

Ring-Opening Metathesis Polymerization of Norbornene with Catecholato Complexes of Tungsten(VI) as Effective Catalyst Precursors

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ABSTRACT: Catalysis of catecholatotungsten(VI) complexes for the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) and dicyclopentadiene (DCPD) was studied. Bis(catecholato) complex, $WCl_2(cat)_2$ (**2**, cat = catecholato), was found to be particularly active for the ROMP of norbornene in the presence of $AlEt_3$ as a cocatalyst to give polymers with relatively narrow molecular weight distributions. A bulky catecholato complex, $WCl_2(^tBucat)_2$ (**3**, ^tBucat = 3,5-di-*tert*-butylcatecholato), afforded poly(NBE) with high *cis*-content. The use of modified methylaluminoxane (MMAO, Type 3A in toluene) as a cocatalyst improved activities at low temperature ($-78^\circ C$). A mono(catecholato) complex, $WCl_4(cat)$ **1**, showed high activity for the ROMP of a bulkier monomer, DCPD, to give poly(DCPD) with high *cis*-content.

KEY WORDS Ring-opening Metathesis Polymerization / Norbornene / Dicyclopentadiene / Tungsten / Catecholato / 2,6-Dimethylphenoxo /

Polynorbornene is an interesting polymer for its special properties such as shape memory resin and oil-absorbing rubber. Hydrogenated polynorbornene derivatives have high transparency and low glass transition point suitable for optical applications. Classical catalysts such as $WCl_6/AlEt_3$ have been used for ring-opening metathesis polymerization (ROMP) of norbornene (NBE).¹ These classical catalyst systems are easily available and highly active, however, they have some disadvantages: high sensitivity to air and moisture, poor controllability of the molecular weight distribution and microstructure of the resulting polymers. Recent development of organometallic chemistry achieved controlled ROMP catalyzed by well-defined alkylidene complexes such as $W(=NAr)(OR)_2(=CHR')$,² but those catalyst systems are also highly sensitive to air and moisture, and are expensive. For practical use, isolation of alkylidene complexes is not necessary and introduction of appropriate supporting ligands is important. For example, $WOCl_{4-n}(OAr)_n/R_3SnH$ is a good catalyst precursor for bulk ROMP of dicyclopentadiene (DCPD).³ We have been interested in the effect of chelating aryloxo ligands on the catalysis of tungsten compounds for ROMP.^{4–8} However, these complexes also contained other ancillary ligands such as oxo and substituted alkyne, which could effect on their ROMP catalyses rather than the chelating aryloxo ligands. In order to clarify the effect of the chelating ligands on ROMP catalysis, we systematically studied a series of tungsten(VI) chloride complexes having chelating aryloxo

ligands without any other ligands. Here we chose a commercially available and inexpensive ligand, catechol, as a practical ancillary ligand for tungsten catalysts. The ROMP catalyses of the catecholatotungsten complexes were compared with those of the monodentate aryloxo complexes and WCl_6 .

EXPERIMENTAL

General

All the operations were performed under argon with standard Schlenk techniques. ¹H NMR spectra were recorded on a JEOL JNM-LA-400 spectrometer, and chemical shifts were calibrated with the residual protons ($\delta = 7.26$ ppm) in $CDCl_3$. The average molecular weights and molecular weight distributions of the polymers were determined by Gel permeation chromatographic (GPC) analyses on a Tosoh model SC-8010 instrument equipped with a RI (Tosoh RI-8012) detector connected to the TSK gel columns G1000, G2500, G4000, and G7000 in THF at $40^\circ C$. Standard polystyrenes were used for calibration. Toluene was purified by distillation from sodium-benzophenone. Tungsten complexes $WCl_{6-2n}(cat)_n$ (**1**: $n = 1$, **2**: $n = 2$, cat = catecholato), $WCl_2(^tBucat)_2$ (**3**, ^tBucat = 3,5-di-*tert*-butylcatecholato), $WCl_{6-n}(dmp)_n$ (**4**: $n = 1$, **5**: $n = 2$, **3**: $n = 3$, dmp = 2,6-dimethylphenoxo), were prepared according to literatures.^{9–12} Norbornene (bicyclo[2.2.1]hept-2-ene) purchased from Aldrich Chemical Company, Inc. was refluxed over sodium and distilled prior to use. DCPD was supplied by Zeon Corporation Co., Ltd., and purified similarly. Triethylaluminum and modified

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methylaluminoxane (MMAO, type 3A in toluene)¹³ were supplied by Tosoh-Finechem co., and used without further purification.

