1. Introduction

Mechanistic and chemical grafting of polyolefins with maleic anhydride and styrene derivatives are used for the introduction of functional groups into hydrocarbon polymers and for industrial modification of polyolefin materials\(^1\),\(^2\). High-pressure radical copolymerization of ethylene and polar monomers such as methyl methacrylate (MMA) also yields functionalized polyolefins, but requires large energy input and lacks selectivity owing to the severe reaction conditions. Late transition metal catalysis now enables copolymerization of ethylene with acrylates under mild conditions to produce polymer with vinylene groups in the polymer chain, and a methyl methacrylate group, \(\text{CH}_2\text{CH(Me)}\text{COOMe}\), at the polymer end. Previous findings of copolymerization catalyzed by Ni complexes with chelating P-O ligands gave a polymer with an unsaturated end group, \(\text{CH}_2\text{C(Me)}\text{COOMe}\). Other alkyl methacrylates such as \(n\)-butyl, \(t\)-butyl, and \(i\)-amyl methacrylates also copolymerized with 1-decene to yield the end-functionalized polymers. Copolymerization of 1-decene with 2-acetyl ethyl methacrylate yielded polymer with a terminal ester group, whereas 2-hydroxyethyl methacrylate did not undergo copolymerization. Allyl methacrylate reacted with 1-decene to produce copolymer via preferential insertion of \(\text{C}=\text{C}\) double bond of the allyl groups into the metal-polymer bond. Copolymer of 1-decene and isoprenyl methacrylate contained comonomer units formed via insertion of \(\text{C}=\text{C}\) double bonds of the methacrylic group and of isoprenyl group in 76 : 24 ratio.

Keywords
Olefin polymerization, Palladium catalyst, Acrylate, Co-polymerization

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* To whom correspondence should be addressed.
* E-mail: osakada.k.aa@m.titech.ac.jp
alkyl, allyl, and isoprenyl methacrylates using Pd-diamo
complex as the catalyst and structures of the resultant
polymers with functional groups at the polymer end.

2. Results and Discussion

2.1. Copolymerization of 1-Decene with MMA
Pd-diamo complexes (1, 2), activated by NaBARF
(BARF = B(C 6 H 3 (CF 3 ) 2 -3,5 ) 4 ,[NaBARF]/[Pd] = 1.2),
catalyzed copolymerization of 1-decene with MMA at
room temperature and 0 °C to produce polymer with the
terminal MMA group, as shown in Eq. (1). An equi-
molar reaction of 1-decene with MMA in the presence
of complex 1 and NaBARF as the catalyst yielded a
mixture of the copolymer of the two olefinic substrates
and a small amount of MMA homopolymer, which was
removed by reprecipitation of the products from
1,1,2,2-tetrachloroethane/acetone. Gel permeation
chromatography (GPC) measurement of the copolymer
showed unimodal elution corresponding to
\[
M_n = 11,000, \quad M_w/M_n = 1.51 \quad \text{(GPC, polystyrene standards)} \quad \text{(Table 1, run 1).}
\]

Higher charged ratio of MMA to 1-decene did not
change the incorporated ratio of the copolymer
(Table 1, run 2-4). The decrease in isolation yield of
the polymer caused by higher MMA amount can be
attributed to strong binding of the carbonyl group of
MMA to retard insertion of 1-decene into the Pd-polymer
bond and/or to increase the low molecular weight frac-
tion not isolated as an insoluble solid. Polymerization
at 0 °C resulted in formation of the copolymer with
higher molecular weight and in higher isolation yield
(Table 1, run 5-8). Melting points of the copolymer
prepared at room temperature (32.6 °C and 34.1 °C)
were lower than those obtained at 0 °C (53.5-62.4 °C).
Pd(II) complexes with common bipyridine and ethylene
diamine ligands did not catalyze such copolymeriza-
tion.

Degree of branching also varied depending on the
temperature of copolymerization, 55-58/1000°C at room
temperature and 42-48/1000°C at 0 °C. Polymerization
catalyzed by Pd complex 2 with bulky N-substituents
gave product with lower MMA incorporation (Table 1,
run 9, 10) because MMA has a 1,1-disubstituted olefin
structure, so coordination to the Pd center is disfavored
by the bulky supporting ligand compared to the sterically
less hindered 1-decene.

