7998 *Macromolecules* **2010**, *43*, 7998–8006
DOI: 10.1021/ma101146j

Macromolecules
ARTICLE

Cyclopolymerization of Monoterminal 1,6-Dienes Catalyzed by Pd Complexes

Takeshi Okada, Daisuke Takeuchi, and Kohtaro Osakada*

Chemical Resources Laboratory R1-03, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan

Received May 25, 2010; Revised Manuscript Received July 24, 2010

ABSTRACT: Pd complexes with chelating diimine ligands promote cyclopolymerization of isopropylidene allyl(1-crotyl)malonate (**I-1**) to afford the polymer having *trans*-1,2-disubstitued five-membered ring and trimethylene spacer in every structural unit. The polymerization of 1,6-dienes with longer *n*-alkyl groups (**I-2**: 1,6-octadiene; **I-3**: 1,6-nonadiene; **I-4**: 1,6-decadiene) also produces the polymers with the five-membered rings located regularly along the linear polymer chain. The cyclopolymerization is applicable to the 1,6-octadienes and 1,6-nonadienes with barbituric acid group, sulfonamide group, and 1,3-indandione group. The polymerization of the 1,6-dienes with isopropyl, isobutyl, and 2-butyl group at a vinyl carbon affords the polymers which are composed of five-membered rings and the spacers with a methyl branch. The polymerization of **I-1** to **I-4** obeys first-order kinetics to the monomer concentration, and the observed rate constants decrease in the order **I-2** $>$ **I-3** $>$ **I-4** $\approx$ **I-1**. Cyclopolymerization of **I-1** under an ethylene atmosphere yields the copolymer of ethylene and the functionalized diene. High reactivity of ethylene monomer for insertion, however, results in low content of the units derived from **I** (4%) and the presence of uncyclized diene units.

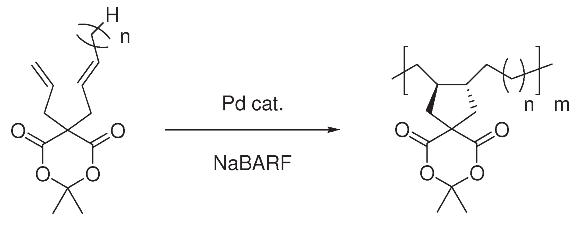
Introduction

Hydrocarbon polymers with cycloalkane groups along the polymer chain exhibit thermal stabilities, optical transparency, and mechanical strength, which could hardly be obtained in common polyolefins.[1] Addition polymerization of cyclic alkenes,[2] metathesis polymerization of norbornenes,[3] and cyclopolymerization of nonconjugated dienes provide general means to produce these polymers.[4] As an extension of the first approach, copolymerization of ethylene and cyclic alkenes, such as cyclopentene and norbornene catalyzed by metal complexes, was studied to produce the polymer with regulated average density of the cyclic unit along the polymer chain and tune the polymer properties.[5] Alternating copolymerization of ethylene with 2-(4-methoxyphenyl)-1-methylenecyclopropane catalyzed by the Co complex yields the polymer having three-membered rings equipped with the functional group.[6] Recently, Wagener chose acyclic functionalized dienes as the monomer of the metathesis polymerization (ADMET) and obtained the polymers having the functional group at regular intervals.[7] Melting point and heat of fusion decrease with increment of the density of the functional group along the polymer. Cyclopolymerization of terminal dienes was studied by using early transition metal catalysts.[4] Recent studies have revealed that late transition metal complexes also catalyze the cyclopolymerization and produce the polymers with high selectivity.[8] We found that the Pd complex-catalyzed cyclopolymerization of functionalized 1,6-dienes[9] and 7-alkyl-1,6-dienes[10] to produce the polymers composed of the alternating cyclic groups and polymethylene spacer. Herein, we report full details of the latter polymerization, reported in a preliminary form,[10] results of the mechanistic studies, and their copolymerization with ethylene.

Results and Discussion

Chart 1 lists precursor of the Pd catalyst and the monomers used in this study. Complexes **1** and **2** in conjunction with NaBARF (BARF = B{$C_6H_3(CF_3)_2$-3,5}$_4$) were reported to catalyze olefin polymerization, copolymerization of ethylene with acrylic esters,[11] and cyclopolymerization of isopropylidene diallylmalonate (**I-0**).[9]

1/NaBARF promotes the cyclopolymerization of isopropylidene allyl(2-butenyl)malonate (**I-1**) and isopropylidene allyl(2-pentenyl)malonate (**I-2**) at room temperature to produce the polymers containing *trans*-1,2-disubstituted five-membered rings separated by trimethylene and tetramethylene spacers, respectively, as shown in eq 1. The results are summarized in Table 1 (runs 1, 2). The polymerization catalyzed by **2**/NaBARF also forms poly-**I-2**, but with a slower rate than that using **1**/NaBARF as the catalyst (run 3). **1**/NaBARF catalyzes the cyclopolymerization of the dienes that contain a longer alkyl group (**I-3**, **I-4**, **I-5**, **I-6**, **I-10**) (Table 1, runs 4−8).



I-n poly-**I-n** (1)

The ^{1}H NMR spectra of poly-**I-*n*** (n = 1−6) do not contain the signals due to vinylene group, indicating complete cyclization of the diene monomers during the polymerization. Figure 1 shows the $^{13}C\{^1H\}$ NMR spectrum of poly-**I-5**.

---

*Corresponding author. E-mail: kosakada@res.titech.ac.jp.

Chart 1

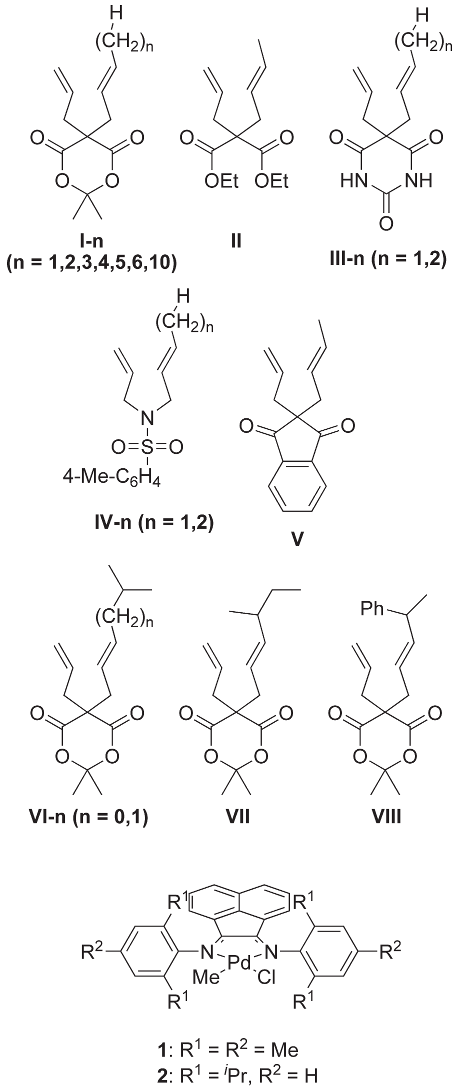


Table 1. Polymerization of 1,6-Dienes Catalyzed by Pd Complexes[a]

run	diene	Pd	time (h)	conv (%)[b]	M_n	M_w/M_n[c]	r (%)[d]
1	**I-1**	**1**	24	quant	7900	1.68	44
2	**I-2**	**1**	24	quant	13600	1.75	48
3	**I-2**	**2**	48	85	5700	2.03	N.D.
4	**I-3**	**1**	24	quant	12200	1.91	N.D.
5	**I-4**	**1**	48	47	10400	1.97	N.D.
6	**I-5**	**1**	48	20	10100	2.31	N.D.
7	**I-6**	**1**	48	27	11500	1.90	N.D.
8	**I-10**	**1**	48	35	6900	1.71	N.D.
9	**II**	**2**	24	trace			
10	**III-1**	**2**	24	34	18900	1.25	55
11	**III-2**	**2**	24	53	N.D.		29
12	**IV-1**	**1**	48	38	10600	1.60	42
13	**IV-2**	**1**	48	49	19900	1.62	45
14	**V**	**2**	48	78	12800	1.92	53
15	**VI-0**	**1**	24	quant	5300	1.57	N.D.
16	**VI-1**	**1**	24	quant	4200	1.73	N.D.
17	**VII**	**1**	24	quant	7400	1.90	N.D.
18	**VIII**	**1**	24	trace			

[a] Reaction conditions: Pd complex = 0.010 mmol, NaBARF = 0.012 mmol, [monomer]/[Pd] = 70, solvent = CH_2Cl_2 (0.5 mL), temperature = rt. [b] Determined by ^1H NMR spectroscopy. [c] Determined by GC using $CHCl_3$ or DMF. [d] Determined by $^{13}C\{^1H\}$ NMR spectroscopy.

