VIP

Cyclopolymerization and Copolymerization of Functionalized 1,6-Heptadienes Catalyzed by Pd Complexes: Mechanism and Application to Physical-Gel Formation

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Abstract: Cationic Pd complexes, prepared from [PdCl(ArN=C$_{12}$H$_6$=NAr)(Me)] and Na[B{3,5(CF$_3$)$_2$C$_6$H$_3$}$_4$] (NaBARF), catalyze the cyclopolymerization of 4,4-disubstituted 1,6-heptadienes. The polymers produced contain a *trans*-fused five-membered ring in each repeating unit. NMR spectroscopy and FAB mass spectrometry of the polymers formed indicated that the initiation end of the chain contains either the cyclopentyl group derived from the preformed Pd–monomer complex or a hydrogen atom left on the Pd center by the chain-transfer reaction. The stable cyclopentylpalladium species are involved in both initiation and propagation steps and undergo isomerization into (cyclopentylmethyl)palladium species followed by the insertion of a CH=CH$_2$ bond of a new monomer molecule into the Pd–CH$_2$ bond. Copolymerization of 1,6-heptadiene derivatives with ethylene, catalyzed by the Pd complexes, yields polymers that contain *trans* five-membered rings and branched oligoethylene units. Copolymerization of isopropylidene diallylmalonate with 1-hexene affords a polymer with 26% diene incorporation. The copolymerization consumes 1-hexene more readily than isopropylidene diallylmalonate, although gel permeation chromatography and NMR spectroscopy of the polymers produced show the formation of copolymers rather than of a mixture of homopolymers. Polymerization of 1-hexene initiated with a Pd–barbiturate complex and terminated with 5-allyl-5-hexylpyrimidine-2,4,6(1H,3H,5H)-trione/Et$_3$SiH leads to polyhexene with barbiturate moieties at both terminal ends. Addition of 5-hexyl-2,4,6-triaminopyrimidine to a toluene solution of the telechelic poly(1-hexene) converts the solution into gel.

**Keywords:** copolymerization · dienes · gels · palladium · polymerization

Introduction

Cationic Pd^{II} and Ni^{II} complexes with bulky diimine ligands have recently attracted attention as new catalysts for olefin polymerization since their discovery in 1995.[1] The reactions with these catalysts yield highly branched polyethylene and poly(α-olefin)s with linear polymethylene chains. This is attributed to a chain-walking reaction, in which alkylnickel and -palladium bonds at the growing-polymer ends undergo repetitive β-hydrogen elimination of vinyl-terminated poly-olefin followed by reinsertion into the metal–hydrogen bond (Scheme 1). The reaction during polymer growth[2] controls the degree of branching of the polyolefins.[3] The polymer end exists as a primary, secondary, or tertiary alkyl group attached to the cationic Pd^{II} center. The group of Brookhart established an equilibrium between the primary and secondary alkyl groups bonded to the palladium complexes and observed higher reactivity of the former toward insertion of ethylene into the Pd–C bond.[4] The Pd catalysts promote copolymerization of ethylene with acrylic esters to give functionalized polyethylene,[5] as well as emulsion polymerization of ethylene in aqueous media; a result of the lower Lewis acidity of Pd^{II} relative to early transition metals in Ziegler–Natta and metallocene catalysts.[6] Stereoselective polymerization of α-olefins is a more recent issue in terms of Ni and Pd catalysis and the number of reports is much smaller than those on the use of early-transition-metal catalysts. For example, a Ni complex with a C_2-symmetric diimine ligand catalyzes the isotactic polymerization of propylene,[7] similarly to C_2-substituted ansa-zirconocenes.[8]

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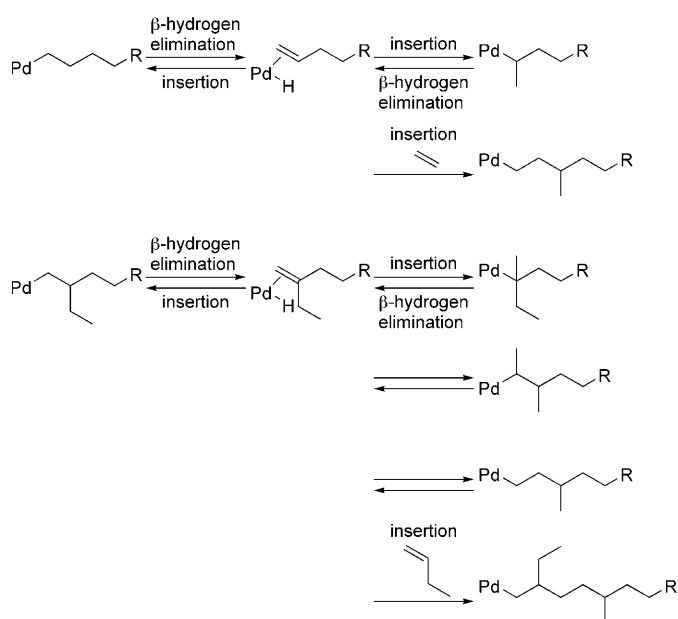
Scheme 1. Chain-walking isomerization in alkyl-palladium species.

Recently, we have applied Pd catalysts to the polymerization of new olefin and diene monomers and observed the characteristics mentioned above: control of branching by chain walking, polymer growth in spite of polar functional groups in the monomer, and stereoselective insertion of α-olefins. 4-Alkylcyclopentenes undergo isomerization polymerization to form polymers with a 1,3-disubstituted five-membered ring in each repeating unit.[9] Use of C_2-symmetric Pd catalysts resulted in selective insertion of a monomer into the Pd–CH$_2$ bond and yielded polymers with an isotactic arrangement of *trans*-fused five-membered rings. Isopropylidene diallylmalonate and related 1,6-heptadiene derivatives with polar functional groups undergo cyclopolymerization to produce polymers with functionalized five-membered rings.[10] The polymerization proceeds smoothly, in spite of the presence of polar ester groups in the monomer. Cyclopolymerization of monoterminal 1,6-dienes affords polymers with 1,2-*trans*-fused five-membered rings linked by polymethylene spacers.[11] These reactions contrast with the cyclopolymerization of 1,6-heptadienes cata-

lyzed by complexes of early transition metals,[12] which form polymers with irregular structures or primarily contain six-membered rings, except for the reactions discussed in recent reports by Coates and co-workers.[13,14] Complexes of other late-transition metals, such as Co and Fe, catalyze cyclopolymerization to form polymers with *trans*- and/or *cis*-fused five-membered rings.[15] Further studies of the cyclopolymerization of functionalized 1,6-heptadiene derivatives catalyzed by Pd complexes have revealed details of the reaction mechanism, copolymerization of the monomer with hexene, and properties of the copolymers with polar functional groups. In this paper, we report the scope of the cyclopolymerization, copolymerization of the dienes with olefins, detailed mechanisms of initiation, polymer growth, and chain transfer, and the synthesis of telechelic poly(1-hexene).

Results and Discussion

Polymerization of functionalized 1,6-heptadienes: Scheme 2 shows a summary of the 1,6-heptadiene derivatives with substituents at the 4-position (**I**–**VI**) and *N,N*-diallylsulfonamides (**VII**–**X**) used as monomers and of the Pd-catalyst precursors (**1a**–**c**, **2a**, **2b**, and **3a**). The cationic methylpalladium complexes formed from **1a**, **1b**, **2a**, **2b**, and **3a** and Na[B{3,5(CF$_3$)$_2$C$_6$H$_3$}$_4$] (NaBARF) catalyze high-mass polymerization of ethylene and α-olefins,[2] whereas **VI** undergoes cycloisomerization and cyclative hydrosilylation cata-
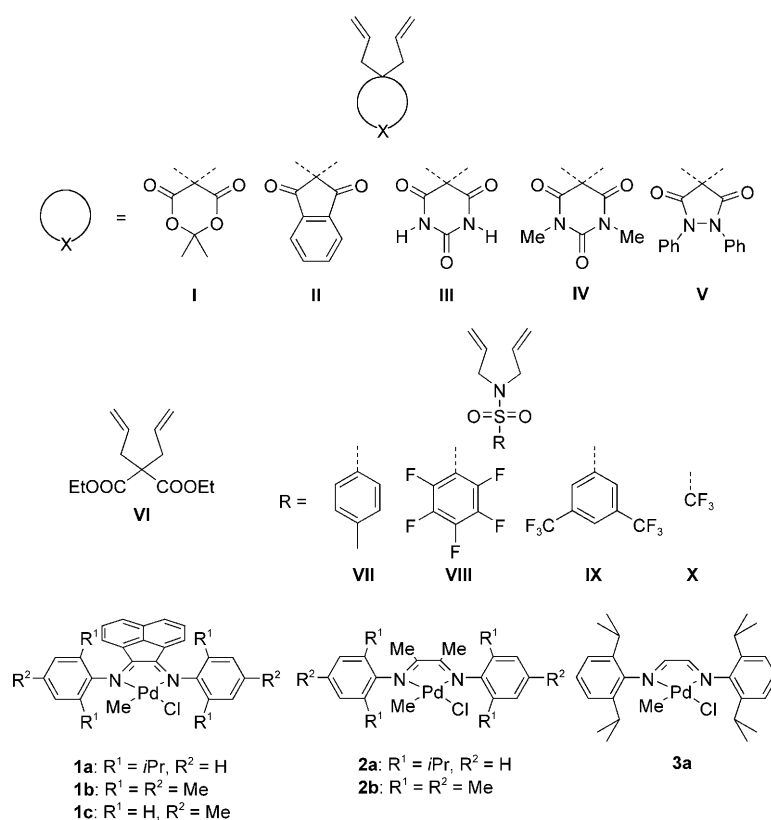
Scheme 2. 1,6-Heptadiene derivatives and Pd catalyst precursors.

lyzed by the cationic Pd–1,10-phenanthroline (phen) complex.[16]

Scheme 3 shows a summary of the cyclopolymerizations in this study. Isopropylidene diallylmalonate (**I**) undergoes smooth cyclopolymerization in the presence of the various
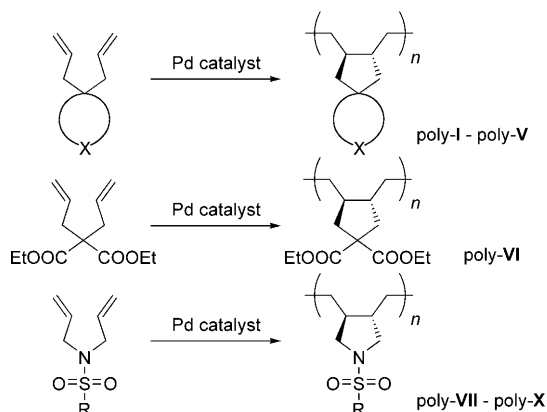
Scheme 3. Cyclopolymerization of 1,6-dienes **I–X** by Pd catalysis.

catalysts, prepared in situ from NaBARF and the Pd diimine complexes **1a**, **1b**, **2a**, and **2b**, to produce a polymer with a five-membered ring in each repeating unit (poly-**I**). The catalysts prepared from **1a** and **2a** exhibit moderate activities toward cyclopolymerization (Table 1, entries 1 and 4), whereas the reactions catalyzed by **1b**/NaBARF and **2b**/

NaBARF form poly-**I** in high yields (Table 1, entries 2 and 5). The complexes **1c** and **3a** do not function as catalyst precursors for cyclopolymerization of **I** (Table 1, entries 3 and 6), although **3a**/NaBARF catalyzes ethylene polymerization smoothly.[2a] Less steric bulkiness (**1c**) and higher flexibility (**3a**) of the ligands may increase the frequency of chain-transfer reactions.

The ^{1}H NMR spectrum of poly-**I** contains no signals due to olefinic hydrogen atoms, which indicates complete cyclization of the monomers during polymer growth. Substituents on the diene monomer may facilitate cyclization in the polymerization (Thorpe–Ingold effect).[17] The ^{13}C NMR spectrum exhibits a single set of signals due to the CH, CH$_2$, and quaternary carbon atoms of the five-membered ring ($\delta = 47.0$, 45.8, and 51.1 ppm, respectively). Comparison of their positions with the positions of model compounds[18] indicates that repeating units of the polymer contain exclusively *trans*-fused 1,2-cyclopentane rings. Molecular weights of poly-**I** prepared by using the **1a**/NaBARF catalyst in CH$_2$Cl$_2$ or toluene ([**I**] = 1.4 M) are in the range $M_n = 6000$–7900 ($M_w/M_n = 1.51$–1.60, gel-permeation chromatography (GPC), polystyrene standard) and the polymerization under bulk conditions yields a product with a higher molecular weight ($M_n = 18400$, $M_w/M_n = 1.43$) (Table 1, entries 1, 7, and 8).

