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Copolymerization of Ethylene with Methylenecyclopropanes Promoted by Cobalt and Nickel Complexes

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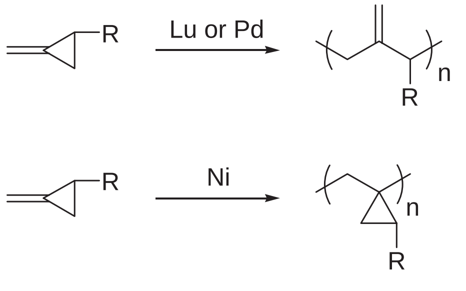
The cobalt and nickel complexes promote addition polymerization of substituted methylenecyclopropanes as well as their copolymerization with ethylene to afford the polymers that contain three-membered rings. The homopolymerization of 2-aryl-1-methylenecyclopropane catalyzed by $[CoCl_2(L)]$–MMAO (L = bis(1-iminoalkyl)pyridine ligand) at −40 °C produces the polymers $-(CH_2-\overline{CCH_2C}HAr)-$ with a narrow molecular weight distribution. The copolymer of ethylene and 2-aryl-1-methylenecyclopropane is also obtained by using the same catalyst. The ratio of the two monomer units varies in the range from 0 to 0.5 depending on the concentration of ethylene and 2-aryl-1-methylenecyclopropane. $^{13}C\{^1H\}$ NMR spectrum of the alternating copolymer exhibits a single sharp signal for each carbon of the repeating units. Ethylene and 7-methylenebicyclo[4.1.0]heptane also undergo alternating copolymerization to produce the polymer having the C4 repeating unit containing a bicyclic group. Heating the polymer at 130 °C causes ring-opening isomerization to afford the polymer having a C=C double bond in the main chain. Mixtures of $[Ni(\pi\text{-}C_3H_5)Br]_2$, a diimine ligand, and cocatalysts such as NaBARF and Et_2AlCl, initiate the copolymerization of ethylene with 2-aryl-1-methylenecyclopropane to give a random copolymer with a low molecular weight ($M_n = 1000–2000$).

Polycycloolefins including polynorbornenes have potential uses as optical materials and engineering plastics because these polymers with regulated structure exhibit optical transparency and a high melting point (T_m) or a glass transition temperature (T_g).[1] Copolymers of ethylene and the cycloolefin show lower T_m and T_g than the homopolymers with a cyclic structure in the monomer units. They could be obtained from the polymerization of a single monomer only with great difficulty. The thermal properties of the copolymers can be controlled by changing the ratio of the two monomer units contained in the polymer chain. Various transition metal complexes copolymerize ethylene with norbornene in the presence of methylaluminoxane (MAO).[2] The copolymerization catalyzed by zirconocenes produces the polymers with high optical transparency. A detailed study of the reaction revealed that successive insertion of norbornene into the metal–polymer bond was much less favored than alternating insertion of the two monomers.[2b] Pd complexes were also reported to catalyze the copolymerization of ethylene and norbornene to give a copolymer with a high norbornene content.[3] Alternating copolymerization of ethylene with cyclopentene was catalyzed by the vanadium complexes,[4] bis(phenoxyimine)titanium complex,[5] and (indenylamido)titanium complex,[6] to afford the polymers composed of the C4 repeating units with a five- or six-membered ring. Random copolymerization of ethylene with norbornene having polar groups was promoted by the Ni complexes.[7]

Copolymerization of ethylene with other cyclic monomers is much less common. Marks et al. reported the copolymerization of ethylene with 7-methylenebicyclo[4.1.0]heptane, which accompanied the ring opening of the bicyclic monomer. The produced polymers have six-membered ring and olefin functionality,[8] although the structure of the polymers is not regulated well. Recently, we reported addition polymerization of 2-aryl- and 2-ethoxycarbonyl-1-methylenecyclopropanes promoted by Ni complexes to form polymers with three-membered rings (Scheme 1).[9] The absence of ring opening during the polymerization contrasts with the results of the ring-opening polymerization of methylenecyclopropane catalyzed by the Zr and Lu catalyst[10] and of 2-aryl-1-methylenecyclopropanes catalyzed by Pd complexes.[11,12] Copolymerization of ethylene with methylenecyclopropanes without ring-opening would afford polymers having the three-membered rings in lower density than the homopolymers of methylenecyclopropanes. Herein, we report the new living polymerization of 2-phenyl-1-methylenecyclopropane promoted by Co complexes and the copolymerization of ethylene with methylenecyclopropanes promoted by Co and Ni complexes. A part of this study was presented in a preliminary form.[13]

Results and Discussion

Addition Polymerization of 2-Aryl-1-methylenecyclopropanes by Cobalt Complexes. The cobalt complexes with bis(1-iminoalkyl)pyridine ligands have been known to catalyze ethylene polymerization in the presence of modified methyl-



Scheme 1. Polymerization of methylenecyclopropanes.

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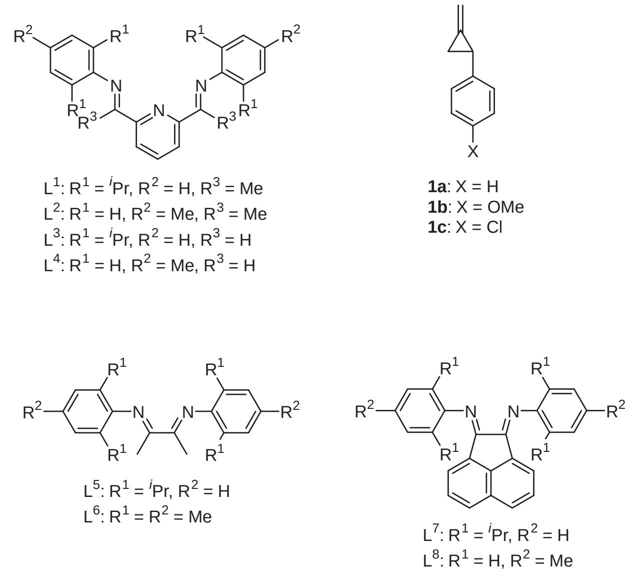


L^1: $R^1 = {}^i\text{Pr}$, $R^2 = \text{H}$, $R^3 = \text{Me}$
L^2: $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{Me}$
L^3: $R^1 = {}^i\text{Pr}$, $R^2 = \text{H}$, $R^3 = \text{H}$
L^4: $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{H}$

1a: X = H
1b: X = OMe
1c: X = Cl

L^5: $R^1 = {}^i\text{Pr}$, $R^2 = \text{H}$
L^6: $R^1 = R^2 = \text{Me}$

L^7: $R^1 = {}^i\text{Pr}$, $R^2 = \text{H}$
L^8: $R^1 = \text{H}$, $R^2 = \text{Me}$

Chart 1.

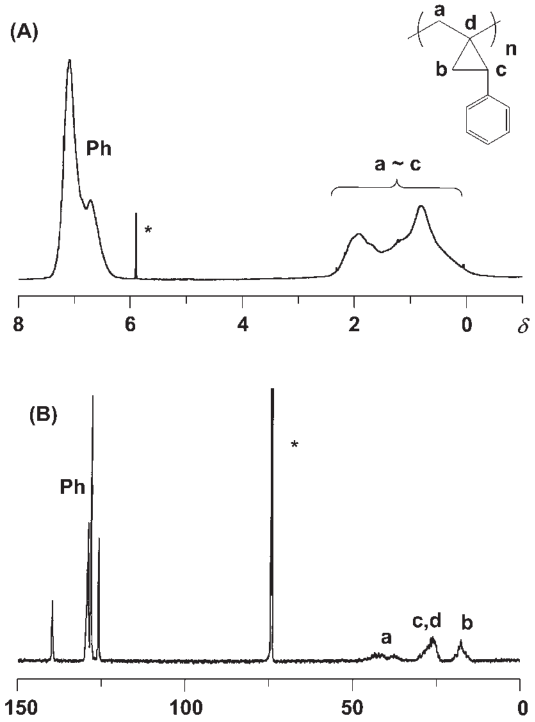
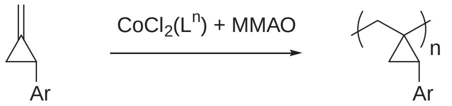


Fig. 1. (A) ^{1}H (rt) and (B) ^{13}C{^{1}H} NMR (130 °C) spectra of **2a** in $C_2D_2Cl_4$ at 130 °C. The signals marked by an asterisk are due to the solvent.

aluminoxane (MMAO),[14,15] although they are not suited for the catalyst of polymerization of propylene and α-olefins.[16] Polymerization of 2-aryl-1-methylenecyclopropanes was conducted by using the Co complexes as catalysts. Chart 1 lists the ligands of the Co complexes employed in this study. 2-Aryl-1-methylenecyclopropanes, **1a**–**1c**, undergo addition polymerization in the presence of [$CoCl_2(L^1)$] ($L^1 = C_5H_3N\{\text{–(Me)C=N–}C_6H_3{}^iPr_2\text{-2,6}\}_2\text{-2,6}$) and MMAO to afford the polymers containing cyclopropylidene groups, **2a**–**2c** (Eq. 1).



(1)

1a: Ar = C_6H_5
1b: Ar = C_6H_4OMe-4
1c: Ar = C_6H_4Cl-4

2a: Ar = C_6H_5
2b: Ar = C_6H_4OMe-4
2c: Ar = C_6H_4Cl-4

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a** contain broad signals assigned to the hydrogens and carbons of the cyclopropane rings at δ −0.1–2.4 (^{1}H) and δ 13–47 (^{13}C{^{1}H}), as shown in Fig. 1. The peak positions are similar to those of the polymer of 2-phenyl-1-methylenecyclopropane obtained from Ni complex-promoted polymerization. The absence of the signals of olefinic carbons and hydrogens indicates no occurrence of ring opening during the polymerization.

