Polymerization of *trans*-2-Butene with (α-Diimine)Ni(II) Complex in Combination with Et$_2$AlCl

Kiyoshi ENDO[†] and Yoshiyuki KONDO

Department of Applied Chemistry and Bioengineering, Graduate School of Engineering,
Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

ABSTRACT: Polymerization of *trans*-2-butene with (α-diimine)Ni(II) complex in combination with R$_3$Al
(R = CH$_3$, C$_2$H$_5$, *i*-C$_4$H$_9$), Et$_2$AlCl, EtAlCl$_2$ and methylaluminoxane (MAO) was investigated. Et$_2$AlCl and EtAlCl$_2$
as well as MAO were found to be an effective cocatalyst for the polymerization of *trans*-2-butene to give a high
molecular weight of the polymer in good yields, but R$_3$Al did not give any polymers. In contrast to MMAO catalyst
system, a less amount of Et$_2$AlCl to (α-diimine)Ni(II) is enough to reach a high active for the polymerization, and
(α-diimine)Ni(II)/Et$_2$AlCl catalyst gave an optimum rate at the Al/Ni mole ratio of about 20 for the polymerization
of *trans*-2-butene. The results obtained from a kinetic study demonstrate that the control of molecular weight is possible
in the polymerization of *trans*-2-butene with (α-diimine)Ni(II)/Et$_2$AlCl catalyst. The polymer obtained with (α-di-
imine)Ni(II)/Et$_2$AlCl catalyst at 20 °C consists of –CH$_2$–CH$_2$–CH(CH$_3$)– units and minor units derived from 1-butene
produced by isomerization from *trans*-2-butene. Such minor structures can be negligible by decreasing the polymeriza-
tion temperature.   [doi:10.1295/polymj.PJ2006058]
    KEY WORDS   (α-Diimine)Ni(II) Complex / Et$_2$AlCl / 2-Butene / Catalyst / Polymer Structure /
        Molecular Weight Control /

A large amount of 2-olefins such as 2-butene is
produced by naphtha cracking products, but they have
not been utilized as monomers because of their low re-
activity toward polymerization catalysts. If these ole-
fins polymerize easily to give high molecular weight
polymers, a large amount of 2-olefins will be expected
to become new polymer materials. Nevertheless, a
few studies on the polymerization of 2-olefins by tran-
sition metal complexes have been reported.[1–5] One ex-
ample is a copolymerization of 2-butene with ethylene
by transition metal catalysts.[1–3] Monomer-isomeriza-
tion polymerization of 2-olefins with Ziegler-Natta
catalysts is another example. In the monomer-isomer-
ization polymerization, various 2-olefins including
cis-2-butene and *trans*-2-butene give high molecular
weight polymers with a recurring unit of the corre-
sponding 1-olefins. This polymerization mechanism
can be explained by the polymerization of 1-olefins
produced by isomerization of charged 2-olefins prior
to the polymerization,[4,5] and consumed 1-olefins are
supplied by isomerization through a equilibrium of
the isomers.

Recently, Brookhart *et al.*[6] discovered a new type
polymerization of *trans*-2-butene with some kinds
of (α-diimine)Ni(II) complexes in combination with
modified-methylaluminoxane (MMAO). In the poly-
merization, *trans*-2-butene gave a high molecular
weight polymer having a microstructure with one
methyl branch for every four carbon atoms. This poly-

merization mechanism can be explained by a series
of β-hydride elimination/re-addition reactions instead
of a direct opening of double bond. Moreover, the ef-
fect of MAO as a cocatalyst for the (α-diimine)Ni(II)
complexes on the polymerization of *trans*-2-butene
was examined. The polymerization proceeded with
MMAO, although a large amount of MMAO was also
needed to reach a high activity for the polymeri-
zation. On the other hand, when methylaluminoxane
(P-MAO) was used as a cocatalyst, no polymerization
was induced. This indicates that the cocatalyst play
a role in the polymerization of *trans*-2-butene with
(α-diimine)Ni(II) complexes.