2,2-Diallylindane-1,3-dione (**II**) undergoes smooth polymerization in the presence of the **1a**/NaBARF catalyst to afford poly-**II** with molecular weights of $M_n = 12000$ and 9200 ($M_w/M_n = 1.64$ and 1.12) at room temperature and $-10\,^\circ$C, respectively (Table 1, entries 9 and 10). Re-addition of the monomer after the polymerization ($M_n = 10800$ and $M_w/M_n = 1.10$) at $-10\,^\circ$C causes the resumption of polymer growth to yield a product with $M_n = 18500$ and $M_w/M_n = 1.24$ (conversion = 93%), which indicates living cyclopolymerization at that temperature. Cyclopolymerization of the monomers with cyclic imide groups (**III–V**) affords the corresponding five-membered ring polymers (Table 1, entries 11–13). Diethyl diallylmalonate (**VI**), without a cyclic group in the monomer, also undergoes the cyclopolymerization catalyzed by **1b**/NaBARF to produce poly-**VI**, at a lower rate than the polymerization of **I** (Table 1, entry 14 versus 2). The sulfonamide groups of **VII–X** do not inhibit the Pd-catalyzed cyclopolymerizations of these compounds (Table 1, entries 15–18). The glass-transition temperatures (T_g) of poly-**VII**–poly-**X** (84–101 $^\circ$C) are lower than that of poly-**II** (134 $^\circ$C), which has a rigid spirocyclic structure.

All of these polymers contain *trans*-fused 1,2-disubstituted five-membered rings and the pathway for their formation is shown in Scheme 4. The polymer growth involves initial 2,1-insertion of the C=C double bond of the diene into the Pd–polymer bond, which forms a *sec*-alkylpalladium intermediate with a pendant vinyl group (**A**). Subsequent cyclization by intramolecular 1,2-insertion of the second C=C bond into the Pd–C bond produces (cyclopentylmethyl)palladium species **B**. A sequence of alternating inter- and intra-molecular insertion reactions of C=C bonds into Pd–C bonds yields a polymer with five-membered rings. The polymer of 1,6-hep-

Table 1. Polymerization of 1,6-heptadienes by Pd complexes.[a]

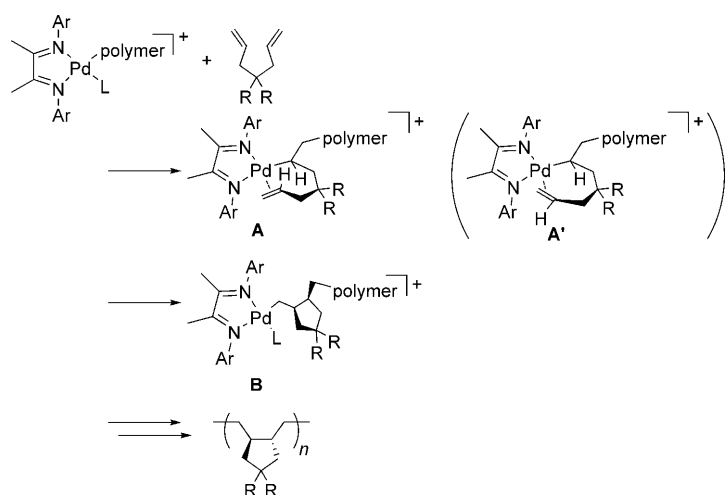|	Diene	Pd	Solvent [mL]	t [h]	Conv.[b] [%]	M_n[c]	M_w/M_n[c]	T_g[d] [°C]
1	**I**	**1a**	CH$_2$Cl$_2$ (0.5)	24	56	7900	1.51	–
2	**I**	**1b**	CH$_2$Cl$_2$ (0.5)	24	95	9200	1.75	–
3	**I**	**1c**	CH$_2$Cl$_2$ (0.5)	24	trace	–	–	–
4	**I**	**2a**	CH$_2$Cl$_2$ (0.5)	24	58	6400	1.47	–
5	**I**	**2b**	CH$_2$Cl$_2$ (0.5)	24	92	9800	1.59	–
6[e]	**I**	**3a**	CH$_2$Cl$_2$ (1)	12	trace	–	–	–
7	**I**	**1a**	toluene (0.5)	48	57	6000	1.60	–
8	**I**	**1a**	bulk	24	31	18400	1.43	–
9	**II**	**1a**	CH$_2$Cl$_2$ (0.25)	11	85	12000	1.64	134
10[f]	**II**	**1a**	CH$_2$Cl$_2$ (0.25)	80	quant	9200	1.12	–
11	**III**	**1a**	CH$_2$Cl$_2$ (0.5)	24	40[g]	23000[h]	1.22[h]	–
12	**IV**	**1b**	CH$_2$Cl$_2$ (0.5)	24	71	2800	1.73	143
13	**V**	**1b**	CH$_2$Cl$_2$ (0.5)	65	33	9400	1.50	–
14	**VI**	**1b**	CH$_2$Cl$_2$ (0.25)	48	53	9400	1.71	20
15	**VII**	**1b**	CH$_2$Cl$_2$ (0.25)	72	56	7100	1.56	90
16	**VIII**	**1b**	CH$_2$Cl$_2$ (0.25)	36	32	8300[h]	1.12[h]	101
17	**IX**	**1b**	CH$_2$Cl$_2$ (0.25)	24	38	–[i]	–[i]	84
18	**X**	**1b**	CH$_2$Cl$_2$ (0.25)	18	53[g]	8200[h]	1.17[h]	89

[a] Reaction conditions: Pd cat (0.010 mmol), NaBARF (0.012 mmol), diene (0.70 mmol), RT. Results in entries 1–3, 14, and 15 are reported in a preliminary communication (see reference [10]). [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Determined by gel-permeation chromatography (GPC), CHCl$_3$ as the eluent. [d] Determined by differential scanning calorimetry (DSC). [e] Pd cat (0.025 mmol), NaBARF (0.030 mmol), diene (1.75 mmol), RT. [f] Diene (0.40 mmol), $-10\,^\circ$C. [g] Yield of isolated polymer. [h] Determined by GPC, DMF as the eluent. [i] Not determined due to low solubility.

Scheme 4. Pathway for the formation of *trans*-fused 1,2-disubstituted five-membered rings.

tadiene prepared by using Ti or Zr catalysts contains 1,3-disubstituted six-membered rings formed by intermolecular 1,2-insertion of a C=C bond of the diene into the metal–polymer bond followed by the cyclization of the polymer end.[12] Preferential 1,2-insertion is common in polymerizations of α-olefins catalyzed by early-transition-metal complexes, however, Pd–diimine complexes are reported to cause both 1,2- and 2,1-insertion in olefin polymerization.[2] *Trans*-selective cyclization is also observed for the cyclative hydrosilylation of diallylmalonates catalyzed by a Pd–phen complex.[16] Formation of thermodynamically stable *trans* five-membered rings in the polymerization can be explained by cyclization via intermediate **A** rather than **A′**, which has more severe steric congestion.[14a,d]

Mechanism of cyclopolymerization: Previously, we carried out an equimolar reaction of **I** with **1a**/NaBARF at −40 °C and proposed a structure **C**, with a seven-membered chelate ring, for the complex (Scheme 5).[10] However, further stud-
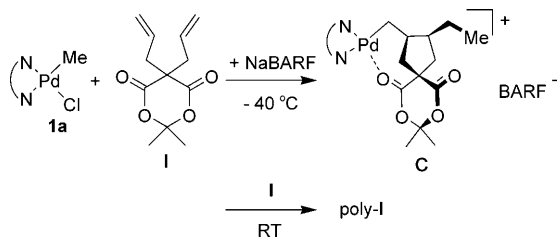
Scheme 5. Reaction pathway proposed in reference [10].

ies of the reaction, isolation and X-ray crystallography of the complex produced, and detailed NMR analyses revealed the actual structure of the complex. Features of the initiation and propagation of the cyclopolymerization are described below.

Reaction of **1a** (1 equiv) with **I** (5 equiv) in the presence of NaBARF at −20 °C followed by recrystallization of the products yielded a complex with a five-membered C,O-chelate ring, **4a-I**, in 27% yield, as shown in Scheme 6. The
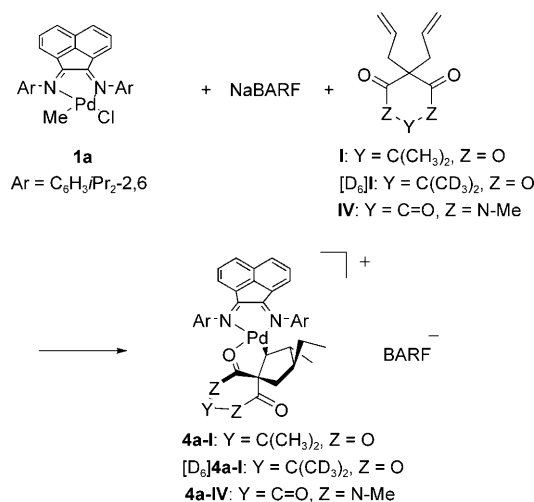
Scheme 6. Equimolar reaction of **1a** with **I** in the presence of NaBARF.

analogous reaction with [D₆]**I**, which contains two CD₃ groups, produced [D₆]**4a-I**. The diene monomer containing *N*-methylimide groups (**IV**) also reacts with **1a** in the presence of NaBARF at −40 °C to produce **4a-IV**, which also contains a five-membered C,O-chelate ring.

Figure 1 shows the structure of **4a-I** determined by X-ray crystallography. The chelating C,O-ligand contains a six-membered isopropylidene malonate ring as well as a *trans*-fused five-membered ring formed by cyclization of the 1,6-diene in **I**. The structure of the chelating ligand is similar to [Pd{CHCH(Me)CH(Et)CH₂C(COOMe)COOMe}(phen)]-[BARF] (**5**, Scheme 7), which was obtained by Widenhoefer et al., in the course of their studies on the mechanism of the cycloisomerization of dimethyl diallylmalonate catalyzed by [Pd(Me)(NCMe)(phen)][BARF].[16] The distance between
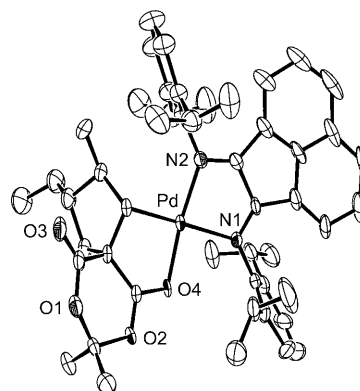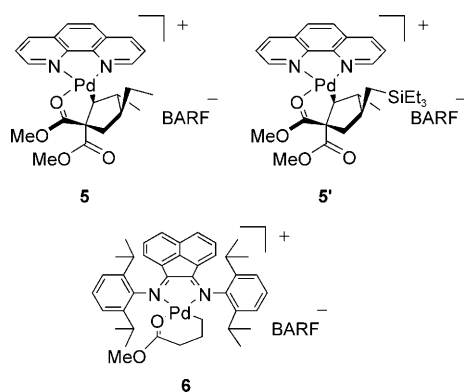

Figure 1. X-ray crystal structure of **4a-I**. The counteranion is omitted.

Scheme 7. Pd-Diimine complexes with a C,O-chelating ligand.

the Pd and O atoms in **4a-I** (2.068 Å) is close to that of **5** (2.064 Å);[16j] the Pd–cyclopentyl carbon atom bond length is 1.974 Å.

The isolated complexes **4a-I** and **4a-IV** were stable at room temperature in solution and have been characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra exhibited signals for the CH$_2$ and CH–Pd hydrogen atoms of the five-membered ring at reasonable positions ($\delta = 2.68$, 2.46, and 2.04 ppm for **4a-I** and $\delta = 2.71$, 2.26, and 2.03 ppm for **4a-IV**). Signals due to the two magnetically non-equivalent *ortho* hydrogen atoms of the acenaphthene group are observed at $\delta = 6.74$ and 6.17 ppm (**4a-I**) and $\delta = 6.84$ and 6.08 ppm (**4a-IV**). Twenty-two ^{13}C NMR signals in the range $\delta = 180–120$ ppm, due to the aromatic carbon atoms of the acenaphthene unit and N-aryl groups, also indicate unsymmetrical coordination of the C,O-chelating ligand to the Pd center in these complexes. The ^{13}C NMR signals of the carbonyl group coordinated to the Pd center ($\delta = 187.6$ (**4a-I**) and 187.9 ppm (**4a-IV**)) are observed at similar positions to the diimine complex with a C,O-chelating ligand formed from the reaction of methyl acrylate with the methylpalladium complex (**6**, $\delta = 183.5$ ppm).[5b] The carbon atoms of the free-carbonyl group show signals significantly upfield ($\delta = 164.4$ (**4a-I**) and 167.9 ppm (**4a-IV**)). The NMR data obtained from DEPT, COSY, and HMBC measurements on the three Pd complexes are consistent with the structure of **4a-I** obtained by X-ray crystallography. Although the yield of **4a-I** can be as low as 27%, the ^{1}H and ^{13}C NMR data of the isolated complex are similar to those observed for the reaction mixture of **1a**, NaBARF, and **I** at −20°C. Thus, the main species obtained from the stoichiometric reaction of **I** and **1a**/NaBARF is **4a-I**, rather than complex **C** with a seven-membered C,O-chelate ring proposed previously (Scheme 5).[10] The dynamic behavior of **4a-I** with the chelate structure **C** was not observed, at least not below room temperature.

