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Notable Effects of Aluminum Alkyls and Solvents for Highly Efficient Ethylene (Co)polymerizations Catalyzed by (Arylimido)-(aryloxo)vanadium Complexes

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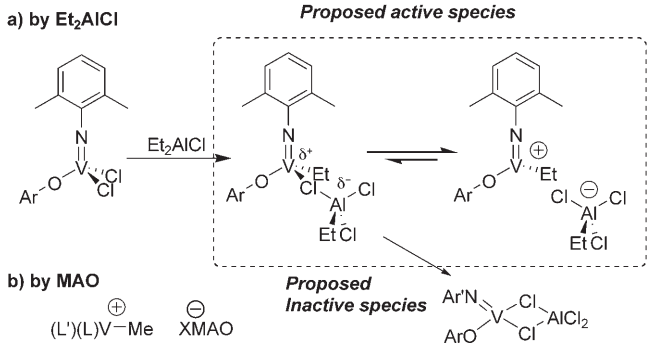
Abstract: The effects of both Al cocatalyst and solvent on catalytic activity in the ethylene polymerization by the (arylmido)(aryloxo)vanadium(V) complex, VCl_2(N-2,6-$Me_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1**), have been explored in detail. The activity of 5.84×10^5 kg PE/mol V·h (TOF 2.08×10^7 h^{-1}) has been achieved by **1**/$EtAlCl_2$ catalyst in CH_2Cl_2 at 0 °C, and the activity in toluene increased in the order: *i*-Bu_2AlCl > $EtAlCl_2$ > Me_2AlCl > Et_2AlCl > $Et_2Al(OEt)$, $AlEt_3$, $AlMe_3$ (negligible activities). Both aluminum alkyl cocatalyst and solvent also affected the catalytic activity and the norbornene (NBE) incorporation in the ethylene/NBE copolymerization using complex **1**, whereas the NBE contents were not strongly affected by the kind of aryl oxide ligand in VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) [OAr = O-2,6-$Me_2C_6H_3$ (**1**), O-2,6-*i*-$Pr_2C_6H_3$ (**2**), O-2,6-$Ph_2C_6H_3$ (**3**)].

Keywords: cocatalyst effect; ethylene; norbornene; olefin polymerization; vanadium

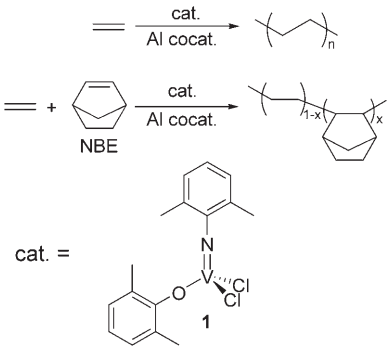
Introduction

Topics concerning precise olefin polymerization by a new generation of transition metal catalysts have attract considerable attention,[1] because the evolution of new polyolefins that have never been prepared by ordinary catalysts is highly expected. Since the classical Ziegler-type vanadium catalyst systems introduced unique characteristics,[2–5] especially for the syntheses of high molecular weight polymers with narrow polydispersities,[3] ethylene/α-olefin copolymers with high α-olefin contents,[3a,4] and propylene-methyl methacrylate diblock copolymers by living polymerization,[5] the design and synthesis of new vanadium catalysts for controlled olefin polymerization have thus been one of the most attractive targets.[2b]

Although many reports are known for olefin polymerization, especially using vanadium(III) and vanadium (IV) complexes,[2b] we focused on the high oxidation state (arylimido)vanadium(V) complexes containing an anionic donor ligand as promising candidates.[6,7] We recently reported that the (arylimido)(aryloxo)-vanadium(V) complexes, VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) [Ar = 2,6-$Me_2C_6H_3$ (**1**), 2,6-*i*-$Pr_2C_6H_3$ (**2**), 2,6-$Ph_2C_6H_3$ (**3**)], exhibited high catalytic activities for ethylene polymerization,[6b] and the activities in the presence of Et_2AlCl were higher than those in the presence of methylaluminoxane (MAO).[6a] Moreover, the catalytic activities, the NBE incorporations, and the dominant chain transfer reactions in the copolymerizations of ethylene with NBE catalyzed by the above complexes were dependent upon the cocatalyst [MAO or Et_2AlCl] employed.[7] Encouraged by the above findings, we further explored the effect of aluminum cocatalyst towards the catalytic activity for ethylene polymerization, because we assumed that a reason for the observed difference in the activities in the presence of between MAO and Et_2AlCl cocatalyst might be due to the different catalytically-active species, a catalyst/cocatalyst nuclearity effect[8] generated in the two systems as exemplified in Scheme 1, and the equilibrium should be dependent upon both solvent and Al alkyls employed. In this paper, we thus report that an exceptionally high catalytic activity for ethylene polymerization has been achieved with these catalyses, and that both the aluminum alkyls and solvents *directly affect* the catalytic activities and NBE incorporation in ethylene (co)polymerizations (Scheme 2). The results presented here represent one



Scheme 1.