Signals at δ 51.0, 46.3, and 45.7 are assigned to quaternary, secondary, and tertiary carbons of the five-membered ring, respectively, based on comparison of the positions with the polymer of **I-0** and on the DEPT spectra. The signals at δ 32.5−27.8 are assigned to CH_2 carbons of heptamethylene spacer and CH_3 carbons of the acetal group. The polymers of the other monomers show three signals due to *trans*-1,2-cyclopentane ring in the region of δ 45.7−51.3 and the spacer carbon signals in the region of δ 26.5−33.0. The spacer part is composed of linear polymethylene chain and does not contain CH_3 or CH carbons which would exhibit the $^{13}C\{^1H\}$ NMR signals δ 20−10 and δ 37−34, respectively. Only poly-**I-10** among the above polymers shows small $^{13}C\{^1H\}$ NMR signals at close positions to the chemical shifts of the vinylene group of **I-10** (δ 122.5 and 137.5) and the CH_2 carbon signals of a decyl group attached to the vinylene carbon. The signals due to vinyl group, however, were not observed.

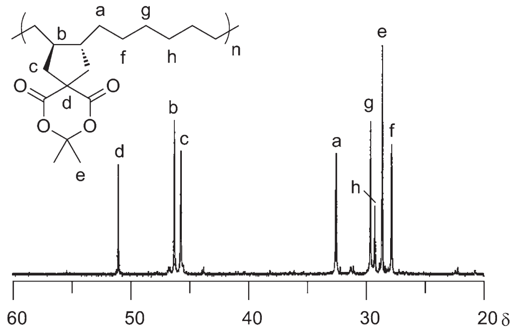
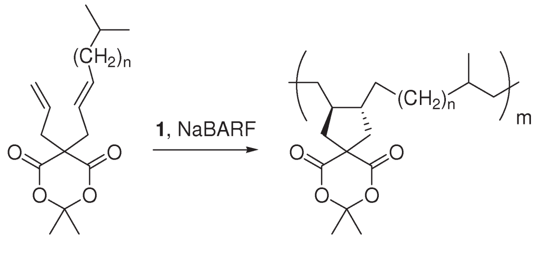


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of poly-**I-5** (in $CDCl_3$, rt).

In contrast to **I-1**, 1,6-octadiene with ester groups (**II**) does not undergo smooth polymerization in the presence of **1**/NaBARF (run 9). The 1,6-diene derivatives with other substituents are also employed for the cyclopolymerization. The 1,6-dienes with a barbituric acid group (**III-1** and **III-2**) polymerize in the presence of **2**/NaBARF catalyst and form poly **III-*n*** (n = 1, 2), which is separated as a solid from the reaction mixture due to low solubility (runs 10 and 11). *N*-Allyl-*N*-(2-alkenyl)sulfonamides (**IV-*n***) (n = 1, 2) and the 1,6-diene with a 1,3-indandione group (**V**) also undergo the cyclopolymerization to produce the corresponding polymers (runs 12−14). Isomerization cyclopolymerization of the 1,6-dienes with branched alkyl groups, **VI-0** and **VI-1**, is catalyzed by **1**/NaBARF to produce poly-**VI-0** and poly-**VI-1** with M_n = 5300 and 4200, respectively (eq 2) (runs 15, 16).



(2)

Figure 2 shows the $^{13}C\{^1H\}$ NMR spectra of poly-**VI-0** and poly-**VI-1**. Signals due to the spacer carbons were assigned based on the spectra in DEPT mode. Signals at δ 40.6−40.0, 36.7−36.5, and 30.0 (poly-**VI-0**) and at δ 35.9−35.0 and 30.1 (poly-**VI-1**) are assigned to CH_2 carbons of the spacer, while CH_3 (δ 21.8−18.5 (poly-**VI-0**) and δ 19.8−19.1 (poly-**VI-1**)) and CH (δ 31.7 (poly-**VI-0**) and δ 33.4−33.1 (poly-**VI-1**)) are observed at close positions to those of methyl branch carbons (δ 19.0 and 33.1) of the polyethylene prepared by using the Ni-diimine catalyst.[12]

Chart 2 summarizes possible diad structures of poly-**VI-0** and poly-**VI-1**. The signal due to CH carbon of poly-**VI-0** (δ 31.7) appears apparently as two peaks, while four CH_3 signals are

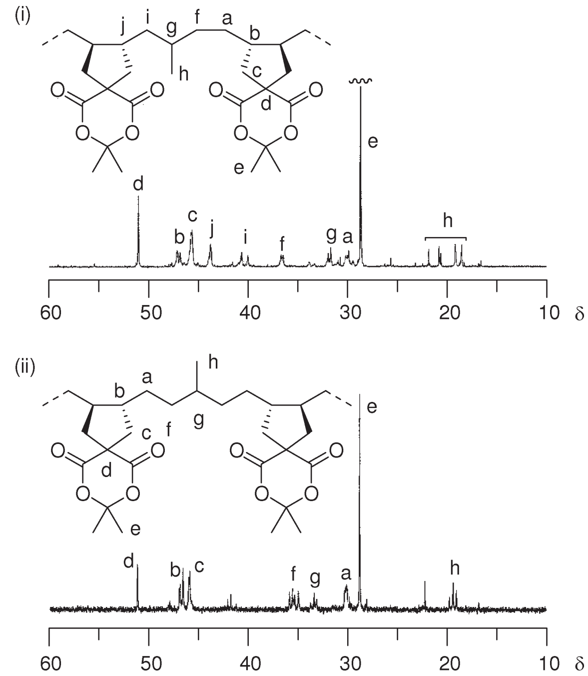
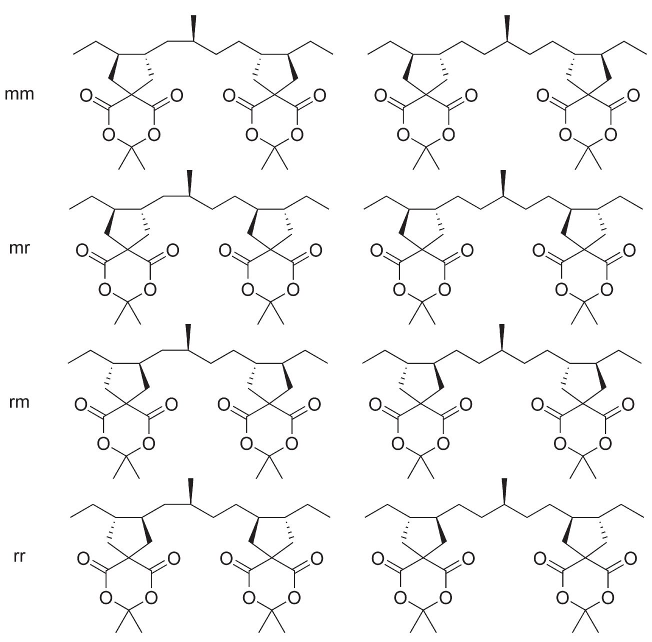


Figure 2. $^{13}C\{^1H\}$ NMR spectra of (i) poly-**VI-0** and (ii) poly-**VI-1** (in $CDCl_3$, rt).