After a discovery of the polymerization of *trans*-
2-butene with (α-diimine)Ni(II)/MMAO catalyst, a
chiral catalyst could be used for the iso-selective poly-
merization of *trans*-2-butene.[7] Moreover, Cavallo
et al. elucidated a rationalization of different reactiv-
ity in the polymerization of (*E*)- and (*Z*)-2-butene
with (α-diimine)Ni(II)/MMAO catalyst by quantum
mechanics calculation.[8,9] They also reported living
polymerization of propylene with C_2-Symmetric (α-
diimine)Ni(II)/MMAO catalyst.[10]

Brookhart *et al.* reported that Et$_2$AlCl as well as
MMAO was an effective to produce active cationic
catalyst for the polymerization of ethylene and pro-
pylene. The activity for the polymerization of ethyl-
ene and propylene with (α-diimine)Ni(II) complex/
Et$_2$AlCl catalyst was lower than that with (α-diimine)-

[†]To whom correspondence should be addressed (Tel/Fax: +81-6-6605-2697, E-mail: endo@a-chem.eng.osaka-cu.ac.jp).
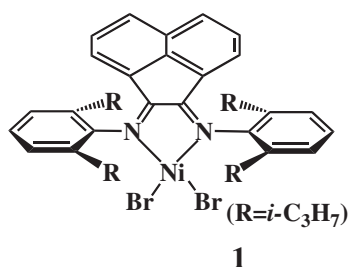
Scheme 1. (α-Diimine)Ni(II) complex.

Ni(II) complex/MMAO catalyst. This suggests that conventional alkylaluminums such as R$_3$Al (R:Et, *i*-Bu, Me), Et$_2$AlCl, and EtAlCl$_2$ will also effective for the polymerization of *trans*-2-butene. However, the effect of these alkylaluminums as a cocatalyst in the polymerization of *trans*-2-butene with (α-diimine)Ni(II) complex was not investigated. We report on the polymerization of *trans*-2-butene with (α-diimine)Ni(II) complex (**1**) in combination with of R$_3$Al (R:Et, *i*-Bu, Me), Et$_2$AlCl, and EtAlCl$_2$.

EXPERIMENTAL

Materials

(α-Diimine)Ni(II) complex (**1**) was synthesized by the reaction of *o*-aryl-substituted α-diimine ligand and (dimethoxyethylene)NiBr$_2$ according to the literature.[10] Commercially available *trans*-2-butene monomer was purchased from Wako Pure Chemical and used without purification. MMAO diluted with toluene (2.53 mol/L) (Tosoh-Fine Chem. Co.) and commercially available alkylaluminums were used as received. Solvents and the other chemicals were used after purification by conventional methods.

Polymerization Procedure

Polymerization was carried out in a sealed glass tube with a rubber septum and a vacuum system. The required amounts of solvent, complex **1** and alkylaluminum were introduced into the tube by syringes under nitrogen atmosphere through a rubber septum. Then *trans*-2-butene was admitted into a glass tube under vacuum after purification over a calcium hydride. Polymerization was carried out in a thermostat at a constant temperature for a given time. After the polymerization, the tube was opened and the contents in the tube were poured into 200 mL of methanol containing 0.4 wt % hydrochloric acid to precipitate the polymer formed. The polymers were washed with a large amount of methanol and dried under vacuum. Polymer yields were calculated by gravimetry.

Polymer Characterization

The number average molecular weight (M_n), weight

Table I. Polymerization of *trans*-2-butene with **1**/ alkylaluminum catalyst in toluene at 20 °C for 24 h[a]

Alkylaluminum	[Al]/[Ni]	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	f[b]
*i*Bu$_3$Al	2	0	—	—	
	10	0	—	—	
Et$_3$Al	2	0	—	—	
	10	0	—	—	
Me$_3$Al	2.5	0	—	—	
	10	0	—	—	
Et$_2$AlCl	2	0	0	—	—
	10	49.3	16.0	2.7	0.69
	15	95.3	20.8	1.8	1.03
EtAlCl$_2$	2	0	0	—	—
	10	24.0	2.9	1.9	1.86
	15	78.3	5.6	2.4	3.13
MMAO	250	10.8	7.9	2.2	0.31
	500	15	8.9	2.1	0.39