Scheme 2.

of the rare examples where Al cocatalyst as well as solvent affect not only the catalytic activity but also the monomer reactivity in ethylene (co)polymerization.[8]

Results and Discussion

Effect of Cocatalyst and Solvent on Ethylene Polymerization Catalyzed by VCl_2(N-2,6-$Me_2C_6H_3$)-(O-2,6-$Me_2C_6H_3$) (1)/Al Cocatalyst Systems

Complex **1** was chosen because this complex exhibited the highest catalytic activity among three complexes with different aryloxo group in the presence of MAO cocatalyst.[6b] The ethylene polymerization results in toluene (ethylene 8 atm, at 0 °C) in the presence of chlorinated aluminum alkyls with different molar ratios are summarized in Table 1, and Table 2 summarizes the results explored for the effect of Al alkyls towards the activity under the optimized conditions.

As summarized in Table 1, the catalytic activities were affected by the Al concentrations (Al/V molar ratios), and the activities obtained in the polymerizations in the presence of 250 μmol of Al alkyls (Al/V molar ratio = 5000) seemed to be the optimized conditions in all cases.[9] It should be noted that the catalytic activity was highly dependent upon the Al cocatalyst employed, and the activities in toluene increased in the order: *i*-Bu_2AlCl (52000 kg PE/mol V·h) > $EtAlCl_2$ (37400) > Me_2AlCl (27500) > Et_2AlCl (11700) > MAO (2930) > $Et_2Al(OEt)$, Me_3Al, Et_3Al (trace or less). Partially chlorinated aluminum alkyl compounds were particularly effective for exhibiting high catalytic activities, and the use of trialkylaluminum or $Et_2Al(OEt)$ showed negligible (or no) catalytic activities under the same conditions. The activities in the presence of Me_2AlCl and *i*-Bu_2AlCl were higher than that in the presence of Et_2AlCl, suggesting that the alkyl group also affected the activity. The catalytic activity did not decrease after 30 min (run 14).

The resultant polymers (runs 5, 13) are linear polyethylene as confirmed by ^1H and ^{13}C NMR spectra, and the polymers possessed ultrahigh molecular weights with unimodal molecular weight distributions. Most of the resultant polymers were, however, hardly soluble even in the hot *o*-dichlorobenzene required for GPC measurement, and this was due to the fact that the polymers possessed ultrahigh molecular weights as estimated by viscosity.[10] For example, the PE prepared by **1**/*i*-Bu_2AlCl catalyst possessed M_η values of $9.87-12.5 \times 10^6$, and an M_η of 8.98×10^6 was also observed for the resultant PE prepared by **1**/Me_2AlCl catalyst.

The polymerization in the co-presence of CCl_3CO_2Et (10.0 equivs. to V) was also employed, because it has been known that the co-presence of a mild oxidizing reagent, like CCl_3CO_2Et, plays an important role in restarting the catalytic cycle from the deactivated catalyst by re-oxidation to a higher oxidation state, when vanadium(III) and/or vanadium(IV) complexes like $V(acac)_3$ (acac = acetylacetonato), V(β-diketonate)$_3$/halogenated aluminum alkyls catalyst systems are employed as the catalyst for the (co)polymerization.[2b,11] However, in contrast to the results by vanadium(III) or vanadium(IV) catalysts, a significant decrease in the catalytic activity was observed upon the addition of oxidizing agent (under the same conditions as in run 14, CCl_3CO_2Et 10 equivs., PE yield *ca.* 9 mg), and the activity decreased upon further addition. These results clearly suggest that the catalytically active species here were thus apparently different from those prepared from vanadium(III), (IV) complexes.[12]

We assumed in the previous paper that a plausible reason for the observed difference in the catalytic activities in the presence of between MAO and Et_2AlCl cocatalyst might be due to the different catalytically-active species, a catalyst/cocatalyst nuclearity effect[8] generated in the two systems as exemplified in Scheme 1. Since it was also assumed that the cationic vanadium alkyl species generated from the precursor complex and Et_2AlCl may not be stable and thus stay in an equilibrium between chloro-bridged and cationic alkyl species due to the less steric bulk and stronger nucleophilic nature of Et_2AlCl, whereas an isolated cationic species would be