Chart 2. Diad Structures of Poly-VI-0 and Poly-VI-1



observed at δ 21.8−18.5 in almost similar intensities. The signal at δ 43.8, assigned to the CH_2 group between the cyclopentane group and methyl branch, is also split into two peaks with 56:44 intensity ratio. These results indicate that poly-**VI-0** contains four possible diads with similar probabilities and adopts atactic structure. The CH_3 and CH signals (h and g) of poly-**VI-1** are split into three peaks, and the intensity ratio of the former peaks for h is 23:50:27 from downfield to upfield. Relative stereochemistry between the methyl branch and two neighboring *trans*-fused five-membered rings (rr, rm + mr, and mm in Chart 2) is responsible for the peak appearance, and the results indicate atactic structure of poly-**VI-1**.

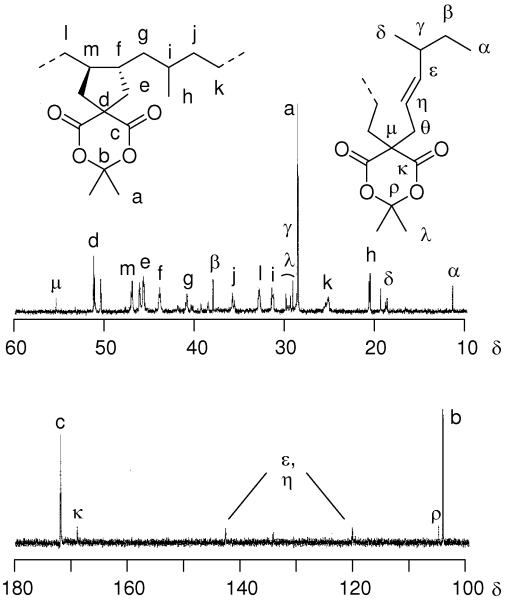
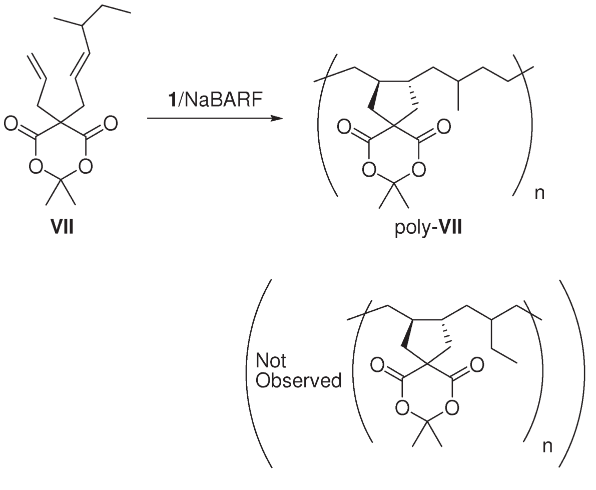


Figure 3. $^{13}C\{^1H\}$ NMR spectrum of poly-**VII** obtained by the reaction catalyzed by **1**/NaBARF (in $CDCl_3$, rt).

The polymerization of **VI-0** and **VI-1** produces the polymer with methyl branch and involves the isomerization of the growing terminal to the species with a Pd−CH_2 bond. Monomer **VII** also undergoes smooth polymerization in the presence of **1**/NaBARF catalyst to attain quantitative conversion of the monomer in 24 h to produce **poly-VII**, as shown in eq 3.



(3)

The $^{13}C\{^1H\}$ NMR spectrum of poly-**VII** shows the signals due to CH_2 (δ 46.2−45.7) and CH (δ 47.1 and 44.0) and quaternary (δ 51.3−50.6) carbons of the cyclopentane ring at similar positions to those of poly-**I-*n*** (Figure 3). Signals at δ 20.8 and 31.6 are assigned to the CH_3 and CH carbons of the methyl branch of the polymer. The ethyl branch of polyolefins was known to show the $^{13}C\{^1H\}$ NMR signal due to the CH_2 carbon at δ 27. The spectrum of poly-**VII** does not contain signals at the position, indicating the absence of ethyl branch in the polymer. The spectrum contains sharp signals with weaker intensities (α−λ). Among three CH_3 carbon signals at δ 11.6, 19.6, and 20.7−20.8 in the spectrum, the two former signals are observed with smaller intensities than the other and at similar positions to the CH_3 carbons of the monomer (δ 11.7 and 19.7). These results suggest the presence of 4-methylhex-2-enyl group due to uncyclized monomer unit and/or the polymer end. In contrast to the diene with aliphatic alkyl groups, the monomer with phenyl group **VIII** does not yield the polymer, probably due to the formation of stable π-benzyl-Pd species as the result of chain-walking isomerization.[13]

Table 2 summarizes thermal properties of the polymers analyzed by DSC and TG measurements. Increase of the alkyl chain length of the monomer lowers the glass transition temperature of the polymers, regardless of the substituents on the five-membered rings.

Mechanism of the Isomerization Cyclopolymerization. Recently, we proposed the mechanism on the cyclopolymerization of isopropylidene diallylmalonate catalyzed by the Pd complexes, as shown in Scheme 1.[9b]

Table 2. Thermal Properties of Polymers

run	diene	M_n	M_w/M_n	T_g/°C	T_d^5/°C
1	poly-**I-1**	7900	1.68	116	150
2	poly-**I-2**	16500	1.75	96	190
3	poly-**I-3**	12200	1.91	71	185
4	poly-**I-4**	14000	1.97	82	198
5	poly-**I-5**	10100	2.31	50	142
6	poly-**I-6**	11500	1.90	31	142
7	poly-**I-10**	6900	1.71	15	148
8	poly-**III-1**	18900	1.25	195	210
9	poly-**III-2**	14000	1.25	161	204
10	poly-**IV-1**	10600	1.60	94	352
11	poly-**IV-2**	7800	1.55	60	218
12	poly-**V**	7900	1.42	115	226

