

Efficient ring-opening metathesis polymerization of norbornene by vanadium-alkylidenes generated *in situ* from $V(\text{NAr})\text{Cl}_2(\text{L})$ (L: ketimide, aryloxo)

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Abstract

Ring-opening metathesis polymerization (ROMP) of norbornene (NBE) using a catalyst system consisting of $V(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2(\text{N}=\text{C}'\text{Bu}_2)$ (**1a**), MeMgBr , and PMe_3 proceeded at a remarkable rate, and the catalytic activities (TON values, TON = turnover number) were low when MeLi or AlMe_3 was used in place of MeMgBr . The activities increased upon increasing the polymerization temperature, and were dependent upon the molar ratio(s) of the catalyst component(s) employed. The resultant polymers prepared at 25 °C under the optimized conditions possessed high molecular weights with unimodal molecular weight distributions ($M_n = 1.31\text{--}1.66 \times 10^6$, $M_w/M_n = 1.40\text{--}1.59$), and contained a mixture of *cis/trans* olefinic double bonds. The effects of anionic donor ligands (L) and substituents on the arylimido ligands on the activity in the ROMP using $V(\text{NAr})\text{Cl}_2(\text{L})$ [Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**1**), 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ (**2**); L = N=C'Bu₂ (**a**), N=C(CH₂SiMe₃)'Bu (**b**), O-2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**c**), O-2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ (**d**), O-2,6- $\text{tBu}_2\text{-4-MeC}_6\text{H}_2$ (**e**)]- MeMgBr-PMe_3 were explored; both **1a** and **1c** showed the remarkable activities, and the observed trends were similar to those observed in ethylene polymerization using $V(\text{NAr})\text{Cl}_2(\text{L})\text{-MAO}$ catalyst systems.

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Keywords: Metathesis; Vanadium; Ring-opening metathesis polymerization; Alkylidene

1. Introduction

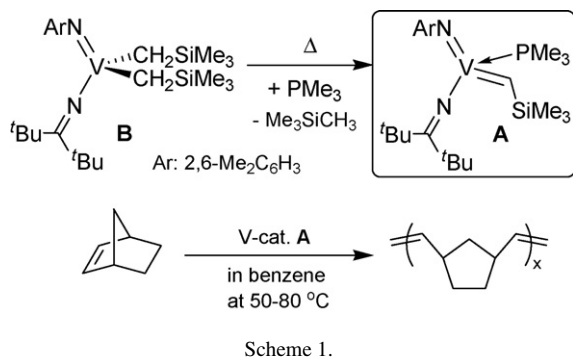
The classical Ziegler type vanadium catalyst systems displayed promising characteristics [1–4] due to the high reactivity toward olefins in olefin coordination insertion polymerization [1b,c]; therefore, the design and synthesis of new vanadium complex catalyst for the controlled polymerization attract considerable attention [1b,c]. Olefin metathesis such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM) and cross metathesis (CM) reactions have recently introduced promising possibilities for synthesis of functional polymers as well as of valuable organic compounds [5], as demonstrated by molybdenum [6] and ruthenium [7] catalyst systems. However, examples of the olefin metathesis with homogeneous vanadium catalysts were rare [8,9]. For instance, polymerization of 3-methylcyclobutene using $\text{VCl}_4\text{-AlEt}_3$, MgEt_2 , and GaEt_3 catalyst systems (so-called

Ziegler-type systems) afforded a mixture of polymers via coordination insertion (vinyl addition) and metathesis (ring opened) mechanisms, whereas $\text{VCl}_4\text{-}^t\text{BuLi}$ catalyst system afforded the ring-opened polymers with extremely low conversion (ca. 3%) [8]. Polymerizations of cyclopentene using $\text{VCl}_4\text{-AlEt}_3$, $\text{VOCl}_3\text{-Et}_2\text{AlCl}$, or $\text{V}(\text{acac})_3\text{-Et}_2\text{AlCl}$ catalyst systems gave mixtures of metathesis and vinyl addition polymerization products with low catalytic activities [9]. Therefore, the descriptions for olefin metathesis using homogeneous vanadium catalysts were rare, and no other examples were reported until 2000.

We recently focused on the high oxidation state (arylimido)vanadium(V) complexes containing anionic donor ligands as the promising catalysts for both olefin coordination insertion polymerization and olefin metathesis [10–15], although many reports are known for olefin insertion polymerization especially for vanadium(III) and vanadium(IV) complexes-cocatalyst systems [1b,c]. We reported that (arylimido)(aryloxo)vanadium(V) complexes of the type, $V(\text{NAr})\text{Cl}_2(\text{OAr}')$ [Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (Ar^1), 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ (Ar^2), etc.; Ar' = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$, 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$, etc.], exhibited high catalytic activities not only for ethylene polymerization but also for ethylene/norbornene (NBE)

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copolymerization in the presence of Al cocatalysts [10,11]; both the Al alkyls and solvents affected the catalytic activity (and NBE incorporation) [11].