Table 1. Effect of Al/V molar ratio on the catalytic activity in ethylene polymerization by VCl_2(N-2,6-$Me_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1**)/Al alkyls catalyst systems.[a]

Run No.	Cat.**1** [μmol]	Al cocat. (Al/V $\times 10^{-3}$)[b]	Polymer Yield [mg]	Activity[c] $\times 10^{-3}$	TOF[d] $\times 10^{-5}$
1	0.05	Me_2AlCl (2.0)	201	24.1	8.61
2	0.05	Me_2AlCl (5.0)	229	27.5	9.80
3	0.05	Me_2AlCl (10.0)	195	23.4	8.36
4	0.05	Et_2AlCl (2.0)	47	5.64	2.01
5[e]	0.05	Et_2AlCl (5.0)	97	11.7	4.15
6	0.05	Et_2AlCl (10.0)	46	5.52	1.97
7	0.05	*i*-Bu_2AlCl (2.0)	375	45.0	16.1
8	0.05	*i*-Bu_2AlCl (5.0)	433	52.0	18.5
9	0.05	*i*-Bu_2AlCl (10.0)	303	36.4	13.0
10	0.05	$EtAlCl_2$ (2.0)	151	18.1	6.47
11	0.05	$EtAlCl_2$ (5.0)	312	37.4	13.3

[a] *Conditions:* toluene + cocatalyst solution = 30 mL, 10 min, 0 °C, ethylene 8 atm, 100-mL scale autoclave.
[b] Molar ratio of Al/V.
[c] Activity in kg polymer/mol V·h.
[d] TOF = (molar amount of ethylene consumed)/(mol V·h).
[e] Cited from ref.[7]

Table 2. Effect of Al alkyls on ethylene polymerization by VCl_2(N-2,6-$Me_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1**).[a]

Run No.	Cat. **1** [μmol]	Al cocat.	Time [min]	Polymer yield [mg]	Activity[c] $\times 10^{-3}$	TOF[d] $\times 10^{-5}$	M_w[e] $\times 10^{-5}$	M_w/M_n[e]	M_η[f] $\times 10^{-6}$
13[g]	1	MAO	10	488	2.93	1.04	28.7	1.64	
2	0.05	Me_2AlCl	10	229	27.5	9.8	–[h]	–	8.98
5[g]	0.05	Et_2AlCl	10	97	11.7	4.15	36.5	1.42	
14	0.05	Et_2AlCl	30	284	11.4	4.06			
15[i]	0.05	Et_2AlCl	10	9	1.08	0.4			
8	0.05	*i*-Bu_2AlCl	10	433	52.0	18.5	–[h]	–	9.87
16	0.01	*i*-Bu_2AlCl	10	108	64.8	23.1	–[h]	–	12.5
11	0.05	$EtAlCl_2$	10	312	37.4	13.3	6.02	3.04	
17	1.0	Et_2AlOEt	10	none	–	–			
18	1.0	Me_3Al	10	trace	–	–			
19	1.0	Et_3Al	10	trace	–	–			
20	1.0	*i*-Bu_3Al	10	trace	–	–			

[a] *Conditions:* toluene + cocatalyst solution = 30 mL, 0 °C (run 13, 25 °C), ethylene 8 atm, Al cocatalyst 250 μmol (run 13, MAO 2.5 mmol; runs 17–20, 500 μmol).
[b] Molar ratio of Al/V.
[c] Activity in kg polymer/mol V·h.
[d] TOF = (molar amount of ethylene consumed)/(mol V·h).
[e] GPC data in *o*-dichlorobenzene *vs.* polystyrene standards.
[f] Molecular weight by viscosity.
[g] Cited from ref.[7]
[h] Insoluble in *o*-dichlorobenzene for GPC measurement.
[i] Polymerization in the co-presence of CCl_3CO_2Et (10.0 equivs. to V).

formed when MAO was employed as the cocatalyst: the equilibrium by Et_2AlCl would stabilize the catalytically-active species, leading to the higher catalytic activity. This would also be based on an assumption that the formed monochloro-bridged species are relatively stable to avoid the formation of the catalytically inactive dichloro-bridged species by reduction. Since an equilibrium between a cationic alkyl (proposed active) and chloro-bridged (dormant) species should exist based on the above assumption and should be affected by the solvent employed,[2b] effect of solvent towards the activity in the ethylene polymerization was thus explored. The results are summarized in Table 3.

