulky ligands. When **2d**–EtMgBr was used for the polymerization of **1b**, a high molecular mass polymer ($M_n = 3.7 \times 10^5$) was obtained in moderate yield. Poly(but-1-yne) with high molecular mass ($M_n = 9.4 \times 10^4$) was achieved using the catalyst system of **2c**–EtMgBr. These values of M_n were about ten times larger than those reported with WCl₆ catalyst.^{6b} Similarly, high molecular mass polymers of **1d** ($M_n = 1.7 \times 10^5$) and **1e** ($M_n = 3.5 \times 10^5$) were obtained by using **2d**–EtMgBr as a catalyst. These polymers were rubbery solids while those obtained by

WCl₆ were viscous oily materials. Until now, metathesis polymerization of n-alkylacetylenes such as **1c**, **d**, or **e** has resulted in the formation of rather low molecular mass polymers ($M_n = 10^3$ – 10^4).⁶ This work demonstrates that the polymers of simple alk-1-yne with high molecular mass can also be obtained by metathesis reactions. Thus, the steric effect of the ligands in **4** becomes more important by systematically increasing the number of aryloxo ligand on tungsten.

Similarly, the ligation of 2,6-dimethylphenoxo to niobium also plays an important role in polymerization. When mono- or bis-(aryloxo)niobium complexes (**3a** and **b**) with a Grignard reagent were used as catalysts for the polymerization of **1a**, a high molecular mass polymer ($M_n > 2 \times 10^6$) was obtained in modest yield. The results are in sharp contrast to the fact that complexes of NbCl₅ have been used as catalysts for the formation of cyclotrimers of alk-1-yne.⁷ The steric effect of the ligand might block the coordination site and prevent formation of the trimers. A less bulky alk-1-yne **1c** did not afford polymers but yielded only cyclotrimers in quantitative yield by using **3a**-EtMgBr or **3b**-EtMgBr.

Thus, we have found that the bulkiness around the active metal centre dramatically enhances the molecular mass of the resulting polymer with narrow molecular mass distribution ($M_w/M_n \cong 1.2$) and prevents side reactions such as cyclotrimerization.

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