Polymerization of Norbornene with Tungsten Complex/*AlEt*₃

Into a schlenk tube were placed the catalyst (0.02 mmol) and toluene (1.0 mL) to form a homogeneous solution. After the solution was cooled to -78 °C, *AlEt*₃ (40 mM, 0.5 mL) was added to the reactor, and the mixture was stirred for 30 min for activation. After the reaction mixture was warmed to room temperature, polymerization was started by introducing a norbornene solution (4 M, 0.5 mL). The polymerization mixture was quenched with a large amount of methanol containing a small amount of hydrochloric acid. The precipitates were collected by centrifugation and dried *in vacuo*. NMR and GPC measurements of the polymers were performed.

Polymerization of Norbornene with Tungsten Complex/*MMAO*

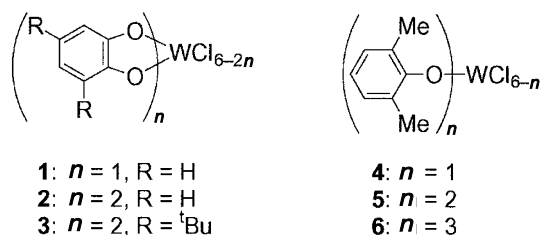
Into a schlenk tube were placed the catalyst (0.02 mmol) and toluene (0.41 mL) to form a homogeneous solution. After the solution was cooled to -78 °C, *MMAO* (5.7 wt%, 1.09 mL) was added to the reactor, and the mixture was stirred for 30 min for activation. After the reaction mixture was warmed to room temperature, polymerization was started by introducing a norbornene solution (4 M, 0.5 mL). The polymerization mixture was quenched with a large amount of methanol containing a small amount of hydrochloric acid. The precipitates were collected by centrifugation and dried *in vacuo*. NMR and GPC measurements of the polymers were performed.

RESULTS AND DISCUSSION

Catecholatotungsten(VI) complexes, $WCl_{6-2n}(cat)_n$ (**1**: $n = 1$, **2**: $n = 2$, *cat* = catecholato) and WCl_2 -(^tBucat)₂ (**3**, ^tBucat = 3,5-di-*tert*-butylcatecholato), were prepared according to literatures (Scheme 1).^{9,10} For comparison, monodentate aryloxotungsten complexes, $WCl_{6-n}(dmp)_n$ (**4**: $n = 1$, **5**: $n = 2$, **6**: $n = 3$, *dmp* = 2,6-dimethylphenoxy), were also prepared (Scheme 1).^{11,12}

Polymerization of Norbornene with Tungsten Complexes/*AlEt*₃

Catecholato complexes **1–3** were inactive for the ROMP of norbornene in the absence of cocatalyst, while one equivalent of *AlEt*₃ effectively activated the catecholato complexes. Table I summarizes the poly-



Scheme 1.

Table I. ROMP of norbornene by tungsten complexes activated with *AlEt*₃

Complex	Temp. (°C)	Yield (%)	M_n^a (/10 ⁵)	M_w/M_n^a	<i>cis</i> -cont. ^b (%)
(cat)WCl ₄ (1)	-78	no polym.	—	—	—
	0	74	17.75	1.99	65
	25	69	13.70	1.68	42
	60	74	8.47	1.83	51
(cat) ₂ WCl ₂ (2)	-78	trace	—	—	—
	0	98	3.55	1.31	73
	25	85	2.94	1.40	69
	60	98	4.71	1.89	53
(^t Bucat) ₂ WCl ₂ (3)	-78	no polym.	—	—	—
	0	48	8.45	1.88	80
	25	49	6.88	1.89	86
	60	50	3.43	1.34	63

Conditions; [W] = 10 mM, [NBE]₀ = 1 M, [*AlEt*₃] = 10 mM, Solvent: 2 mL of toluene, Time = 10 min. ^aDetermined by GPC, ^bDetermined by ¹H NMR.