The ethylene polymerization in CH_2Cl_2 and C_6H_5Cl (chlorobenzene) exhibited higher catalytic activities than that in toluene, and the activities in *n*-hexane

Table 3. Solvent effect in ethylene polymerization by **1**/Al cocatalyst systems.[a]

Run No.	Cat.**1** [μmol]	Al cocat.	Solvent	Ethylene [atm]	Temp. [°C]	Polymer Yield [mg]	Activity[b] $\times 10^{-3}$	TOF[c] $\times 10^{-4}$	M_w[d] $\times 10^{-5}$	M_w/M_n[d]	M_η[e] $\times 10^{-5}$
21	0.05	Me_2AlCl	*n*-Hexane	8	0	20	2.40	8.56	–	–	
22	0.05	Et_2AlCl	*n*-Hexane	8	0	23	2.76	9.86	–	–	
23	0.05	*i*-Bu_2AlCl	*n*-Hexane	8	0	56	6.72	24.0	26.1	3.19	
24	0.05	$EtAlCl_2$	*n*-Hexane	8	0	394	47.3	169	13.7	3.85	
2	0.05	Me_2AlCl	Toluene	8	0	229	27.5	98.0	–[f]	–	89.8
5[g]	0.05	Et_2AlCl	Toluene	8	0	97	11.7	41.5	36.5	1.42	
8	0.05	*i*-Bu_2AlCl	Toluene	8	0	433	52.0	185	–[f]	–	98.7
16	0.01	*i*-Bu_2AlCl	Toluene	8	0	108	64.8	231	–[f]	–	125
11	0.05	$EtAlCl_2$	Toluene	8	0	312	37.4	133	6.02	3.04	
25	0.05	Me_2AlCl	C_6H_5Cl	8	0	162	19.4	69.4	20.0	3.46	55.1
26	0.05	Me_2AlCl	C_6H_5Cl	8	0	165	19.8	70.6	–	–	
27	0.05	Et_2AlCl	C_6H_5Cl	8	0	158	19.0	67.7	–[f]	–	38.3
28	0.05	*i*-Bu_2AlCl	C_6H_5Cl	8	0	132	15.8	56.5	5.63	3.80	
29	0.05	$EtAlCl_2$	C_6H_5Cl	8	0	537	64.4	230	24.4	3.14	
30	0.05	$EtAlCl_2$	C_6H_5Cl	8	0	503	60.4	216	–	–	
31	0.05	Me_2AlCl	CH_2Cl_2	8	0	164	19.7	70.2	24.2	3.38	
32	0.05	Et_2AlCl	CH_2Cl_2	8	0	110	13.2	47.1	13.4	3.93	
33	0.05	*i*-Bu_2AlCl	CH_2Cl_2	8	0	377	45.2	161	–[f]	–	58.5
34	0.05	$EtAlCl_2$	CH_2Cl_2	8	0	1198	144	512	–	–	
35	0.01	$EtAlCl_2$	CH_2Cl_2	8	0	973	584	2080	–[f]	–	
36	0.01	$EtAlCl_2$	CH_2Cl_2	2	0	373	224	800	12.2	2.33	
37	0.01	$EtAlCl_2$	CH_2Cl_2	2	25	322	193	690	12.2	2.83	
38	0.01	$EtAlCl_2$	CH_2Cl_2	2	40	52	31.2	111	7.04	2.86	
39	0.01	$EtAlCl_2$	CH_2Cl_2	2	−30	51	30.6	109	14.6	2.32	

[a] *Conditions:* solvent + cocatalyst solution = total 30 mL, ethylene 8 atm, 10 min, Al cocatalyst 250 μmol.
[b] Activity in kg polymer/mol V·h.
[c] TOF = (molar amount of ethylene consumed)/(mol V·h).
[d] GPC data in *o*-dichlorobenzene *vs.* polystyrene standards.
[e] Molecular weight by viscosity.
[f] Insoluble in *o*-dichlorobenzene for GPC measurement.
[g] Cited from ref.[7]

were low. These results may suggest that polar solvents may play a role to shift the equilibrium as well as to stabilize the (assumed catalytically active) cationic species.[8] Under the optimized conditions, a notable activity for ethylene polymerization in CH_2Cl_2 could be achieved ($EtAlCl_2$ cocatalyst, 584 ton polymer/mol V·h), and the observed activity did not show first-order dependence upon the ethylene pressure (activity 584 *vs.* 224 kg PE/mol V·h at ethylene 8 *vs.* 2 atm, runs 35 and 36) probably due to the fact that control of the exotherm may be difficult under these conditions (due to extremely high catalytic activity even under low catalyst concentration conditions). The activities decreased at higher temperatures (25 and 40 °C) probably due to the partial deactivation as reported previously,[6a,7] and the activity also decreased at −30 °C.