Addition of acetonitrile to a CDCl$_3$ solution of **4a-I**, formed in situ from **1a**, **I**, and NaBARF, causes change in the ^{13}C NMR spectrum. Two signals due to uncoordinated carbonyl groups are observed at $\delta = 172.0$ and 171.1 ppm. Signals due to coordinated acetonitrile ($\delta = 104.8$ and

12.1 ppm) are also observed. Two tertiary carbon atom signals ($\delta = 47.8$ and 49.4 ppm), two secondary carbon atom signals ($\delta = 47.0$ and 45.8 ppm), and one quaternary carbon atom signal ($\delta = 49.9$ ppm) of the cyclopentane ring, in addition to the above results, suggest a structure for the complex with coordinated acetonitrile and cyclopentylmethyl ligands, but no coordination of the CO group. CH$_2$Cl$_2$ may also assist chelate-ring opening of **4a-I** but to a much less significant extent, although it was not observed (Scheme 10, see later).

The complexes **4a-I**, [D$_6$]**4a-I**, and **4a-IV** initiate cyclopolymerization of **I** and **IV** similarly to the catalyst prepared from **1a** and NaBARF. Addition of **I** (or [D$_6$]**I**) to a CH$_2$Cl$_2$ solution of isolated **4a-I** causes cyclopolymerization to afford poly-**I** and poly-([D$_6$]**I**), respectively, as shown in Scheme 8. Poly-**I** obtained by using [D$_6$]**4a-I** as the initiator shows a ^{2}H NMR signal due to the CD$_3$ end group at $\delta = 1.73$ ppm, whereas initiation by **4a-IV** produces a polymer that exhibits a ^{1}H NMR signal at $\delta = 3.27$ ppm due to the N–CH$_3$ end group (Figure 2).
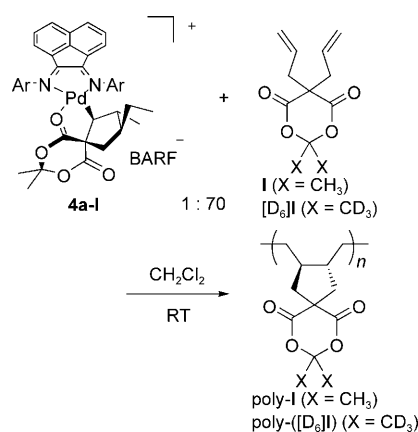
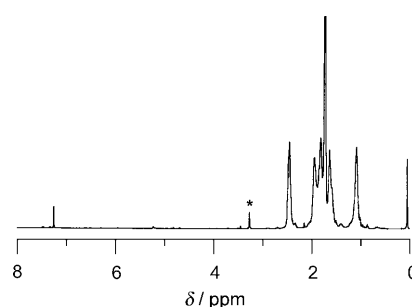Scheme 8. Cyclopolymerization of **I** and [D$_6$]**I** with **4a-I**.

Figure 2. ^{1}H NMR spectrum of poly-**I** obtained from **4a-IV**. The peak marked with * is due to N–CH$_3$ hydrogen atoms derived from **4a-IV**.

The molecular weight of the polymer ($M_n = 11600$), estimated from the ^{1}H NMR peak-intensity ratio of the N–CH$_3$ group to the polymer chain, is close to that calculated from the molar ratio of the amount of monomer consumed versus the amount of **4a-IV** ($M_{n\ calcd} = 11900$), although both are

larger than values from GPC ($M_n = 8100$ with $M_w/M_n = 1.74$, polystyrene standard). The results suggest that the complex **4a-IV** initiates cyclopolymerization quantitatively.

MALDI-TOF MS analysis of poly-**IV** obtained by initiation with **4a-IV** revealed the precise molecular weights and structures of the initiating end of the polymer. The spectrum in Figure 3 contains two series of peaks with a difference of
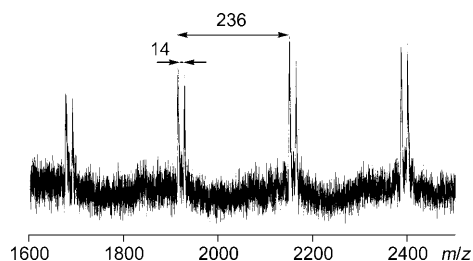

Figure 3. MALDI-TOF mass spectrum of poly-**IV** obtained from **4a-IV**.

235.17–237.12 mass units, which corresponds to the molecular weight of the monomer (236.12). The m/z values of the two parent peaks between 1800 and 2000 are determined to be 1927.20 and 1913.21 by reflect-mode measurement and are assigned to Na adducts of the polymer molecules with a 2-ethylcyclopentyl (1927.18) and a 2-methylcyclopentyl end group (1913.16), respectively (Scheme 9). Products of the cyclopolymerization of **IV** after initiation with **1a**/NaBARF gave similar results to the mass-spectrometry measurements.
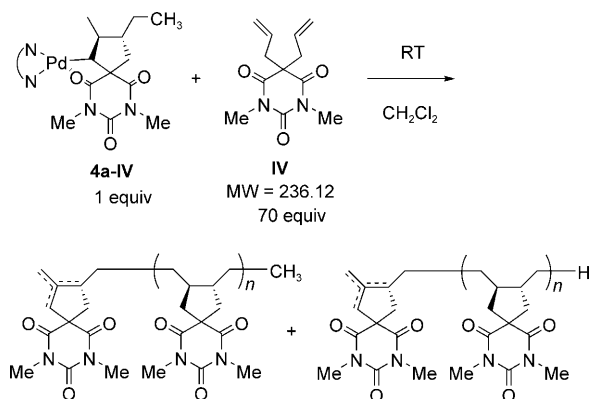
Scheme 9. Polymerization of **IV** by **4a**.

Scheme 10 depicts a pathway for the initiation of the cyclopolymerization of **I**. Complex **4a-I** is formed by the reaction of **I** with the Pd–Me complex, as shown in Scheme 6. The carbonyl group coordinated to the cationic Pd center is displaced and isomerization occurs by chain-walking from the (cyclopentylmethyl)palladium species. The vacated coordination site is occupied by solvent (as discussed earlier) or a vinyl group of the monomer, although a seven-membered ring C,O-chelate complex (**C** in Scheme 5) may also be present in the mixture. The isomerization of the intermediates
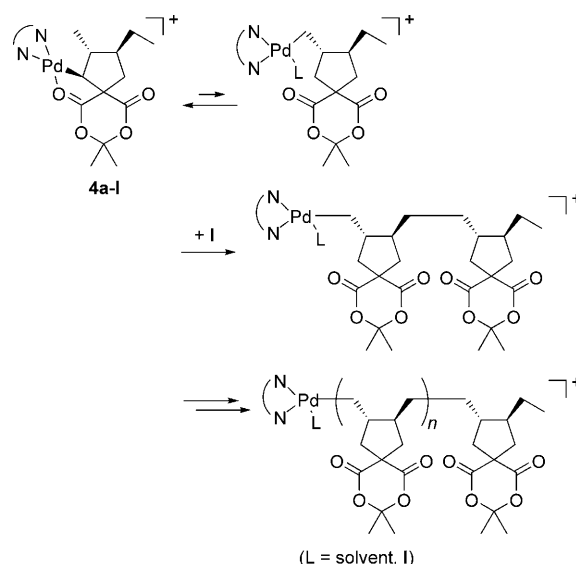

Scheme 10. Initiation of the cyclopolymerization of **I**.

can occur reversibly by repeated β-hydrogen elimination of methylenecyclopentane or methylcyclopentene derivatives and reinsertion of their C=C bond into the Pd–H bond. Although this intermediate is less stable than **4a-I**, insertion of a new monomer into the Pd–CH$_2$ bond occurs smoothly. The polymer structure determined by NMR spectroscopy indicates that no direct insertion of the monomer into the cyclopentyl CH–palladium bond occurs during polymerization. Mechanistic studies of the polymerization of α-olefins revealed that insertion of a vinyl group into the Pd–CH$_2$ bond occurs more easily than insertion into the Pd–CH bond.[4,19]

Room temperature ^{13}C NMR spectroscopy of the polymerization reaction of **I** catalyzed by **1a**/NaBARF revealed the presence of signals due to the carbonyl carbon atom attached to Pd ($\delta = 187.5$ ppm). The polymer end maintains coordination of the carbonyl group to Pd in the resting state, indicated by the similarity of the peak position to isolated and fully characterized **4a-I** and **4a-IV** ($\delta = 187.6$ and 187.9 ppm, respectively). Scheme 11 shows a plausible structure of the end group of the growing polymer. The cyclopentyl–palladium complex with a five-membered C,O-chelate ring is thermodynamically more favorable than the cyclopentylmethyl–palladium complex. The structures of the observed intermediate of the polymerization and actual polymer obtained indicate that polymer growth also takes place by isomerization of the cyclopentylpalladium intermediate to the (cyclopentylmethyl)palladium species and preferential insertion of a vinyl group of the new diene monomer into the Pd–CH$_2$ bond of the latter.

Monomer consumption in the cyclopolymerization of **I** catalyzed by **1a**/NaBARF was monitored by ^{1}H NMR spec-
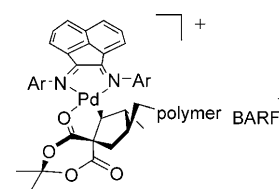
Scheme 11. Plausible structure of the end group of the growing polymer.

troscopy, as shown in Figure 4. The monomer consumption at a lower initial concentration of the monomer ($[I]_0 = 0.50\,\text{M}$) obeys first-order kinetics, whereas consumption
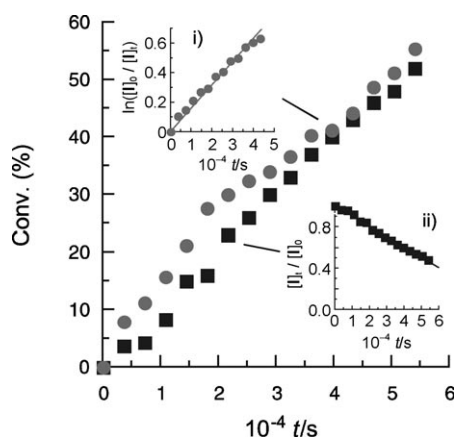

Figure 4. Monomer consumption in the polymerization of **I** in CDCl$_3$ at 20°C catalyzed by **1a**/NaBARF ([Pd] = 20 mM) ($[I]_0 = 0.50\,\text{M}$ (●) and 1.0 M (■)). Inset: i) First-order plot (●) and ii) zero-order plot (■).

when $[I]_0 = 1.0\,\text{M}$ proceeds linearly and suggests apparent zero-order kinetics. Scheme 12 shows a summary of a plausible mechanism for polymer growth. Compound **D**, with a similar structure to **4a-I**, exists in a stable resting state in the reaction mixture. The cyclopentylpalladium complex should isomerize to an intermediate with a cyclopentylmethyl ligand and a π-coordinated monomer, **E^1**, prior to the insertion of a new monomer molecule (Scheme 12 a). Initial formation of the intermediate **E^2**, with a cyclopentylmethyl ligand and a ligated solvent molecule,[20] may occur in the formation of **E^1** (Scheme 12 b)). Coordination of the remaining vinyl group to the cationic Pd center (Scheme 12 c) and subsequent intramolecular insertion result in the formation of a five-membered ring (Scheme 12 d). Cyclization by 1,2-insertion of the vinyl group yields an intermediate with the cyclopentylmethyl group bonded to the Pd center. The intermediate formed is either converted into its thermodynamically stable resting state (**D**) or reacts with a new

monomer directly. At low concentrations of the diene monomer, the formation of **E^1** is the rate-determining step in the polymerization. At higher initial concentrations of the monomer ($[I]_0 = 1.0\,\text{M}$), apparent zero-order kinetics are observed because formation of **E^1** becomes faster than isomerization of **E^1** into the (cyclopentylmethyl)palladium intermediate or intramolecular insertion of the vinyl group.