The 1H nuclear magnetic resonance (NMR) spectrum
of the polymer from the reaction of Table 1, run 1
included signals of OCH 3 hydrogen at 3.60 ppm and
vinylene (\'_{CH} - CH_{2}) and allylic (\'_{C - CH_{2}}) hydrogens at
5.34 ppm and 1.91 ppm, respectively. No signals
assigned to vinyl hydrogens (\'_{CH_{2} - CH}) and vinylene
hydrogens of the \(\alpha\),\(\beta\)-unsaturated ester group (\'_{CH = C(Me)-COOMe}) were observed. Ratio of the OMe
hydrogen signal to the other hydrogens corresponded to
the incorporation of MMA at 1.4 mol%.

\[\text{Figure 1(a)}\]
shows the 13C{1H} NMR spectrum of the 1-decene/
MMA copolymer. Small signals at 51.6, 39.7, 32.8,

| Run | Catalyst | [Pd]/[MMA]/[1-decene] | Temp. \[^{\circ}\text{C}\] | Yield [mg] | MMA incorp.\[^{\text{b}}\] [mol\%] | \(M_n\) by GPC\[^{\text{c}}\] | Branch\[^{\text{d}}\] | \(T_m\) \[^{\circ}\text{C}\] |
|-----|----------|------------------------|-----------------|-----------|----------------|-----------------|----------|----------|
| 1   | 1        | 1/100/100              | r.t.            | 33.4      | 1.4            | 11000 (1.51)    | 58       | 34.1     |
| 2   | 1        | 1/200/100              | r.t.            | 45.0      | 1.3            | 10000 (1.51)    | 55       | 32.6     |
| 3   | 1        | 1/400/100              | r.t.            | 11.0      | 1.6            | 5100 (1.52)     | 55       | -        |
| 4   | 1        | 1/1000/100             | r.t.            | N.D.      | -              | -               | -        | -        |
| 5   | 1        | 1/10/100               | 0               | 187       | 0.3            | 20000 (1.75)    | 42       | -        |
| 6   | 1        | 1/100/100              | 0               | 105       | 0.6            | 31000 (1.88)    | 48       | 53.5     |
| 7   | 1        | 1/200/100              | 0               | 96.1      | 0.7            | 25000 (1.53)    | 46       | 62.4     |
| 8   | 1        | 1/300/100              | 0               | 37.0      | 0.8            | 17400 (1.85)    | 46       | 61.7     |
| 9   | 2        | 1/100/100              | r.t.            | 27.3      | 0.3            | 16000 (1.52)    | 60       | 37.2     |
| 10  | 2        | 1/200/100              | r.t.            | 24.0      | 0.5            | 11000 (1.50)    | 61       | 35.0     |
| 11  | 1        | 1/0/100                | r.t.            | 201       | -              | -               | 53       | 29.4     |

\[^{\text{a}}\] Reaction condition: [Pd] = 0.020 mmol, [NaBARF] = 0.024 mmol, solvent = CH 2 Cl 2 (2.0 mL), 72 h. \[^{\text{b}}\] Molar fraction of MMA unit in the isolated copolymer. \[^{\text{c}}\] Polystyrene standard. \[^{\text{d}}\] Per 1000 carbons. Determined by 1H NMR of the reaction mixture.
and 17.2 ppm were assigned to the methoxy(d), methine(b), methylene(a), and methyl(c) carbons of the MMA unit at the polymer end. The carbonyl carbon signal was observed at 177.3 ppm. These signals were assigned based on the distortionless enhancement by polarization transfer (DEPT) spectrum (135°) and similarity of the positions to those of a model compound (methyl 2-methylpentanoate, 50.9, 39.3, 33.6, and 16.6 ppm). The 1H and 13C{1H} NMR spectra of the copolymer indicated terminal methacrylate unit rather than α, β-unsaturated ester structure, as observed in the copolymer formed via polymerization catalyzed by Ni complexes with chelating P-O ligands13,14).

Figure 1 shows the 13C{1H} NMR spectrum of the 1-decene/MMA copolymer containing carbonyl carbon enriched with 13C. The signal of the methine carbon of the terminal MMA group (b') was observed as a doublet with 13C-13C coupling of 52.5 Hz.

Scheme 1 shows the pathway for successive insertion of MMA and 1-decene in the copolymerization. 2,1-Insertion of MMA into the Pd-CH2 bond forms the intermediate (A), as shown in Scheme 1.

The intermediate with a four-membered ring undergoes isomerization via a chain-walking mechanism to a more stable five-membered cyclic intermediate (B) and into a six-membered cyclic intermediate (C).