[a][*trans*-2-butene] = 2.0 mol/L, [Ni] = 5.0×10^{-4} mol/L, Total volume = 10 mL. [b]Calculated by $f = ([trans$-2-butene]$_0 \times$ Polymer yield $\times 56.1)/([**1**] \times M_{n,obs}$).

average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymer were determined by gel permeation chromatography using Tosoh 8000 series system in THF as calibrated with polystyrene standards. The polymer structure was determined from ^{13}C NMR spectra taken in CDCl$_3$ at 20 °C on α-400NMR spectrometer.

RESULT AND DISCUSSION

Effect of Cocatalyst on the Polymerization

Polymerization of *trans*-2-butene with **1** in combination with alkylalminiums was examined, and the results are shown in Table I. The polymerization of *trans*-2-butene with **1**/Et$_2$AlCl and **1**/EtAlCl$_2$ catalysts as well as **1**/MMAO catalyst was induced to give a high molecular weight polymer. When Me$_3$Al, Et$_3$Al and (*i*-Bu)$_3$Al were used as a cocatalyst, no polymerization was induced. This may be explain by a strong reduction ability of R$_3$Al to Ni(0) species which is inactive for the polymerization of *trans*-2-butene.[12] Since an initiation efficiency of catalysts is one important factor to determine the activity for the polymerizations with transition metal complexes, we estimated it by the number of chain per one Ni atom (f) calculated by the following equation for the polymerization of *trans*-2-butene with **1**/Et$_2$AlCl catalyst;

$$f = ([trans\text{-}2\text{-butene}]_0 \times \text{Polymer yield} \times 56.1)/([**1**] \times M_{n,obs})$$

In where, [*trans*-2-butene]$_0$ is the initial concentration of charged *trans*-2-butene, and [**1**] is the concentration of complex **1**, and the results are listed in Table I. If
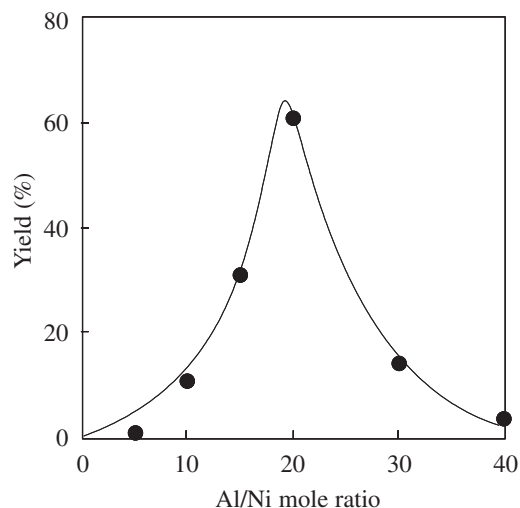
Figure 1. Relationship between Et_2AlCl/Ni mole ratio and polymer yield in the polymerization of *trans*-2-butene with **1**/Et_2AlCl in toluene at $20\,^{\circ}C$ for 5 h: [*trans*-2-butene] $= 2.0\,mol/L$, [Ni] $= 5.0 \times 10^{-4}\,mol/L$.

Figure 2. First order plot for the polymerization of *trans*-2-butene with **1**/Et_2AlCl catalyst in toluene at $20\,^{\circ}C$; [*trans*-2-butene] $= 2.0\,mol/L$, [Ni] $= 1.0 \times 10^{-3}\,mol/L$, Al/Ni $= 15$ mole ratio. M indicates *trans*-2-butene.

the polymerization may neglect chain transfer and termination reactions, the values can be used as an index of initiation efficiency. Interestingly, the *f* of **1**/Et_2AlCl catalyst for the polymerization of *trans*-2-butene was higher than that of **1**/MMAO catalyst.