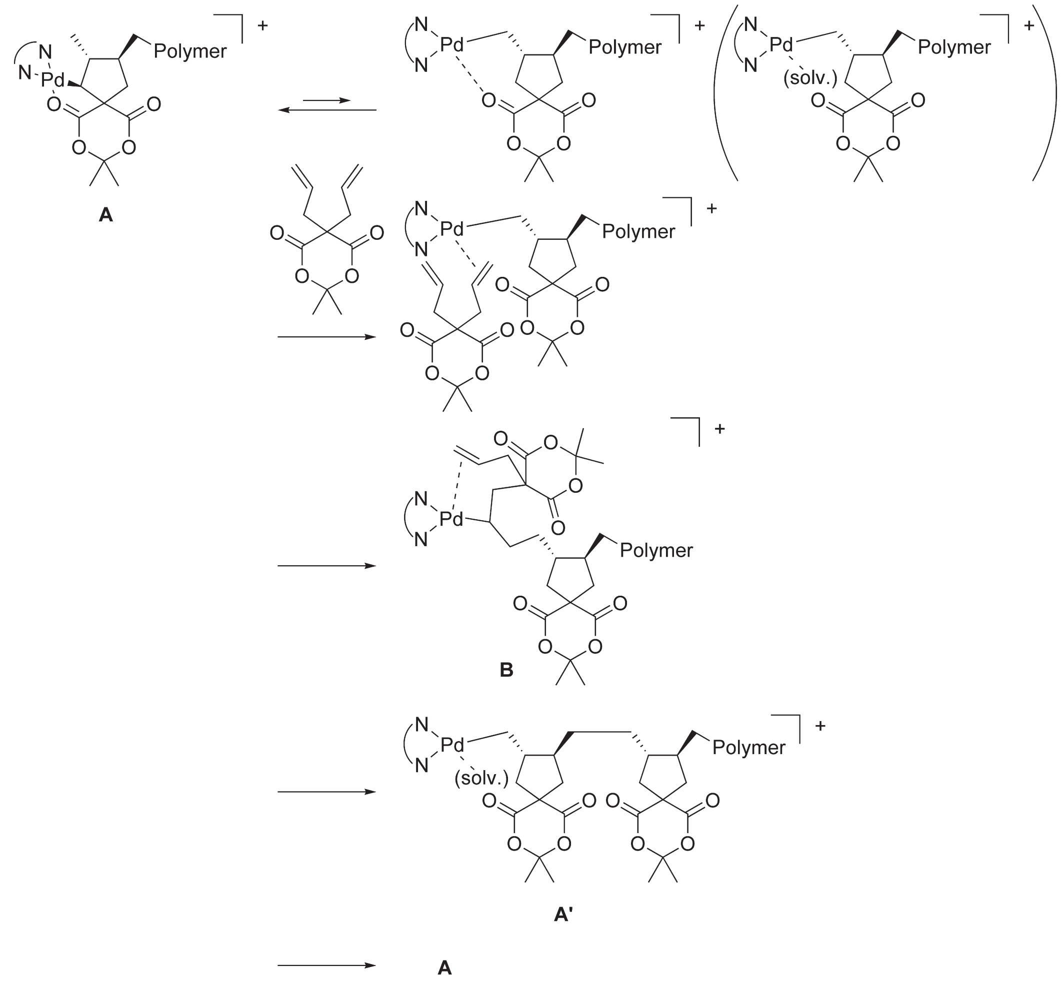
Cyclopentylpalladium species **A** is involved as the resting state of the cyclopolymerization and is stabilized by coordination of a carbonyl group to the Pd center. Migration of the Pd to form cyclopentylmethylpalladium species occurs prior to insertion of a new monomer. Insertion of a vinyl group into the Pd$-$CH$_2$ bond produces alkylpalladium species with pendant vinyl group **B**. Subsequent cyclization, forming **A′**, and its isomerization regenerates **A** as the resting state.

Mechanism of the cyclopolymerization of **I-*n*** can be explained similarly, as shown in Scheme 2. The cyclopentylmethylpalladium species **C** probably functions as the resting state of the catalytic cycle. Migration of Pd along the polymer chain via chain-walking forms the intermediate **C′** having a CH$_2$$-$Pd bond. Insertion of a vinyl group of the monomer and subsequent cyclization forms intermediate **C″**, which is isomerized into the stable resting state **C** via chain-walking.

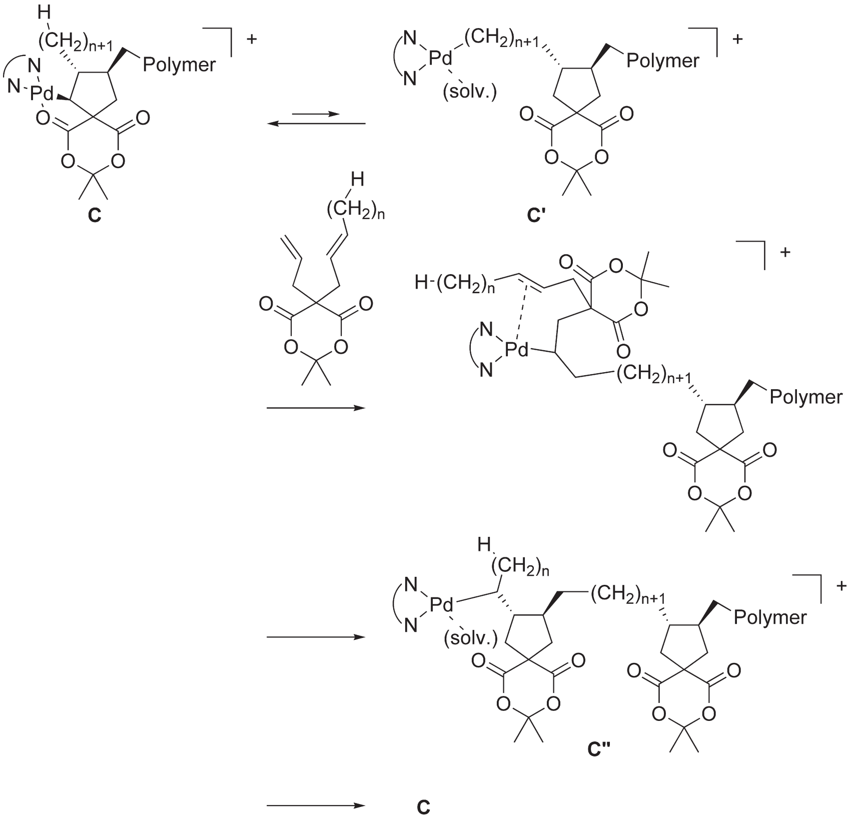
Brookhart compared stability of the primary and secondary alkyl ligand bonded to Pd as well as their reactivity toward ethylene insertion into the Pd$-$C bond.[14] The complexes having secondary alkyl ligand is more stable than that with primary alkyl ligand, while the former exhibits lower reactivity for ethylene insertion, as shown in Scheme 3. In the cyclopolymerization of **I-*n***, intermediate **C″** with secondary alkyl group bonded to Pd is much less reactive with ethylene. Intermediate species **C′** with a CH$_2$$-$Pd bond undergoes smooth insertion of a vinyl group.

The polymerization of **I-10** affords the polymer containing 2-tridecenyl group attached to the six-membered ring due to

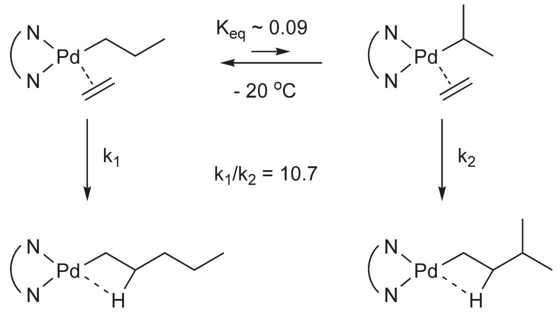
Scheme 1. Mechanism of Cyclopolymerization of Isopropylidene Diallylmalonate (I-0)



Scheme 2. Mechanism of Cyclopolymerization of Monoterminal Diene (I-*n*)



Scheme 3. Thermodynamic and Kinetic Features of the Primary and Secondary Alkyl−Palladium Complexes[14b]



incomplete cyclization. This result suggests occurrence of the termination and/or chain transfer reaction prior to the cyclization. Bulky decyl group may inhibit smooth cyclization of the diene monomer. NMR evidence for the chain transfer reaction was not obtained in the polymerization of the other monomers.