Table II. ROMP of norbornene by tungsten complexes activated with *AlEt*₃

Complex	Temp. (°C)	Yield (%)	M_n^a (/10 ⁵)	M_w/M_n^a	<i>cis</i> -cont. ^b (%)
WCl ₆	-78	no polym.	—	—	—
	0	61	0.41	20.03	26
	25	52	5.12	8.84	24
	60	75	25.54	4.76	43
(dmp)WCl ₅ (4)	-78	trace	—	—	—
	0	37	7.06	1.72	44
	25	39	5.62	1.88	44
	60	47	2.33	2.43	36
(dmp) ₂ WCl ₄ (5)	-78	no polym.	—	—	—
	0	54	3.24	1.45	61
	25	56	3.58	1.51	71
	60	58	3.03	1.53	54
(dmp) ₃ WCl ₃ (6)	-78	no polym.	—	—	—
	0	6	1.87	1.45	79
	25	48	1.91	1.31	79
	60	29	2.53	1.54	65

Conditions; [W] = 10 mM, [NBE]₀ = 1 M, Solvent : 2 mL of toluene, Time = 10 min. (*dmp*) = 2,6-dimethylphenoxy. ^aDetermined by GPC, ^bDetermined by ¹H NMR.

merization of norbornene by catecholato complexes **1–3** in the presence of *AlEt*₃. Table II shows the polymerization by monodentate *dmp* complexes **4–6** and WCl₆ for comparison. When *AlEt*₃ was used as a co-

catalyst, catecholato complexes **1–3** showed high activities. Especially, the bis(catecholato) complex **2** was remarkably more active than any other catecholato, dmp complexes, and WCl_6 . When the monomer solution in toluene was added to the mixture of **2**/ $AlEt_3$ in toluene, gelation of the reaction mixture immediately occurred. The molecular weights of the polymers obtained with **2**/ $AlEt_3$ were rather lower than those obtained with **1** and **3**/ $AlEt_3$, indicating higher initiator efficiency of **2**/ $AlEt_3$ than complexes **1** and **3** systems. The polymers obtained with bis(catecholato) complexes **2** and **3** had significantly narrower molecular weight distributions than those obtained with WCl_6 . Chelating coordination of two catecholato ligands should be appropriate both for enhancement of the catalytic activity and for suppression of side reactions such as secondary metathesis.¹⁴ The mono(catecholato) complex **1** gave polymers with broader molecular weight distributions compared with the corresponding bis(catecholato) complex **2**. Coordination of only one catecholato ligand in **1** might be insufficient for effective stabilization of the active species. The bulky bis(catecholato) complex **3** yielded polymers with relatively high *cis*-content, while the corresponding unsubstituted bis(catecholato) complex **2** did not show *cis/trans* selectivity. The bulky substituents of **3** were essential for control of the microstructure of the polymers, although the activity of **3** was lower than that of **2**. Thus, chelating catecholato ligands showed better activity and control of ROMP than the monodentate dmp complexes (Table II).

Figure 1 shows GPC profiles of the polymers obtained with catecholato complexes **1–3** and WCl_6 based systems. The polymers obtained with complex **1** and WCl_6 had shoulder peaks, indicating existence of two or more active species. In contrast, the bis(catecholato) complexes **2** and **3** based systems could be regarded as single site catalysts. The $AlEt_3$ cocatalyst should alkylate the tungsten complexes followed by α -H elimination to generate alkylidene species as catalytically active species. We are assuming that the alkylidene species from bis(catecholato) complexes **2** and **3** could be formulated as $WL_2(=CHCH_3)$ ($L = cat$ or tBucat), while the mono(catecholato) complex **1**/ $AlEt_3$ could generate $WX_2(cat)(=CHCH_3)$ ($X = Cl$ and/or Et) and $WCl_6/AlEt_3$ system could give a more complicated mixture. This multiplicity of active species in **1** and WCl_6 systems should be the reason for the shoulder peaks of their GPC profiles.

