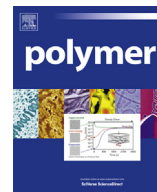




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## Feature article

## Controlled isomerization polymerization of olefins, cycloolefins, and dienes

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## ARTICLE INFO

## Article history:

Received 19 August 2015

Received in revised form

26 September 2015

Accepted 29 September 2015

Available online xxx

## Keywords:

Isomerization polymerization

Pd catalyst

Polyolefin

## ABSTRACT

This article features recent studies on Pd-catalyzed isomerization polymerization of dienes, cyclopentenes and alkenylcyclohexanes. Pd complexes with diimine ligands promote controlled cyclopolymerization of functionalized 1,6-dienes to afford the polymers with repeating *trans*-1,2-bis(methylene)cyclopentylene units. The dienes copolymerize with various olefins, such as ethylene,  $\alpha$ -olefin, and cyclopentene, to yield the polymers containing the *trans*-fused five membered rings. The polymerization of 7-alkyl-1,6-dienes by the Pd catalysts involves stereoselective cyclization as well as chain-walking, and the produced polymers contain 1,2-*trans*-cyclopentylene units separated by oligomethylene spacer along the polymer chain. Trienes with 1,6-diene moieties undergo double cyclizative isomerization polymerization to give the polymers with two cyclopentylene units connected directly or by oligomethylene spacer. The density and distribution of the cyclopentylene units in the polymer can be accurately controlled by changing the monomer. Polymerization of 4-alkylcyclopentenes by the Pd complex, produces the polymers composed of 1,3-*trans*-cyclopentylene units and oligomethylene spacer. The Pd complexes with pseudo- $C_2$  symmetrical structure bring about isospecific polymerization of the cyclopentenes. The isotactic polymers of 4-alkylcyclopentene show liquid crystalline properties. Isomerization polymerization of alkenylcyclohexanes by the Pd catalysts leads to the polymers with high melting point caused by regulated alignment of 1,4-*trans*-cyclohexylene units. Homopolymerization of methylenecyclohexanes also proceeds smoothly in the presence of the Pd catalyst in spite of general low reactivity of the 1,1-disubstituted olefins.

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## 1. Introduction

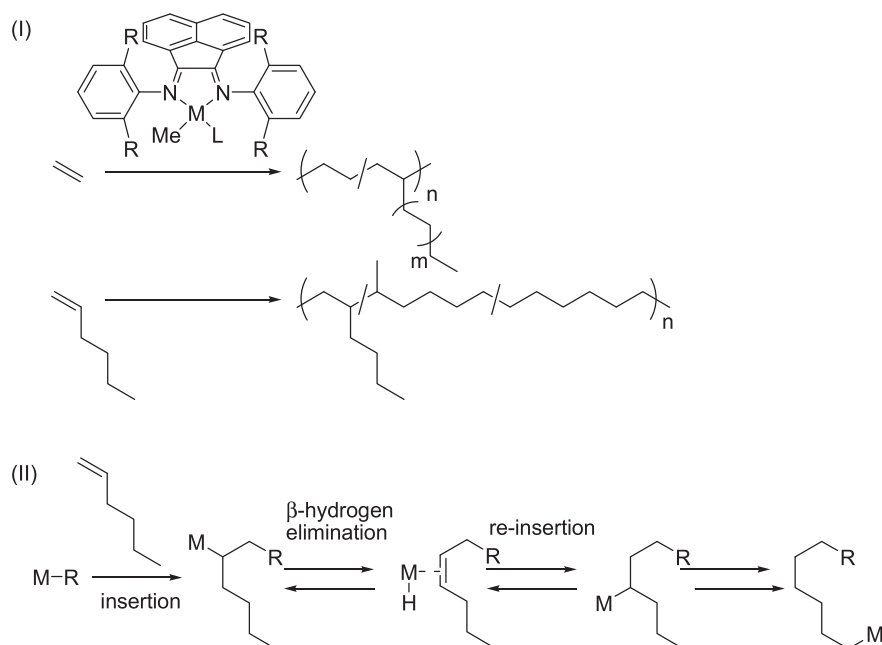
Isomerization polymerization of olefins can lead to a polymer which cannot be directly obtained by the vinyl polymerization of olefin monomers. The reaction often provides the polymers whose structures differ by choice of the catalyst and reaction conditions. Late transition metal complexes were established as a new generation of catalysts for olefin polymerization [1–4]. Pd and Ni complexes with diimine ligands catalyze ethylene and  $\alpha$ -olefin polymerization [5–11], which yields highly branched polyethylene and poly( $\alpha$ -olefin)s with less branched repeating units than expected from the monomer structure (Scheme 1(I)). This is in

contrast with the formation of linear polyethylene and poly( $\alpha$ -olefin)s having alkyl groups in every two carbons of the polymer chain by catalysis using early transition metal compounds.