Further 1,2- or 2,1-insertion of 1-decene into the Pd-C bond of (B) produces the polymer structure with the -CH(CH2CH2R)-C(CH3)-COOCH3 group as the pendant (Scheme 2).

Insertion of 1-decene into the Pd-C bond of (C) produces the polymer with the -CH2-C(CH3)-COOCH3 end group, as shown in Scheme 3. The 13C{1H} NMR results shown in Fig. 1 are consistent with this end structure. Thus, successive insertion of MMA and 1-decene involves isomerization of the initially formed intermediate (A) with a four-membered ring structure into intermediate (C) with a six-membered metallacyclic structure prior to insertion of 1-decene.

Insertion of MMA into a Pd-C bond was found to in-
volve the methyl-palladium complex with the diimine ligand undergoing 1,2-insertion of MMA to form the resulting cyclic Pd complex (D), as shown in Scheme 4 (16).

However, structure (D) was not observed in the $^{13}$C NMR spectrum of the copolymer. Thus, insertion of MMA into the Pd-poly(1-decene) bond occurs by 2,1-insertion preferentially, whereas the insertion of MMA into the Pd-Me bond proceeds via 1,2-insertion, as reported before.

### 2.2 Copolymerization of 1-Decene with Other Methacrylates

Pd-diimine complexes catalyzed the copolymerization of 1-decene with other alkyl methacrylates, as shown in Chart 1 and summarized in Table 2. The copolymers were obtained using $t$-butyl methacrylate ($t$-BMA, Table 2, run 1), $n$-butyl methacrylate ($n$-BMA, Table 2, run 2) and $i$-amyl methacrylate (IAMA, Table 2, run 3), and the $^{13}$C($^1$H) NMR spectra of the comonomer suggest the terminal saturated ester structure similar to the copolymer of 1-decene with MMA.

The results suggested 2,1-insertion of the comonomer and the chain-walking reaction occurred prior to further insertion of a new monomer. 2-Acetoxyethyl methacrylate (HEMA-Ac, Table 2, run 4) with an acetyl group attached to the ethyl methacrylate also co-

### Table 2 Copolymerization of Methacrylate Monomers with 1-Decene by Pd-diimine Catalysts (17)

| Run | Methacrylate | [Pd]/[comonomer]/[1-decene] | Time [h] | Conv.[a] [mol%] | MMA incorp.[b] [mol%] | Yield [mg] | MMA incorp.[c] [mol%] | $M_n$ by GPC[d] | Branch[e] | $T_m$ [°C] |
|-----|--------------|-----------------------------|----------|-----------------|----------------------|------------|----------------------|-----------------|----------|------------|
| 1   | $t$-BMA      | 1/200/100                   | 24       | 1.8             | 81.0                 | 75         | 1.00                 | 7800 (1.51)     | 53       | 35.4       |
| 2   | $n$-BMA      | 1/200/100                   | 72       | 14.8            | 66.2                 | 60         | 1.40                 | 5600 (1.52)     | 51       | 33.4       |
| 3   | IAMA         | 1/200/100                   | 72       | 0.7             | 53.0                 | 64.1       | 1.40                 | 6200 (1.48)     | 59       | 34.1       |
| 4   | HEMA-Ac      | 1/200/100                   | 72       | 11.0            | 62.0                 | 117        | 1.54                 | 6900 (1.89)     | 49       | 32.1       |
| 5   | HEMA         | 1/200/100                   | 48       | N.D.            | 90.1                 | -          | -                    | -               | -        | -          |
| 6   | MAA          | 1/200/100                   | 3        | 43.7[c]        | 99.0[c]              | 159        | N.D.                | 10000 (1.59)    | 56       | 34         |
| 7   | IPEMA        | 1/200/100                   | 48       | 10.1            | 72.4                 | 70.1       | 2.80                 | 6600 (1.51)     | 57       | 32.8       |
| 8   | AMA          | 1/10/100                    | 48       | 38.8            | 88.5                 | 116        | 1.30                 | 8500 (1.50)     | 51       | 19.6       |
| 9   | AMA          | 1/50/100                    | 48       | 17.8            | 21.8                 | 32         | 7.30                 | 4900 (1.46)     | 51       | 26.8       |
| 10  | AMA          | 1/100/100                   | 48       | 5.7             | 10.2                 | 18         | -                    | 3600 (1.42)     | -        | 21.5       |
| 11  | AMA          | 1/200/100                   | 72       | 2.8             | 5.1                  | 6.7        | 18.5                 | 2600 (1.26)     | 53       | -          |
| 12  | allyl acetate| 1/10/100                    | 72       | 24.3            | 73.3                 | 172        | 1.29                 | 9400 (1.46)     | 55       | 34.6       |
| 13  | allyl acetate| 1/100/100                   | 72       | 5.1             | 7.6                  | N.D.      | -                    | -               | -        | -          |