We also reported that ROMP of NBE by $V(NAr^1)(CH_2Ph)_2(O-2,6-iPr_2C_6H_3)$ took place affording ultra high molecular weight polymer with a unimodal molecular weight distribution [10], and that the ROMP using $V(NAr^1)Cl_2(OAr^1)-AlMe_3$ (5–10 equiv. to V) catalyst system also proceeded exclusively [10]. Moreover, we communicated that the vanadium(V)-alkylidene, $V(CH_2SiMe_3)(NAr^1)(N=C^tBu_2)(PMe_3)$ (**A**), which was isolated from $V(NAr^1)(CH_2SiMe_3)_2(N=C^tBu_2)$ (**B**) by α -hydrogen elimination in the presence of PMe_3 , initiated ROMP of NBE affording the high molecular weight polymers with unimodal molecular weight distributions (Scheme 1) [12]. The activity of **A** for the ROMP increased upon increasing the polymerization temperature, and the fact clearly suggested that the vanadium-alkylidene was thermally stable under these conditions. The dialkyl analogue (**B**), which was prepared from the dichloro analogue, $V(NAr^1)Cl_2(N=C^tBu_2)$ (**1a**), by treating with $LiCH_2SiMe_3$, also exhibited relatively high catalytic activity for the ROMP of NBE, and the activity increased upon addition of PMe_3 ; the activity also increased at higher temperature [13]. The results strongly suggested a formation of

the alkylidene complex (**A**) *in situ*, which was independently isolated from the C_6D_6 solution containing **B** and PMe_3 upon heating [12].

More recently, as described below, we found that a catalyst solution, which was prepared *in situ* from $V(NAr^1)Cl_2$ ($N=C^tBu_2$) (**1a**), $MeMgBr$ and PMe_3 , exhibited both remarkable catalytic activity and promising thermal stability in the ROMP of NBE [14]. Therefore, we herein introduce our detailed results concerning various factors affecting the activity of $V(NAr)Cl_2(L)$ [$Ar = 2,6-Me_2C_6H_3$ (Ar^1 , **1**), $2,6-iPr_2C_6H_3$ (Ar^2 , **2**); $L = N=C^tBu_2$ (**a**), $N=C(CH_2SiMe_3)^tBu$ (**b**), $O-2,6-Me_2C_6H_3$ (**c**), $O-2,6-iPr_2C_6H_3$ (**d**), $O-2,6-tBu_2-4-MeC_6H_2$ (**e**)]- $MeMgBr$ - PMe_3 catalyst systems for the ROMP of NBE (Scheme 2).

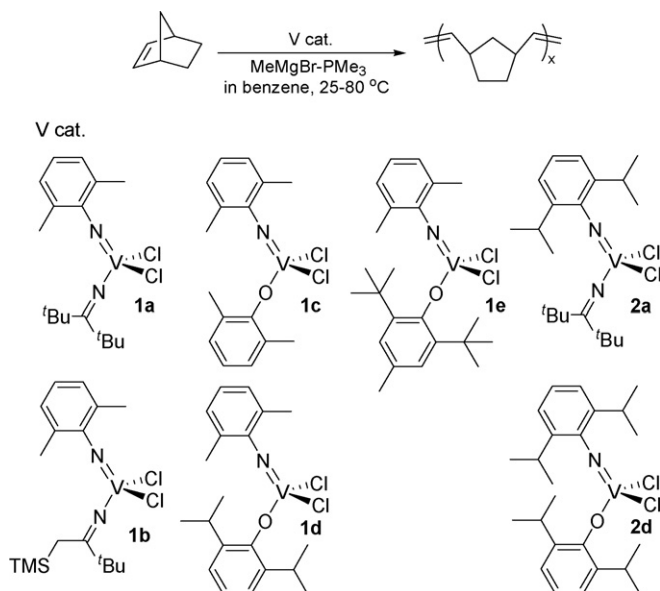
2. Results and discussion

2.1. Reactions of $V(N-2,6-Me_2C_6H_3)Cl_2(N=C^tBu_2)$ (**1a**) with $MeMgBr$, PMe_3 : ring-opening metathesis polymerization (ROMP) of norbornene (NBE) by **1a**-cocatalyst systems

$V(NAr^1)Cl_2(N=C^tBu_2)$ (**1a**) was prepared by treating $V(NAr^1)Cl_3$ with $LiN=C^tBu_2$ in Et_2O in high yield (84%) [12], and was identified by 1H -, ^{13}C -, and ^{51}V -NMR spectra, and elemental analysis [12]. The structure for **1a** determined by X-ray crystallography indicates that **1a** folds a distorted tetrahedral geometry around V and the results suggest that **1a** is a 14 electron species [12]. Complex **1a** reacted with 1.0 equiv. of PMe_3 to afford $V(NAr^1)Cl_2(N=C^tBu_2)(PMe_3)$ (**1a-PMe₃**) exclusively confirmed by 1H , ^{13}C and ^{51}V NMR spectra [12]. The crystal structure for **1a-PMe₃** showed that the complex folds a distorted trigonal bipyramidal structure around V, and that P atom is positioned *trans* to the N atom in the ketimide ligand; PMe_3 in **1a-PMe₃** was dissociated exclusively *in vacuo* affording analytically pure **1a** [12].