Table 1 summarizes the results of the polymerization. The reaction of 2-phenyl-1-methylenecyclopropane promoted by [$CoCl_2(L^1)$] ([monomer]/[Co] = 200) at room temperature forms polymer **2a** with $M_n = 24000$ ($M_w/M_n = 1.45$) (Run 1). The complex with the ligand without substituents at ortho position of phenyl group (L^2) gives the polymer with $M_n = 31000$ ($M_w/M_n = 2.04$) (Run 2). The bulky ortho substituents facilitate the formation of narrow molecular weight distribution. The Co complexes with ligands L^3 and L^4 and a mixture of $CoCl_2$ and diimine ligand, L^5, show negligible catalytic activity for the polymerization (Runs 3–5), which indicates that the rigid structure of bis(1-iminoalkyl)pyridine ligand is necessary for smooth polymerization. The reaction using PMAO cocatalyst affords the polymer with $M_n = 24000$ ($M_w/M_n = 1.45$) in a higher yield (85%) (Run 6) than that using MMAO as the cocatalyst (55%) (Run 1). Although Me_3Al or Et_2AlCl was not effective as the cocatalyst of the polymerization (Runs 7 and 8), the polymerization using ${}^iBu_3Al$/NaBARF (NaBARF = NaB{$C_6H_3(CF_3)_2$-3,5}$_4$) initiated the polymerization to produce **2a** quantitatively (Run 9). The amount of MMAO can be reduced to ten times molar amount of Co (Run 13). The reaction with [Al]/[Co] = 30 results in the highest yield of the polymer among Runs 10–14.

The polymers obtained from the reaction at 0 °C and −40 °C have narrow molecular weight distribution (M_w/M_n = 1.15 and 1.16) (Runs 15 and 16). Figure 2A plots the relationship between the conversion of the monomer **1a** in the polymerization at −40 °C and the molecular weight of the polymer determined by GPC (gel permeation chromatography). The molecular weights of **2a** are close to those calculated from the monomer-to-catalyst ratio and increase in proportion to the conversion of the monomer. A decrease of the M_w/M_n ratio of the growing polymer from 1.31 to 1.12 is noted during the reaction. These results indicate the living polymerization with slower initiation than propagation of the polymer. As shown in Fig. 2B, the polymer obtained from the reactions with different initial molar ratios of **1a** to Co shows a linear relationship between M_n and the monomer-to-catalyst ratio. In each reaction, the produced polymer had a narrow molecular weight distribution (M_w/M_n = 1.10–1.20). The growing end of the polymer is stable at −40 °C; this stability was examined by the polymer growth caused by stepwise addition of the monomer. Polymerization of **1a** promoted by [$CoCl_2(L^1)$]/MMAO with [**1a**]/[Co] = 50 at −40 °C causes complete consumption

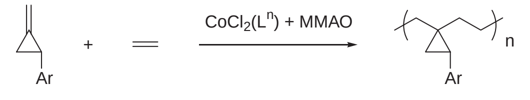
Table 1. Polymerization of Methylenecyclopropanes by Co Complexes[a)]

Run	Monomer	Co catalyst	cocatalyst	Al/Co	Temp /°C	Time /min	Yield /%	M_n[b)] /g mol^{-1}	M_w/M_n[b)]
1	**1a**	$[CoCl_2(L^1)]$	MMAO	300	rt	15	55	24000	1.45
2	**1a**	$[CoCl_2(L^2)]$	MMAO	300	rt	15	38	31000	2.04
3	**1a**	$[CoCl_2(L^3)]$	MMAO	300	rt	15	trace	—	—
4	**1a**	$[CoCl_2(L^4)]$	MMAO	300	rt	15	trace	—	—
5	**1a**	$CoCl_2 + L^5$	MMAO	300	rt	30	trace	—	—
6	**1a**	$[CoCl_2(L^1)]$	PMAO	300	rt	15	85	24000	1.45
7	**1a**	$[CoCl_2(L^1)]$	Me_3Al	300	rt	30	trace	—	—
8	**1a**	$[CoCl_2(L^1)]$	Et_2AlCl	300	rt	30	trace	—	—
9[c)]	**1a**	$[CoCl_2(L^1)]$	$^iBu_3Al$	30	rt	30	quant	51000	1.59
10	**1a**	$[CoCl_2(L^1)]$	MMAO	1000	rt	15	46	33000	1.34
11	**1a**	$[CoCl_2(L^1)]$	MMAO	100	rt	15	61	55000	1.41
12	**1a**	$[CoCl_2(L^1)]$	MMAO	30	rt	15	80	39000	1.39
13	**1a**	$[CoCl_2(L^1)]$	MMAO	10	rt	15	48	64000	1.60
14	**1a**	$[CoCl_2(L^1)]$	MMAO	3	rt	15	trace	—	—
15	**1a**	$[CoCl_2(L^1)]$	MMAO	300	0	15	quant	29000	1.16
16	**1a**	$[CoCl_2(L^1)]$	MMAO	300	−40	15	63	20000	1.15
17	**1b**	$[CoCl_2(L^1)]$	MMAO	300	−40	30	26	19000	1.54
18	**1c**	$[CoCl_2(L^1)]$	MMAO	300	rt	10	80	40000	1.24

a) Reaction conditions: $[Co] = 1.7 \times 10^{-6}$ M, [monomer]/[Co] = 200, in toluene (5 cm^3). b) Determined by GPC based on polystyrene standard. c) In the presence of NaBARF, [NaBARF]/[Co] = 1.

of the monomer after 0.5 h and produces the polymer with $M_n = 8300$ ($M_w/M_n = 1.16$). Further addition of the monomer ([**1a**]/[Co] = 100) leads to an increase of the molecular weight of the growing polymer to $M_n = 26000$ ($M_w/M_n = 1.14$). $[CoCl_2(L^1)]$/MMAO promotes the polymerization of 2-(4-methoxyphenyl)-1-methylenecyclopropane (**1b**) and 2-(4-chlorophenyl)-1-methylenecyclopropane (**1c**), giving the polymers with cyclopropylidene groups, **2b** and **2c**, also (Table 1, Runs 17 and 18).

Copolymerization of Ethylene with 2-Aryl-1-methylenecyclopropanes by Cobalt Complexes. Co complexes with bis(1-iminoalkyl)pyridine ligand promote the polymerization of both ethylene and 2-aryl-1-methylenecyclopropanes. The catalysis is applied to the copolymerization of these monomers. The copolymerization of ethylene (1 atm) with **1a** (0.11 g, 0.027 M in toluene) in the presence of $[CoCl_2(L^1)]$ and MMAO ([**1a**]/[Co]/[Al] = 200/1/300) at room temperature for 2 min produces the alternating copolymer of these monomers **3a** (0.046 g), as shown in Eq. 2. GPC traces of **3a** detected by RI and by UV (254 nm) show the identical unimodal elution pattern ($M_n = 58000$, $M_w/M_n = 2.84$ (RI)), suggesting the absence of polyethylene in the product. The ^{1}H NMR spectrum of **3a** shows the signals of the aliphatic hydrogens (δ 0.5–1.8) and the aromatic hydrogens (δ 6.9–7.3) (Fig. 3A). The pattern of the signals is quite different from that of the homopolymer of **1a**. These GPC and ^{1}H NMR data and the $^{13}C\{^1H\}$ NMR spectrum mentioned below all indicate that the product is a copolymer with regulated structure. The relative peak area ratios of the signals of **3a** indicating the monomer unit from ethylene and that from **1a** are in almost a 1:1 ratio. The $^{13}C\{^1H\}$ NMR spectrum of **3a** exhibits six sharp peaks due to the aliphatic carbons in the range: δ 17.2–38.3, as shown in Fig. 3B.[13a] The peaks were reasonably assigned to the carbons of the repeating unit of the alternating copolymer based on the $^{13}C\{^1H\}$ and DEPT (Distortionless Enhancement by Polarization Transfer) spectra as well as on a comparison of them with that of a model compound (1,1-dibutyl-2-phenylcyclopropane). The copolymerization of **1b** and **1c** with ethylene also proceeds smoothly. The $^{13}C\{^1H\}$ NMR spectra of **3b** and **3c** exhibit sharp signals, indicating the alternating copolymerization.



(2)

1a: Ar = C_6H_5
1b: Ar = C_6H_4OMe-4
1c: Ar = C_6H_4Cl-4

3a: Ar = C_6H_5
3b: Ar = C_6H_4OMe-4
3c: Ar = C_6H_4Cl-4

The copolymer of ethylene (1 atm) and **1a** (0.17 M in toluene) contains the monomer units of ethylene and of **1a** in 45:55, while the reaction with [**1a**] = 1.23 M produces the polymer having the monomer units in 26:74 ratio. Thus, an increase in the initial concentration of **1a** changes the ratio of the two monomer units in the copolymer. Figure 4 shows T_g of the copolymers. Homopolymer **2a** and the alternating copolymer exhibit glass transitions at 178 °C and at 71 °C, respectively. The T_g value of the copolymers increases with increase of the monomer unit from **1a**. The high T_g of **2a** is ascribed to the rigid polymer chain having the cyclopropylidene group and the aryl substituents.