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**Footnotes:**

- **a)** Reaction condition: [Pd] = 0.020 mmol, [NaBARF] = 0.024 mmol, in CH$_2$Cl$_2$ (2.0 mL), temp. = r.t..
- **b)** Determined by GC of the reaction mixture.
- **c)** Molar fraction of methacrylate unit in the isolated copolymer.
- **d)** Polystyrene standard. $M_n$ and $M_w$ are in parenthesis.
- **e)** Per 1000 carbons. Determined by $^1$H NMR of the reaction mixture.
polymerizes with 1-decene under similar conditions. 
$^{13}$C{$^1$H} NMR suggested 2,1-insertion of HEMA-Ac at
the terminal of the polymer. On the other hand,
polymerization of 1-decene in the presence of 2-
hydroxyethyl methacrylate (HEMA, Table 2, run 5)
produced poly(1-decene) without the comonomer unit.
We think that coordination of the hydroxyl groups of
HEMA or methacrylic acid (MAA) to the palladium
inhibited the insertion of new monomers. Isoprenyl
methacrylate with two different vinylidene groups also
copolymerized with 1-decene (Table 2, run 7).

Figure 2(a) shows the $^1$H NMR spectrum of the
copolymer. Signals of both unreacted isoprenyl and
methacryloyl groups were observed in the ratio of 76 : 24.
Copolymerization of 1-decene and isoprenyl acetate
is reported to form polymers with comonomer units
in both the polymer chain and at the polymer end.

The methacryloyl group in the difunctional comonomer
reacts more readily than the isoprenyl group, probably
because coordination of the carbonyl group to Pd center
induces insertion of the methacryloyl group into the
Pd-polymer bond. On the other hand, allyl methacryl-
ate (AMA), which also has two olefin structures, reacted
at the allyl group preferentially probably due to less
severe steric hindrance and much less significant polar-
ization of the olefinic group of the allyl group than
the methacryloyl group. The $^1$H NMR spectrum of 1-
decene/AMA copolymer shows the methacryloyl signal
does not show the allyl signal due to unreacted copoly-
mer (Fig. 2(b)). The allyl signal (CH$_2$O, 4.07 ppm,
$^1$I = 6.0 Hz) was observed as a triplet, which suggested
2,1-insertion and incorporation at the polymer chain
terminal of AMA. These results suggested that inser-
tion of olefin groups becomes less easy in the order,
allyl $>$ methacryloyl $>$ isoprenyl.

Use of a large amount of AMA comonomer caused
lower yield of the polymeric product, attributed to
$\beta$-carboxylate elimination from the intermediate formed
by insertion of the comonomer (Scheme 5).

3. Conclusions

Pd-diimine complexes catalyzed copolymerization of
1-decene with MMA to form a polymer with the $\text{CH}_2$-
C(Me)COOMe group via 2,1-insertion of MMA and
the chain-walking reaction. These catalysts can incor-
porate not only MMA but also other methacrylates with
various functional groups into polyolefins. In particu-
lar, AMA with two olefin structures reacted at one ole-
finic group only and IPEMA reacted at both olefinic
groups. Therefore, polyolefins with terminal olefin
units can be obtained. In the future, synthesis of ter-
minaly functionalized branch polyolefins may be car-
ried out through reactions at the terminal olefin.

4. Experimental Section

4.1. General Method

All synthetic manipulations were carried out under
nitrogen or argon using standard Schlenk techniques.
$^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a
Bruker AVANCE-400 spectrometer (400 MHz),
JEOL400YH spectrometer (400 MHz) or JEOL JNM-500 spectrometer (500 MHz). The peaks were referenced to residual nondeuterated solvents as follows: CDCl$_3$, 7.26 ppm ($^1$H) and 77.0 ppm ($^{13}$C), C$_2$D$_2$Cl$_4$, 5.91 ppm ($^1$H) and 74.2 ppm ($^{13}$C). GPC was performed at 40 °C on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV/Vis detector, using tetrahydrofuran as eluent at a flow rate of 0.6 mL min$^{-1}$ with TSKgel SuperHM-L and SuperHM-M columns. The molecular weights were calibrated based on polystyrene standards. DSC was recorded on a METTLER TOLEDO DSC822e instrument.