The complexes **4–6** having monodentate dmp ligands also afforded polymers with narrower molecular weight distributions in comparison with WCl_6 (Table II), but they were less active than bis(catecholato) complex **2**. Among the three dmp complexes **4–6**, bis(dmp) com-

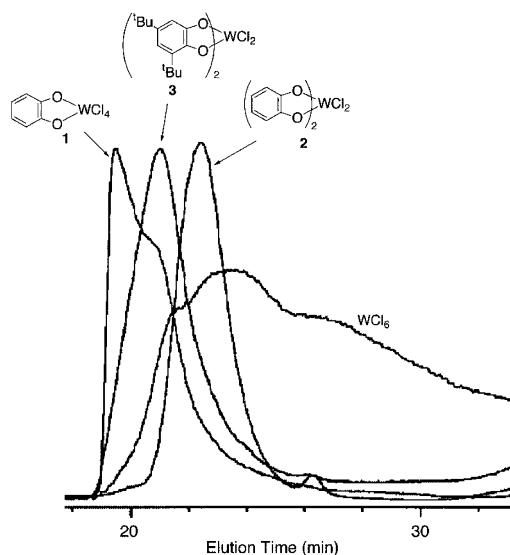


Figure 1. GPC profiles of poly(norbornene)s obtained with tungsten catalysts/ $AlEt_3$ at 0 °C.

plex **5** was most active. With increasing dmp ligands on tungsten, the molecular weights of the resulting polymers decreased, suggesting that the initiation became faster and propagation slower with increasing the dmp ligands. This could be attributed to the steric effect of the dmp ligands, which also enhanced *cis* selectivity with increasing the dmp ligands. It is noteworthy that only the monoaryloxo complex **4** gave polynorbornene at 60 °C without any cocatalyst although the polymer yield was rather low (22% yield under similar conditions in Table II except for the polymerization time of 3 h).

Polymerization of Norbornene with Tungsten Complexes/MMAO

We have recently found that {bis(imino)pyridine} $MoCl_3$ (**7**)/MMAO system promoted ROMP of norbornene to give polymers with high *cis*-contents, while **7**/ $AlEt_3$ resulted in low *cis* selectivity.¹⁵ This encouraged us to use MMAO as a cocatalyst for the complexes **1–6** (Tables III and IV). The polymerization of NBE by MMAO-activated systems also proceeded in ROMP fashion and vinyl addition polymerization of norbornene did not occur. The catecholato complexes **1–3**/MMAO systems were active for the ROMP of NBE at -78 °C. At this temperature, the bis(catecholato) complex **2**/MMAO was particularly active, although the molecular weight distribution of the polymer was rather broad in comparison with those obtained with **2**/ $AlEt_3$. On the other hand, the bulky complex **3** became most active among these complexes at 0–60 °C to give polymers with relatively narrow molecular weight distributions. This might partly result from the thermal stabilities of

Table III. ROMP of norbornene by tungsten complexes activated with MMAO

Complex	Temp. (°C)	Yield (%)	M_n^a ($/10^5$)	M_w/M_n^a	<i>cis</i> -cont. ^b (%)
(cat)WCl ₄ (1)	-78	40	2.44	1.82	53
	0	84	2.85	1.63	43
	25	71	3.83	1.46	44
	60	20	3.62	1.46	45
(cat) ₂ WCl ₂ (2)	-78	86	2.02	1.74	45
	0	65	1.57	1.27	44
	25	63	2.26	1.30	52
	60	74	1.79	1.31	36
^t Bucat) ₂ WCl ₂ (3)	-78	10	2.78	1.26	54
	0	> 99	1.85	1.68	52
	25	91	1.49	1.36	43
	60	> 99	2.13	1.30	40

Conditions; [W] = 10 mM, [NBE]₀ = 1 M, [MMAO] = 1 M, Solvent : 2 mL of toluene, Time = 10 min. ^aDetermined by GPC. ^bDetermined by ¹H NMR.