The olefin polymerization by the Pd and Ni catalysis includes isomerization of the growing chain end via  $\beta$ -hydrogen elimination and re-insertion of the vinyl-terminated polymer (chain walking), in addition to simple coordination/insertion of the monomer (Scheme 1(II)). The  $\beta$ -hydrogen elimination of the growing terminal could lead to chain transfer reaction via the exchange of the coordinated olefin-terminated polymer chain with the monomer. The Pd catalyst with the diimine ligand having bulky *N*-aryl groups, however, suppress the chain transfer and promotes the formation of the above poly( $\alpha$ -olefin)s. Ethylene insertion occurs both to  $-\text{CH}_2-\text{Pd}$  bond and  $-\text{CH}(\text{R})-\text{Pd}$  bond, giving the branched polyethylene.  $\alpha$ -Olefins, on the other hand, insert preferentially to  $-\text{CH}_2-\text{Pd}$  bond rather than  $-\text{CH}(\text{R})-\text{Pd}$  bond [10]. The Pd-catalyzed

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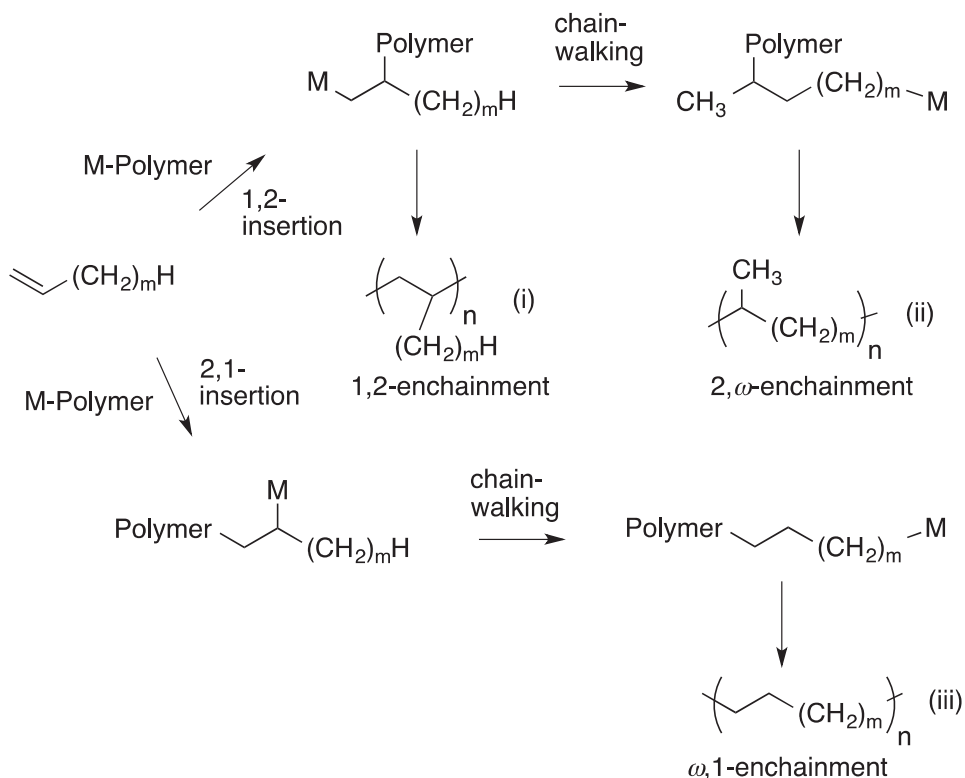
E-mail address: [dtakeuch@res.titech.ac.jp](mailto:dtakeuch@res.titech.ac.jp) (D. Takeuchi).