Kinetic Study of the Polymerization

Since the activity for the polymerization of *trans*-2-butene with **1**/Et_2AlCl catalyst showed the highest among the catalysts examined, we choice **1**/MMAO catalyst to study on the polymerization of *trans*-2-butene in detail. In the polymerizations with binary catalysts, the mole ratios of both catalyst components were known to give an influence to an activity for the polymerization. To check this, the effect of the Al/Ni mole ratio on the polymerization of *trans*-2-butene with **1**/Et_2AlCl catalyst was examined. The results are depicted in Figure 1. Both components are required for the formation of active species for the polymerization. The activity for the polymerization of *trans*-2-butene depended on the Al/Ni mole ratios, and gave an optimum at the Al/Ni ratio of about 20, which is contrast to that a high Al/Ni mole ratios are required to reach a high active for the polymerization of *trans*-2-butene with **1**/MMAO catalyst.[6] The activity for the polymerization decreased by a further addition of Et_2AlCl in the polymerization of *trans*-2-butene with the **1**/Et_2AlCl catalyst. This may be explained by that an excess of Et_2AlCl is able to reduce Ni(II) complex to Ni(0) species that is inactive species for the polymerization of *trans*-2-butenee. Otherwise, a small amount of Et_3Al contained in Et_2AlCl serve as a reducing agent.[12]
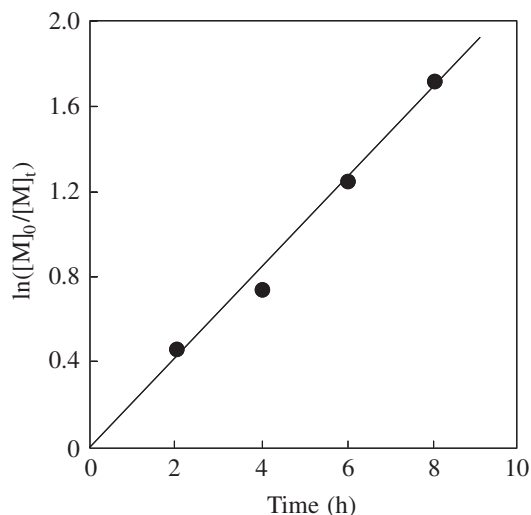
A kinetic study of the polymerization of *trans*-2-

butene with **1**/Et_2AlCl catalyst at the Al/Ni molar ration of 15 was performed to elucidate a possibility of molecular weight control of polymer. Figure 2 shows the first-order plot (ln[*trans*-2-butene]$_0$/[*trans*-2-butene]$_t$ against reaction time) for the polymerization of *trans*-2-butene with **1**/Et_2AlCl catalyst, in where [*trans*-2-butene]$_0$ and [*trans*-2-butene]$_t$ indicate the initial monomer concentration and the monomer concentration at the stated time calculated from the polymer time, respectively. A good linear relationship between ln[*trans*-2-butene]$_0$/[*trans*-2-butene]$_t$ and reaction time was observed, which indicates that the concentration of the active ends kept constant during the course of the polymerization. Namely, the termination reactions or chain transfer reactions may be negligible.

A control of molecular weight of polymer in the polymerization of *trans*-2-butene with **1**/Et_2AlCl catalyst was examined by plotting the M_n of the polymers against the polymer yield, and the results are shown in Figure 3. It is clear that the M_n of the polymers increased linearly with polymer yields, and the line passed through the origin. Although the GPC elution curves of polymers obtained with **1**/Et_2AlCl catalyst showed a monomodal, but M_w/M_n values of the polymers were not narrow. Nevertheless, M_w/M_n values of the polymers became narrow as a function of polymer yields. These results demonstrate that the polymerization of *trans*-2-butene with the **1**/Et_2AlCl catalyst has a living character. In the polymerization of ethylene and propylene with **1**/Et_2AlCl catalyst, the active metal cationic species was reported to be produced in the presence of Et_2AlCl as well as MMAO.[12] The function of MAO is known to stabilize active cationic species of polymerizations as a counter anion
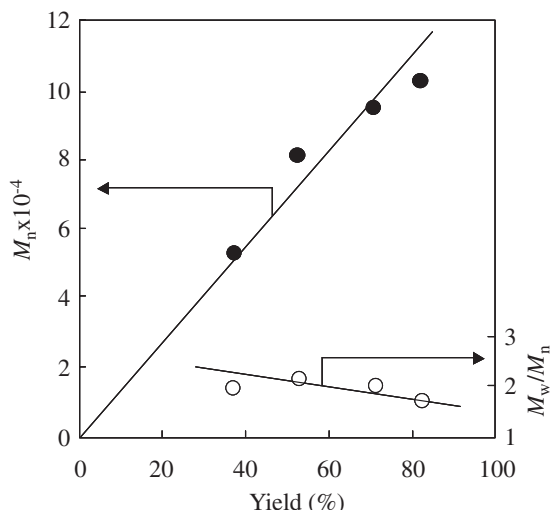
Figure 3. Relationship between the polymer yield and M_n, M_w/M_n in the polymerization of *trans*-2-butene with **1**/Et$_2$AlCl catalyst in toluene at 20 °C: [*trans*-2-Butene] = 2.0 mol/L, [Ni] = 1.0×10^{-3} mol/L, Al/Ni = 15 mole ratio.