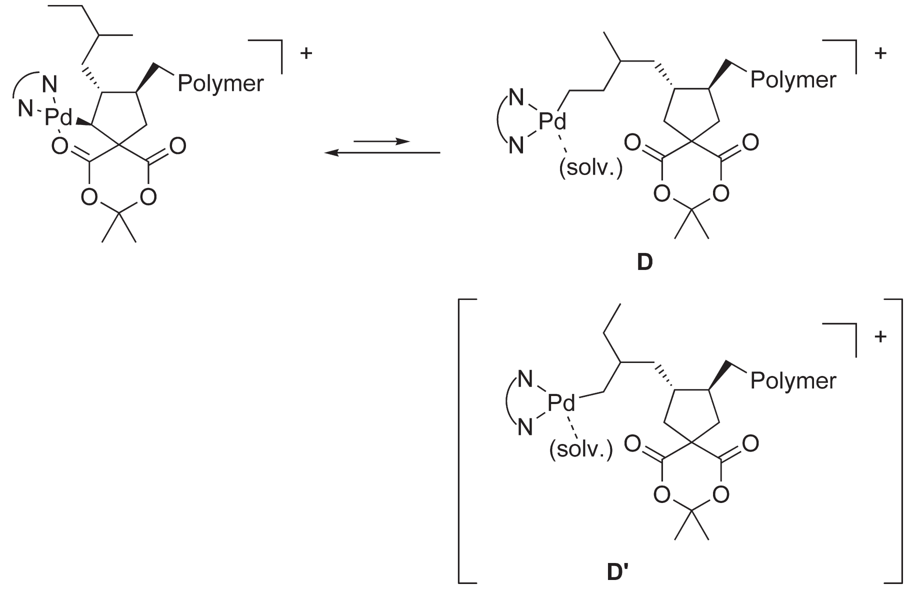
Monomers with branched alkyl group attached to a vinyl carbons **VI-0**, **VI-1**, and **VII** are polymerized smoothly to produce the polymers having five-membered rings. Chain-walking proceeds smoothly even for branched alkyl group. Monomer **VII** forms the polymer with the spacer having methyl branch and the diene units, as shown in eq 3 and Figure 3.

Scheme 4 shows chain-walking of the intermediate of the reaction, which causes formation of intermediate **D**, having the Pd$-CH_2-CH_2$ bond. Formation of intermediate **D′** with a Pd$-CH_2-CH(CH_3)-$ bond and its further reaction with the monomer would afford the polymer having ethyl branches. However, the obtained polymer does not contain the ethyl branch, and formation of **D′** is depressed, or monomer insertion to **D′** occurs much less smoothly than that of **D**. Formation of uncyclized monomer unit in the polymerization of **VII** is explained in Scheme 5. Cyclization from intermediate **E** forms the five-membered ring (Scheme 5 (i)). Steric congestion due to the 2-butyl group may cause β-elimination to form the polymer end having 4-methylhex-2-enyl group (ii). Insertion of a new monomer into the Pd−C bond of **E** prior to the cyclization produces the polymer having uncyclized monomer unit as the pendant group (iii).

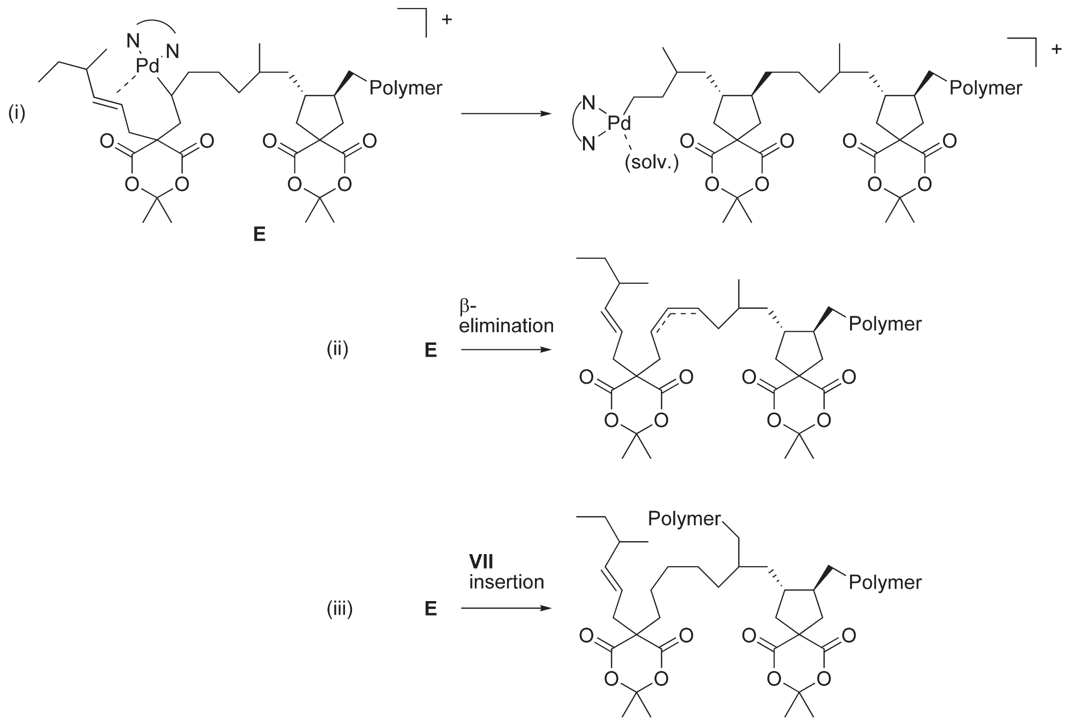
Kinetic studies of the polymerization of monoterminal dienes (**I-*n***, n = 1−4) as well as diterminal diene (**I-0**) were performed by using **1**/NaBARF as the catalyst in $CDCl_3$ at 20 °C ([Pd] = 20 mM, [monomer]/[Pd] = 50). Figure 4 shows time−conversion curve and corresponding first-order kinetic plots of the polymerization. Under the reaction conditions, the polymerization of all the monomers obeys first-order kinetics to the monomer concentration, which suggests that the rate-determining step of the polymer growth resides in the coordination and insertion of 1,6-dienes into the Pd−alkyl bond rather than intramolecular cyclization or chain-walking reaction.

Polymerization of **I-2** (k_{obsd} = 6.20 × 10^5 s^{-1}) and **I-3** (k_{obsd} = 6.27 × 10^5 s^{-1}) is faster than that of **I-0** (k_{obsd} = 4.76 × 10^5 s^{-1}) and **I-1** (k_{obsd} = 4.58 × 10^5 s^{-1}) with shorter alkyl chain and than **I-4** (k_{obsd} = 4.24 × 10^5 s^{-1}) with longer alkyl chain.

Copolymerization of Ethylene with I-1. **1**/NaBARF promotes the copolymerization of **I-1** with ethylene (1 atm) at room temperature to produce the copolymer (M_n = 5800, M_w/M_n = 1.85) (Table 3, run 1). The $^{13}C\{^1H\}$ NMR spectrum of the produced poly(**I-1**-*co*-ethylene) is shown in Figure 5. The signals at δ 169.2, 131.9, 124.1, 105.5, 55.7, 41.6, and 17.8 are quite similar positions to the corresponding signals of the diene monomer (**I-1**), and the signals observed at δ 131.9 and 124.1 are assigned to carbons of internal olefin, Scheme 4. Mechanism of Cyclopolymerization of VII



Scheme 5. Mechanism for the Formation of Uncyclized Monomer Unit



which indicates incomplete cyclization of **I-1** during the copolymerization.

Scheme 6 shows possible pathways for ethylene insertion in the copolymerization. Insertion of vinyl group of **I-1** and further insertion of ethylene into the Pd−CH bond before cyclization forms unit **F**, having a vinylene group in the pendant group. Cyclization of diene unit and subsequent chain-walking form a Pd−CH_2 bond which undergoes insertion of ethylene to produce unit **H**. The signals appeared atδ 172.2, 104.6, 51.3, 46.5, 46.0, and 32.8 are assigned to this unit **H**.

The signals of δ 46.5 and 46.0 correspond to trans-fused cyclopentane ring, and the signal of δ 32.8 is secondary carbon formed by chain-walking isomerization. The molar ratio of **I-1** and ethylene incorporated in the copolymer is estimated to be 4:96 based on the ^{1}H NMR spectrum, and the ratio of units **F** and **H** is estimated to be 1:0.9. The NMR data of the copolymer are consistent with the presence of the two structural units. The cyclization followed by direct insertion of ethylene into the Pd−CH bond would form unit **G**, but the NMR results indicate the absence of branch in the polymer chain. Ethylene insertion competes with cyclization of the alkyl intermediate to form the copolymer with uncyclized structural unit. These reactions occur much slowly than the chain-walking and produce the polymer with units **F** and **H** as the crossing points of the polymer.