Figure 5A shows the relationship between the initial molar ratio of the two monomers in the polymerization at 0 °C and the ratio of the two monomer units in the copolymer formed at early stage. The reaction of **1a** at a concentration lower than 82 mM ($[\text{ethylene}]_0/([\text{ethylene}]_0 + [\mathbf{1a}]_0) > 0.71$) produces the copolymer consisting of the two monomer units with a ratio close to unity. In contrast, the copolymer prepared from the reaction with $[\mathbf{1a}]_0$ at a concentration higher than 150 mM ($[\text{ethylene}]_0/([\text{ethylene}]_0 + [\mathbf{1a}]_0) < 0.57$) contains a portion

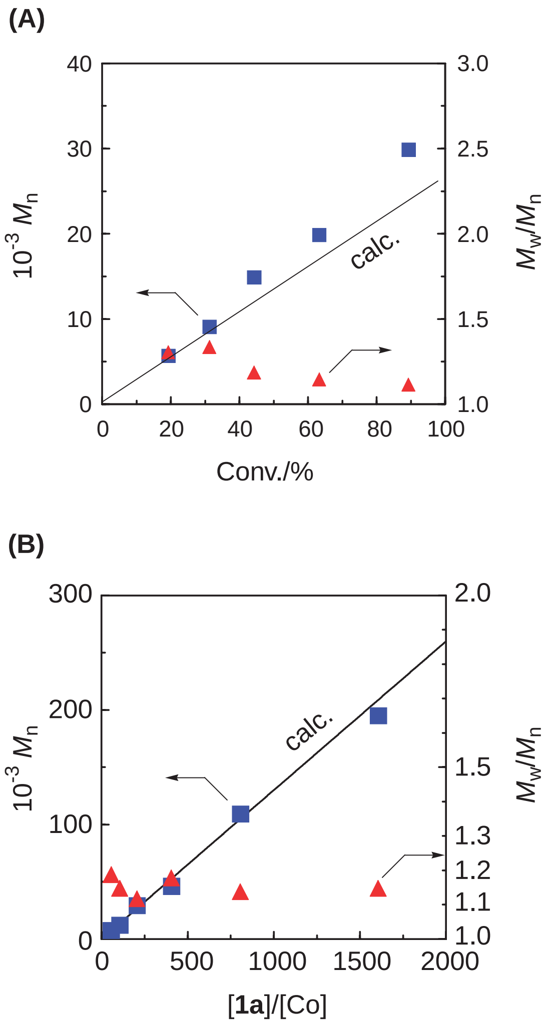


Fig. 2. Relationship between molecular weight and (A) conversion and (B) initial monomer-to-Co molar ratio of the polymerization of **1a** by $[CoCl_2(L^1)]$–MMAO. (A) $[\mathbf{1a}]_0/[Co]/[Al] = 200/1/300$ in toluene (5 mL) at −40 °C.

of the monomer unit from **1a** larger than that of the ethylene monomer unit. The copolymerization of **1c** with ethylene showed a similar relationship between the ratio of the initially charged monomers and the two monomer units in the formed copolymer. The copolymerization of ethylene with **1b** produces the polymer with lower content of ethylene than the other two copolymers prepared under the same conditions. Figure 5B displays linear Fineman–Ross plots of the copolymerization. The relative monomer ratios of $r_{\mathbf{1a}}$ and r_{ethylene} were calculated to be 0.30 and 0.01, respectively. ($r_{\mathbf{1b}}$, r_{ethylene}) and ($r_{\mathbf{1c}}$, r_{ethylene}) were obtained similarly to be (1.1, 0.05) and (0.18, 0.03), respectively.

Scheme 2 depicts the mechanism proposed for the alternating copolymerization. The growing polymer with the Co–CH_2–CH_2– bond (**A**) undergoes coordination of methylenecyclopropane and 1,2-insertion of its C=C bond into the Co–C bond to form intermediate **B**. The C=C bond of 2-aryl-1-methylenecyclopropane undergoes smooth coordination to Co of **A** and subsequent insertion of it into the Co–C bond. Both the coordination and the insertion of methylenecyclopropanes to transition metal are thermodynamically favored processes owing to the releases of ring strains of the molecules caused by the reactions.

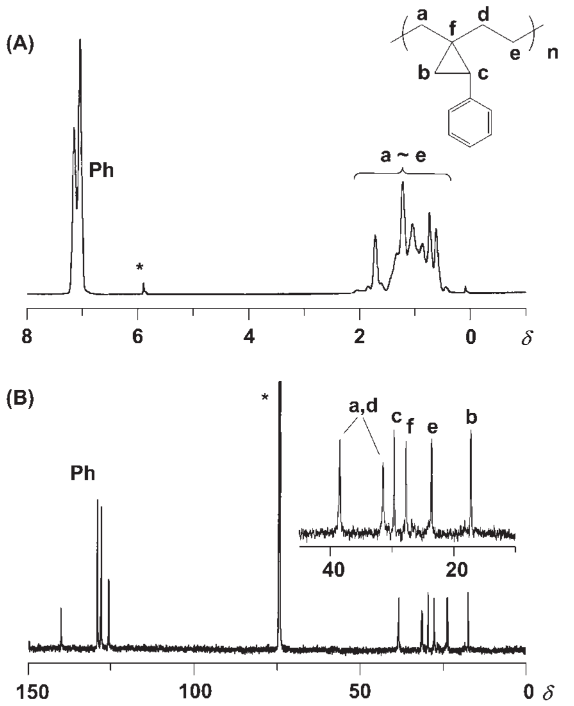


Fig. 3. (A) ^1H and (B) ^{13}C NMR spectra of **3a** in $C_2D_2Cl_4$ at 130 °C. The signals marked by an asterisk are due to the solvent.

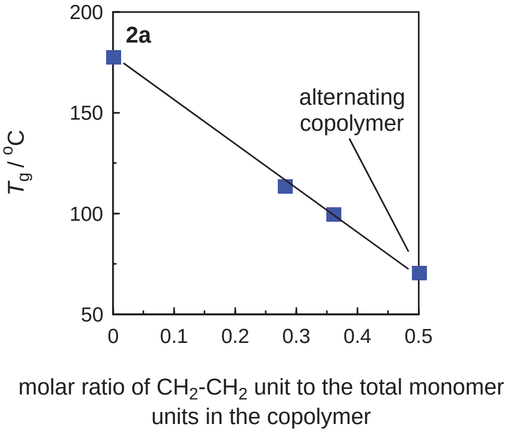


Fig. 4. Relationship between glass transition temperature of the produced copolymer and content of the monomer unit from ethylene in the copolymer.

Small r_{ethylene} values (0.01–0.05) calculated from the Fineman–Ross plots are consistent with selective insertion of methylenecyclopropanes into the Co–CH_2–CH_2– bond. This is in contrast with the alternating copolymerization of ethylene with norbornene catalyzed by the Zr and Ti complexes, in which double insertion of ethylene is much easier than that of the cyclic monomer ($r_{\text{ethylene}} > 1$). Coordination of methylenecyclopropane to transition metal is generally favored due to the release of the strained energy of the C=C double bond attached to the three-membered ring.[17]

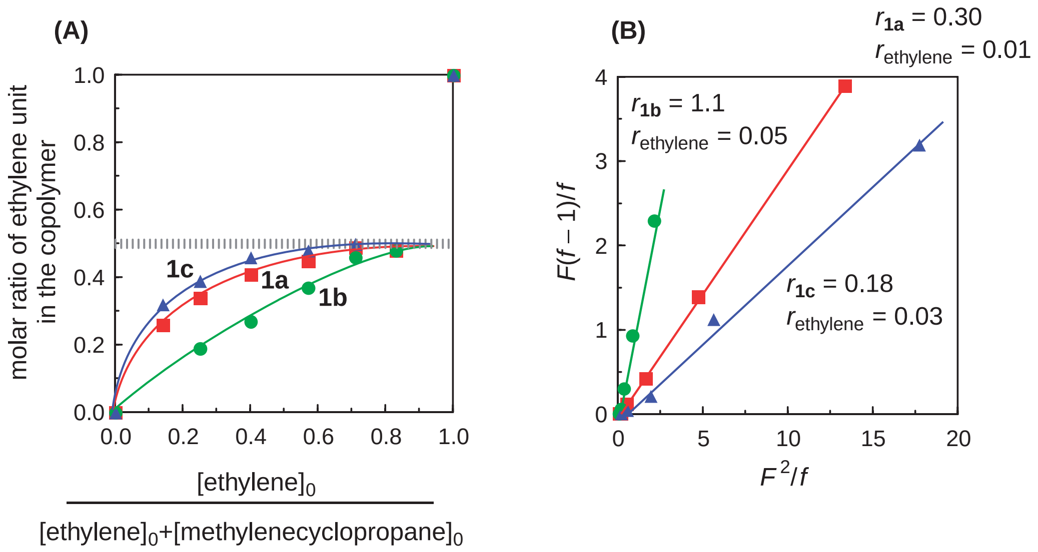
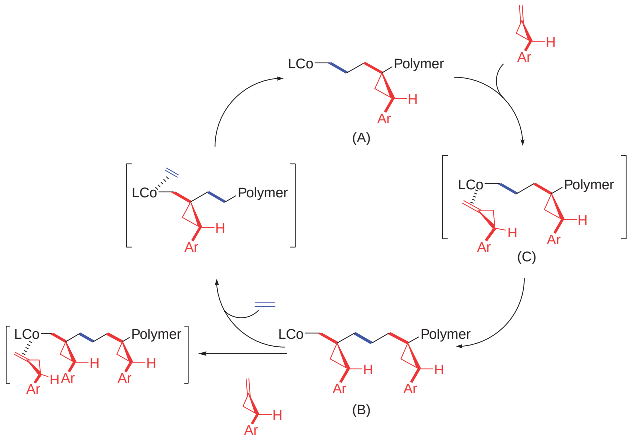


Fig. 5. (A) Relationship between ethylene content in the monomers and the content of the monomer unit from ethylene in the copolymer of ethylene with methylenecyclopropanes and (B) Fineman–Ross plots of the copolymerization. F = [methylenecyclopropane]$_0$/[ethylene]$_0$ in monomer. f = [methylenecyclopropane]/[ethylene] in polymer.