Scheme 13 displays the pathway of chain transfer in the cyclopolymerization of **IV**. β-Hydrogen elimination in the polymer with a methylcyclopentene end group takes place during polymer growth. Displacement of the coordinated polymer by coordination of a new diene molecule to the Pd center of the hydride–palladium intermediate leads to the formation of a new (2-methylcyclopentyl)methylpalladium intermediate. Further insertion of the diene into the Pd–C bond and subsequent cyclization produce a polymer with a methylcyclopentyl end group.

We carried out the reaction with deuterated monomer to obtain further insights into the propagation step of the cyclopolymerization. The catalyst **1a**/NaBARF promotes cyclopolymerization of [D$_2$]**I**, deuterated at the internal vinyl bonds, to produce poly-([D$_2$]**I**) ($M_n = 4200$, $M_w/M_n = 1.34$). The polymerization requires 72 h to attain 15% conversion of [D$_2$]**I**, which is slower than the reaction of **I** (27% conversion, 12 h). Figure 5 displays the ^{1}H and ^{13}C NMR spectra of poly-([D$_2$]**I**). The peak-area ratio of H$_a$/H$_{a'}$/H$_c$ in the
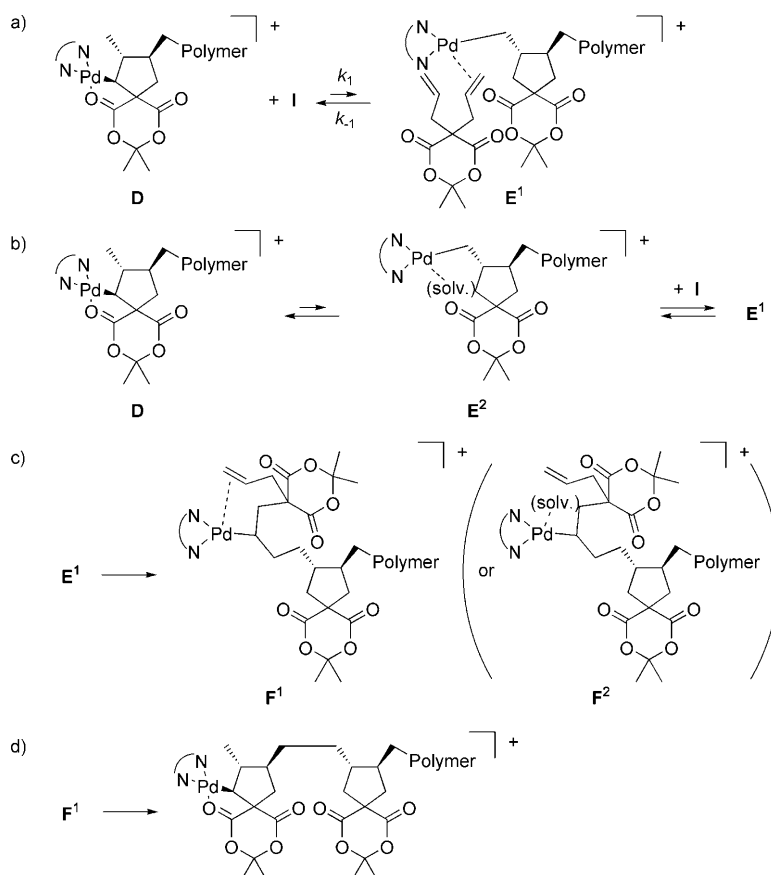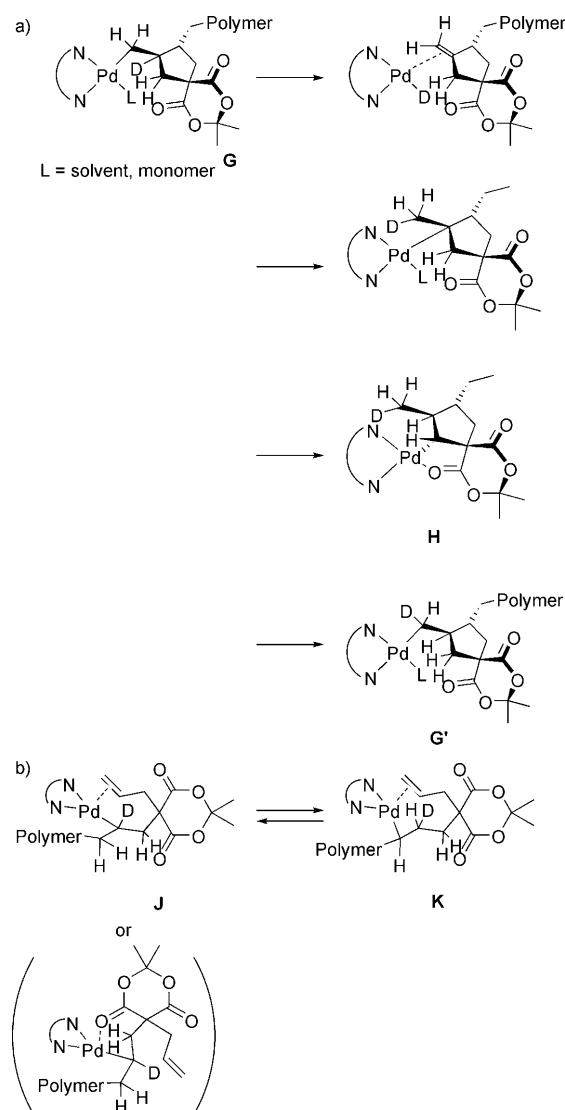

Scheme 12. Plausible mechanism of cyclopolymerization of **I**.
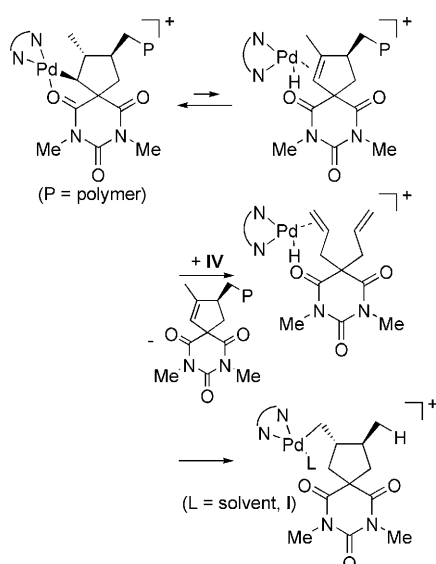
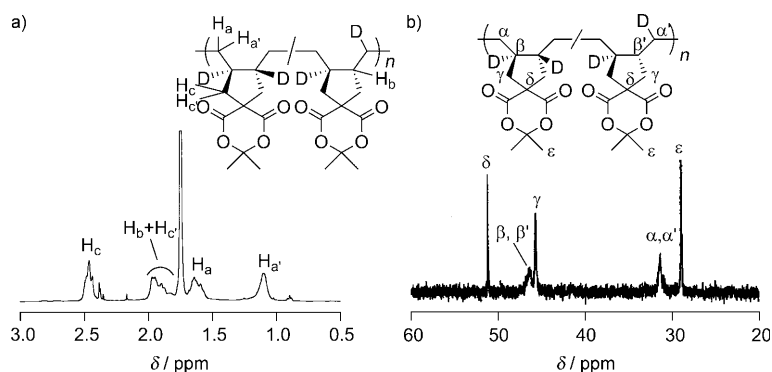Scheme 13. Chain transfer in the cyclopolymerization of **IV**.

Scheme 14. Possible mechanisms for H/D scrambling.

^{1}H NMR spectrum of poly-([D$_2$]**I**) is 1.0:0.75:0.95 (Figure 5a)). ^{13}C NMR signals at $\delta = 31.3$ and 46.4 ppm assigned to the secondary (α, α′) and tertiary carbon atoms (β and β′) of the polymer chain are broadened as a result of the bonded deuterium atoms (Figure 5b). These results indicate atom exchange between the CH$_2$ and CD groups of the polymer chain during polymer growth. The H/D ratio for the tertiary carbon atom in the five-membered ring is 0.43:1, based on the ratios of the peak areas in the ^{1}H NMR spectrum.

Scheme 14 shows possible pathways for hydrogen-atom scrambling. Cyclization of the polymer end group by intramolecular insertion of the C=C bond produces an intermediate with a cyclopentylmethyl ligand attached to Pd (**G**, Scheme 14a). Subsequent isomerization of the intermediate into the resting state with a CH$_2$D substituent on the five-membered ring (**H**) and regeneration of the (cyclopentylmethyl)palladium intermediate with deuterium at a different position (**G′**) take place as described previously (Scheme 13). Mutual isomerization between **G** and **G′** occurs prior to the insertion of a C=C bond of the monomer

into the Pd−CH$_2$ bond. The slower cyclopolymerization of [D$_2$]**I** compared to **I** may be partly due to slower activation of the C−D bond relative to the C−H bond in these equilibrium reactions. Another possible pathway for H/D scrambling involves chain walking of the intermediate prior to cyclization (Scheme 14b). The secondary alkyl ligand bonded to Pd in **J** is isomerized to the isotopomer, with a deuterium atom located on the β-carbon atom, via intermediate **K** with a CHD−CH−Pd linkage. The quantitative cyclization of the diene during the polymerization as a result of rapid cyclization may support the former mechanism.

Figure 5. a) ^{1}H and b) ^{13}C NMR spectra of poly([D$_2$]**I**).

All of the reaction steps in the cyclopolymerization (initiation, propagation, and chain transfer) involve isomerization between the cyclopentyl- and cyclopentylmethyl-palladium species by a chain-walking process. Scheme 15 shows a summary of reactions of the cyclopentylpalladium com-
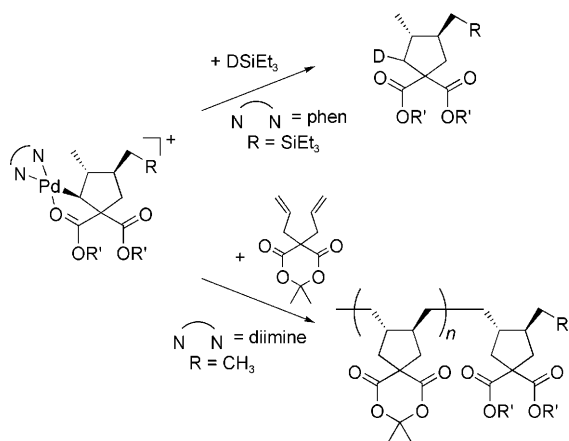
Scheme 15. Reactions of the cyclopentyl palladium species.

plexes related to this study. Perch and Widenhoefer reported the reaction of DSiEt$_3$ with Pd complex **5′** (Scheme 7), which has a similar structure to **5** and **4a-I**. The organic product contains deuterium incorporated from the silane at the 3-position of the five-membered ring, which suggests that the cyclopentylpalladium complex undergoes σ-bond metathesis with DSiEt$_3$ or oxidative addition of DSiEt$_3$ followed by C−D coupling to form the deuterated cyclopentane derivative.[16h] The complexes **4a-I** and **4a-IV** in this study will initiate cyclopolymerization but insertion of a new diene monomer only takes place after chain-walking isomerization of the ligand to generate a (cyclopentylmethyl)palladium species, as shown in Schemes 10 and 12. Thus, the diverse reactivity of the cyclopentylpalladium complexes enables both cyclative hydrosilylation and cyclopolymerization of dienes, catalyzed by Pd complexes.