In order to explore the possibility of generation of vanadium-alkylidene species *in situ*, the reaction of **1a** with $MeMgBr$ in the presence of PMe_3 was monitored by ^{51}V NMR spectra (Fig. 1a–c). $MeMgBr$ was chosen because it was quite effective in preparing the monomethyl analogue, $V(NAr^1)Me(N=C^tBu_2)_2$, from $V(NAr^1)Cl(N=C^tBu_2)_2$ [15]. As shown in Fig. 1a and b, the resonance observed at 47.3 ppm (ascribed to **1a**) was moved to 494 ppm, when **1a** was treated with 2.0 equiv. of $MeMgBr$ in C_6D_6 at 25 °C. The observed chemical shift (494 ppm) was close to that in $V(NAr^1)(CH_2SiMe_3)_2(N=C^tBu_2)$ (**B**, 495 ppm) reported previously [12], and the fact would strongly suggest formation of the dimethyl complex *in situ*, although we could not isolate the desired complex in a pure form. A broad resonance at ca. 413 ppm (Fig. 1c) was observed in the ^{51}V NMR spectrum upon addition of PMe_3 (1.0 equiv. to V) into the solution containing **1a** and $MeMgBr$, and the spectra did not change even if excessive amount of NBE (10.0 equiv. to V) was added into the solution at 25 °C [16].

Note that a consumption of (cyclic) olefinic double bonds in NBE was observed when a mixed solution consisting of **1a**,



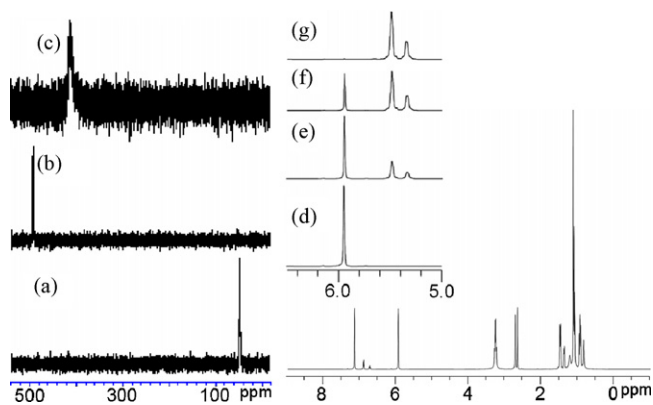


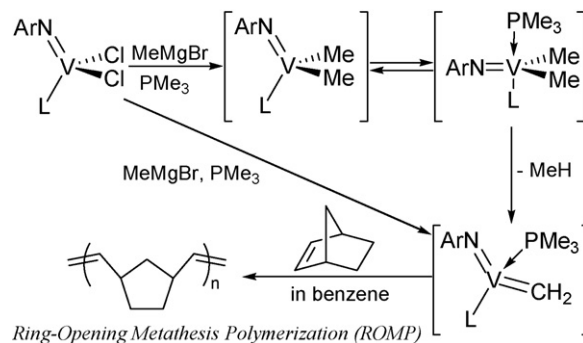
Fig. 1. [Left (a–c)] ^{51}V NMR spectra (in C_6D_6 at 25°C) for (a) $\text{V}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**1a**), (b) **1a** + MeMgBr (2.0 equiv.), (c) **1a** + MeMgBr (2.0 equiv.) + PMe_3 (1.0 equiv.). [Right, d–g] ^1H NMR spectra (in C_6D_6 at 25°C) for time course in ROMP of NBE: (d) **1a** + MeMgBr (2.0 equiv.) + PMe_3 (1.0 equiv.) + NBE (10.0 equiv.) at 25°C [(c) + NBE]; heating solution (d) for (e) 0.5 h, (f) 1.0 h, and (g) 4.0 h at 50°C .

MeMgBr , PMe_3 , and of NBE was heated at 50°C . The resonances ascribed to NBE disappeared after 4 h (Fig. 1d–g), and resonances assigned to the ring-opened poly(NBE) were appeared. NBE was not consumed if the same reaction was employed in the absence of PMe_3 . The results clearly indicate that ROMP of NBE took place, as depicted in Scheme 3, although we could not isolate and identify the active species (vanadium-alkylidene) at this moment [16].

2.1.1. ROMP of NBE by **1a**-cocatalyst systems

Based on the above preliminary experiments, effects of alkylating reagents, PMe_3 , solvent on the catalytic activities for the ROMP of NBE were explored. The results at 25°C are summarized in Table 1.

The ROMP of NBE proceeded with high catalytic activity, if **1a** was treated with 2.1 equiv. of MeMgBr in benzene in the presence of PMe_3 (run 2). The polymerization did not take place or was extremely slow in the absence of PMe_3 (run 1), and the activity decreased upon the excessive addition of PMe_3 (3–5



Scheme 3. Proposed reaction scheme for ROMP of NBE initiated by *in situ* generated vanadium-alkylidene derived from $\text{V}(\text{NAr})\text{Cl}_2(\text{L})\text{-MeMgBr-PMe}_3$.

equiv., runs 3–4). The observed effect of PMe_3 was analogous to that in the ROMP by $\text{V}(\text{NAr}^1)(\text{CH}_2\text{SiMe}_3)_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**B**) [13], and this decrease in the activity by the excessive addition can be explained by assuming that the coordination of PMe_3 into the V retards the propagation (coordination of NBE for propagation), leading to the lower activities; in contrast, PMe_3 was necessary to generate the catalytically active species *in situ*, as reported previously [12,13].