It should also be noted that the most effective Al cocatalyst was dependent upon the solvent employed (Figure 1): **1**/$EtAlCl_2$ catalyst showed the highest catalytic activity among these Al alkyl in *n*-hexane, chlorobenzene, and in CH_2Cl_2, whereas *i*-Bu_2AlCl was the most effective Al alkyl as cocatalyst in toluene. The resultant polymers possessed high molecular weights (with unimodal molecular weight distributions for samples measured by GPC), and the M_w values prepared by **1**/$EtAlCl_2$ were lower than those prepared in the presence of the other Al cocatalysts. The molecular weight distributions for the resultant polymers prepared in the presence of $EtAlCl_2$ (at ethylene 2 atm) were 2.32–2.86 with unimodal distributions, suggesting that these polymerizations proceed with single catalytically-active species accompanied by some extent of chain-transfer reactions.[10]

Effect of Cocatalyst and Solvent for Ethylene/Norbornene Copolymerization Catalyzed by VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) (1–3)/Al Cocatalyst Systems

Based on the above results, copolymerizations of ethylene with norbornene (NBE) by **1** were conducted in toluene, chlorobenzene, CH_2Cl_2 in the presence of various Al cocatalysts. The results are summarized in Table 4.[13]

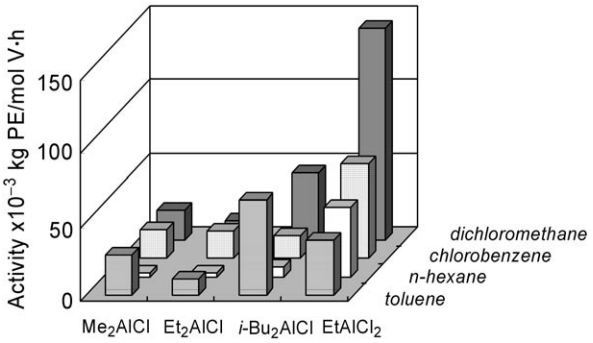


Figure 1. Effects of Al cocatalysts and solvents on ethylene polymerization by **1** (ethylene 8 atm, 0 °C, 10 min).

The copolymerization results (in toluene) by using the other aryl oxide analogues, VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) [OAr = O-2,6-*i*-$Pr_2C_6H_3$ (**2**), O-2,6-$Ph_2C_6H_3$ (**3**)] are also cited[7] for comparison.

The activity by **1** in toluene increased in the order: Et_2AlCl (31700 kg polymer/mol V·h) > *i*-Bu_2AlCl (30100) > Me_2AlCl (23400) > $EtAlCl_2$ (690). The order was different from that observed for the ethylene homopolymerization shown in Table 2 (*i*-Bu_2AlCl > $EtAlCl_2$ > Me_2AlCl > Et_2AlCl > MAO). In particular, the activity for the copolymerization in the presence of $EtAlCl_2$ was low irrespective of the kind of solvent employed (runs 43, 50, 54), although the catalytic activity for ethylene homopolymerization in the presence of $EtAlCl_2$ showed remarkable catalytic activities (entries 11, 24, 29, 30, 34, 35). Note that the activity was affected by the solvent employed, and the activities with Me_2AlCl and Et_2AlCl in CH_2Cl_2 were higher than those in toluene and chlorobenzene. The use of CH_2Cl_2 showed higher catalytic activity than toluene in the copolymerization by the **1**/Me_2AlCl catalyst, whereas the use of toluene was more effective than CH_2Cl_2 for the copolymerization in the presence of *i*-Bu_2AlCl.