It is contrasted with copolymerization of ethylene and isopropylidene diallylmalonate (**I-0**), which forms the copolymer having the cyclized diene units only because of facile cyclization

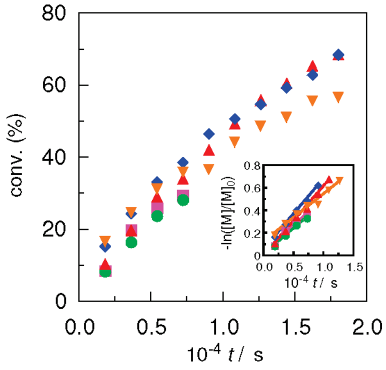


Figure 4. Time−conversion plots of the polymerization of **I-0** (pink square), **I-1** (green circle), **I-2** (red triangle), **I-3** (blue square), and **I-4** (orange triangle) catalyzed by **1**/NaBARF ($CDCl_3$, 20 °C). First-order plots are shown in the inset.

Table 3. Copolymerization of I-1 with Ethylene by Pd Complexes[a]

run	Pd	time (h)	conv (%)[b]	incorp (%)[b]	cyclization (%)[c]	M_n[d]	M_w/M_n[d]
1	**1**	3	24	6	47	5800	1.85
2	**2**	1	18	4	68	8300	1.91

[a] [NaBARF]/[Pd] = 1.2, [monomer]/[Pd] = 70, ethylene = 1 atm, temperature = rt. [b] Determined by ^1H NMR. [c] Determined by $^{13}C\{^1H\}$ NMR. [d] Determined by GPC based on polystyrene standard.

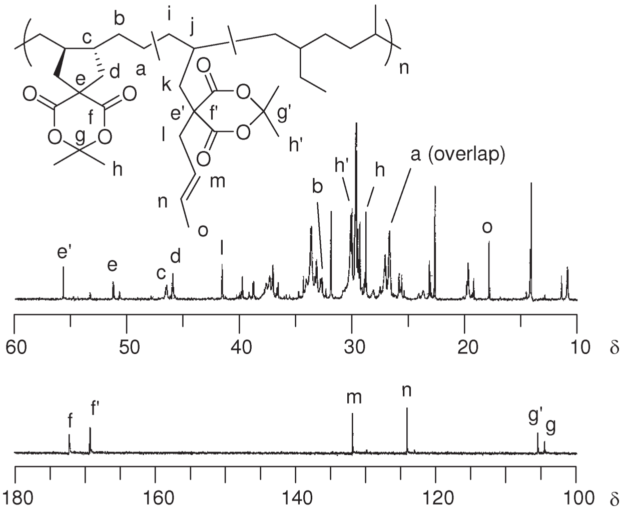


Figure 5. $^{13}C\{^1H\}$ NMR spectrum of poly(**I-1**-*co*-ethylene).

via intermolecular insertion of the terminal vinyl group into the Pd−CH bond. Use of **2**/NaBARF as the catalyst also promoted the copolymerization of **I-1** with ethylene to afford the corresponding polymer. Incorporation of **I-1** in the copolymer, however, is lower than that obtained by **1**/BARF, and the cyclization efficiency of **I-1** is 68%.

In summary, we found smooth isomerization polymerization of the functionalized monoterminal dienes catalyzed by the Pd complexes. The polymerization involves selective formation of trans-five-membered rings with the same intervals along the polymer chain in most cases. Chain-walking takes place smoothly along the long alkyl chain or the branched alkyl chain. Facile insertion of ethylene into the Pd−CH_2 bond resulted in the polymers with the regulated structures.

Experimental Section

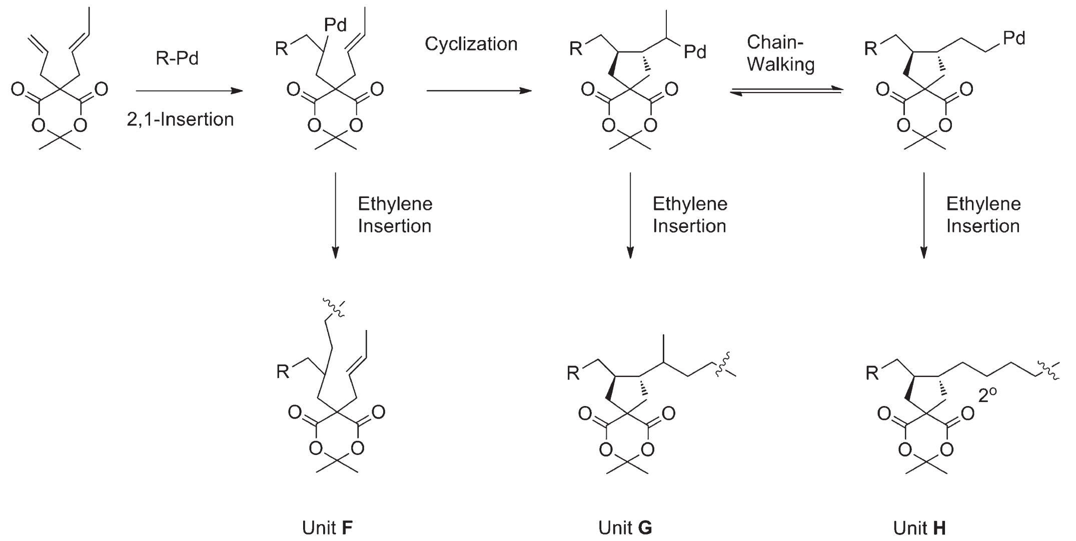
General Method. All manipulations of air- and water-sensitive compounds were carried out with standard high-vacuum or Schlenk techniques. NMR spectra were recorded on a Varian Mercury 300 and JEOL JNM-500 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to the signals of solvents. Gel permeation chromatography (GPC) measurement was conducted at 40 °C on a JASCO high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using $CHCl_3$ as eluent at a flow rate of 1.0 mL min^{-1} with Shodex-806 L column. Molecular weights were calculated relative to polystyrene standards. DSC and TG were recorded on Seiko DSC 6200R and TG/DTA 6200R, respectively.

Materials. Dry solvents were purchased and used as received unless otherwise noted. $CDCl_3$ dried over CaH_2, vacuum-transferred, and degassed by repeated freeze−pump−thaw cycles was used for kinetic studies. Diimine ligands,[11,15,16] Pd complexes,[11,15] and NaBARF[17] were synthesized according to the literature method. Preparation procedure and spectroscopic data are included in the Supporting Information.