MeMgBr was found to be more effective as the alkylating reagent than MeLi , and this may be explained in terms of the fact that the products in the reaction of **1a** with 2.0 equiv. of MeLi in C_6D_6 consisted of **1a** and the other species (125 ppm in ^{51}V NMR spectrum) [16]. As described in Section 1, $\text{V}(\text{NAr}^1)\text{Cl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1d**) showed catalytic activities for the ROMP in the presence of AlMe_3 but the observed activities were low (e.g. TON 29 after 20 min at 25°C) [10]. The catalytic activity by **1a** in the presence of AlMe_3 was, in fact, extremely low (run 8), but the activity increased in the co-presence of PMe_3 (run 7) [17]. The observed lower activity with AlMe_3 than that with MeMgBr may also be explained in terms of the facts that the reaction of **1a** with AlMe_3 afforded another species (108 ppm in ^{51}V NMR spectrum), and that a relatively sharp resonance peak was observed at 116 ppm upon addition of PMe_3 into a mixed C_6D_6 solution containing **1a** and AlMe_3 [16]; the results

Table 1

Effect of molar ratios, alkylating reagents, and solvents for ROMP of NBE using $\text{V}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**1a**)-cocatalyst systems

Run	Reagent	M/V ^a	PMe_3/V^b	Solvent	Yield (mg (%))	TON ^c	$M_n^d \times 10^{-4}$	M_w/M_n^d
1	MeMgBr	2.1	–	Benzene	Trace	–		
2	MeMgBr	2.1	1.0	Benzene	129 (65)	6850	158	1.50
3	MeMgBr	2.1	3.0	Benzene	75 (38)	3980	131	1.48
4	MeMgBr	2.1	5.0	Benzene	86 (43)	4570	144	1.41
5	MeMgBr	5.0	1.0	Benzene	2 (1)	85	82	2.28
6	MeLi	2.1	1.0	Benzene	Trace	–		
7	AlMe_3	2.1	1.0	Benzene	20 (10)	1060		
8	AlMe_3	2.1	0.0	Benzene	Trace	–		
9	MeMgBr	2.1	1.0	Toluene	90 (45)	4780	Insoluble	
10	MeMgBr	2.1	1.0	Chlorobenzene	139 (70)	7380	74	1.95
11	MeMgBr	2.1	1.0	THF	Trace	–		

Conditions: complex **1a** 0.20 μmol , benzene 4.8 mL, NBE 200 mg (NBE/V molar ratio = 10600), 25°C , 1 h.

^a MeMgBr , MeLi , or AlMe_3/V molar ratio.

^b PMe_3/V molar ratio.

^c TON = (molar amount of NBE consumed)/(mol V).

^d GPC data in THF vs. polystyrene standards.

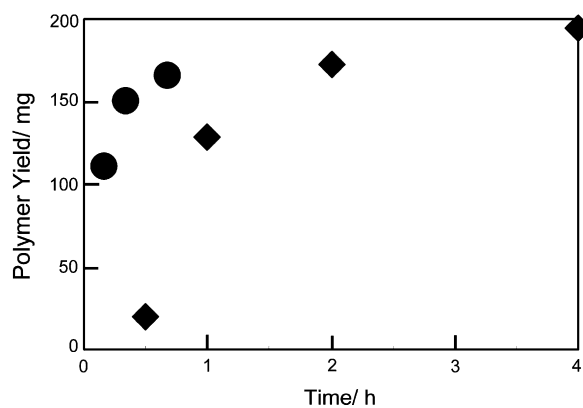


Fig. 2. Time course plots of polymer yields for ROMP of NBE using V(N-2,6-Me₂C₆H₃)Cl₂(N = C'Bu₂) (**1a**)-MeMgBr-PMe₃ catalyst system in benzene at 25 °C (◆) or 50 °C (●). The detailed results are also shown in Table 2.

suggested the formation of another catalytically active species [17].

The molar ratio of Mg/V affected the catalytic activity, and the observed activity became low at a high Mg/V ratio (run 5, Mg/V = 5.0), probably due to the partial decomposition of the catalytically active species and/or formation of other species by excessive addition of MeMgBr. The activity was also affected by the solvent employed (runs 2, 9–11); chlorobenzene and toluene were found to be suitable as the solvents. However, the polymerization did not take place in THF, probably due to the coordination of THF to the metal center, thus disturbing the coordination of monomers. The resultant polymer prepared in toluene was hardly soluble in THF for GPC measurement, probably due to the formation of ultrahigh molecular weight polymer in this catalysis.

Time course of polymer yields in the ROMP by **1a**-MeMgBr-PMe₃ catalyst system under the optimized molar ratios (PMe₃/MeMgBr/V = 1.0/2.1/1.0, molar ratio) at 25 and 50 °C are summarized in Table 2 and Fig. 2. The polymerization proceeded at remarkable rates at the beginning, and the rates decreased gradually probably due to the decrease in the NBE concentration in the reaction mixture. As also shown in Fig. 3, time course plots of log[NBE]/[NBE]₀ {[NBE]₀: initial NBE concentration}, it is clear that the observed catalytic activities (NBE consumption rates) were first order with respect to the NBE concentration employed. The molecular weight dis-