Copolymerization of functionalized 1,6-dienes with ethylene and 1-hexene: The Pd–diimine complexes were reported to catalyze the copolymerization of ethylene with ethyl acrylate to produce a polymer with ester groups incorporated. Insertion of ethyl acrylate into the Pd−C bond is followed by chain walk-

ing to produce a Pd species with a C,O-chelated polymer end (similar structure to **6** in Scheme 7); no direct insertion of monomer into the Pd−CHCOOEt bond takes place.[5a,b] Copolymerization of ethylene or α-olefins with the functionalized dienes would form polymers with five-membered rings and polar functional groups along the polymer chain because the cyclopolymerization in this study involves insertion of a C=C bond of the new diene monomer into the cyclopentylmethyl CH$_2$−Pd bond,[10,21]

The monomer **I** copolymerizes with ethylene under mild conditions, as shown in Scheme 16. Stirring a CH$_2$Cl$_2$ solution of **I** (0.18 M), **1a** (2.5 mM), and NaBARF under an ethylene atmosphere (1 atm) at room temperature yields the copolymer with a 3:97 ratio of **I**/ethylene incorporation (Table 2, entry 1). The copolymer exhibits signals in the ^{1}H and ^{13}C NMR spectra assigned to the hydrogen and carbon atoms of the five-membered ring at $\delta = 1.82$–2.44 and 46.0–51.3 ppm, respectively, as well as those due to the ethylene units at $\delta = 0.84$–1.25 and 10.8–37.4 ppm, respectively (Figure 6). The absence of signals in the NMR spectra due to olefinic carbon and hydrogen atoms indicates complete cyclization of the diene monomer in the copolymerization, in spite of facile insertion of ethylene into the Pd−polymer bond. The appearance of ^{13}C NMR signals at $\delta = 10.8$, 14.1, and 19.2 ppm indicates that the oligoethylene groups in the
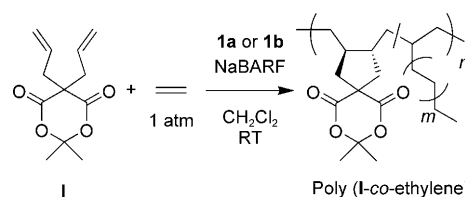
Scheme 16. Copolymerization of **I** with ethylene.

Table 2. Copolymerization of the 1,6-heptadiene derivatives with ethylene[a] and 1-hexene[b] catalyzed by Pd complexes.

	Pd	Diene	Olefin	t [h]	TON[c,d] Diene	TON[c,d] Olefin	Diene unit in polymer[d,e] [%]	M_n[f]	M_w/M_n[f]	T_g[g] [°C]	Me/1000C[h]
1[i]	**1a**	I	ethylene	12	25	808	3	9500	1.48	decomp[j]	106
2	**1a**	II	ethylene	3	42	158	21	18500	1.81	–	–
3	**1a**	III	ethylene	3	26	1274	2	11200	1.94	–	–
4	**1b**	IV	ethylene	6	38	912	4	24700	1.72	–	–
5	**1a**	V	ethylene	6	17	196	8	7400	1.42	–	–
6	**1b**	VI	ethylene	3	13	204	6	5200	1.29	–	–
7	**1b**	VII	ethylene	2	8	28	22	4600	1.42	–	–
8	**1b**	IX	ethylene	2	14	126	10	3600	1.63	−18	112
9	**1b**	X	ethylene	2	17	226	7	5200	1.68	–	–
10	**1a**	I	1-hexene	2	25	70	26	9800	1.59	–	86
11	**1b**	I	1-hexene	3	24	67	30	3200	1.99	–	74
12	**1a**	VI	1-hexene	7	13	49	21	6000	1.46	–	–
13	**1b**	VI	1-hexene	7	24	59	29	5400	1.60	–	–

[a] Reaction conditions: Pd cat (0.010 mmol), NaBARF (0.012 mmol), diene (0.70 mmol), ethylene (1 atm), CH$_2$Cl$_2$ (0.5 mL). Results in entry 1 were partially reported in a preliminary communication (see reference [10]). [b] Reaction conditions: Pd cat (0.010 mmol), NaBARF (0.012 mmol), diene (0.70 mmol), 1-hexene (0.70 mmol), CH$_2$Cl$_2$ (0.5 mL). [c] Turnover number. [d] Determined by ^{1}H NMR spectroscopy. [e] Molar ratio of the diene unit in the isolated copolymer. [f] Determined by GPC, CHCl$_3$ as the eluent. [g] Determined by DSC. [h] Number of methyl branches (including terminal Me groups) per 1000 carbon atoms of the repeating unit of the olefin. [i] CH$_2$Cl$_2$ (4 mL) used. [j] Decomposition observed at approximately 150 °C.
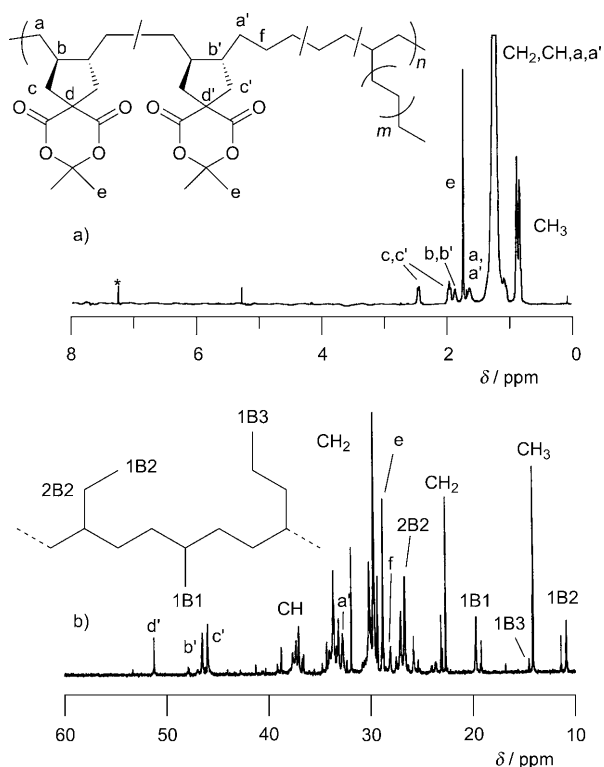
Figure 6. a) ^1H and b) ^{13}C NMR spectra of poly(**I**-*co*-ethylene) in CDCl$_3$.

polymer have branched structures; their positions are similar to those of the CH$_3$ carbon atoms of the ethyl, propyl, and methyl branches of polyethylene obtained from polymerization catalyzed by Ni–diimine complexes.[22] A branched structure of the polymer indicates that ethylene insertion into the secondary alkylpalladium species also takes place in the copolymerization. The ^{13}C NMR signal due to the CH carbon atom of the five-membered ring attached to the oligoethylene unit (b′) appears at $\delta = 46.5$ ppm. The resonance is at a higher magnetic field than that of poly-**I** ($\delta = 47.0$ ppm) and is similar to the polymer of isopropylidene allyl(2-pentyl)malonate (shown here), which has an alternating sequence of the cyclized diene unit and a −(CH$_2$)− group ($\delta = 46.4$ ppm).[11] Diene **II**, which has a cyclic diketone group, also forms a copolymer, which contains 21% of the repeating units from **II** (Table 2, entry 2). Dienes **III–VII**, **IX**, and **X**, containing a polar group, also copolymerize with ethylene to give the respective copolymers (Table 2, entries 3–9). In all of these cases, the dienes undergo cyclization during the copolymerization and form a copolymer with a *trans*-fused five-membered ring along the polymer chain.

Copolymers of ethylene with norbornene and cyclopentene, obtained by using Ti, Zr, and Pd catalysts, show a high T_g (205–237 °C), which is ascribed to the presence of cyclic

units in the polymer.[23] Ethylene polymerization catalyzed by **1a**/NaBARF produces polyethylene with 116 branches per 1000 carbon atoms and $T_g = −85$ °C.[2a] Poly-(**IX**-*co*-ethylene) obtained by catalysis with **1a**/NaBARF (Table 2, entry 8) has branched oligoethylene groups (112 branches per 1000 C) and shows a T_g of −18 °C.

Copolymerization of dienes **I** and **VI** with 1-hexene is catalyzed by **1a**/NaBARF and **1b**/NaBARF to afford the respective copolymers (Table 2, runs 10–13). The copolymerization of **VI** with 1-hexene proceeds more slowly than that of **I** with 1-hexene but the ratios of incorporated diene/1-hexene in the copolymers are within the range 0.21–0.30 for both diene monomers. Figure 7 shows a plot of the con-
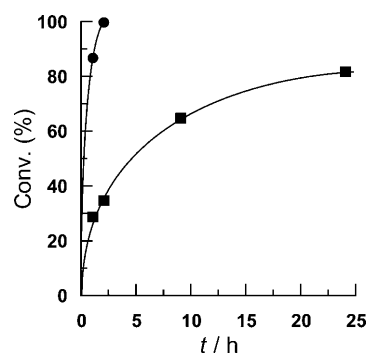

Figure 7. Time versus conversion curve of the copolymerization of **I** (■) and 1-hexene (●) catalyzed by **1a**/NaBARF at room temperature.

sumption of **I** and 1-hexene in the copolymerization catalyzed by **1a**/NaBARF. 1-Hexene is consumed rapidly at the initial stage, followed by a decrease in the amount of **I** present. The copolymer isolated after reaction for 2 h contains the unit from **I** at 26% incorporation (Table 2, entry 10). Unimodal elution in GPC of $M_w/M_n = 1.59$ suggests that the polymer produced is the copolymer of the two monomers, in spite of their different reactivities, and that it is composed of two monomer units with a gradient composition. The ^{13}C NMR spectra revealed the composition and structure of the copolymer in greater detail (Figure 8).

Scheme 17 shows a summary of possible partial structures of the copolymer; two neighboring units from **I** (Scheme 17 a), alternating sequences of **I** and 1-hexene (Scheme 17 b–d)), and oligo(1-hexene) units (Scheme 17 e). 1-Hexene units adjacent to the diene unit have three possible structures, −(CH$_2$)$_6$−, −(CH$_2$)$_4$−CHMe−, and −CH$_2$−CHBu−, which are similar to the monomer units of poly(1-hexene) obtained in the reaction catalyzed by Pd–diimine complexes. The two latter structures correspond to units (3) and (4) (Scheme 17), respectively. The ^{13}C NMR spectra of poly(**I**-*co*-1-hexene), obtained by using **1a**/NaBARF and **1b**/NaBARF catalysts (Table 2, entries 10 and 11), show signals due to the CH$_2$ (a, a′) and CH (b, b′) carbon atoms of the diene unit at $\delta = 31.6$, 32.8, 47.0, and 46.6 ppm respectively (Figure 8). The former polymer shows a peak at $\delta = 47.0$ due to the diene block portrayed in Scheme 17 a). The peak has a
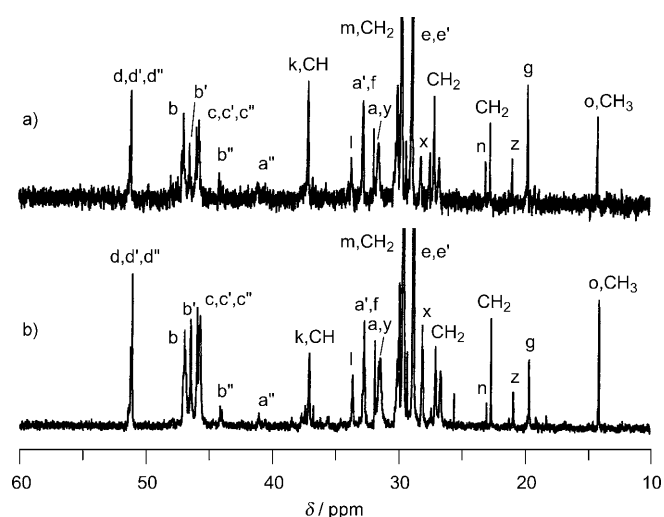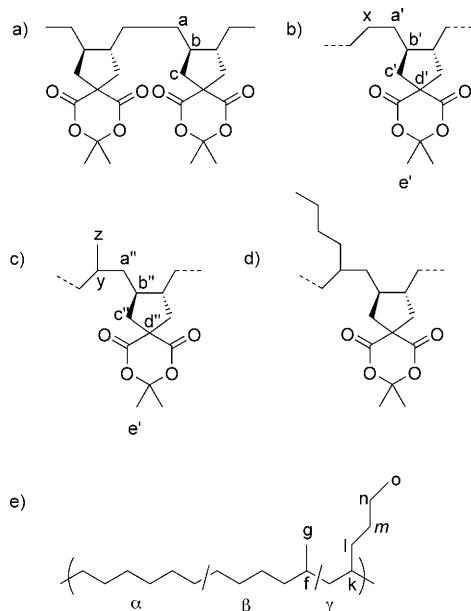
Figure 8. ^{13}C NMR spectra of poly(I-co-1-hexene) obtained by using a) **1a**/NaBARF and b) **1b**/NaBARF catalysts. Assignment of signals corresponds to the formula in Scheme 17.