4.2. Materials

Anhydrous dichloromethane, 1-decene and methacrylate esters (MMA, HEMA, AMA, MAA) were purchased and used as received. Diimine ligands$^{(18)}$, Pd-diimine complexes$^{(19)}$, and NaBARF$^{(20)}$ were synthesized according to previously reported methods.

4.3. Copolymerization of 1-Decene with Methacrylate

To a 25 mL Schlenk tube containing a CH$_2$Cl$_2$ solution (2 mL) of Pd complexes 1 or 2 (0.020 mmol) NaBARF (0.024 mmol, 21.3 mg) was added under Ar or N$_2$. After stirring for 2 min at r. t., a methacrylate ester (0.20, 1.00, 2.00, 4.00, 6.00, 8.00 or 20.0 mmol) and 1-decene (2.00 mmol, 281 mg) were added to the solution. The mixture was stirred for 72 h. HSIE$_3$ was added to quench the polymer growth, and the reaction mixture was poured into a large amount of methanol. After filtration, the precipitate was dissolved in 1,1,2,2-tetrachloroethane (1.0 mL) and diethylammonium N,N-diethyldithiocarbamate (0.08 mmol, 17.8 mg) was added. After stirring for 1 h at 70 °C, the reaction mixture was poured into a large amount of methanol. After filtration, the precipitate was dissolved in 1,1,2,2-tetrachloroethane (1.0 mL) at 70 °C, and the reaction mixture was poured into a large amount of acetone. The volatile fractions were removed in vacuo at 80 °C to give the polymer as colorless grease.

4.4. Calculation of Degree of Branching

The degree of branching was estimated by $^1$H NMR as follows

$$\text{branches} = \frac{I_{\text{CH}_3} + 1000 \times I_{\text{CH}}}{3} - I_{\text{CH}} - I_{\text{CH}_3+\text{CH}}$$

where $I_{\text{CH}_3}$ is the intensity of the signals at $\delta$ 0.6 to 1.0, $I_{\text{CH}_3+\text{CH}}$ is the intensity of the signals at $\delta$ 1.0 to 1.5, $I_{\text{CH}} = I_{\text{CH}_3}/3$, and $I_X$ is the intensity of the signals at $\delta$ 0.6 to 1.5 due to the unit from the comonomer.