Scheme 2. Mechanism of alternating copolymerization of ethylene with methylenecyclopropane. LCo denotes Co^{III} bonded to the bis(imino)pyridine ligand.

The intermediate **B** undergoes insertion of ethylene into the $\mathrm{Co{-}CH_2{-}\overline{CCH_2C}HAr{-}}$ bond to regenerate **A** when the concentration of methylenecyclopropane is low (<82 mM for **1a**). The copolymerization with high concentration of **1a** (>82 mM) produces the polymer with higher content of the monomer unit from **1a** than that of the ethylene monomer unit. Figure 5A shows that the copolymer of ethylene with **1b** has a lower content of ethylene monomer unit than that obtained from copolymerization of ethylene with **1a** and **1c**, which is consistent with r_{1b} (1.1) being larger than r_{1a} (0.30) and r_{1c} (0.18). At present, the reason for different reactivities of **1a**–**1e** toward the copolymerization is not clear. The ^{13}C{^{1}H} NMR spectrum of the alternating copolymer (Fig. 3B) shows a single sharp peak for each carbon of the structural units, although the signals of the homopolymer (Fig. 1B) are significantly broadened. The copolymer has regulated orientation of the aryl substituents, which is governed by the structure of the intermediate **C** having π-coordinated methylenecyclopropane in Scheme 2.

The polymerization of 2-aryl-1-methylenecyclopropane catalyzed by the Co complex/MMAO probably involves 1,2-insertion of the monomer in order to release steric interaction between the three-membered ring of the monomer and the ligands of the catalysts. The growing polymer end, $\mathrm{Co{-}CH_2{-}\overline{CCH_2C}HAr{-}}$, has no β-hydrogens and does not undergo β-hydrogen elimination. Gibson reported that chain transfer of ethylene polymerization by [CoCl$_2$(L^1)]/MMAO takes place by β-hydrogen elimination rather than by chain transfer of the growing polymer from Co to Al.[15c] Living polymerization of **1a** at 0 °C and −40 °C is ascribed to the polymer end that has no β-hydrogen. Copolymer of **1a** and ethylene has a larger polydispersity ($M_w/M_n = 1.35$) than that of **2a** obtained at 0 °C. The β-hydrogen of the growing polymer **A** in Scheme 2 may be responsible to the chain transfer of the copolymer.

The alternating copolymerization, which is initiated by the living polymer of **1a** ([**1a**]/[Co] = 60, $M_n = 12000$, $M_w/M_n = 1.09$), affords an AB block copolymer, $\mathrm{{-}(CH_2{-}\overline{CCH_2C}HPh{-}CH_2{-}CH_2)_{\mathit{m}}{-}(CH_2{-}\overline{CCH_2C}HPh)_{\mathit{n}}{-}}$ ($M_n = 75000$, $M_w/M_n = 1.76$). GPC of the block copolymer showed a single elution peak, indicating complete consumption of the prepolymer. In a similar manner, addition of **1b** and ethylene to the living polymer of **1a** ([**1a**]/[Co] = 50, $M_n = 9300$, $M_w/M_n = 1.14$) forms the block copolymer $\mathrm{{-}(CH_2{-}\overline{CCH_2C}H(C_6H_4OMe\text{-}4)\text{-}CH_2{-}CH_2)_{\mathit{m}}{-}(CH_2{-}\overline{CCH_2C}HPh)_{\mathit{n}}{-}}$ ($M_n = 28000$, $M_w/M_n = 1.77$) (Eq. 3). ^{1}H and ^{13}C{^{1}H} NMR spectra showed the signals assignable to both $\mathrm{{-}(CH_2{-}\overline{CCH_2C}HPh){-}}$ and $\mathrm{{-}(CH_2{-}\overline{CCH_2C}H(C_6H_4OMe\text{-}4)\text{-}CH_2{-}CH_2){-}}$ segments (Fig. 6).[18] GPC of the obtained copolymers showed a single elution peak. TLC (silica gel) of the copolymer (eluent: CHCl$_3$) showed a single spot at $R_f = 0.16$, which differs from that of **2a** ($R_f = 1.0$) and **3b** ($R_f = 0.12$). All these results indicate that the obtained polymer is not a blend of **2a** and **3b**, but rather the block copolymer shown in Eq. 3.

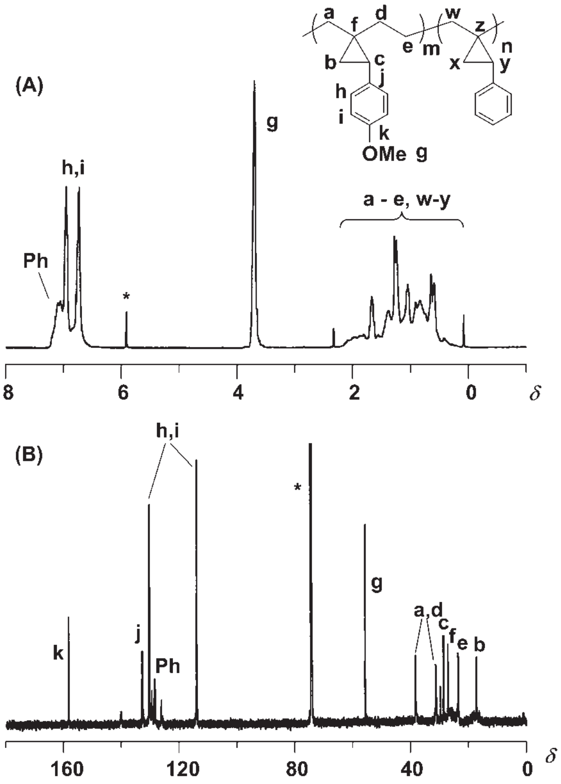
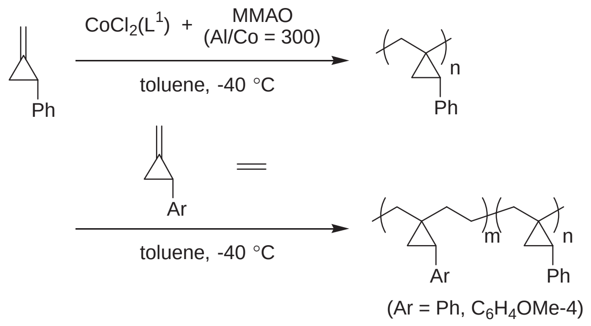
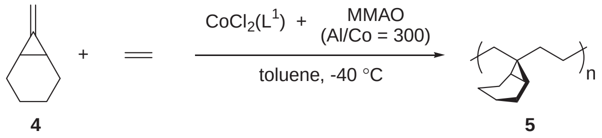


Fig. 6. (A) ^{1}H and (B) ^{13}C{^{1}H} NMR spectra of poly{**1a**-*block*-(**1b**-*alt*-ethylene)} in $C_2D_2Cl_4$ at 130 °C. Broad ^{13}C NMR signals at δ 0–50 are assigned to w–z. The peaks by an asterisk are due to the solvent.



(3)

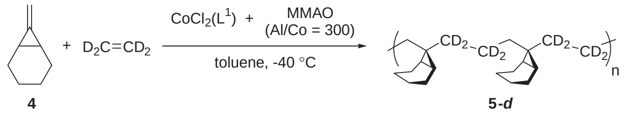
Copolymerization of 7-Methylenebicyclo[4.1.0]heptane with Ethylene by Cobalt Complexes. Homopolymerization of 7-methylenebicyclo[4.1.0]heptane (**4**) in the presence of [$CoCl_2(L^1)$] and MMAO at −40 °C is slow and produces the polymer in 16% yield after 1 h. The polymer probably has a structure with three-membered rings similar to those of **2a**–**2c**, although low solubility of the polymer in common organic solvent prevented detailed NMR analysis of it. The reaction of ethylene (1 atm) with **4** (0.18 g) in the presence of [$CoCl_2(L^1)$] and MMAO ([Co] = 1.7 mM, [Co]/[**4**]/[Al] = 1/200/300) at −40 °C leads to the alternating copolymer **5** in 0.18 g (67% based on **4**) after 1 h (Eq. 4). The copolymerization for 10 min at −40 °C produces 0.11 g of copolymer and is completed within 1 h. The yield of the copolymer is low above 0 °C.