Scheme 17. Possible partial structures of the copolymer of **I** and 1-hexene.

higher intensity than that at $\delta = 46.6$ ppm, which results from the diene units bonded to a 1-hexene unit (as in partial structures in Scheme 17 b–d), in spite of the low diene unit content (26%). This result is consistent with the different reactivities between the **I** and 1-hexene monomers, shown in Figure 7. The ^{13}C NMR spectrum of the copolymer obtained by catalysis with **1b**/NaBARF (Figure 8 (ii)) shows that the relative ratio of the alternating sequence to the diene block is larger than that for the copolymer formed by using the **1a**/NaBARF catalyst, although the diene block

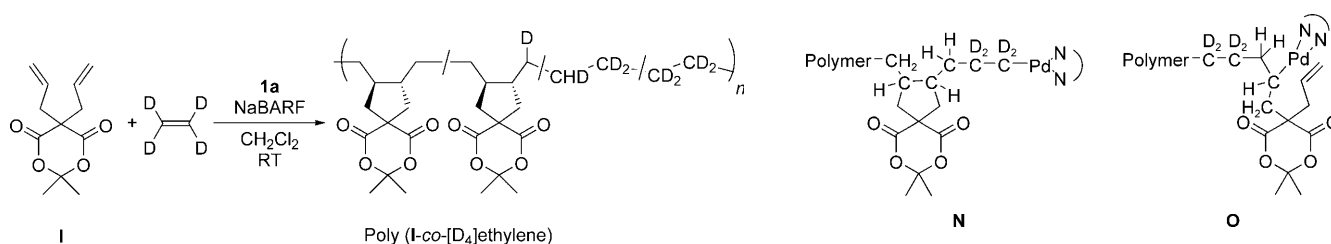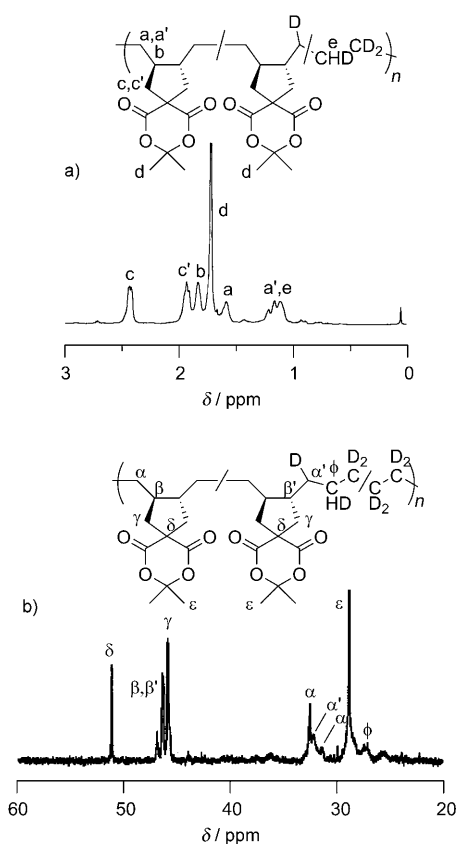(Scheme 17 a) is still comparable to the alternating sequences (Scheme 17 b–d).

Copolymerization of ethylene with [D$_2$]**I** catalyzed by **1a**/NaBARF produces poly([D$_2$]**I**-co-ethylene) with the diene units and branched oligoethylene units at a ratio of 3:97 (Scheme 18). The ratio of monomer units is similar to that of the copolymer of ethylene and **I** obtained with the same catalyst.
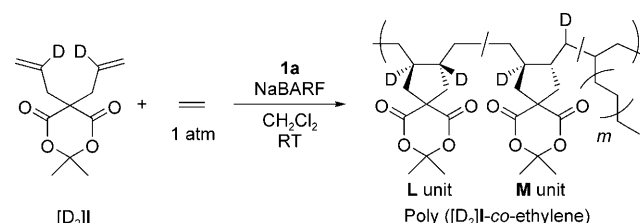
Scheme 18. Copolymerization of [D$_2$]**I** with ethylene catalyzed by **1a**/NaBARF.

The ^{1}H NMR spectrum of poly([D$_2$]**I**-co-ethylene) (Figure 9 a) shows a small peak at $\delta = 1.82$ ppm due to the CH hydrogen atom of the five-membered ring (b) and in the ^{2}H NMR spectrum signals are observed at $\delta = 1.84$, 1.20, and 0.95 ppm. The two latter peaks are assigned to the CHD (or CH$_2$D) group formed by H/D scrambling. DEPT NMR spectroscopy verified that the signal at $\delta = 46.3$ ppm resulted from CH and quaternary carbon atoms and that at $\delta = 32.6$ ppm was due to CH$_2$ and CH carbon atoms. These results suggest that the polymer contains **M** units and **L** units (Scheme 18) and that scrambling of deuterium (derived from the diene monomer) takes place to form a polymer chain that contains partially deuterated methylene carbon atoms.

Polymerization of **I** under a [D$_4$]ethylene atmosphere (1 atm) catalyzed by **1a**/NaBARF proceeds to give poly(I-co-[D$_4$]ethylene) with $M_n = 16000$ ($M_w/M_n = 1.27$) after reaction for 3 h (Scheme 19). The resulting polymer contains 15% of the unit from **I**, as estimated by elemental analysis (H, C). The ^{1}H NMR spectrum signals (Figure 10 a) at $\delta = 2.43$ (c), 1.84 (b), 1.59 (a), and 1.16 ppm (a′, e) are observed with a peak ratio of 1:1.08:0.64:1.25. Relative signal intensities, $H_a < H_b \approx H_c$, are attributed to deuterium scrambling of the [D$_4$]ethylene with the vinylic CH$_2$ hydrogen atoms of **I** during copolymerization. No deuteration of the CH group of the five-membered ring of the copolymer was observed. The ^{13}C NMR spectrum (Figure 10 b) exhibits broad signals at $\delta = 32.3$–31.3 ppm due to secondary carbon atoms attached to the five-membered ring. The contribution of CH$_2$ and CHD carbon atoms to the peaks was confirmed by DEPT NMR spectroscopy. Two possible structures of the alkylpalladium species subjected to H/D scrambling in the copolymerization of C$_2$D$_4$ with **I** are suggested (**N** and **O**). Chain walking in alkylpalladium species **N** explains the scrambling between the CH$_2$ and CD$_2$ groups at the polymer end. Alkylpalladium species **O**, formed by the insertion of a
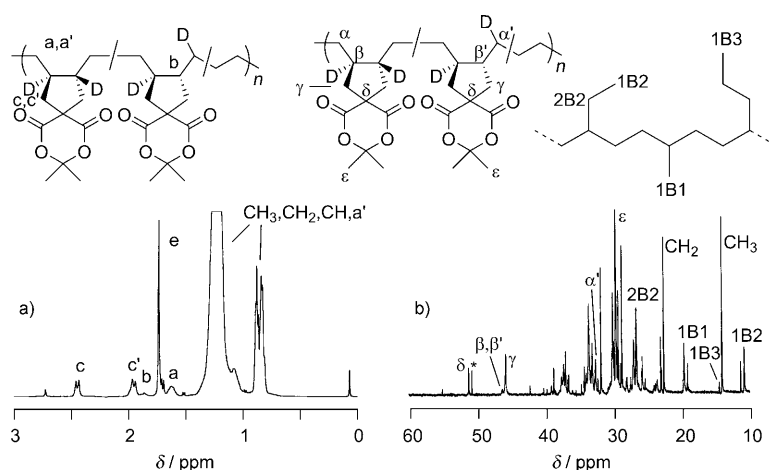
Figure 9. a) [^1^]H and b) [^13^]C NMR spectra of poly([D_2]**I**-*co*-ethylene).

vinyl group into a Pd−CD_2 bond, may also undergo H/D scrambling prior to cyclization. Rapid and reversible chain walking of **O**, however, would lead to deuteration of the CH group bonded to Pd and result in deuteration of the five-membered ring. The latter is less feasible because deuteration is only observed for the CH_2 groups attached to the five-membered ring of the copolymer.

Scheme 19. Copolymerization of **I** with [D_4]ethylene catalyzed by **1a**/NaBARF.

Figure 10. a) [^1^]H and b) [^13^]C NMR spectra of poly(**I**-*co*-[D_4]ethylene).

Synthesis and gelation of telechelic poly(1-hexene): The complexes **4a-I** and **4a-IV** undergo insertion of the vinyl groups of 1,6-heptadiene derivatives to initiate their cyclopolymerization. The copolymerization of **I** (or **IV**) with 1-hexene should also involve formation of intermediate **D** (see Scheme 12) and subsequent insertion of 1-hexene into the Pd−C bond of the intermediate. These observations suggest that 1-hexene polymerization is initiated by complexes having C,O-chelated cyclopentyl ligands. We prepared end-functionalized poly(1-hexene) by using Pd complexes with a C,O-chelating cyclopentyl ligand and polar imide groups.

The palladium complex **4a-III**, formed by the reaction of **1a**, NaBARF, and **III** (1:1.2:7.5 equiv) at −40°C in CH_2Cl_2, promoted polymerization of 1-hexene at −20°C in CH_2Cl_2 to attain quantitative monomer conversion in 68 h. The polymerization proceeded in living fashion and gave a polymer with a narrow molecular-weight distribution (GPC, $M_n = 9900$, $M_w/M_n = 1.09$), similar to 1-hexene polymerization catalyzed by **1a**/NaBARF.[19] The [^1^]H NMR spectrum of the polymer obtained showed a signal at $\delta = 2.36$ ppm, assigned to the CH_2 of the cyclopentane ring, as well as a peak at $\delta = 1.99$ ppm, assigned to the CH_2 and CH carbon atoms of the cyclopentane ring at an intensity ratio of 2:4, which indicates the incorporation of the barbiturate unit of **4a-III** into the polymer end. The relative-intensity ratio of the signal at $\delta = 2.36$ ppm to the signals of the hydrogen atoms of the 1-hexene unit ($\delta = 1.5$–0.65 ppm) is 1:801, which corresponds to $M_n = 11000$. The efficiency of the initiator based on these results is 60%. Addition of 5-allyl-5-hexylbarbituric acid (**XI**) and Et_3SiH to the living polymer