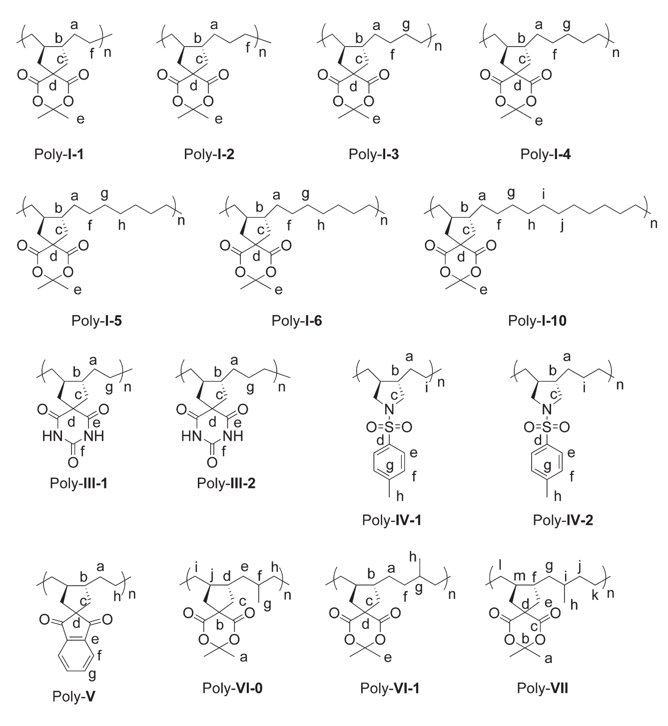
Polymerization of 1,6-Dienes. Typically, to a 25 mL Schlenk flask containing a CH_2Cl_2 solution (0.5 mL) of Pd complex **1** (0.01 mmol, 5.7 mg) was added NaBARF (0.012 mmol, 10.6 mg) under Ar. After stirring for several minutes, 5-allyl-5-((2*E*)-butenyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**I-1**, 166.7 mg, 0.70 mmol) was added, and the reaction mixture was stirred at room temperature. The portion of the reaction mixture was periodically taken out from the flask and subjected to ^1H NMR and GPC analysis to determine conversion of **I-1** and molecular weight of poly-**I-1** (24 h, quant conversion). After 24 h reaction, the reaction mixture was poured into large amount of methanol (ca. 50 mL). A white solid formed was collected and dried in vacuo at 25 °C to give poly-**I-1** (117 mg, 76% yield, M_n = 7900, M_w/M_n = 1.68). ^1H NMR (500 MHz, $CDCl_3$): δ 2.42 (br, 2H, CH_2 (cyclopentane)), 1.92 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)), 1.71 (s, 6H, CH_3), 1.62 (br, 2H, CH_2 (main chain)), 1.13 (br, 4H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.0 (C=O), 104.7 (O−C−O), 51.2(C_d), 46.9 (C_b), 45.8 (C_c), 33.0 (C_a), 28.8(C_e), 26.7(C_f).

Other dienes are polymerized similarly. Poly-**I-2**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (br, 2H, CH_2 (cyclopentane)), 1.92 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)), 1.72 (s, 6H, CH_3), 1.60 (br, 2H, CH_2 (main chain)), 1.18 (br, 6H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.1 (C=O), 104.7 (O−C−O), 51.2(C_d), 46.4 (C_b), 45.8 (C_c), 32.8 (C_a), 28.8(C_e), 26.5(C_f). Poly-**I-3**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (br, 2H, CH_2 (cyclopentane)), 1.89 (br, 2H, CH_2 (cyclopentane)), 1.82 (br, 2H, CH (cyclopentane)), 1.70 (s, 6H, CH_3), 1.59 (br, 2H, CH_2 (main chain)), 1.13 (br, 8H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.1 (C=O), 104.6 (O−C−O), 51.2(C_d), 46.4 (C_b), 45.8 (C_c), 32.7 (C_a), 30.2 (C_g), 28.7(C_e), 28.0 (C_f). Poly-**I-4**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.44 (br, 2H, CH_2 (cyclopentane)), 1.94 (br, 2H, CH_2 (cyclopentane)), 1.85 (br, 2H, CH (cyclopentane)), 1.73 (s, 6H, CH_3),1.62 (br, 2H, CH_2 (main chain)), 1.19 (br, 10H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2 (C=O), 104.7 (O−C−O), 51.3(C_d), 46.5 (C_b), 46.0 (C_c), 32.8 (C_a), 30.0 (C_g), 28.8(C_e), 28.1 (C_f). Poly-**I-5**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.36 (br, 2H, CH_2 (cyclopentane)), 1.87 (br, 2H, CH_2 (cyclopentane)), 1.78 (br, 2H, CH (cyclopentane)), 1.66 (s, 6H, CH_3), 1.55 (br, 2H, CH_2 (main chain)), 1.12 (br, 12H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.9 (C=O), 104.4 (O−C−O), 51.0(C_d), 46.3 (C_b), 45.7 (C_c), 32.5 (C_a), 29.6 (C_g), 29.2 (C_h), 28.6(C_e), 27.8 (C_f). Poly-**I-6**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (br, 2H, CH_2 (cyclopentane)), 1.94 (br, 2H, CH_2 (cyclopentane)), 1.84 (br, 2H, CH (cyclopentane)), 1.72 (s, 6H, CH_3), 1.61 (br, 2H, CH_2 (main chain)), 1.18 (br, 14H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2 (C=O), 104.6 (O−C−O), 51.2(C_d), 46.5 (C_b), 46.0 (C_c), 32.7 (C_a), 29.9 (C_g), 28.8(C_e), 28.1 (C_j). Poly-**I-10**: ^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (br, 2H, CH_2 (cyclopentane)), 1.93 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)),

Scheme 6. Copolymerization of Ethylene with I-1



1.71 (s, 6H, CH_3), 1.62 (br, 2H, CH_2 (main chain)), 1.21 (br, 22H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2 (C=O), 104.6 (O−C−O), 51.2(C_d), 46.5 (C_b), 46.0 (C_c), 32.7 (C_a), 29.9 (C_g,C_h,C_i), 28.8(C_e), 28.1 (C_f). Poly-**III-1**: ^1H NMR (500 MHz, DMF-d_7, rt): δ 11.1 (br, 2H, NH), 2.38 (br, 2H, CH2 (cyclopentane)), 1.80 (br, 2H, CH_2 (cyclopentane)), 1.73 (br, 2H, CH (cyclopentane)), 1.66 (br, 2H, CH_2 (main chain)), 1.31 (br, 2H, CH_2 (main chain)), 1.13 (br, 2H, CH2 (main chain)). $^{13}C\{1H\}$ NMR (125 MHz, DMF-d_7, r.t.): δ 175.6 (C_e), 151.2 (C_f), 55.0 (C_d), 46.8 (C_b), 44.0 (C_c), 33.9 (C_a), 27.4 (C_g). Poly-**III-2**: ^1H NMR (500 MHz, DMF-d_7, rt): δ 11.1 (br, 2H, NH), 2.38 (br, 2H, CH_2 (cyclopentane)), 1.77 (br, 2H, CH_2 (cyclopentane)), 1.71 (br, 2H, CH (cyclopentane)), 1.65 (br, 2H, CH_2 (main chain)), 1.37 (br, 4H, CH_2 (main chain)), 1.13 (br, 2H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, DMF-d_7, rt): δ 175.1 (C_e), 150.7 (C_f), 55.2 (C_d), 46.7 (C_b), 44.0 (C_c), 33.4 (C_a), 28.6 (C_g) Poly-**IV-1**: ^1H NMR (500 MHz, $CDCl_3$, rt): δ 7.65 (br, 2H, H_e), 7.34 (br, 2H, H_f), 3.38 (br, 2H, CH_2 (cyclopentane)), 2.74 (br, 2H, CH_2 (cyclopentane)), 2.43 (s, 3H, H_h), 1.52 (br, 2H, CH (cyclopentane)), 1.33 (br, 2H, CH_2 (main chain)), 1.04 (br, 4H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, rt): δ 143.4 (C_g), 133.4 (C_d), 130.0 (C_f), 127.4 (C_e), 53.0 (C_c), 44.3 (C_b), 32.6 (C_a), 26.6 (C_i), 21.5 (C_h). Poly-**IV-2**: ^1H NMR (500 MHz, $CDCl_3$, rt): δ 7.68 (br, 2H, H_e), 7.33 (br, 2H, H_f), 3.40 (br, 2H, CH_2 (cyclopentane)), 2.76 (br, 2H, CH_2 (cyclopentane)), 2.42 (s, 3H, H_h), 1.55 (br, 2H, CH (cyclopentane)), 1.38 (br, 2H, CH_2 (main chain)), 1.12 (br, 6H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.4 (C_g), 133.6 (C_d), 129.6 (C_f), 127.4 (C_e), 53.1 (C_c), 44.3 (C_b), 32.4 (C_a), 28.3 (C_i), 21.5 (C_h). Poly-**V**: ^1H NMR (500 MHz, $CDCl_3$, rt): δ 7.90 (br, 2H, H_f), 7.78 (br, 2H, H_g), 2.05 (br, 2H, CH_2 (cyclopentane)), 1.77 (br, 2H, CH_2 (cyclopentane)), 1.58 (br, 2H, CH (cyclopentane)), 1.58 (br, 2H, CH_2 (main chain)), 1.20 (br, 4H, CH_2 (main chain)). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, rt): δ 204.7 (C=O), 141.4 (C_e), 135.2 (C_g), 123.3 (C_f), 58.5 (C_d), 46.7 (C_b), 40.8 (C_c), 33.7 (C_a), 27.0 (C_h). Poly-**VI-0**: ^1H NMR (500 MHz, $CDCl_3$, rt): δ 2.38 (br, 2H, CH_2 (cyclopentane)), 1.88 (br, 2H, CH_2 (cyclopentane)), 1.59 (s, 6H, CH_3), 1.24−1.10 (br, 7H, CH_2 (main chain) and CH (main chain)), 0.81 (br, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, rt): δ 172.0 (C=O), 104.6 (O−C−O), 51.1 (C_b), 47.2−46.9 (C_j), 45.8 (C_c), 43.8 (C_d), 40.6−40.0 (C_e), 36.7−36.5 (C_h), 31.7 (C_f), 30.0 (C_i), 28.7 (C_a), 21.8−18.5 (C_g). Poly-**VI-1**: ^1H NMR (500 MHz, $CDCl_3$, rt): δ 2.44 (br, 2H, CH_2 (cyclopentane)), 1.93 (br, 2H, CH_2 (cyclopentane)), 1.83 (br, 2H, CH (cyclopentane)), 1.73 (s, 6H, CH_3), 1.24−1.06 (br, 7H, CH_2 (main chain) and CH (main chain)), 0.83 (br, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, rt): δ 172.2 (C=O), 104.7 (O−C−O), 51.2 (C_d), 47.0−46.6 (C_b), 45.8 (C_c), 35.9−35.0 (C_f), 33.4−33.1 (C_g), 30.1 (C_a), 28.8 (C_e), 19.8−19.1 (C_h).