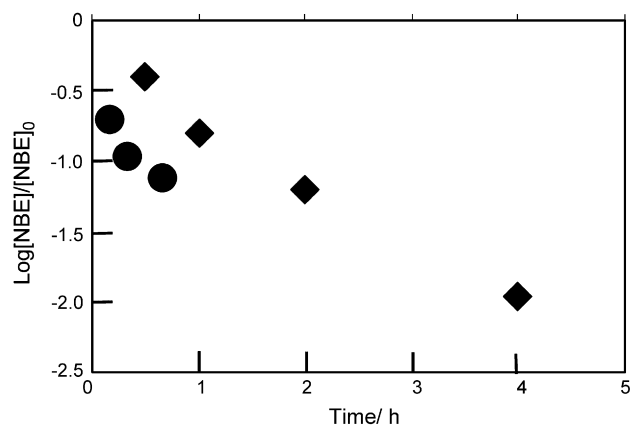


Fig. 3. Time course plots of NBE concentration, Log[NBE]/[NBE]₀, for ROMP of NBE using V(N-2,6-Me₂C₆H₃)Cl₂(N = C'Bu₂) (**1a**)-MeMgBr-PMe₃ catalyst system in benzene at 25 °C (◆) or 50 °C (●). The detailed results are also shown in Table 2. [NBE]₀: initial NBE concentration.

tributions for the resultant polymers prepared at 25 °C were rather narrow ($M_w/M_n = 1.43$ – 1.59); however, the M_n values did not increase with conversion (polymer yields). Therefore, the results suggest that these polymerizations took place without deactivation and accompanied with a certain degree of chain-transfer reactions under these conditions. It is also assumed from these results that the polymerization took place with single (uniform) catalytically active species. These assumptions would also be supported by the facts that the M_n values for the resultant polymers prepared at 50 °C decreased ($M_n = 1.31$ – 1.66×10^6 at 25 °C versus 6.6 – 7.9×10^5) and that the M_w/M_n values became rather broad ($M_w/M_n = 1.43$ – 1.59 at 25 °C; $M_w/M_n = 1.99$ – 2.34 at 50 °C) probably due to the increased extent of chain-transfer reactions.

Note that the catalytic activity increased at 80 °C, and the resultant polymer possessed relatively high molecular weight with a unimodal molecular weight distribution (run 18). The fact suggests that the catalytically active species in the present catalyst system were thermally stable. Moreover, the observed catalytic activities in the ROMP under the optimized conditions [ex. TON 8820 after 40 min at 50 °C (run 17), 7010 after 10 min at 80 °C (run 18)] were significantly higher than (or similar to) those observed in the ROMP initiated by the isolated alkylidene, V(NAr¹)(CHSiMe₃)(N = C'Bu₂)(PMe₃) (**A**, ex. TON 1275 after

Table 2
Time course for ROMP of NBE using V(N-2,6-Me₂C₆H₃)Cl₂(N = C'Bu₂) (**1a**)-MeMgBr-PMe₃ catalyst system

Run	Temperature (°C)	Time (min)	Yield (mg (%))	TON ^a	$M_n^b \times 10^{-4}$	M_w/M_n^b
12	25	30	20 (10)	1060	131	1.54
2	25	60	129 (65)	6850	158	1.50
13	25	120	172 (86)	9130	140	1.59
14	25	240	195 (98)	10360	166	1.43
15	50	10	111 (56)	5900	66	2.34
16	50	20	151 (76)	8020	79	1.99
17	50	40	166 (83)	8820	67	2.13
18	80	10	132 (66)	7010	91	1.87

Conditions: **1a** 0.20 μmol, benzene 4.8 mL, NBE 200 mg (NBE/V molar ratio = 10600), PMe₃/MeMgBr/V = 1.0/2.1/1.0 (molar ratio).

^a TON = (molar amount of NBE consumed)/(mol V).

^b GPC data in THF vs. polystyrene standards.

Table 3
Effect of monomer concentration, temperature in ROMP of NBE using V(N-2,6-Me₂C₆H₃)Cl₂(N=C^tBu₂) (**1a**)-MeMgBr-PMe₃ catalyst system

Run	NBE/V ^a	Benzene (mL)	Temperature (°C)	Time (min)	Yield (mg (%))	TON ^b	M _n ^c × 10 ⁻⁴	M _w /M _n ^c
2	10600	4.8	25	60	129 (65)	6850	158	1.50
19	10600	7.5	25	60	181 (91)	9610	160	1.40
20	10600	2.4	50	40	174 (87)	9240	70	2.34
17	10600	4.8	50	40	166 (83)	8820	67	2.13
21	21200 ^d	4.8	50	20	396 (99)	21100	37	3.06

Conditions: complex **1a** 0.20 μmol, NBE 200 mg, PMe₃/MeMgBr/V = 1.0/2.1/1.0 (molar ratio).

^a NBE/V molar ratio.

^b TON = (molar amount of NBE consumed)/(mol V).

^c GPC data in THF vs. polystyrene standards.

^d NBE charged 400 mg.

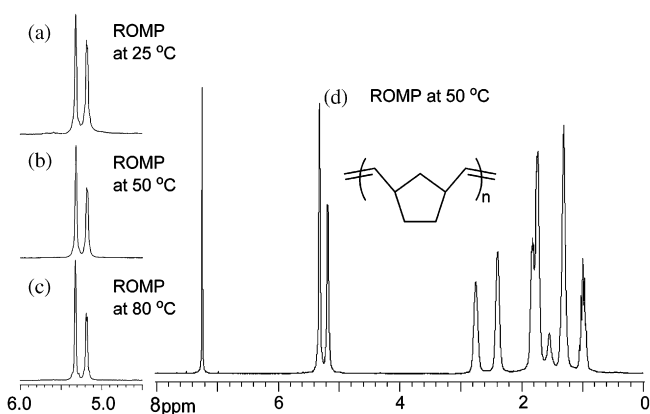


Fig. 4. ¹H NMR spectra for ring-opened poly(NBE)s prepared by V(N-2,6-Me₂C₆H₃)Cl₂(N=C^tBu₂) (**1a**)-MeMgBr-PMe₃ catalyst system. Poly(NBE)s prepared at (a) 25 °C (run 2), (b) 50 °C (run 16), (c) 80 °C (run 18), and (d) 50 °C (run 16, full spectrum).