forms poly(1-hexene) with two terminal barbituric acid groups (**XI**-polyhexene-**III**) (Scheme 20). GPC analysis of the polymer showed a narrow molecular-weight distribution ($M_n = 10\,700$, $M_w/M_n = 1.17$). The ^{1}H NMR spectrum of the polymer obtained showed signals at $\delta = 2.43$ ppm, assigned to the CH_2 of the initiating end, and at $\delta = 1.99$ ppm, assigned to the cyclopentane ring of the initiating end and the CH_2 attached to the barbiturate group of the terminating end. The relative intensity ratio of these signals is 2:11, which is close to the calculated value based on the quantitative functionalization of the terminating end (2:10). A similar telechelic polymer (**III**-polyhexene-**III**) is obtained using **5a-III**, formed by the reaction of **2a** with **III** as the initiator and the terminating agent. The polymer was isolated as a semi-solid after precipitation from MeOH, washing with acetone and acetonitrile, and decolorization with activated carbon.
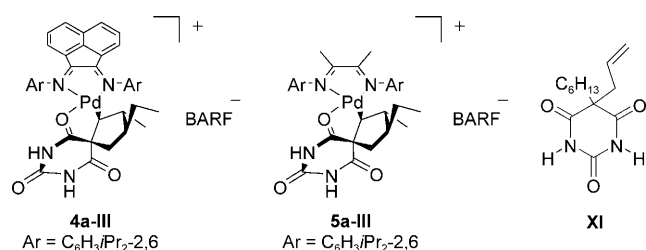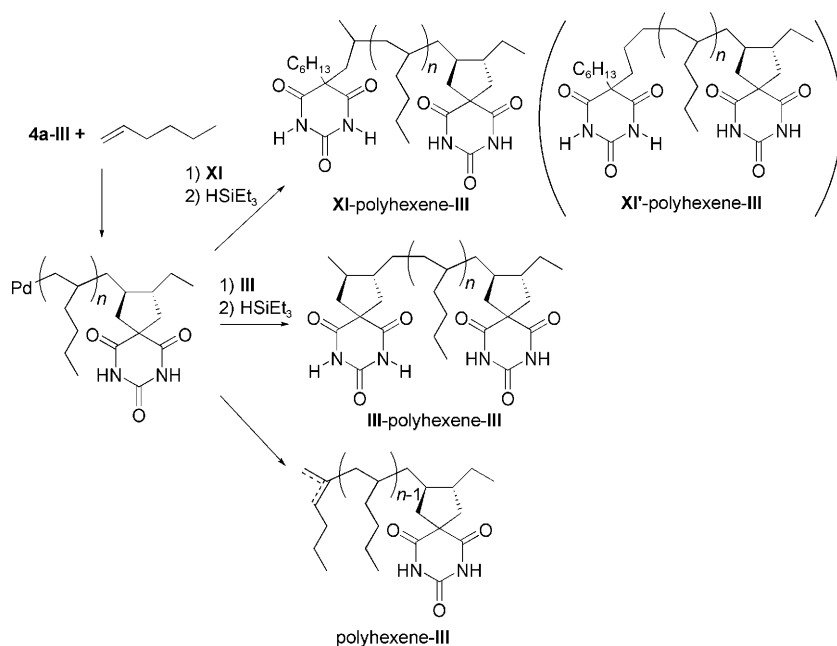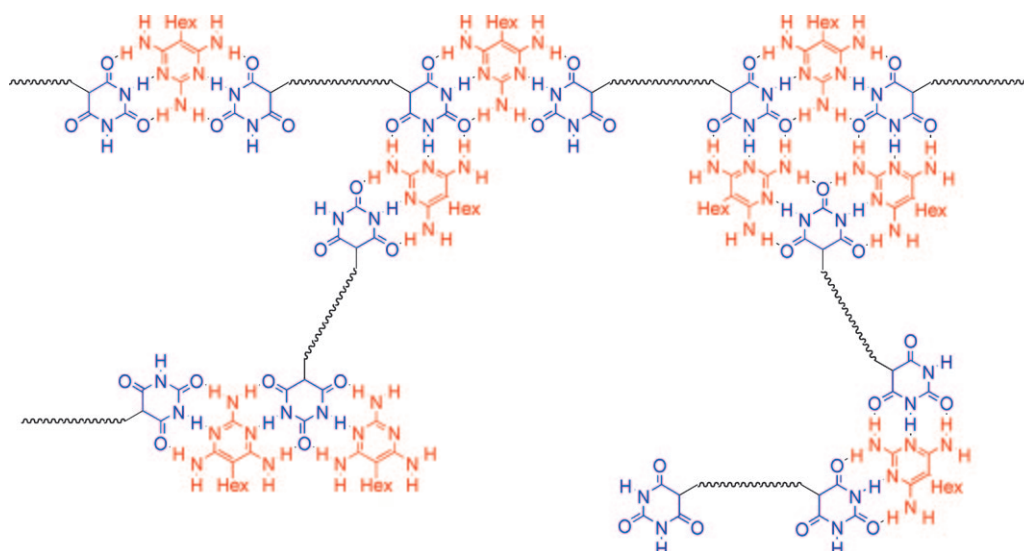
parent gel formed changed reversibly to a sol at RT, which indicated the formation of a thermoreversible network. A similar reaction of the polymer **XI**-polyhexene-**III** (5 mol equiv of TAP with respect to the terminal units in the polymer) leads to the formation of a gel at RT, which was transformed into a sol upon heating to 55 °C. The use of polyhexene-**III**, with only one end functionalized with a barbiturate group (Scheme 20), did not bring about a marked change in viscosity upon addition of TAP to the solution. This result indicates the importance of hydrogen bonding in the polymer for gel formation. Barbiturates have been reported to form a variety of structural motifs in the presence of melamines or triaminopyrimidines, such as linear tape, crinkled tape, and rosette, dependent on the substituents.[24] Formation of such aggregated structures through hydrogen bonding between the barbiturate end groups and TAP is proposed to cause crosslinking, and thereby result in the formation of a thermoreversible gel (Scheme 21).

Conclusion

The Pd-complex-catalyzed cyclopolymerization in this study afforded polymers with *trans*-fused five-membered rings along the polymer chain. Intermolecular 1,2-insertion and intramolecular 2,1-insertion of the vinyl groups of 1,6-diene derivatives occurred in an alternating fashion to produce polymers with regulated structures. Spectroscopic observation of the reaction mixtures and isolation of the Pd species formed in the polymerizations of **I** and **IV** revealed the structure of the resting state, which contains a cyclopentyl ligand bonded to the cationic Pd center through both a Pd–CH bond and the coordination of a carbonyl group. Polymer growth involves isomerization of the resting state into the (cyclopentylmethyl)palladium species and insertion of a vinyl group of the monomer into the Pd–CH$_2$ bond. Both the polymerization of α-olefins reported by Brookhart et al. and this cyclopolymerization involve the smooth isomerization between two intermediates with either primary or secondary alkyl ligands bonded to a Pd center and preferential insertion of the monomer into the latter Pd–polymer bond. Copolymerization of the functionalized diene with ethylene or 1-hexene provided a unique means for the introduction of polar functional groups into polyolefins. The functionalized five-membered rings are included in the polymer chain because of facile in-

4a-III
Ar = C$_6$H$_3$iPr$_2$-2,6

5a-III
Ar = C$_6$H$_3$iPr$_2$-2,6

XI

Addition of 5-hexyl-2,4,6-triaminopyrimidine (TAP) (4 mol equiv with respect to the terminal units in the polymer) to a solution of the telechelic polymer **III**-polyhexene-**III** (80 mg) in toluene (1 mL) afforded a clear solution. Cooling the solution to −20 °C induced gelation. The trans-

Scheme 20. Synthesis of end-functionalized poly(1-hexene).

Scheme 21. Crosslinking of the telechelic polyhexene by aggregation.

sertion of olefin into the Pd−CH$_2$ bond formed by cyclization of the diene-derived polymer end. This compatibility of the polar diene derivatives and 1-hexene in the Pd-catalyzed polymerization enabled the synthesis of telechelic poly(1-hexene). This polymer can be used as a component of physical gels, formed by addition of polyaminoaromatic compounds, as shown in this study. Other applications of the functionalized polyolefins will continue to be explored.

Experimental Section

General: All manipulations of air- and water-sensitive compounds were carried out with standard high-vacuum or Schlenk techniques. NMR spectra were recorded on Varian Mercury 300 and JEOL JNM-500 spectrometers. ^{1}H, ^{2}H, and ^{13}C NMR chemical shifts (δ, ppm) were referenced to residual solvent signals. Mass spectra were acquired by MALDI-TOF mass spectrometry with a Shimadzu Axima CFR MALDI-TOF mass spectrometer, equipped with a nitrogen laser that delivered 3 ns laser pulses at 337 nm. Mass spectra were recorded in linear (or reflector) delayed-extraction mode with an accelerating voltage of 20 kV and a delay time of 100 ns. Elemental analyses were performed with a Yanaco MT-5 CHN autorecorder. Gel permeation chromatography (GPC) measurements were conducted at 40 °C on a JASCO high-speed liquid-chromatograph system equipped with a Shodex-806L column, a differential refractometer detector, and a variable-wavelength UV/Vis detector, with CHCl$_3$ as the eluent (flow rate of 1.0 mL min^{-1}). Molecular weights were calculated relative to polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were performed on Seiko DSC6200R and TG/DTA6200R instruments, respectively.

Materials: Dry solvents were purchased and used as received unless otherwise noted. Hexane distilled over sodium metal and CHCl$_3$ were used in the recrystallization of Pd complexes. CDCl$_3$ and CD$_2$Cl$_2$ (dried over CaH$_2$, vacuum-transferred, degassed by repeated freeze–pump–thaw cycles) were used for low-temperature NMR spectroscopy measurements. Diimine ligands,[25] **1a–c**,[2,5,26] [PdCl(1,5-cyclooctadiene)(Me)],[27] NaBARF,[28] and monomers **I**,[29] **II**,[30] **III**,[31] **V**,[32] and **VII–X**[33] were synthesized according to literature methods. Monomer **IV** was purchased and distilled from anhydrous CaH$_2$; monomer **III** was purchased and used as received.

Synthesis of [D$_6$]I and [D$_2$]I: Monomers [D$_6$]**I** and [D$_2$]**I** were synthesized in two steps, according to the reported procedures with and without modification.[29,34–36]

Monomer [D$_6$]I: Overall yield = 67 %; D content > 95 %; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.70 (m, 2 H; CH$_2$=CH), 5.21 (m, 4 H; CH$_2$=CH), 2.74 ppm (d, J = 7.8 Hz, 4 H; CHCH$_2$C); ^{2}H NMR (500 MHz, CHCl$_3$): δ = 1.66 ppm (s, 6 D; CD$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 168.5 (C=O), 130.9 (CH$_2$CHCH$_2$), 121.4 (CH$_2$CHCH$_2$), 105.7 (OCO), 55.5 (CH$_2$CCH$_2$), 42.8 (CH$_2$CHCH$_2$), 29.3 ppm (q, CD$_3$).

Monomer [D$_2$]I: Overall yield = 21 %; D content = 92 %; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.22 (m, 4 H; CH$_2$=CD), 2.74 (s, 4 H; CH$_2$C), 1.69 ppm (s, 6 H; CH$_3$); ^{2}H NMR (500 MHz, CHCl$_3$): δ = 5.75 ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ = 168.5 (C=O), 130.5 (t, CD), 121.3 (CH$_2$=CD), 105.9 (C(CH$_3$)$_2$), 55.5 (CH$_2$CCH$_2$), 42.7 (CH$_2$C), 29.9 ppm (CH$_3$).

Polymerization of I catalyzed by 1a/NaBARF (Table 1, entry 1): Under an argon atmosphere, NaBARF (10.6 mg, 0.012 mmol) was added to a solution of Pd complex (6.6 mg, 0.010 mmol) in CH$_2$Cl$_2$ (0.5 mL) in a 25 mL Schlenk flask. After stirring for several minutes, compound **I** (0.156 g, 0.70 mmol) was added and the reaction mixture was stirred at RT. Small portions of the reaction mixture were periodically removed from the flask and subjected to ^{1}H NMR spectroscopy and GPC analysis to determine the conversion of **I** and molecular weight of poly-**I**. After 24 h, the reaction mixture was poured into MeOH (50 mL). The solid formed was collected and dried in vacuo at 25 °C to give poly-**I** (56 % conversion, M_n = 7900, M_w/M_n = 1.51). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.46 (brs, 2 H; CH$_2$ (cyclopentane)), 1.95 (brs, 2 H; CH$_2$ (cyclopentane)), 1.82 (brs, 2 H; CH), 1.73 (s, 6 H; CH$_3$), 1.64 (brs, 2 H; CH$_2$ (main chain)), 1.09 ppm (brs, 2 H; CH$_2$ (main chain)); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.0 (C=O), 104.8 (OCO), 51.1 (CH$_2$CCH$_2$), 47.0 (CH), 45.8 (CH$_2$ (cyclopentane)), 31.5 (CH$_2$ (main chain)), 28.8 ppm (CH$_3$). Polymerization of other dienes was carried out in a similar manner.[37]

Copolymerization of I with ethylene (Table 2, entry 1): Under an argon atmosphere, NaBARF (15.95 mg, 0.018 mmol) was added to a solution of **1a** (9.86 mg, 0.015 mmol) in CH$_2$Cl$_2$ (6 mL) in a 25 mL Schlenk flask. The polymerization was initiated by transfer of the solution (4 mL) to a flask that contained **I** (0.156 g, 0.70 mmol) under an ethylene atmosphere (1 atm). After 12 h, the reaction mixture was poured into a large amount of MeOH (≈ 200 mL). The supernatant was decanted from the precipitated polymer and the residue was washed with methanol. The oily substance formed was collected and dried in vacuo at 25 °C to give poly(**I**-*co*-ethylene) (diene conversion = 35 %, M_n = 9500, M_w/M_n = 1.48, diene incorporation = 3 %). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.44 (m, 2 H; CH$_2$

(cyclopentane)), 1.96 (br s, 2H; CH$_2$ (cyclopentane)), 1.82 (br s, 2H; CH), 1.73 (s, 6H; CH$_3$), 1.65 (br s, 2H; CH$_2$ (main chain)), 1.25 (br s; CH$_2$, CH), 1.10 (br s, 2H; CH$_2$ (main chain)), 0.84 ppm (m; CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.2 (C=O), 104.8 (OCO), 51.3 (CH$_2$CCH$_2$), 46.5 (CH), 46.0 (CH$_2$ (cyclopentane)), 37.4–37.1 (brB3-brBn), 36.6 (3B3), 34.4 (brB1), 33.7 (4B4), 32.8 (CH$_2$ (main chain)), 32.0 (1,4-αBn), 29.7 (CH$_2$ backbone of ethylene unit), 29.5–29.3 (3B4, 4Bn), 28.8 (CH$_3$), 28.1 (CH$_2$ (main chain) adjacent to **I** unit), 27.1 (βB2), 26.7 (2B2), 23.1(2B4), 22.7 (2Bn), 19.7 (2B3), 19.2 (1B1), 14.1 (1B4+1B5+1Bn), 10.8 ppm (1B2). Copolymerizations of [D$_2$]**I** with ethylene and **I** with [D$_4$]ethylene were performed analogously.[37]