(4)

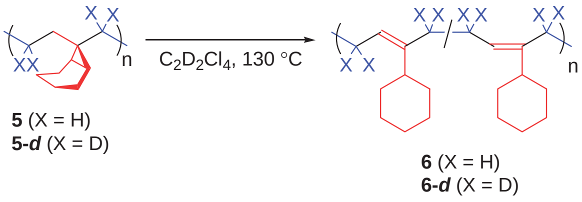
The limited solubility of **5** in THF and in $CHCl_3$ prevented determination of the molecular weight by GPC. The ^{13}C{^{1}H} NMR spectrum, however, was obtained by dissolving the polymer in $C_2D_2Cl_4$ at 130 °C, cooling the resulting solution, and measuring the spectrum at room temperature soon. Seven sharp signals are assigned to the aliphatic carbons of the alternating copolymer unit, based on comparisons of the peak positions with those of 7,7-dibutylbicyclo[4.1.0]heptane. The signals at δ 26.4 and 40.2 are attributed to the CH_2 carbons bonded to the three-membered ring of the polymer. The former signal is assigned to the carbon on the same side of the cyclohexane-1,2-diyl group, while the latter is due to that on the opposite side.[19]

The reaction using C_2D_4 as the comonomer produces the deuterated polymer **5-*d***. The ^{13}C{^{1}H} NMR spectrum of **5-*d*** shows five sharp signals at δ 19.1, 19.5, 22.7, 25.0, and 26.2, and two weak signals at δ 22.1 and 39.1 with broadening. The positions of the latter signals are shifted from the corresponding signals of **5** (δ 23.0 and 40.2) with large isomer shifts (0.921 and 1.012 ppm, respectively). Thus, they are assigned to the CD_2 carbons derived from C_2D_4 monomer. All these results indicate that the copolymer of C_2D_4 and 7-methylenebicyclo[4.1.0]heptane, **5-*d***, has the partial structure shown in Eq. 5 exclusively.



(5)

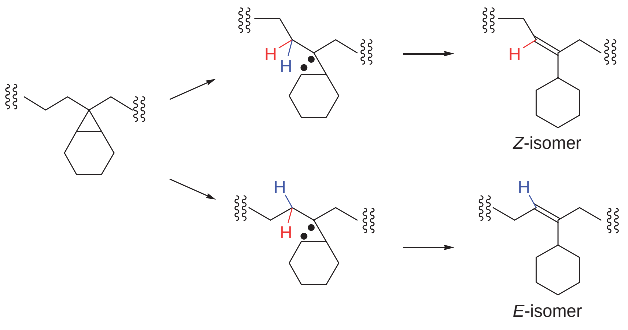
Chain growth of the copolymerization is considered to proceed similarly to that of ethylene with 2-phenyl-1-methylenecyclopropane as shown in Scheme 2. The growing polymer with the Co–CH_2–CH_2– bond (**A** in Scheme 2) undergoes 1,2-insertion of 7-methylenebicyclo[4.1.0]heptane into the Co–C bond. Pre-coordination of the C=C double bond of the bicyclic monomer occurs at the opposite side of the six-membered ring of the monomer in order to avoid any steric repulsion between the coordinated monomer and the polymer end. The formed intermediate, having a Co–CH_2–C(C_6H_{10})– bond, undergoes preferential insertion of ethylene into the Co–C bond. Strong coordination of C=C bond of **4** to the Co center prevents double insertion of ethylene, similar to the copolymerization of ethylene with **1a**. Double insertion of **4** is also inhibited due to the steric bulkiness of the monomer. In fact, reaction (4) produces the alternating copolymer even at high concentrations of **4**.



(6)

Heating a $C_2D_2Cl_4$ solution of **5** at 130 °C for 12 h causes disappearance of the $^{13}C\{^1H\}$ NMR signals at δ 19.2–25.2 of **5** and generation of new signals of olefinic carbon at δ 123.4 and 144.8 and of a pair of the CH carbons at δ 41.0 and 45.4. The product of the thermal reaction is assigned to **6**, having a structure of poly(2-cyclohexyl-1,3-butadiene), based on comparison of the spectrum with those of 2-cyclohexyl-2-butene[20] and poly(isoprene) (Eq. 6).[21] A pair of the signals for each carbon of the cyclohexyl ring are assigned to the trans and cis C=C groups in the polymer chain. GPC analysis of **6** shows $M_n = 5800$ and $M_w/M_n = 1.69$. **5-*d*** also undergoes the thermal isomerization to afford the corresponding deuterated polymer **6-*d***. ^2H NMR spectrum of **6-*d*** show broad signals at δ 1.15 and 1.93 (CD_2) and a much smaller signal at δ 5.05 (=CD). Organic compounds with similar structures also undergo the ring-opening isomerization. 2-Methyl-1-phenylcyclopropane was reported to undergo photo-isomerization into 4-phenyl-1-butene.[22] We conducted thermal reactions of 7,7-dimethylbicyclo[4.1.0]heptane and 7,7-dibutylbicyclo[4.1.0]heptane in $C_2D_2Cl_4$ at 130 °C for 12 h, and observed clean formation of 1-isopropylcyclohexane and (*E*)-5-cyclohexyl-4-nonene, respectively.[23] The first DSC scan of **5** shows an endothermic peak at 100 °C on heating and no exothermic peak on cooling. The second scan exhibits a transition at 52 °C (T_g) only. The results suggest that the ring-opening isomerization of **6** occurs in the solid state also.

These isomerization reactions are considered to proceed via formation of biradical species followed by 1,4-migration of a hydrogen atom. The thermal isomerization reaction of **5** and **5-*d*** also involves homolytic cleavage of C–C bond of the three-membered ring to form the biradical species, as shown in Scheme 3. Abstraction of a hydrogen from the CH_2 group by the cyclohexyl radical forms the C=C double bond in the main chain. Results of the thermal reaction of **5-*d*** indicates that the hydrogen is abstracted from the CH_2 group on the same side of the cyclohexane-1,2-diyl group with respect to the cyclopropane plane. 1,4-Migration of a hydrogen of the CH_2 group results in formation of *Z* and *E*-olefinic groups in **6** and **6-*d***.



Scheme 3. Mechanism of thermal isomerization.

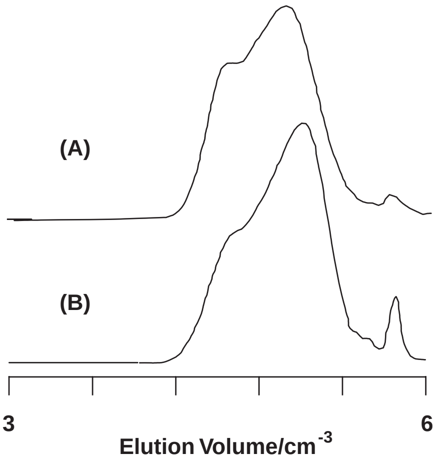
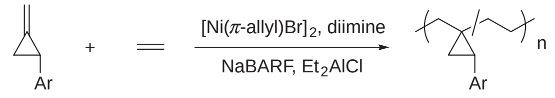


Fig. 7. GPC profiles of **7a** by (A) UV (254 nm) detector and (B) RI detector.

Polymerization of 2-Aryl-1-methylenecyclopropane and Their Copolymerization with Ethylene Catalyzed by Nickel Complexes. Addition of NaBARF to a mixture of $[Ni(\pi\text{-}C_3H_5)Br]_2$ and L^7 does not cause ethylene polymerization. The two mixtures, $[Ni(\pi\text{-}C_3H_5)Br]_2$–$L^6$–$Et_2AlCl$ and $[Ni(\pi\text{-}C_3H_5)Br]_2$–$L^7$–NaBARF–$Et_2AlCl$, in contrast, afforded the polyethylene in the respective yields of 0.36 and 0.37 g.[24] The polymerization of **1a** by $[Ni(\pi\text{-}C_3H_5)Br]_2$–$L^5$–NaBARF–$Et_2AlCl$ also takes place at room temperature in CH_2Cl_2 to give the corresponding polymer with three-membered rings in 65% yield. Based on the above results, we conducted the copolymerization of ethylene with 2-aryl-1-methylenecyclopropanes using the Ni catalysts. Copolymerization of ethylene (1 atm) and **1a** (1.7 M) in the presence of $[Ni(\pi\text{-}C_3H_5)Br]_2$ (0.0083 mmol), L^8 (0.0083 mmol), NaBARF (0.01 mmol), and Et_2AlCl (0.83 mmol) produce the copolymer (**7a**) in 0.31 g (Eq. 7). GPC profiles obtained by UV (254 nm) and RI detectors (Fig. 7) show similar elution in the high molecular weight region. A minor elution, observed by RI detector, is assigned to oligoethylenes (C4–C14) with a molecular weight of $M_n = 1200$.



1a: Ar = C_6H_5
1b: Ar = C_6H_4OMe-4
1c: Ar = C_6H_4Cl-4
1d: Ar = C_6H_4Me-4

7a: Ar = C_6H_5
7b: Ar = C_6H_4OMe-4
7c: Ar = C_6H_4Cl-4
7d: Ar = C_6H_4Me-4

(7)

The ^1H NMR spectrum of **7a** shows a broad signal assigned to the phenyl hydrogen at δ 6.3–7.9 and a less broad signal assigned to polyethylene segment at δ 0–3.7 (Fig. 8A). Relative intensity of the signals indicates the content of ethylene segment to be 90% of the copolymer. These results of the NMR and GPC measurements indicate that the product is a copolymer of the two monomers rather than a mixture of the homopolymers. The broad signals of the methylenecyclopropane unit are in contrast to the alternating copolymer obtained by the reaction catalyzed by Co complex and suggest a random sequence of the two monomer units. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **7a** show the signals due to branched polyethylene segments: (δ 0.8) for ^1H, and δ 14.3 and 30.0 for $^{13}C\{^1H\}$ (Fig. 8B). Similar branching in high density was reported also for the polyethylene obtained by the Ni catalyst.[23] The minor signals at δ 12.3, 17.9, and 43.0 are assigned to the methylenecyclopropane segment. Comparison of the $^{13}C\{^1H\}$ NMR spectrum with the DEPT spectrum (45° pulse) indicates that the signals at δ 32.4 and

33.7 are due to the cyclopropylidene carbon next to the terminal olefinic unit formed by β-hydrogen elimination.