3 h at 50 °C, 1583 after 1 h at 80 °C) [12], suggesting that the active species could be efficiently generated *in situ* under these conditions.

As shown in Fig. 4, the resultant polymer possessed ring-opened structures (Fig. 4d) containing a mixture of *cis*- and *trans*-olefinic double bonds, and the significant differences in the *cis/trans* ratios were not seen in the resultant polymers prepared at various temperatures (25–80 °C, Fig. 4a–c). We are not sure at this moment whether the control of olefinic double bonds in the resultant polymer would be explained as a result of the degree of *syn/anti* rotational isomers and/or the coordination mode of

NBE into the vanadium metal center, as proposed in the ROMP by the molybdenum-alkylidene catalysts [6].

The polymerization results under various NBE concentration conditions are summarized in Table 3. The observed catalytic activity (TON value) at 25 °C increased at lower monomer concentration conditions (runs 2, 19), although, as shown in Figs. 2 and 3, the NBE consumption rate was first order with respect to the NBE concentration. Since the observed activity decreased under higher NBE concentrations (TON 5900 after 60 min, benzene 2.4 mL in stead of 4.8 mL in run 2), the fact (improved catalytic activity) would be probably explained by the improvement in the viscosity [due to the formation of high molecular weight poly(NBE)] in the solution. Similarly, no significant differences in the activity (TON values) at 50 °C were seen upon the decrease in the NBE concentration (runs 17, 20); the polymerization reached to completion even if the ROMP was employed at a higher NBE concentration (yield 99%, run 21).

2.2. Effect of ligand in ROMP of norbornene (NBE) by V(NAr)Cl₂(L)-cocatalyst systems

ROMP of NBE using various (arylimido)vanadium(V) complexes containing aryloxo or ketimide ligands, V(NAr)Cl₂(L)-MeMgBr-PMe₃ catalyst systems were conducted to explore the effect of ligands on both the catalytic activity and the M_n value in the resultant ring-opened poly(NBE). The results are summarized in Table 4.

Both V(NAr¹)Cl₂(N=C^tBu₂) (**1a**) and V(NAr¹)Cl₂(O-2,6-Me₂C₆H₃) (**1c**) showed the remarkable catalytic activities;

Table 4
ROMP of NBE by various vanadium complexes, V(NAr)Cl₂(L) (**1,2**)-MeMgBr-PMe₃ catalyst systems

Run	Complex (μmol)	Ar	L	Yield (mg (%))	TON ^a	M _n ^b × 10 ⁻⁴	M _w /M _n ^b
17	1a (0.2)	2,6-Me ₂ C ₆ H ₃	NC ^t Bu ₂	166 (83)	8820	67	2.13
22	2a (1.0)	2,6- ⁱ Pr ₂ C ₆ H ₃	NC ^t Bu ₂	12 (6)	130	17	2.21
23	1b (1.0)	2,6-Me ₂ C ₆ H ₃	NC(CH ₂ SiMe ₃) ^t Bu	31 (16)	330	69	1.83
24	1c (0.2)	2,6-Me ₂ C ₆ H ₃	O-2,6-Me ₂ C ₆ H ₃	140 (70)	7440	154	1.46
25	1d (1.0)	2,6-Me ₂ C ₆ H ₃	O-2,6- ⁱ Pr ₂ C ₆ H ₃	37 (19)	390	35	2.25
26	2d (1.0)	2,6- ⁱ Pr ₂ C ₆ H ₃	O-2,6- ⁱ Pr ₂ C ₆ H ₃	14 (7)	150	16	2.27
27	1e (1.0)	2,6-Me ₂ C ₆ H ₃	O-2,6- ^t Bu ₂ C ₆ H ₃	Trace	–	–	–

Conditions: complex 0.20 or 1.0 μmol, benzene 4.8 mL, NBE 200 mg (NBE/V molar ratio = 10600 or 2120), 50 °C, 40 min, PMe₃/MeMgBr/V = 1.0/2.1/1.0 (molar ratio).

^a TON = (molar amount of NBE consumed)/(mol V).

^b GPC data in THF vs. polystyrene standards.

Table 5
ROMP of NBE using complex V(N-2,6-Me₂C₆H₃)Cl₂(N=C'Bu₂) (**1a**)-MeMgBr-PMe₃ catalyst system or Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆H₃)(O^tBu)₂ (**Mo**)

Run	Complex	Temperature (°C)	Time (min)	Yield (mg (%))	TON ^a	$M_n^b \times 10^{-4}$	M_w/M_n^b
2 ^c	1a	25	60	129 (65)	6850	158	1.50
28 ^d	Mo	25	60	161 (81)	8550	160	1.15
17 ^c	1a	50	40	166 (83)	8820	67	2.13
29 ^d	Mo	50	40	trace			
18 ^c	1a	80	10	132 (66)	7010	91	1.87
30 ^d	Mo	80	10	30 (15)	1590	49	2.06

Conditions: **1a** or **Mo** 0.20 μmol, benzene or toluene 4.8 mL, NBE 200 mg.