Copolymerization of I with 1-hexene (Table 2, entry 10): Under an argon atmosphere, NaBARF (15.95 mg, 0.018 mmol) was added to a solution of **1a** (9.86 mg, 0.015 mmol) in CH$_2$Cl$_2$ (0.75 mL) in a 25 mL Schlenk flask. The polymerization was initiated by transfer of the Pd-complex solution (0.5 mL) to a flask that contained **I** (0.156 g, 0.70 mmol) and 1-hexene (0.087 mL, 0.70 mmol) under N$_2$ at RT. After 2 h, the reaction mixture was poured into a large amount of MeOH ($\approx$200 mL). The supernatant was decanted from the precipitated polymer and the remaining residue was washed with methanol. The powdery solid formed was collected and dried in vacuo at 25°C to give poly(**I**-co-1-hexene) (conversion of **I** = 35%, conversion of 1-hexene = quant, M_n = 9800, M_w/M_n = 1.59, diene incorporation = 26%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.43 (br s, 2H; CH$_2$ (cyclopentane)), 1.94 (br s, 2H; CH$_2$ (cyclopentane)), 1.84 (br s, 2H; CH), 1.73 (s, 6H; CH$_3$), 1.62 (br s, 2H; CH$_2$ (main chain)), 1.23 (br s, 2H; CH$_2$, CH, CH$_2$ (main chain)), 0.83 ppm (m; CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.1 (C=O), 104.6 (OCO), 51.2 (CH$_2$CCH$_2$), 47.0 (CH adjacent to **I** unit), 46.6 (CH adjacent to 1-hexene unit), 46.0–45.8 (CH$_2$ (cyclopentane)), 37.1 (αB1), 33.7 (4B4), 32.8 (CH$_2$ (main chain) adjacent to 1-hexene unit, brB1), 31.6 (CH$_2$ (main chain) adjacent to **I** unit), 30.0–29.7 (CH$_2$ backbone of 1-hexene unit), 29.3 (3B4), 28.8 (CH$_3$), 28.2 (CH$_2$ (main chain) adjacent to **I** unit), 27.4–26.7 (βB1, 2), 22.7 (2B4), 20.9 (CH$_3$ adjacent to **I** unit), 19.7 (1B1), 14.1 ppm (1B4, CH$_3$ terminal).

Preparation of 4a-I: A flame-dried Schlenk flask was charged with **1a** (50 mg, 0.075 mmol) and NaBARF (80 mg, 0.09 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) (solution A). A solution of **I** (84 mg, 0.375 mmol) in dry CH$_2$Cl$_2$ (0.25 mL) was precooled to −20°C in a second Schlenk flask (solution B). Solution A was filtered by cannula to afford a clear orange solution and then solution B was added to solution A by microsyringe at −20°C under an argon atmosphere. The solution was then cooled to −40°C. After standing for 12 h, hexane (5 mL) was layered on top of the reaction mixture. The solution was kept at −40°C for a week to afford **4a-I** as an orange solid (17.1 mg, 27%). ^{1}H NMR (CDCl$_3$, 500 MHz, RT): δ = 8.05 (d, J(H,H)=8.55 Hz, 1H; H$_p$), 8.03 (d, J(H,H)=8.55 Hz, 1H; H$_p$), 7.69–7.39 (m, 8H; H$_m$, H$_{m'}$, H$_{p'}$), 6.74 (d, J(H,H)=7.35 Hz, 1H; H$_o$), 6.17 (d, J(H,H)=7.30 Hz, 1H; H$_o$), 3.71 (t, J(H,H)=6.75 Hz, 1H; CHMe$_2$), 3.15 (sept, 2H; CHMe$_2$), 3.05 (t, J(H,H)=6.75 Hz, 1H; CHMe$_2$), 2.68 (s, 1H; H$_a$), 2.46 (m, 1H; H$_d$), 2.04 (m, 1H; H$_d$), 1.78 (m, 9H; H$_c$, H$_g$, H$_l$), 1.54, 1.45 (d, J(H,H)=6.1 Hz, 3H; CHMe$_2$), 1.42 (d, J(H,H)=6.1 Hz, 3H; CHMe$_2$), 1.35 (d, J(H,H)=6.1 Hz, 3H; CHMe$_2$), 1.27 (m; 4H; H$_b$, H$_f$), 1.10, 0.98, 0.90 and 0.68 ((each) d, J(H,H)=5.50–6.10 Hz, 3H; CHMe$_2$), 0.98 ppm (s, 3H; H$_h$); ^{13}C NMR (CDCl$_3$, 125 MHz, RT): δ = 187.6 (C$_i$), 175.6 (N=C), 169.4 (N=C), 164.4 (C$_j$), 145.9 (C$_r$), 140.9 (C$_t$), 140.8 (C$_t$), 140.0 (C$_t$), 139.9 (C$_t$), 138.5 (C$_{o'}$), 137.7 (C$_{o'}$), 133.4 (C$_o$), 132.7 (C$_o$), 131.3 (C$_q$), 130.2, 129.2, 129.0, 128.9 and 128.7 (C$_{p'}$, C$_m$), 126.0, 125.9, 125.6, 125.5, 124.7 and 124.6 (C$_s$, C$_p$, C$_{m'}$), 111.6 (C$_k$), 60.9 (C$_e$), 49.6 (C$_c$), 48.1 (C$_b$), 46.9 (C$_a$), 46.6 (C$_d$), 29.7 (CHMe$_2$), 29.4 (CHMe$_2$), 29.35 (CHMe$_2$), 29.32 (CHMe$_2$), 28.3 (C$_l$), 28.0 (C$_l$), 27.8 (C$_g$), 25.3 (CHMe$_2$), 24.9 (CHMe$_2$), 24.1 (CHMe$_2$), 24.0 (CHMe$_2$), 23.4 (CHMe$_2$), 23.1 (CHMe$_2$), 22.7 (CHMe$_2$), 22.5 (CHMe$_2$), 19.3 (C$_f$), 12.4 ppm (C$_h$); elemental analysis calcd for C$_{88}$H$_{87}$BCl$_2$F$_{24}$N$_2$O$_4$Pd: C 56.20, H 4.66, N 1.49; found: C 56.12, H 4.44, N 1.54. [D$_6$]**4a-I**, **4a-III**, and **4a-IV** were prepared in an analogous manner by using [D$_6$]**I**, **III**, and **IV** in approximately 30, 20, and 50% yield, respectively. Compound **5a-III** was prepared from **5a**, NaBARF, and **III** in 91% yield.

Polymerization of [D$_6$]I by 4a-I: The above polymerization procedure of **I** by **1a**/NaBARF was followed for the reaction of [D$_6$]**I** (0.35 mmol) with **4a-I** (0.005 mmol) in CH$_2$Cl$_2$ (0.20 mL) over 3 d. Poly-[D$_6$]**I** was obtained
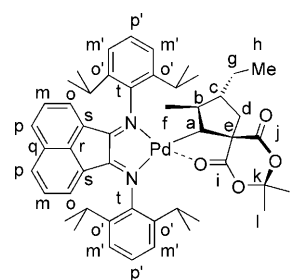
4a-I

as a powder, which was dried in vacuo overnight (M_n = 8600, M_w/M_n = 1.70). ^{2}H NMR (500 MHz, CHCl$_3$): δ = 1.74 ppm (s, 6D; CD$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.1 (C=O), 104.7 (OCO), 51.1 (CH$_2$CCH$_2$), 47.1 (CH), 45.7 (CH$_2$ (cyclopentane)), 31.6 (CH$_2$ (main chain)), 28.2 ppm (br s; CD$_3$ and CH$_3$). Polymerization of **I** by [D$_6$]**4a-I** or **4a-IV** was performed similarly.

Reaction intermediate observed in the reaction between 1a/NaBARF and I: Under an argon atmosphere, NaBARF (53.2 mg, 0.06 mmol) was added to a distilled solution of **1a** (33 mg, 0.05 mmol) in CDCl$_3$ (1.0 mL) in a 25 mL Schlenk flask. After stirring for several minutes, compound **I** (0.22 g, 1.0 mmol) was added and the reaction mixture was briefly shaken in the flask. The reaction mixture was transferred to a well-dried NMR tube at RT. ^{13}C NMR spectroscopy was conducted at RT over 4 h. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 187.5 (C$_i$), 171.8 (C=O, polymer) 175.5 (N=C), 169.3 (N=C), 163.8 (C$_j$), 145.5 (C$_r$), 140.9 (C$_t$), 140.6 (C$_t$), 139.8 (C$_t$), 139.6 (C$_t$), 138.4 (C$_{o'}$), 137.2 (C$_{o'}$), 133.3 (C$_o$), 132.6 (C$_o$), 131.4 (C$_q$), 111.6 (C$_k$), 104.5 (OCO, polymer), 60.6 (C$_e$), 51.0 (CH$_2$CCH$_2$, polymer), 49.5 (C$_c$), 47.7 (C$_b$), 46.7 (CH, polymer), 46.3 (C$_a$), 46.2 (C$_d$), 45.5 (CH$_2$ (cyclopentane), polymer), 31.2 (CH$_2$ (main chain), polymer), 28.8 (CH$_3$, polymer), 25.2, 25.0 (CHMe$_2$), 24.5 (CHMe$_2$), 24.1 (CHMe$_2$), 23.7 (CHMe$_2$), 23.2 (CHMe$_2$), 22.8 (CHMe$_2$), 22.1 (CHMe$_2$), 19.0 (C$_f$), 12.0 ppm (C$_h$). After the experiment, poly-**I** was obtained (30% conversion, M_n = 1900, M_w/M_n = 1.10). The letters in the NMR assignment refer to those of **4a-I**.

Polymerization of 1-hexene by 4a-III: 1-Hexene (0.059 g, 0.7 mmol) was added to a solution of **4a-III** (17 mg, 0.010 mmol) and a trace amount of NaBARF in CH$_2$Cl$_2$ (0.5 mL) in a 25 mL Schlenk flask. The mixture was stirred at −20°C under Ar. 1-Hexene was quantitatively consumed after 68 h. The reaction was quenched with small amount of Et$_3$SiH, and the reaction mixture was poured into acetone ($\approx$50 mL). The oil formed was collected and dried in vacuo at 25°C to give **III**-polyhexene (M_n = 9900, M_w/M_n = 1.09). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.36 (br s 2H, CH$_2$ (cyclopentane) of the initiating end group), 2.1–1.8 (CH$_2$ (cyclopentane), CH of the initiating end group), 1.8–0.8 (CH, CH$_2$, and CH$_3$ from the initiating end group and the unit from 1-hexene). The molecular weight of the isolated polymer determined by ^{1}H NMR spectroscopy (M_{NMR}) was estimated to be 11 200, which was very close to that determined by GPC with THF as eluent (polystyrene standard, M_n = 9900, M_w/M_n = 1.09).

Synthesis of XI-polyhexene-III: Monomer **XI** (19 mg, 0.075 mmol) in CH$_2$Cl$_2$ (1.0 mL) was added to a living polymer of 1-hexene (0.059 g, 0.7 mmol) and **4a-III** (17 mg, 0.010 mmol) (M_n = 9900, M_w/M_n = 1.09) and the reaction mixture was stirred for 6 h at −20°C. The reaction was quenched by small amount of Et$_3$SiH then poured into acetone ($\approx$50 mL). The resultant semi-solid was collected and dried in vacuo at 25°C to give **XI**-polyhexene-**III** (M_n = 10 700, M_w/M_n = 1.17). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.43 (br s, 2H, CH$_2$ (cyclopentane) of the initiating end group), 2.1–1.8 (CH$_2$ (cyclopentane), CH of the initiating end group, α-CH$_2$ of the terminating end group from the quaternary carbon atom), 1.80–0.61 (CH, CH$_2$, and CH$_3$ from α,ω-end groups and the unit from 1-hexene).

Gelation reaction of XI-polyhexene-III with TAP: TAP (4.60 mg, 0.022 mmol) was added to a solution of **XI**-polyhexene-**III** (50 mg) in toluene (0.5 mL) and the reaction mixture was heated at 90°C for 10 min with shaking. The solution was allowed to stand at room temperature for

1 h. Further addition of TAP (3.14 mg, 0.015 mmol) to the solution, followed by the heating at 90 °C, then cooling to RT gave rise to gelation.

Crystal structure determination: Crystals of **4a-I** suitable for an X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/hexane at -40 °C and mounted in glass capillary tubes under Ar. The data were collected at a temperature of -160 °C to a maximum 2θ value of 55.0° on a Rigaku Saturn CCD area detector. Calculations were carried out with the program package CrystalStructure for Windows. The structure was solved by direct methods and expanded using Fourier techniques. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Atomic scattering factors were defined from the literature.[38]

CCDC-765655 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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