Table IV. ROMP of norbornene by tungsten complexes activated with MMAO

Complex	Temp. (°C)	Yield (%)	M_n^a ($/10^5$)	M_w/M_n^a	<i>cis</i> -cont. ^b (%)
(dmp)WCl ₅ (4)	-78	33	2.29	1.44	41
	0	28	2.04	1.56	51
	25	66	2.31	1.54	31
	60	37	2.18	1.49	32
(dmp) ₂ WCl ₄ (5)	-78	11	2.02	1.50	63
	0	68	2.78	1.49	36
	25	79	2.71	1.49	30
	60	69	2.83	1.54	27
(dmp) ₃ WCl ₃ (6)	-78	8	2.33	1.55	57
	0	26	4.29	1.42	49
	25	89	4.13	1.34	46
	60	67	4.62	1.33	28

Conditions; [W] = 10 mM, [NBE]₀ = 1 M, [MMAO] = 1 M, Solvent : 2 mL of toluene, Time = 10 min. ^aDetermined by GPC. ^bDetermined by ¹H NMR.

the active species in these systems. The *cis*-contents of the polymers obtained with catecholatotungsten complex/MMAO systems were 36–54%, lower than those obtained with the AlEt₃-activated system. The structure of the active species in the MMAO systems should differ from that in the AlEt₃ systems. In the polymerization by the monodentate phenolato complexes **4–6**, the mono(dmp) complex **4**/MMAO showed rather low activities, while activities of the bis- and tris(dmp) complexes **5** and **6** were similar to those of bis(catecholato) complex **2**.

Polymerization of Dicyclopentadiene with Tungsten Complexes/AlEt₃

The catecholato complexes/AlEt₃ systems were applied to the polymerization of dicyclopentadiene (DCPD) (Table V). The catecholato complexes **1–3**

Table V. ROMP of dicyclopentadiene by tungsten complexes activated with AlEt₃

Complex	Temp. (°C)	Time (h)	Yield (%)	M_n^a ($/10^5$)	M_w/M_n^a	<i>cis</i> -cont. ^b (%)
(cat)WCl ₄ (1)	-78	24	no polym.	—	—	—
	0	6	53	1.57	1.38	90
	25	6	65	1.38	2.04	90
	60	6	56	1.61	2.25	81
(cat) ₂ WCl ₂ (2)	-78	24	no polym.	—	—	—
	0	24	3	6.49	1.67	93
	25	24	29	3.76	1.56	88
	60	24	56	1.23	2.52	93
^t Bucat) ₂ WCl ₂ (3)	-78	24	no polym.	—	—	—
	0	24	27	6.60	1.96	96
	25	24	31	3.83	2.10	90
	60	24	52	1.29	2.16	88

Conditions; [W] = 10 mM, [NBE]₀ = 1 M, [MMAO] = 1 M, Solvent : 2 mL of toluene, Time = 10 min. ^aDetermined by GPC. ^bDetermined by ¹H NMR.

successfully polymerized DCPD to give soluble polymers. For the polymerization of this bulky monomer, less bulky monocatecholato complex **1** exhibited significantly higher activity than the bis(catecholato) complexes **2** and **3**. Thus, the catalytic behavior of the catecholato complexes could be tuned by the number of the catecholato ligands depending on the monomer. The poly(DCPD)s obtained with these catalyst systems had high *cis*-contents in comparison with the poly(NBE)s.

CONCLUSION

Introduction of two catecholato ligands into the tungsten metal center is quite effective not only on the control of molecular weight distribution but also on the enhancement of the catalytic activity for ROMP of norbornene. Bis(catecholato) complex gave polymers with narrower molecular weight distributions than those observed in monodentate 2,6-dimethylphenoxo complexes. Chelating coordination and conjugated structure of catecholato ligands could adequately affect the reactivity of the active species. The use of bulky catecholato ligand ^tBucat resulted in higher *cis*-selectivity in comparison with unsubstituted catecholato ligand, although its activity was lower than the unsubstituted bis(catecholato) complex. In the case of polymerization of DCPD, mono(catecholato)complex was particularly active to give soluble poly(DCPD) with high *cis*-content. Thus, catecholato ligands were found to be quite effective to improve ROMP catalysis of tungsten complexes as practical catalyst precursors.

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