Table 2 summarizes the results of the copolymerization. The reaction under 1 atm of ethylene in the presence of Et_2AlCl cocatalyst gives the polymer in a low yield (Run 1). The polymerization with addition of NaBARF affords the polymer having both monomer units after 2 h (Run 2). Addition of NaBARF increases both the content of the ethylene unit and the polymer yield. A longer reaction (15 h) causes partial formation of polyethylene with high molecular weight (M_n = 7330000). The reactions using $AgPF_6$ or $AgBF_4$ instead of NaBARF and those using $^iBu_3Al$ or PMAO instead of Et_2AlCl produce the polymer in low or negligible yields. The reaction under ethylene at 15 atm affords the polymer with the ethylene content of 40% (Run 4), while the polymer obtained under ethylene at 30 atm is insoluble in $CHCl_3$ and THF, due to partial formation of polyethylene (Run 5). Ligands L^6–L^8 form the copolymer with different contents of the ethylene unit: 23, 11, and 87%, respectively (Runs 6–8). Chlorobenzene and toluene were also usable as the solvent for the polymerization (Runs 9 and 10). The ratio of the two monomer units of the copolymer varies significantly depending on the ligand used and the reaction conditions, indicating that the copolymerization occurs in random fashion.

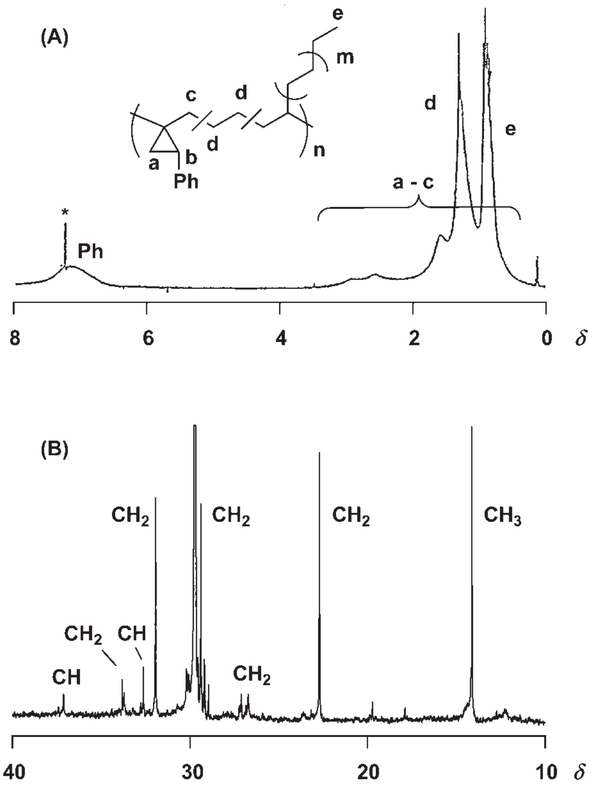


Fig. 8. (A) ^1H and (B) $^{13}C\{^1H\}$ NMR spectra of **7a** in $CDCl_3$ at 25 °C. The signal marked by an asterisk is due to solvent.

The copolymerization of ethylene with **1b**, **1c**, and **1d** by $[Ni(\pi\text{-}C_3H_5)Br]_2$ (0.0083 mmol)/L^5 (0.0083 mmol)/NaBARF (0.01 mmol) in CH_2Cl_2 (5 cm^3) for 15 h gives the copolymers in lower yields (0.06–0.15 g) than the copolymerization with **1a** (0.31 g). The content of the ethylene unit in the copolymers was also decreased in the case of these monomers (9–71%). **1a** and **1d** gave the copolymer with ethylene in higher yields than **1b** and **1c**, which is similar to Ni complex-catalyzed homopolymerization of 2-aryl-1-methylenecyclopropanes.[9b]

Conclusion

The Co and Ni complexes promote copolymerization of ethylene and substituted methylenecyclopropanes, as revealed by this study. The Co complex with bis(1-iminoalkyl)pyridine ligand initiates both polymerization of ethylene and that of methylenecyclopropanes in the presence of MAO as the cocatalyst. Preferential coordination of C=C bond of methylenecyclopropane to the Co center of the Co–CH_2–CH_2 growing end inhibits the double insertion of ethylene during the polymerization. This is the primary reason for the selective alternating copolymerization, while double insertion of methylenecyclopropane is also restricted under the conditions with high ethylene/methylenecyclopropane ratios. This copolymerization affords the polymer having one three-membered ring in every four carbons of the main chain. Copolymerization of ethylene with 2-aryl-1-methylenecyclopropane promoted by Ni–diimine complexes forms the polymer having three-membered rings randomly along the polymer chain. Although the

Table 2. Copolymerization of 2-Phenyl-1-methylenecyclopropane with Ethylene by Ni Catalysts[a)]

Run	Ni catalysts		Conditions				Products		
	Ligand	Cocat.	**1a** /g	Ethylene /atm	Solvent	Time /h	Yield /g	Ethylene /%	$M_n(M_w/M_n)^{b)}$ /g mol^{-1}
1	L^5	—	0.076	1	CH_2Cl_2	15	0.056	9	1600 (1.50)
2	L^5	NaBARF	0.11	1	CH_2Cl_2	2	0.068	17	—
3	L^5	NaBARF	0.11	1	CH_2Cl_2	15	0.31	>99	1200 (1.4)
4	L^5	NaBARF	0.22	15	CH_2Cl_2	3	0.02	40	1300 (1.6)
5	L^5	NaBARF	0.22	30	CH_2Cl_2	3	0.09	insoluble	2900 (1.6)
6	L^6	NaBARF	0.11	1	CH_2Cl_2	5	0.08	23	1200 (1.6)
7	L^7	NaBARF	0.11	1	CH_2Cl_2	2	0.07	11	1300 (1.8)
8	L^8	NaBARF	0.11	1	CH_2Cl_2	15	0.31	87	1200 (2.61)
9	L^8	NaBARF	0.11	1	C_6H_5Cl	15	0.04	38	1200 (1.36)
10	L^8	NaBARF	0.11	1	Toluene	15	0.08	71	1200 (1.40)

a) Reaction conditions: [Ni] = 1.7×10^{-6} M, [ligand]/[Ni]/[Et_2AlCl] = 1/1/100, [Ni]/[NaBARF] = 1:1.2 for Runs 2–9, solvent 5 cm^3. b) Determined by GPC based on polystyrene standard.

cocatalysts are different between that used for polymerization of ethylene and that used for polymerization of 2-aryl-1-methylenecyclopropane, proper choice of the reaction conditions has achieved successful random copolymerization of these monomers. The molecular weight of the copolymer is limited due to facile β-hydrogen elimination of the polymer chain bonded to the Ni center.

Experimental

General Methods. Anhydrous toluene and deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$) were used as received. CH_2Cl_2 was washed successively with conc. H_2SO_4, water, and brine, dried over $CaCl_2$, and distilled over CaH_2 under Ar. Ethylene was used as received. PMAO and MMAO was purchased from TOSOH FINECHEM and used as received. Co and Ni complexes,[14] 2-aryl-1-methylenecyclopropanes, 2-methyl-2-phenyl-1-methylenecyclopropane, and 7-methylenebicyclo[4.1.0]heptane were prepared according to the reported procedures.[25] 7,7-Dimethylbicyclo[4.1.0]heptane and 7,7-dibutylbicyclo[4.1.0]heptane were prepared according to the reported procedure.[26]

NMR spectra (^{1}H and ^{13}C) were recorded on Varian Mercury 300 and JEOL JNM-500 spectrometers, where the chemical shifts were determined with respect to C_2DHCl_2 (δ 5.91) for ^{1}H and $C_2D_2Cl_4$ (δ 74.2) for ^{13}C. Gel permeation chromatography (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 THF as an eluent at a flow rate of 0.6 $cm^3\,min^{-1}$ with TSKgel SuperHM-L and SuperHM-M columns. The molecular weights were calibrated based on polystyrene standards. DSC and TG were recorded on Seiko DSC6200R and Seiko TG/DTA6200R instruments.

Homopolymerization of 1a by [CoCl$_2$(L^1)]–MMAO at Room Temperature. Typically, to a 25-cm^3 Schlenk flask containing a toluene solution (3.9 cm^3) of [$CoCl_2(L^1)$] (0.0083 mmol, 0.0050 g), **1a** (1.75 mmol, 0.228 g), and a magnetic stirring bar under Ar, was added a toluene solution of MMAO (1.1 cm^3, 2.5 mmolAl) with a syringe. The mixture was then stirred at room temperature for 15 min. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol (ca. 100 cm^3). The white precipitates that formed were collected and dried in vacuo at room temperature. Yield 55%. ^{1}H NMR ($C_2D_2Cl_4$): δ −0.1–2.4 (5H, br, CH, CH$_2$) and 6.2–7.5 (5H, br, Ph). ^{13}C{^{1}H} NMR ($C_2D_2Cl_4$): δ 13–21 (C, CH$_2$ (cyclopropyl)), 23–31 (CH), 34–47 (CH$_2$), 126.0 (*p*-Ph), 128.2, 129.1 (*o*-, *m*-Ph), and 139.9 (*ipso*-Ph).