Poly-**VII**: ^1H NMR (500 MHz, $CDCl_3$, rt): δ 2.42 (br, 2H, CH_2 (cyclopentane)), 1.91 (br, 2H, CH_2 (cyclopentane)), 1.81 (br, 2H, CH (cyclopentane)), 1.58 (s, 6H, CH_3), 1.36−1.08 (br, 9H, CH_2 (main chain) and CH (main chain)), 0.83 (br, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, rt): δ 172.1 (C=O), 104.6 (O−C−O), 51.3−50.6 (C_d), 47.1 (C_m), 46.2−45.7 (C_e), 44.0 (C_f), 41.1 (C_g), 35.9 (C_j), 33.0 (C_l), 31.6 (C_i), 28.7 (C_a), 26.5 (C_k), 20.8−20.7 (C_h).

Kinetic Study. To a 25 mL Schlenk flask containing a $CDCl_3$ solution (1.0 mL) of Pd complex **1** (0.02 mmol, 11.5 mg) was added NaBARF (0.024 mmol, 21.3 mg) and naphthalene (internal standard, 0.25 mmol, 32.0 mg) under Ar. After stirring for several minutes, 5-allyl-5-((2*E*)-butenyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**I-1**, 238.1 mg, 1.00 mmol) was added at room temperature, and 0.5 mL of the reaction mixture was transferred to NMR tube. The mixture was allowed to stand at 20 °C and was subjected to ^1H NMR measurement with appropriate intervals to determine conversion of **I-1**. k_{obsd}(**I-0**) $= 4.76 \times 10^5\ \mathrm{s}^{-1}$, k_{obsd}(**I-1**) $= 4.58 \times 10^5\ \mathrm{s}^{-1}$, k_{obsd}(**I-2**) $= 6.20 \times 10^5\ \mathrm{s}^{-1}$, k_{obsd}(**I-3**) $= 6.27 \times 10^5\ \mathrm{s}^{-1}$, k_{obsd}(**I-4**) $= 4.24 \times 10^5\ \mathrm{s}^{-1}$.

Acknowledgment. This work was supported by a Grant-in-Aid for Young Scientist (No. 20750085) for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Preparation procedure and spectroscopic data of monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Janiak, C.; Lassahn, P. G. *Macromol. Rapid Commun.* **2001**, *22*, 479. (b) Yamazaki, M. *J. Mol. Catal. A: Chem.* **2004**, *213*, 81. (c) Li, X.; Hou, Z. *Coord. Chem. Rev.* **2008**, *252*, 1842.

(2) (a) Collins, S.; Kelly, W. M. *Macromolecules* **1992**, *25*, 233. (b) McLain, S. J.; Feldman, J.; McCord, E. F.; Gardner, K. H.; Teasley, M. F.; Coughlin, E. B.; Sweetman, K. J.; Johnson, L. K.; Brookhart, M. *Macromolecules* **1998**, *31*, 6705. (c) Fujita, M.; Coates, G. W. *Macromolecules* **2002**, *35*, 9640.

(3) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(4) (a) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (b) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (c) Naga, N.; Shiono, T.; Ikeda, T. *Macromolecules* **1999**, *32*, 1348. (d) Choo, T. N.; Waymouth, R. M. *J. Am. Chem. Soc.* **2002**, *124*, 4188. (e) Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 11578.

(5) (a) Kim, I.; Shin, Y. S.; Lee, J. K.; Won, M.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1520. (b) Kiesewetter, J.; Kaminsky, W. *Chem.—Eur. J.* **2003**, *9*, 1750. (c) Hasan, T.; Ikeda, T.; Shiono, T. *Macromolecules* **2004**, *37*, 8503. (d) Wang, W.; Fujiki, M.; Nomura, K. *J. Am. Chem. Soc.* **2005**, *127*, 4582. (e) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(6) (a) Takeuchi, D.; Anada, K.; Osakada, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1233. (b) Takeuchi, D.; Anada, K.; Osakada, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1868.

(7) (a) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 8963. (b) Rojas, G.; Inci, B.; Wei, Y.; Wagener, K. B. *J. Am. Chem. Soc.* **2009**, *131*, 17376. (c) Baughman, T. W.; Wagener, K. B. *Adv. Polym. Sci.* **2005**, *176*, 1. (d) Rojas, G.; Berda, E. B.; Wagener, K. B. *Polymer* **2008**, *49*, 2985.

(8) (a) Takeuchi, D.; Matsuura, R.; Park, S.; Osakada, K. *J. Am. Chem. Soc.* **2007**, *129*, 7002. (b) Takeuchi, D.; Matsuura, R.; Osakada, K. *Macromol. Rapid Commun.* **2008**, *29*, 1932. (c) Takeuchi, D.; Fukuda, Y.; Park, S.; Osakada, K. *Macromolecules* **2009**, *42*, 5909. (d) Takeuchi, D.; Matsuura, R.; Fukuda, Y.; Osakada, K. *Dalton Trans.* **2009**, 8955.

(9) (a) Park, S.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2006**, *128*, 3510. (b) Park, S.; Okada, T.; Takeuchi, D.; Osakada, K. *Chem.—Eur. J.*, **2010**, *16*, 8662.

(10) Okada, T.; Park, S.; Takeuchi, D.; Osakada, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6141.

(11) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664. (c) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (d) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(12) Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.

(13) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436.

(14) (a) Tempel, D. J.; Brookhart, M. *Organometallics* **1998**, *17*, 2290. (b) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

(15) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88.

(16) Song, C.-L.; Tang, L.-M.; Li, Y.-G.; Li, X.-F.; Chen, J.; Li, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1964.

(17) (a) Buschmann, W. E.; Miller, J. S. *Chem.—Eur. J.* **1998**, *4*, 1731. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (c) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600.