^a TON = (molar amount of NBE consumed)/(mol V).

^b GPC data in THF vs. polystyrene standards.

^c PMe₃/MeMgBr/V = 1.0/2.1/1.0 (molar ratio), benzene 4.8 mL.

^d Toluene 4.8 mL.

the ROMP by **1c** afforded high molecular weight polymer with a relatively narrow molecular weight distribution ($M_n = 1.54 \times 10^6$, $M_w/M_n = 1.46$, run 24). The activities with 2,6-dimethylphenylimido (Ar¹N) analogues were higher than those with 2,6-diisopropylphenylimido (Ar²N) analogues in all cases (runs 17, 22, runs 25, 26), suggesting that the substituent in the aryylimido ligand affects the catalytic activity. The activity at 50 °C also decreased when **1b** [L = N = C(CH₂SiMe₃)^tBu] was used in stead of **1a** (L: N = C'Bu₂). The order in the catalytic activity with the ketimide ligands is the same as that observed in ethylene polymerization in the presence of MAO at 50 °C [18b]. Moreover, the activities for the ROMP of NBE using the V(NAr¹)Cl₂(OAr¹)-MeMgBr-PMe₃ catalyst systems increased in the order: **1c** (L: O-2,6-Me₂C₆H₃) > **1d** (O-2,6-ⁱPr₂C₆H₃) > **1e** (O-2,6-^tBu₂-4-MeC₆H₂). The order with a series of the aryloxy ligand is also the same as that observed in ethylene polymerization using **1c–e**-MAO catalyst systems at 25 °C [18a], strongly suggesting that the steric bulk in the phenoxy ligand affects the activity.

Well-defined molybdenum-alkylidene, Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆H₃)(O^tBu)₂ (**Mo**) [6,19,20], was chosen to compare the catalytic performance of NBE for ROMP under similar conditions, and the results are summarized in Table 5. The activity with **Mo** at 25 °C was higher than that of **1a**, and the resultant polymer possessed high molecular weight with a narrow molecular weight distribution ($M_n = 1.60 \times 10^6$,

$M_w/M_n = 1.15$). However, significant decrease in the activity for **Mo** was observed at 50 °C, probably due to the rapid decomposition of the catalytically active species. Since the activity by **1a** increased at higher temperature (50–80 °C, runs 17–18), a unique thermal stability in the present catalyst system (containing **1a**) should be thus emphasized.

2.3. Attempts at ring-opening metathesis polymerizations of various cyclic olefins

Polymerizations of various cyclic olefins such as cyclopentene (CPE), cyclooctene (COE), and norbornadiene (NBD) using the **1a**-MeMgBr-PMe₃ catalyst system were attempted at 25–80 °C, and the results are summarized in Table 6. The attempts at polymerization of CPE and COE afforded negligible amount of polymers even if the polymerizations were attempted under bulk (neat) conditions. Moreover, the resultant polymers in the polymerization of NBD were insoluble even in hot *o*-dichlorobenzene, suggesting a possibility of cross-linking (by polymerization/incorporation of residual cyclic olefins in NBD after insertion/incorporation). These results suggest that the present catalytic systems are limited to be effective for norbornene derivatives. Although we could not obtain the positive results for polymerization of COE and CPE, we believe, this can be improved by innovation of more active catalysts in the near future.

Table 6
ROMP of various monomers using V(N-2,6-Me₂C₆H₃)Cl₂(N=C'Bu₂) (**1a**)-MeMgBr-PMe₃ catalyst system

Run	Monomer	1a (μmol)	Monomer (equiv.) ^a	Benzene (mL)	Temperature (°C)	Time	Yield/mg (%)	TON ^b
31	COE	10	425	4.8	80	20 h	None	
32	COE	10	425	– ^c	80	20 h	Trace ^d	
33	CPE	10	425	– ^c	25	20 h	Trace ^d	
16	NBE	0.2	10600	4.8	50	20 min	151 (76)	8020
34	NBD	5.0	850	4.8	50	40 min	116 (30)	250
35	NBD	5.0	850	4.8	80	10 min	274 (70)	600

COE, cyclooctene; CPE, cyclopentene; NBD, norbornadiene. Conditions: PMe₃/MeMgBr/V = 1.0/2.1/1.0 (molar ratio).

^a Monomer/V molar ratio.

^b TON = (molar amount of NBE consumed)/(mol V).

^c Without additional solvent (under bulk conditions).

^d Trace amount of polymer precipitates were collected.

3. Concluding remarks

We have shown that vanadium-alkylidene species *active* in the *olefin metathesis* can be efficiently prepared from V(N-2,6-Me₂C₆H₃)Cl₂(N = C^tBu₂) (**1a**) upon the addition of MeMgBr and PMe₃, and the ROMP of NBE proceeded with remarkably high catalytic activities, affording high molecular weight ring-opened poly(NBE)s with unimodal molecular weight distributions. The activities (TON values) increased upon increasing the polymerization temperature, and the fact should introduce one of the unique characteristics of the vanadium catalysts. We are now exploring the more details concerning the effect of ligands on the activities to find more active catalysts.