leading to the polymerization of olefins, but Et$_2$AlCl is not so enough to stabilize them to control of molecular weight of polymer. We thus assume that the complex of the nickel and *trans*-2-butene is stable to control the molecular weight of polymer even with **1**/Et$_2$AlCl catalyst. The broad M_w/M_n of the polymers can be explained by a slow initiation.

Polymer Structure

Figure 4 shows the ^{13}C NMR spectra of the poly-

mers obtained with **1**/Et$_2$AlCl catalyst. The spectrum of the polymers obtained with **1**/Et$_2$AlCl catalyst at 20 °C is similar to that obtained with **1**/MMAO catalyst.[6] The chemical shifts were calculated by Lindemann-Adams rule[14] for each carbon atom by assuming polymer structure as shown in Figure 4a. The observed chemical shifts were in a good agreement with the assuming polymer structure, and the observed signals were assigned as indicated on Figure 4a. Although the main peaks were assigned as the repeating unit of –CH$_2$–CH$_2$–CH(CH$_3$)–,[6] but very small peaks were also detected. The small signals of *e*, *f*, *g*, h, and *i* could be assigned to repeating unit of 1-butene and methylene sequence –(CH$_2$)$_n$– (n = 5~). The ethyl branch structure corresponding 1-butene unit is formed by the chain walk as a disfavored route.[6,12] The methylene sequence introduced in the chain may be explained by the formation of 1-butene produced by an isomerization from *trans*-2-butene, followed by involving 2,1-insertion and 1,3-chain walking as depicted in Scheme 2.

To suppress these weak peaks, the polymerization of *trans*-2-butene was conducted at −30 °C. As shown in Figure 4b, the small peaks became negligible in the polymer in the ^{13}C NMR spectrum of the polymers obtained at −30 °C. The detail study for the polymerization at −30 °C is now in progress.