Note that the NBE contents for the resultant copolymers were highly affected by both Al cocatalyst and solvent employed. The NBE content in the copolymerization in toluene increased in the order: MAO (23.9 mol %) > Me_2AlCl (15.2) > *i*-Bu_2AlCl (12.4), $EtAlCl_2$ (11.7) > Et_2AlCl (10.4). The NBE contents in the copolymerization in the presence of Me_2AlCl increased in the order: chlorobenzene (17.5 mol %) > toluene (15.2) > CH_2Cl_2 (11.4). The similar solvent effects toward the NBE contents were also observed in the copolymerization in the presence of Et_2AlCl and *i*-Bu_2AlCl. Since the observed difference in the NBE contents were not observed in the copolymerization by varying the aryloxo ligand employed (runs 41, 45, 46, NBE 9.9–10.4 mol %), the facts observed here should represent a rare example that the kind of solvent as well as the Al cocatalyst controls the monomer reactivity for the ethylene/norbornene copolymerization.

Figure 3 shows typical ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s prepared by **1**/Me_2AlCl catalyst system

Table 4. Ethylene/NBE copolymerization by VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) [Ar = 2,6-$Me_2C_6H_3$ (**1**), 2,6-*i*-$Pr_2C_6H_3$ (**2**), 2,6-$Ph_2C_6H_3$ (**3**)]/Al cocatalyst systems: effects of solvent and cocatalyst.[a]

Run No.	Cat. [μmol]	Al cocat.	Solvent	Polymer Yield [mg]	Activity[b] $\times 10^{-3}$	M_w[c] $\times 10^{-6}$	M_w/M_n[c]	NBE cont.[d] [mol %]
40	**1** (0.05)	Me_2AlCl	Toluene	195	23.4	1.75	1.83	15.2
41[e]	**1** (0.05)	Et_2AlCl	Toluene	265	31.7	3.28	1.29	10.4
42	**1** (0.05)	*i*-Bu_2AlCl	Toluene	251	30.1	2.62	2.47	12.4
43	**1** (1.0)	$EtAlCl_2$	Toluene	115	0.69	1.87	2.16	11.7
44[e]	**1** (1.0)	MAO	Toluene	146	0.88	0.54	1.79	23.9
45[e]	**2** (0.05)	Et_2AlCl	Toluene	169	20.3	2.13	2.05	10.2
46[e]	**3** (0.05)	Et_2AlCl	Toluene	125	15	1.82	2	9.9
47	**1** (0.10)	Me_2AlCl	C_6H_5Cl	181	10.9	5.82	2.57	17.5
48	**1** (0.05)	Et_2AlCl	C_6H_5Cl	115	13.8	3.76	2.61	14
49	**1** (0.05)	*i*-Bu_2AlCl	C_6H_5Cl	99	11.9	4.68	2.66	15.8
50	**1** (1.0)	$EtAlCl_2$	C_6H_5Cl	86	0.52	0.845	1.6	17.9
51	**1** (0.10)	Me_2AlCl	CH_2Cl_2	571	68.5	1.35	2.64	11.4
52	**1** (0.20)	Et_2AlCl	CH_2Cl_2	346	41.5	2.41	2.38	9.5
53	**1** (0.20)	*i*-Bu_2AlCl	CH_2Cl_2	103	12.4	2.22	2.51	9.9
54	**1** (1.0)	$EtAlCl_2$	CH_2Cl_2	24	0.14			

[a] *Conditions:* solvent + cocatalyst solution = 30 mL, NBE 15 mmol, 10 min, 0 °C, ethylene 8 atm, Al cocatalyst 250 μmol (MAO 2.5 mmol).
[b] Activity in kg polymer/mol V·h.
[c] GPC data in *o*-dichlorobenzene *vs.* polystyrene standards.
[d] NBE content (mol %) estimated by ^{13}C NMR.
[e] Cited from ref.[7]