4.5. Calculation of Incorporation of the Comonomer

Incorporation of the comonomer was estimated by $^1$H NMR as follows

$$\text{incorporation} = \frac{I_{\text{CH}_3}}{I_X}$$

References

1a) Moad, G., Prog. Polym. Sci., 24, (1), 81 (1999).
1b) Oliphant, K. E., Russell, K. E., Baker, W. E., Polymer, 36, (8), 1597 (1995).
1c) Li, C., Zhang, Y., Zhang, Y., Polym. Test., 22, (2), 191 (2003).
2a) Dong, J. Y., Hong, T. C., Chung, H. C., Wang, H. C., Datta, S. Macromolecules, 36, (16), 6000 (2003).
2b) Wang, Z. M., Hong, H., Chung, T. C., Macromolecules, 38, (22), 8966 (2005).
2c) Oromiehie, A., Ebadi-Dehaghani, H., M infrared, S., Int. J. Chem. Eng. Appl., 5, (2), 117 (2014).
2d) Chung, T. C., Xu, G., Lu, Y., Hu, Y., Macromolecules, 34, (23), 8040 (2001).
3a) Johnson, L. K., Mecking, S., Brookhart, M., J. Am. Chem. Soc., 118, (1), 267 (1996).
3b) Nakamura, A., Anselment, T. M., Claverie, J., Goodall, B., Jordan, R. F., Mecking, S., Rieger, B., Sen, A., van Leeuwen, P. W. N. M., Nozaki, K., Acc. Chem. Res., 46, (17), 1438 (2013).
4) Drent, E., van Dijk, R., van Ginkel, R., van Oort, B., Pague, R. L., Chem. Commun., (7), 744 (2002).
5) Kochi, T., Yoshimura, K., Nozaki, K., Dalton Trans., (1), 25 (2006).
6) Skupov, K. M., Marella, P. R., Simon, M., Yap, G. P. A., Allen, N., Conner, D., Goodall, B. L., Claverie, J. P., Macromol. Rapid Commun., 28, (20), 2035 (2007).
7) Guirondet, D., Roelse, P., Rünzi, T., Göttert-Schnettmann, I., Mecking, S., J. Am. Chem. Soc., 131, (2), 422 (2009).
8) Guirondet, D., Caporaso, L., Neuwald, B., Göttert-Schnettmann, I., Cavallio, L., Mecking, S., J. Am. Chem. Soc., 132, (12), 4410 (2010).
9) Kryuchkov, V. A., Daigle, J.-C., Skupov, K. M., Claverie, J. P., Winnik, F. M., J. Am. Chem. Soc., 132, (44), 15573 (2010).
10) Rünzi, T., Fröhlich, D., Mecking, S., J. Am. Chem. Soc., 132, (50), 17690 (2010).
11) Takano, A., Takouchi, D., Osakada, K., Akamatsu, N., Shishido, A., Angew. Chem. Int. Ed., 53, (35), 9246 (2014).
12) Rünzi, T., Guirondet, D., Göttert-Schnettmann, I., Mecking, S., J. Am. Chem. Soc., 132, (46), 16623 (2010).
13) Gibson, V. C., Tomov, A., Chem. Commun., (19), 1964 (2001).
14) Chen, M., Chen, C., Angew. Chem. Int. Ed., 57, (12), 3094 (2018).
15a) Yasuda, H., Nakano, R., Ito, S., Nozaki, K., J. Am. Chem. Soc., 140, (5), 1876 (2018).
15b) Mitsushige, Y., Yasuda, H., Carnow, B. P., Ito, S., Kobayashi, M., Tayano, T., Watanabe, Y., Okuno, Y., Hayashi, S., Kuroda, J., Okumura, Y., Nozaki, K., ACS Macro Lett., 7, (3), 305 (2018).
16) Borkar, S., Yennawar, H., Sen, A., Organometallics, 26, (19), 4711 (2007).
17) Takeuchi, D., Yamada, T., Nakamura, Y., Osakada, K., Aratani, I., Suzuki, Y., Organometallics, 38, (11), 2323 (2019).
18) van Asselt, R., Elsevier, C. J., Smeets, W. J. J., Spek, A. L., Benedix, R., Recl. Trav. Chim. Pays-Bas., 113, (2), 88 (1994).
19a) Johnson, L. K., Killian, C. M., Brookhart, M., J. Am. Chem. Soc., 117, (23), 6414 (1995).
19b) Rüllke, R. E., Delis, J. G. P., Groot, A. M., Elsevier, C. J., van Leeuwen, P. W. N. M., Vrieze, K., Goubitz, K., Schenk, H., J. Organomet. Chem., 588, (1-2), 109 (1996).
19c) Killian, C. M., Tempel, D. J., Johnson, L. K., Brookhart, M., J.
要 旨

バラジウム-ジイミン錯体触媒による1-デセンとメタクリル酸エステルの共重合

山田 高義1), 2), 竹内 大介1), 3), 小坂田 豊太郎1), 荒谷 一弘1)

1) 東京工業大学化学生命科学研究科，226-8503 横浜市緑区長津田町4259
2) (株) クレレスト研究センター，305-0841 茨城県つくば市御幸が丘41
3) 弘前大学理工学部物質創成化学科，036-8561 青森県弘前市文京町3

後期遷移金属触媒によるオレフィンと極性モノマーとの共重
合によって，炭化水素オリオレフィンに新しい機能を付与することができる。本研究では，Brookhart型のバラジウム-ジイミ
ン錯体を触媒に用いて，1-デセンとメタクリル酸エステルとの共重合を行った。メタクリル酸メチル(MMA)との共重合では，
極性基を末端に有する分歧状の生成物が得られた。共重合体の平均分子量はおよそ10,000 ～ 31,000であった。同位体標識を用
いたNMRスペクトルの解析により，極性基を含む末端構造を決定した。これによって，MMAが高分子生成末端に2,1-挿入
し，続く異性化で生じた六員環バラジウム錯体に1-デセンが挿
入し，その後水素脱離により高分子が生成することが明らかに
なった。各種のメタクリル酸エステルと1-デセンとの共重合体
を得た。メタクリル酸イソブレニルとの共重合体は，極性モノ
マーの二つの炭素炭素二重結合の両方が重合に関与した新しい
構造を有する高分子であった。