CONCLUSION

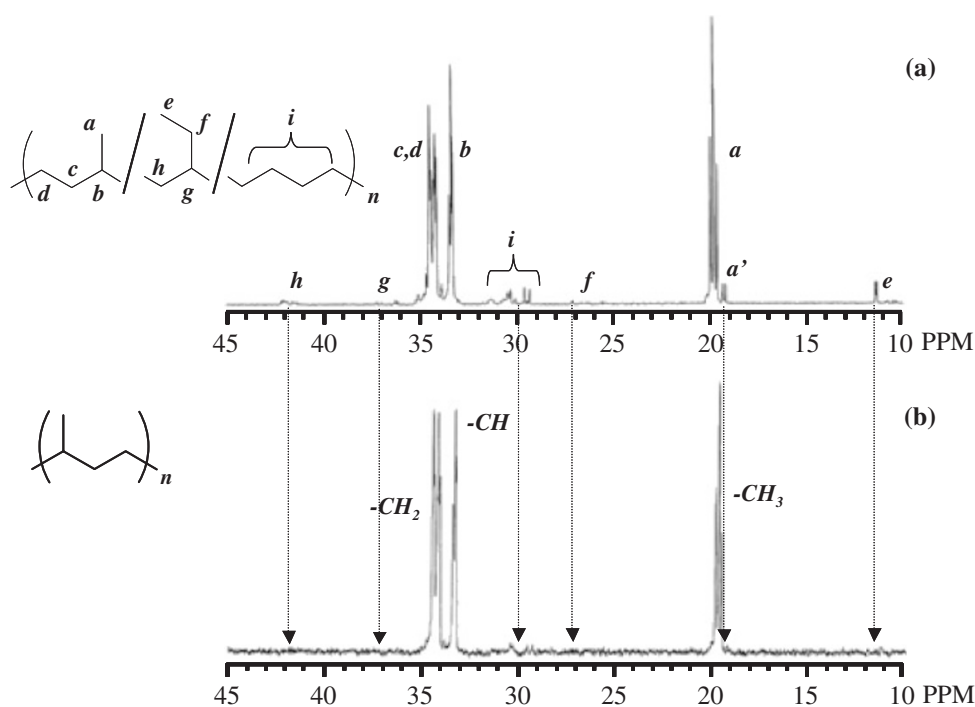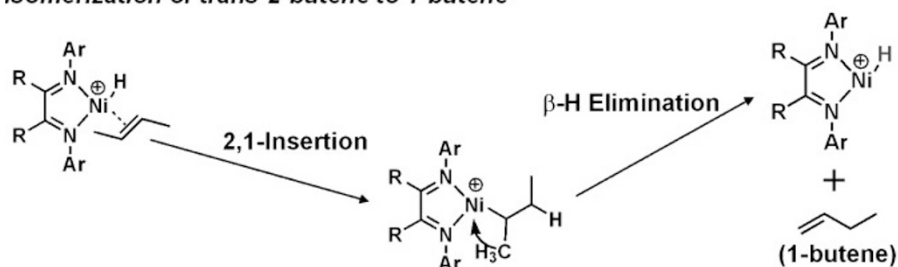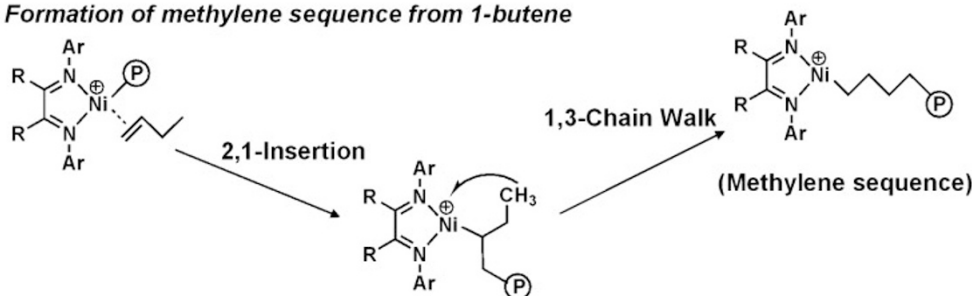The polymerization of *trans*-2-buten with **1**/

Figure 4. ^{13}C NMR spectra of poly(*trans*-2-butene) obtained from polymerization of *trans*-2-butene with **1**/Et$_2$AlCl catalyst in toluene at (a) 20 °C and (b) −30 °C.

Isomerization of trans-2-butene to 1-butene

Formation of methylene sequence from 1-butene

Scheme 2. Possible route for the formation of the methylene sequence in the polymer chain.

Et$_2$AlCl catalyst as well as **1**/M-MAO catalyst gave high molecular weight polymers. In the polymerization of *trans*-2-butene with **1**/Et$_2$AlCl catalyst, an excess of Et$_2$AlCl was not necessary to reach a high active for the polymerization, and gave an optimum at the Al/Ni ratio of about 20. A control of molecular weight was achieved in the polymerization of *trans*-2-butene with **1**/Et$_2$AlCl catalyst. The polymer obtained from the polymerization at 20 °C consists of –CH$_2$–CH$_2$–CH(CH$_3$)– unit and a small amount of other units. Such small amounts of units derived from 1-butene were suppressed significantly by decreasing the reaction temperature.

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