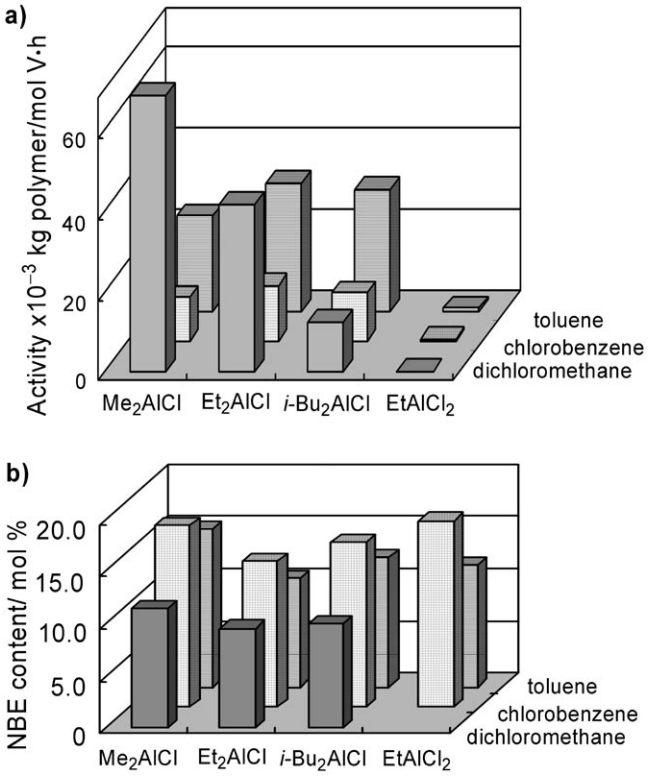


Figure 2. Effects of Al cocatalyst and solvent towards **a)** catalytic activity and **b)** NBE contents for ethylene/NBE copolymerization by **1** (ethylene 1 atm, NBE 15 mmol, 0 °C, 10 min).

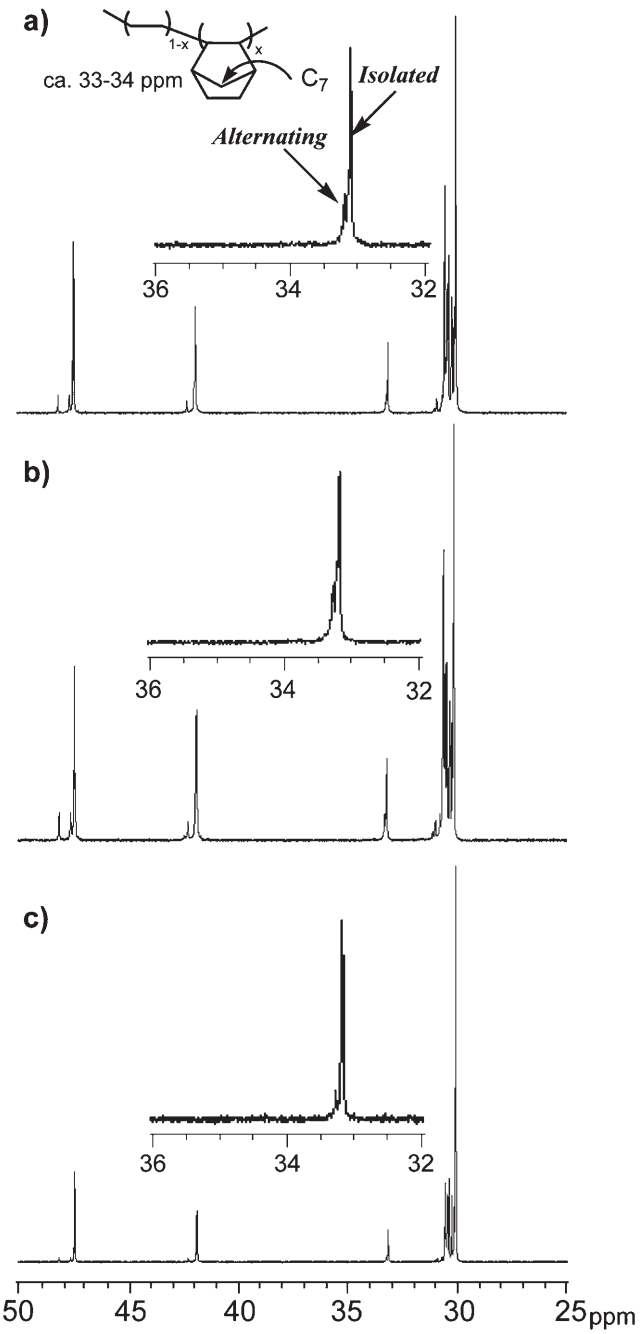


Figure 3. ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) prepared by the **1**/Me_2AlCl catalyst system: (**a**) in toluene, NBE 15.2 mol % (run 40); (**b**) in chlorobenzene, NBE 17.5 mol % (run 47); (**c**) in dichloromethane, NBE 11.4 mol % (run 51).

in various solvent. No significant differences were observed by varying the solvent employed, and the resultant copolymer possessed isolated and alternating NBE sequences, and the facts were related to those observed in the copolymerization in the presence of MAO or Et_2AlCl.[7]