4. Experimental

4.1. General procedure

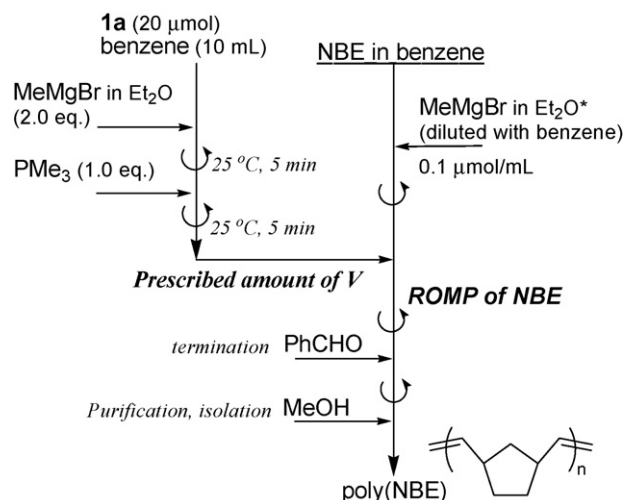
All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grade and were purified by the standard purification procedure. Anhydrous-grade benzene, THF, toluene, and chlorobenzene (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A, 4A 1/16, and 13X) in the drybox under N₂. Polymerization-grade toluene was stored over a sodium/potassium alloy in the drybox, and then passed through an alumina short column before use. V(NAr)Cl₂(L) [Ar: 2,6-Me₂C₆H₃, L: N = C^tBu₂ (**1a**) [12], N = C(CH₂SiMe₃)^tBu (**1b**) [12], O-2,6-Me₂C₆H₃ (**1c**) [10], O-2,6-ⁱPr₂C₆H₃ (**1d**) [10], O-2,6-^tBu₂-4-MeC₆H₂ (**1e**) [10]; Ar: 2,6-ⁱPr₂C₆H₃, L: N = C^tBu₂ (**2a**) [12], O-2,6-ⁱPr₂C₆H₃ (**2d**) [10]] were prepared according to the published methods from (ArN)VC₃. Synthesis of Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆H₃)(O^tBu)₂ was according to the published procedure [20].

All ¹H, ¹³C, and ⁵¹V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ¹H, 100.40 MHz for ¹³C, and 105.31 MHz for ⁵¹V), and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in ppm, and are referenced to SiMe₄ (δ 0.00, ¹H, ¹³C), VOCl₃ (δ 0.00, ⁵¹V).

Molecular weights and the molecular weight distributions of resultant polymers were measured by gel-permeation chromatography (GPC). GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804, and 802, 30 cm × 8.0 mmφ, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from <10² to 2 × 10⁷ MW) were calibrated *versus* polystyrene standard samples.

4.2. ROMP of norbornene (NBE) with **1a**

The typical reaction procedure for ROMP (Table 1, run 2) is as follows (Scheme 4). Benzene (4.5 mL), norbornene (2.12 mmol, 200 mg), and MeMgBr in Et₂O diluted (0.020 μmol, 0.10



Scheme 4. General procedure for ROMP of NBE using V(N-2,6-Me₂C₆H₃)Cl₂(N = C^tBu₂) (**1a**)-MeMgBr-PMe₃ catalyst system. * Additional amount of MeMgBr was added upon the molar ratio employed.

equiv., 3.0 M) with benzene (0.10 μmol/mL) were added into the sealed Schlenk tube. Pre-mixed catalyst solution was independently prepared by adding **1a** (20 μmol) and MeMgBr in Et₂O (40 μmol, 2.0 equiv.), followed by the addition of PMe₃ (20 μmol, 1.0 equiv.) at room temperature. As shown in Scheme 4, the mixture was stirred for 5 min before adding MeMgBr and PMe₃, respectively. Prescribed amount of the prepared catalyst solution was then added into the sealed Schlenk tube, and was magnetically stirred for prescribed time. The polymerization was then quenched by addition of excess PhCHO, and the solution was stirred for additional 1 h at room temperature for completion. The mixture was then poured into MeOH (ca. 100 mL). The resultant polymer was collected on a filter paper, and was adequately washed with MeOH, and was then dried *in vacuo* for several hours. ¹H NMR (CDCl₃): δ 5.19 and 5.33 (br.m, 2H olefinic), 2.77 and 2.42 (br.s, 2H), 1.84 and 1.02 (m, 2H), 1.77 and 1.33 (m, 4H). ¹³C NMR (CDCl₃): δ 133.9, 133.8, and 133.0 and 132.8 (olefinic), 43.4, 43.1, 42.7, 42.1, 41.3, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2.

ROMP with other vanadium complexes were also performed according to the above procedure, and the polymerizations of other cyclic olefins were also attempted similarly.

4.3. Reactions of V(N-2,6-Me₂C₆H₃)Cl₂(N = C^tBu₂) (**1a**) with MeMgBr, PMe₃ (NMR experiment), and the ROMP of NBE monitored by ¹H NMR spectra

Into an NMR tube containing **1a** (38 mg, 0.10 mmol), MeMgBr (2.0 equiv. to **1a**) was added in the dry box at 25 °C. After 5 min, PMe₃ (1.0 equiv. to V) was added, and NBE (10.0 equiv. to V) was then added into the reaction mixture. The tube was then placed in the NMR apparatus, and the measurement was started with stirring at 25 °C. The tube was then heated to 50 °C and collected the data for the prescribed period (after 0.5, 1.0, 2.0, and 4.0 h, respectively).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.05.028.

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