Homopolymerization of 1a Catalyzed by [CoCl$_2$(L^1)]–MMAO at −40 °C. Typically, to a 25-cm^3 Schlenk flask containing a toluene solution (3.9 cm^3) of [$CoCl_2(L^1)$] (0.0083 mmol, 0.005 g), **1a** (1.75 mmol, 0.228 g), and a magnetic stirring bar under Ar, was added a toluene solution of MMAO (1.1 cm^3, 2.5 mmolAl) with a syringe. The mixture was then stirred at −40 °C for 15 min. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol (ca. 100 cm^3). The formed white precipitates that formed were collected and dried in vacuo at room temperature. Yield 63%.

Copolymerization of Ethylene with 1a Catalyzed by [CoCl$_2$(L^1)]–MMAO. Typically, a toluene solution (29.4 cm^3) of [$CoCl_2(L^1)$] (0.0041 mmol, 2.5 mg) and **1a** (0.82 mmol, 0.11 g) in a 25-cm^3 Schlenk flask was subjected to a freeze–pump–thaw cycle, and back-filled with ethylene. A toluene solution of MMAO (0.6 cm^3, 1.23 mmolAl) was added with a syringe. The mixture was then stirred for 2 min under ethylene flow (1 cm^3/min) at room temperature. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3) and poured into a large amount of HCl/methanol (ca. 200 cm^3). The white precipitates that formed were collected and dried in vacuo at room temperature. Yield 0.12 g. Activity 880 $g\,mmol^{-1}\,h^{-1}\,atm^{-1}$. $M_n = 58000$, $M_w/M_n = 2.84$. The molar fraction of ethylene in the polymer was estimated by ^{1}H NMR ($C_2D_2Cl_4$) based on the peak area ratio of the peaks at −0.1–2.4 (CH and CH$_2$ of ethylene unit and **1** unit) and those of 6.2–7.5 (Ph of **1** unit). ^{1}H NMR ($C_2D_2Cl_4$): δ 0.5–1.8 (9H, m, CH, CH$_2$) and 7.07 and 7.17 (5H, s, Ph). ^{13}C{^{1}H} NMR ($C_2D_2Cl_4$): δ 17.2 (CCH$_2$CHPh), 23.5 (CH$_2$CH$_2$CH$_2$), 27.6 (C), 29.5 (CHPh), 31.3, 38.3 (CCH$_2$), 125.6 (*p*-Ph), 128.0, 129.1 (*o*-, *m*-Ph), and 140.3 (*ipso*-Ph).

Copolymerization of Ethylene with 1b. A toluene solution (4.5 cm^3) of [$CoCl_2(L^1)$] (0.0041 mmol, 2.5 mg), **1b** (1.66 mmol, 0.27 g) in a 25-cm^3 Schlenk flask was subjected to a freeze–pump–thaw cycle, and then back-filled with ethylene. A toluene solution of MMAO (0.5 cm^3, 1.23 mmolAl) was added with a syringe, and the mixture was stirred for 2 min under ethylene flow (1 cm^3/min) at 0 °C. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. The white precipitates that formed were collected and dried in vacuo at room temperature. Yield 0.22 g. Activity 1600 $g\,mmol^{-1}\,h^{-1}\,atm^{-1}$. $M_n = 120000$, $M_w/M_n = 2.32$. ^{1}H NMR ($C_2D_2Cl_4$): δ 0.4–1.8 (8H, m, CH, CH$_2$), 3.71 (3H, s, OCH$_3$), and 6.74, 6.76, and 6.97 (4H, s, Ar). ^{13}C{^{1}H} NMR ($C_2D_2Cl_4$): δ 17.2 (CCH$_2$CHPh), 23.6 (CH$_2$CH$_2$CH$_2$), 27.1 (C), 28.7 (CHPh), 31.4, 38.2 (CCH$_2$), 55.6 (OCH$_3$), 114.1, 130.1, 132.5, and 158.2 (Ar).

Copolymerization of Ethylene with 1c by [CoCl$_2$(L^1)]. A toluene solution (1.5 cm^3) of [$CoCl_2(L^1)$] (0.00123 mmol, 0.75 mg), **1c** (1.23 mmol, 0.2 g) in a 25-cm^3 Schlenk flask was subjected to a freeze–pump–thaw cycle, and then back-filled with ethylene. A toluene solution of MMAO (0.6 cm^3, 1.23 mmolAl) was added with a syringe, and the mixture was stirred for 2 min under ethylene flow (1 cm^3/min) at 0 °C. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. The white precipitates that formed were collected and dried in vacuo at room temperature. Yield 0.11 g. Activity 2700 $g\,mmol^{-1}\,h^{-1}\,atm^{-1}$. $M_n = 110000$, $M_w/M_n = 1.81$. ^{1}H NMR ($C_2D_2Cl_4$): δ 0.2–2.2 (8H, m, CH, CH$_2$) and 6.96 and 7.15 (4H, s, Ph). ^{13}C{^{1}H} NMR ($C_2D_2Cl_4$): δ 17.5 (CCH$_2$CHPh), 23.4 (CH$_2$CH$_2$CH$_2$), 27.6 (C), 28.9 (CHPh), 31.3, 38.0 (CCH$_2$), 128.1, 130.4, 131.9, and 140.3 (Ar).

Synthesis of $-(CH_2-\overline{CCH_2C}HPh-CH_2-CH_2)_m-(CH_2-\underline{CCH_2C}HPh)_n-$. A toluene solution (1 cm^3) of [$CoCl_2(L^1)$] (0.002 mmol, 1.2 mg) and **1a** (0.12 mmol, 0.016 g) in a 25-cm^3 Schlenck flask was subjected to a freeze–pump–thaw cycle, and then back-filled with ethylene. A toluene solution of MMAO (0.25 cm^3, 0.6 mmolAl) was added with a syringe, and then the mixture was stirred for 30 min at −40 °C. A part of the reaction mixture was taken out of the flask and subjected to GPC analysis ($M_n = 12000$, $M_w/M_n = 1.09$). After addition of MMAO (2.5 cm^3, 6 mmol) and **1a** (0.11 g, 0.84 mmol), ethylene (1 cm^3/min) was bubbled at 0 °C. After 1 min, the reaction mixture was quenched by adding EtOH (ca. 1 cm^3) and then poured into a large amount of HCl/methanol. The white precipitates that formed were collected and dried in vacuo at room temperature. $M_n = 75000$, $M_w/M_n = 1.76$.

Synthesis of $-(CH_2-\overline{CCH_2CH}(C_6H_4OMe\text{-}4)\text{-}CH_2-CH_2)_m-(CH_2-\overline{CCH_2CH}Ph)_n-$. A 25-cm^3 Schlenk flask containing a toluene solution (2 cm^3) of [$CoCl_2(L^1)$] (0.004 mmol, 2.5 mg) was subjected to a freeze–pump–thaw cycle, and then back-filled with ethylene. A toluene solution of MMAO (0.5 cm^3, 1.2 mmolAl) and 2-phenyl-1-methylenecyclopropane (**1a**) (0.2 mmol, 0.03 g) was successively added with a syringe, and the mixture was stirred for 30 min at −40 °C. A part of the reaction mixture was taken out of the flask and subjected to GPC analysis ($M_n = 9300$, $M_w/M_n = 1.14$). To the reaction mixture was successively added MMAO (2.5 cm^3, 6 mmol) and 2-(4-methoxyphenyl)-1-methylenecyclopropane (**1b**) (0.13 g, 0.8 mmol) and bubbling with ethylene (1 cm^3/min) at 0 °C. After 2 min the reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. The white precipitates that formed were collected and dried in vacuo at room temperature. Yield 0.15 g. $M_n = 28000$, $M_w/M_n = 1.77$. TLC (silica gel) of the produced polymer (eluent: $CHCl_3$) showed single spot at $R_f = 0.16$, which differs from that of poly**1a** ($R_f = 1.0$) and poly(ethylene-*alt*-**1b**) ($R_f = 0.12$).

Copolymerization of Ethylene with 4. Typically, a toluene solution (3.7 cm^3) of [$CoCl_2(L^1)$] (0.0083 mmol, 5 mg) and 7-methylenebicyclo[4.1.0]heptane (**4**) (1.66 mmol, 0.18 g) in a 25-cm^3 Schlenk flask, was subjected to a freeze–pump–thaw cycle, and then back-filled with ethylene. A toluene solution of MMAO (1.3 cm^3, 2.5 mmolAl) was added with a syringe; the mixture was then stirred for 1 h under ethylene flow (1 cm^3/min) at −40 °C. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. The white precipitate thus formed was collected by filtration and dried in vacuo at room temperature. Yield 0.18 g. ^{1}H NMR ($C_2D_2Cl_4$): δ 0.46 (2H, s, CH), 1.15 (8H, br, CH_2), 1.26 (4H, br, CH_2), and 1.74 (2H, s, CH (cyclohexane)). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 19.2 (CH), 19.5 (CH_2 (cyclohexane)), 22.7 (CH_2 (cyclohexane)), 23.0 (CH_2), 25.2 (C), 26.4 (CH_2), and 40.2 (CH_2).

Copolymerization of C_2D_4 with 4. Typically, a toluene solution (3.7 cm^3) of [$CoCl_2(L^1)$] (0.0083 mmol, 5 mg) and 7-methylenebicyclo[4.1.0]heptane (**4**) (1.66 mmol, 0.18 g) in a 25-cm^3 Schlenk flask, was subjected to a freeze–pump–thaw cycle, and then back-filled with C_2D_4. A toluene solution of MMAO (1.3 cm^3, 2.5 mmolAl) was added with a syringe, and the mixture was stirred for 1 h under C_2D_4 atmosphere (1 atm) at −40 °C. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. The white precipitate thus formed was collected by filtration and dried in vacuo at room temperature. Yield 0.18 g. ^{1}H NMR ($C_2D_2Cl_4$): δ 0.51 (2H, s, CH), 1.18 (6H, br, CH_2), 1.30 (2H, br, CH_2), and 1.79 (2H, s, CH (cyclohexane)). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 19.1 (CH), 19.5 (CH_2 (cyclohexane)), 22.1 (CD_2), 22.7 (CH_2 (cyclohexane)), 25.0 (C), 26.2 (CH_2), and 39.1 (CD_2).