Concluding Remarks

We have shown that both Al alkyls and solvents directly affect the catalytic activity as well as M_w values for the resultant polymer in the ethylene polymerization catalyzed by **1**. Both the catalytic activity and NBE incorporation were also influenced not only by the Al cocatalyst employed but also by the solvent used in the ethylene/NBE copolymerization, although modification of aryl oxide ligand did not strongly affect the NBE incorporation. As far as we know, these facts represent a unique example in which the Al alkyl and solvent control the NBE incorporation as well as the catalytic activity. Moreover, the most effective catalyst/Al cocatalyst/solvent systems were different between ethylene polymerization and ethylene/NBE copolymerization by **1**; polymerization in CH_2Cl_2 in the presence of $EtAlCl_2$ showed the highest catalytic activity for ethylene polymerization, whereas copolymerization in the presence of Me_2AlCl in CH_2Cl_2 showed the highest catalytic activity and copolymerization in chlorobenzene showed the most efficient NBE incorporation.

Experimental Section

General Procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres dry box unless otherwise specified. Anhydrous grade toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3 Å and 4 Å, 1/16, and 13X) in the dry box, and was used without further purification. Norbornene of reagent grade (Aldrich) was stored in the dry box, and was used without further purification. Syntheses of VCl_2(N-2,6-$Me_2C_6H_3$)(OAr) [Ar = 2,6-$Me_2C_6H_3$ (**1**), 2,6-*i*-$Pr_2C_6H_3$ (**2**), 2,6-$Ph_2C_6H_3$ (**3**)] were according to the previous reports.[6] Alkylaluminum compounds (Me_3Al, Et_3Al, *i*-Bu_3Al, Me_2AlCl, Et_2AlCl, $EtAlCl_2$ and Et_2AlOEt) in *n*-hexane (1.0 mol/L) were purchased from Kanto Kagaku Co. Ltd., and used as received. *n*-Hexane solution containing *i*-Bu_2AlCl (1.0 mol/L) was prepared by dilution of *i*-Bu_2AlCl (Kanto Kagaku Co. Ltd.) in *n*-hexane. Toluene and Me_3Al in commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at *ca.* 50 °C for removing toluene, Me_3Al, and then heated at > 100 °C for 1 h for completion) in the dry box to give white solids.[6b,7]

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si. ^{13}C NMR spectra for polyethylene and poly(ethylene-*co*-NBE)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients accumulated was *ca.* 6000–7000. The analysis samples of copolymers were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt) and the spectrum was measured at 110 °C. The NBE contents and the monomer sequence distributions in the copolymers were estimated by the ^{13}C NMR spectra of copolymer, and attribution of each resonances and estimation of norbornene contents were according to the previous reports.[7,14]

Molecular weights and molecular weight distributions for polyethylenes and poly(ethylene-*co*-NBE)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm ϕ ID), ranging from $< 10^2$ to $< 2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v % 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. The molecular weights for samples which were hardly soluble in *o*-dichlorobenzene for the GPC measurements were estimated by viscosity (Asahi Kasei Chemicals Co.) according to a procedure established for ultrahigh molecular weight polyethylene.

Ethylene Polymerization, Ethylene/NBE Copolymerization

A typical reaction procedure for ethylene/NBE copolymerization (Table 4, run 41) was as follows. Toluene (29.0 mL), Et_2AlCl (1.0 mol/L solution in *n*-hexane, 250 μmol), and norbornene (15 mmol, 1412 mg) were added into the autoclave (100-mL scale, stainless steel) under stirring in the dry box. The reaction apparatus was then filled with ethylene at 0 °C. A toluene solution (1.0 mL) containing **1** (0.05 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 7 atm (total pressure 8 atm). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after reaction, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH, and was then dried under vacuum for several hours. Ethylene polymerization was carried out in the same procedure in the absence of norbornene.

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[9] A certain amount of Al compounds is necessary to perform the polymerization with high catalytic activity, because not only the Al alkyls act as the cocatalyst in the polymerization, but also a certain amount of the Al compounds is required to remove impurities in the reaction mixture (water, oxygen etc.).

[10] Due to the fact that some polymers were insoluble in the hot *o*-dichlorobenzene required for GPC analysis, the M_η values were estimated by viscosity. Some samples were still difficult for measurement, and it proved very difficult to estimate the molecular weight. Moreover, we previously suggested a possibility that the ethylene polymerization by **1**/Et_2AlCl in toluene took place in a quasi-living manner, but we could not explore the possibility in details under these conditions (both higher catalytic activities affording ultrahigh molecular weight polymers), except for the polymerization in the presence of $EtAlCl_2$. Broad molecular weight distributions for the resultant polyethylenes are probably due to the fact that the resultant polymers were insoluble in the solvent employed.

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