Homopolymerization of 4 at −40 °C. Typically, to a 25-cm^3 Schlenk flask containing a toluene solution (3.7 cm^3) of [$CoCl_2(L^1)$] (0.0083 mmol, 5 mg), 7-methylenebicyclo[4.1.0]heptane (**4**) (1.66 mmol, 0.18 g), and a magnetic stirring bar under Ar, was added a toluene solution of MMAO (1.3 cm^3, 2.5 mmolAl) with a syringe. The mixture was then stirred at −40 °C for 30 min. The reaction mixture was quenched by adding EtOH (ca. 1 cm^3). Pouring the reaction mixture into a large amount of HCl/methanol formed the polymer as a white precipitate; this was collected by filtration and dried in vacuo at room temperature. Yield 0.028 g (16%).

Thermal Isomerization of 5. A $C_2D_2Cl_4$ solution (0.5 cm^3) of **5** (0.05 g) was heated at 130 °C for 12 h. The solution was subjected to NMR and GPC analyses directly. $M_n = 5800$, $M_w/M_n = 1.69$. ^{1}H NMR ($C_2D_2Cl_4$): δ 1.9–2.2 (m, CH_2), 1.12 (br, CH), 1.9–2.2 (m, CH_2), 2.41 (m, CH (cis)), 2.75 (m, CH (trans)), and 5.09 and 5.13 (s, CH=). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 26.7 (CH_2 (cyclohexane)), 26.8 (CH_2 (cyclohexane)), 27.3 (CH$_2$CH= (cis)), 27.3 (CH$_2$CH= (trans)), 30.9 (=CCH$_2$ (cis)), 31.9 (CH_2 (cyclohexane)), 32.1 (CH_2 (cyclohexane)), 33.4 (=CCH$_2$ (trans)), 41.0 (CH (trans)), 45.4 (CH (cis)), 123.4 (CH=), and 144.8 (=C).

Preparation of 7,7-Dimethylbicyclo[4.1.0]heptane. To a 25-cm^3 Schlenk flask containing CuI (3.36 g, 17.5 mmol), Et_2O (70 cm^3), and a magnetic stirring bar, was added MeLi (35 cm^3, 1.0 M solution in ether) with a syringe under Ar at −45 °C. The mixture was stirred for 10 min. An Et_2O solution (3.5 cm^3) of 7,7-dibromobicyclo[4.1.0]heptane (0.9 g, 3.5 mmol) was added to the mixture. After stirring for 1 h at −45 °C and for 18 h at 0 °C, MeI (3.5 cm^3, 56 mmol) was added to the mixture at 0 °C. This was stirred for 16 h. The resulting mixture was poured into water (ca. 50 cm^3). Organic products were extracted with Et_2O; the Et_2O layer was then dried with $MgSO_4$. The volatile fraction was removed by evaporation to afford colorless oil (0.277 g). The ^{1}H NMR analysis results indicated the formation of 7,7-dimethylbicyclo[4.1.0]heptane in ca. 80% purity. The compound was employed for thermal isomerization reaction without further purification. ^{1}H NMR ($C_2D_2Cl_4$): δ 0.45 (2H, d, $J = 7.5$ Hz, CH), 0.87 (3H, s, CH_3), 0.89 (3H, s, CH_3), 1.09 (4H, m, CH_2), 1.28 (2H, m, CH_2), and 1.74 (2H, m, CH_2). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 15.7 (CH_3), 17.4 (C), 19.2 (CH), 19.5 (CH_2 (cyclohexane)), 21.5 (CH_2 (cyclohexane)), and 29.8 (CH_3).

Thermal Isomerization of 7,7-Dimethylbicyclo[4.1.0]heptane. A $C_2D_2Cl_4$ solution (0.5 cm^3) of 7,7-dimethylbicyclo[4.1.0]heptane (0.05 g) was heated at 130 °C for 12 h. The solution was subjected to NMR analysis without isolation of the product. The main product was assigned by comparison of the NMR data with those of isopropylcyclohexane.[23] ^{1}H NMR ($C_2D_2Cl_4$): δ 0.91 (6H, d, $J = 7$ Hz, CH_3), 1.47 (2H, m, CH_2), 1.54 (2H, m, CH_2), 1.86 (2H, s, CH_2), 1.92 (2H, s, CH_2), 2.07 (1H, septet, $J = 7$ Hz, CH), and 5.31 (1H, s, =CH). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 21.7 (CH_3), 23.2 (CH_2 (cyclohexane)), 23.5 (CH_2 (cyclohexane)), 25.6 (CH_2 (cyclohexane)), 26.3 (CH_2 (cyclohexane)), 35.5 (CH), 118.5 (=CH), and 143.8 (C=).

Preparation of 7,7-Dibutylbicyclo[4.1.0]heptane. To a 25-cm^3 Schlenk flask containing CuI (3.36 g, 17.5 mmol), Et_2O (70 cm^3), and a magnetic stirring bar under Ar at −45 °C, were successively added *n*-BuLi (22 cm^3, 1.6 M solution in hexane) and Et_2O solution (3.5 cm^3) of 7,7-dibromobicyclo[4.1.0]heptane (0.9 g, 3.5 mmol) with a syringe. The mixture was stirred at −45 °C for 1 h and at 0 °C for 18 h. *n*-BuI (6.4 cm^3, 56 mmol) was added to the mixture at 0 °C; this mixture was stirred for 16 h. The mixture was then poured into water, extracted with Et_2O, and dried with $MgSO_4$. The volatile fraction was evaporated to afford colorless oil (0.7 g, ca. 70% purity by NMR). It was used for the thermal isomerization reaction without further purification. ^{1}H NMR ($C_2D_2Cl_4$): δ 0.45 (2H, s, CH), 0.81 (3H, s, CH_3), 0.85 (3H, s, CH_3), 1.1–1.4 (18H, m, CH_2), and 1.74 (2H, s, CH_2). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 14.7 (CH_3), 19.1 (CH), 19.5 (CH_2 (cyclohexane)), 22.7 (CH_2 (cyclohexane)), 23.8 (CH$_3$$CH_2$), 25.2 (C), 25.9 ($CH_2$C), 28.7 ($CH_2$), 28.8 ($CH_2$), and 39.3 ($CH_2$C).

Thermal Isomerization of 7,7-Dibutylbicyclo[4.1.0]heptane. A $C_2D_2Cl_4$ solution (0.5 cm^3) of 7,7-dimethylbicyclo[4.1.0]-heptane (0.1 g) was heated at 130 °C for 12 h. The solution was subjected to NMR analysis without isolation of the product. The main product was assigned to be (*E*)-5-cyclohexyl-4-nonene by comparison of the NMR results with the reported data of (*E*)- and (*Z*)-2-cyclohexyl-2-butene.[20b] ^{1}H NMR ($C_2D_2Cl_4$): δ 0.81 (6H, t, $J = 7$ Hz, CH_3), 1.10 (2H, m, CH_2 (cyclohexane)), 1.20 (10H, m, CH_2), 1.50 (2H, m, CH_2 (cyclohexane)), 1.73 (4H, m, $=C\text{–}CH_2$), 1.92 (3H, m, CH, $CH_2\text{–}CH=$), and 5.28 (1H, s, $CH=$). $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4$): δ 14.5 (CH_3), 23.2 (CH_3CH_2), 23.4 (CH_2), 23.5 (CH_2), 24.3 ($CH_2CH=$), 25.7 (CH_2 (cyclohexane)), 30.2 ($=CCH_2$), 33.6 (CH_2 (cyclohexane)), 47.9 (CH), 122.1 ($CH=$), and 140.0 ($=C$).

Copolymerization of Ethylene with 1a Catalyzed by Ni Catalyst. To a 25-cm^3 Schlenk flask containing a CH_2Cl_2 solution (5 cm^3) of $[Ni(\pi\text{-}C_3H_5)Br]_2$ (0.0083 mmolNi, 0.0015 g), diimine ligand (L^8, 0.0083 mmol, 0.003 g), and NaBARF (0.01 mmol, 0.0089 g) was added **1a** (0.11 g, 0.83 mmol) with a syringe at room temperature. The mixture was frozen with liq. N_2, evacuated, backfilled with ethylene, and warm to room temperature. A hexane solution of Et_2AlCl (1 mol/L, 0.83 mL) was added to the mixture, which was stirred for 15 h at room temperature; the reaction mixture was then quenched by adding HCl/MeOH. The produced polymer was isolated by pouring a chloroform solution of the polymer into a large amount of methanol as brown oil.

7a: ^{1}H NMR ($CDCl_3$): δ −0.3–4.2 (br, CH, CH_2, CH_3) and 6.3–7.8 (br, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.7, 14.1 (CH_3 (terminal)), 17.9, 19.7 (CH_2), 22.7 (CH_2 (terminal)), 26.7 (CH_2), 27.1 (CH_2), 28.9–30.2 (CH_2), 31.9 (CH_2 (terminal)), 32.6 (CH), 33.7 (CH_2), 33.8 (CH_2), 37.1 (CH), 43.0, 124–130 (Ph), and 139.3 (*ipso*-Ph).

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