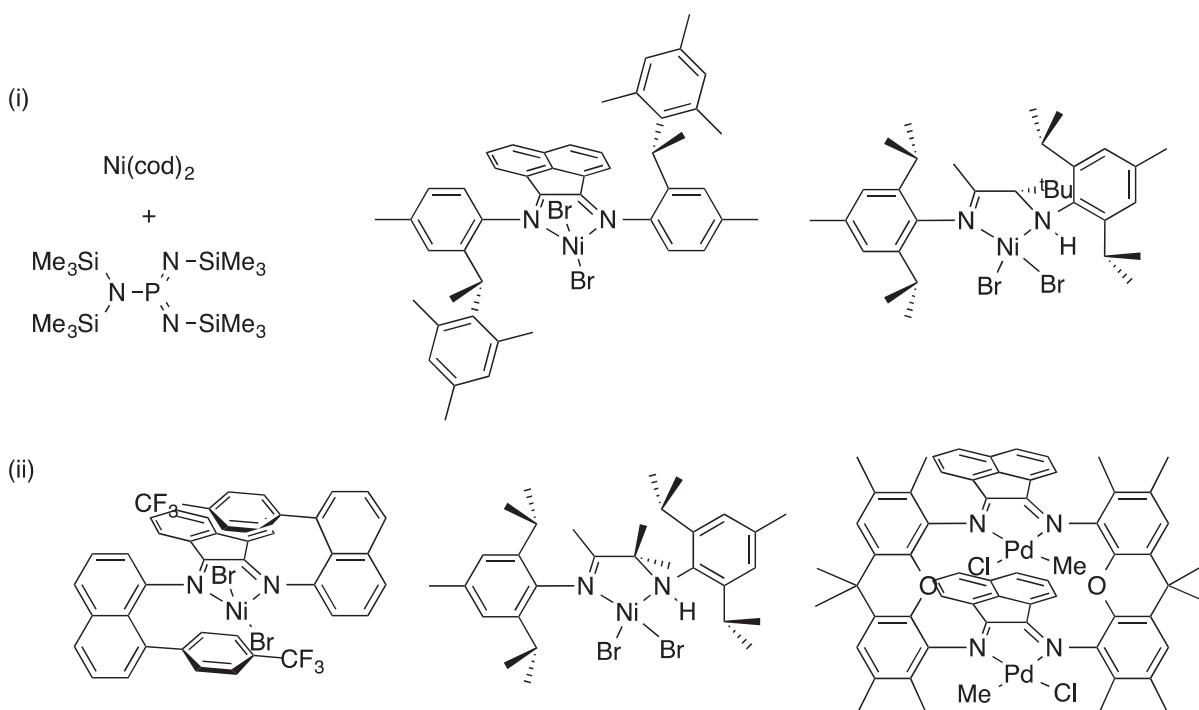
**Scheme 1.** (I) Polymerization of ethylene and 1-hexene by diimine Pd and Ni complexes and (II) mechanism of chain-walking reaction.

polymerization of  $\alpha$ -olefins ( $\text{CH}_2=\text{CH}-(\text{CH}_2)_m\text{H}$ ) produced the polymer composed of three repeating units,  $-\text{CH}_2-\text{CH}((\text{CH}_2)_m\text{H})-$  having alkyl side chain (i) (1, 2 unit),  $-\text{CH}(\text{CH}_3)-(\text{CH}_2)_m-$  having methyl branch (ii) (2, $\omega$  unit), and  $-(\text{CH}_2)_{m+2}-$  without branch (iii)

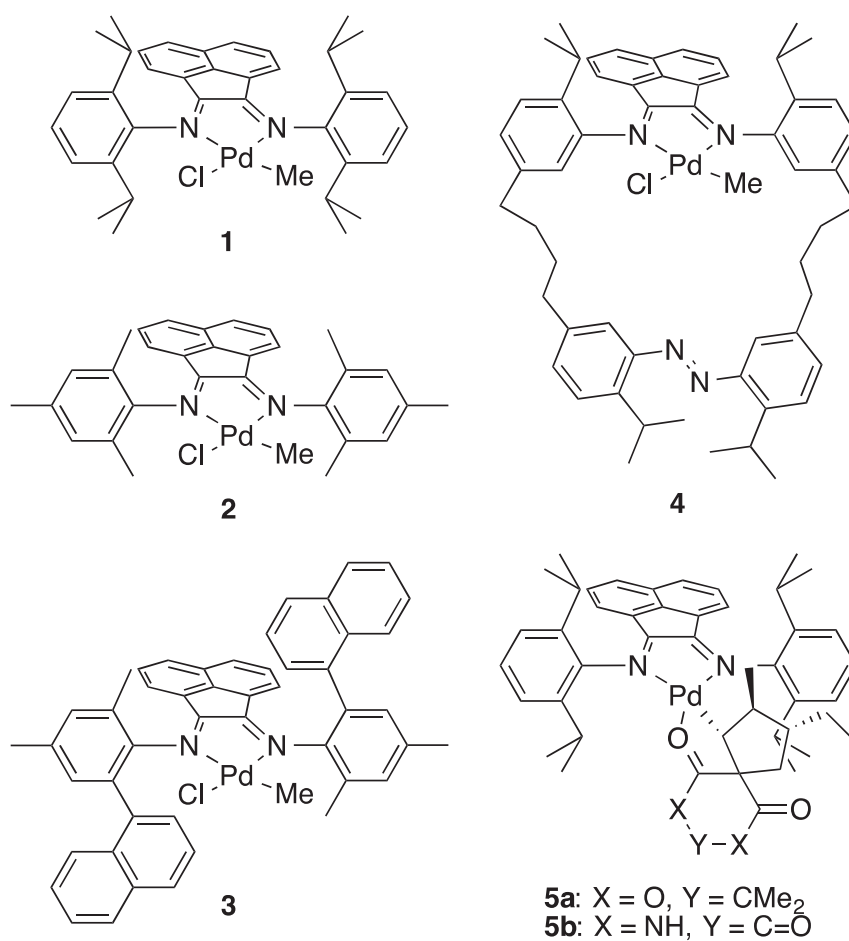
( $\omega$ ,1 unit) (Scheme 2). Chain-walking reaction isomerizes the growing polymer end having  $-\text{CH}(\text{R})-\text{Pd}$  bond into that having  $-\text{CH}_2-\text{Pd}$  bond that undergoes further insertion of the monomer more easily.



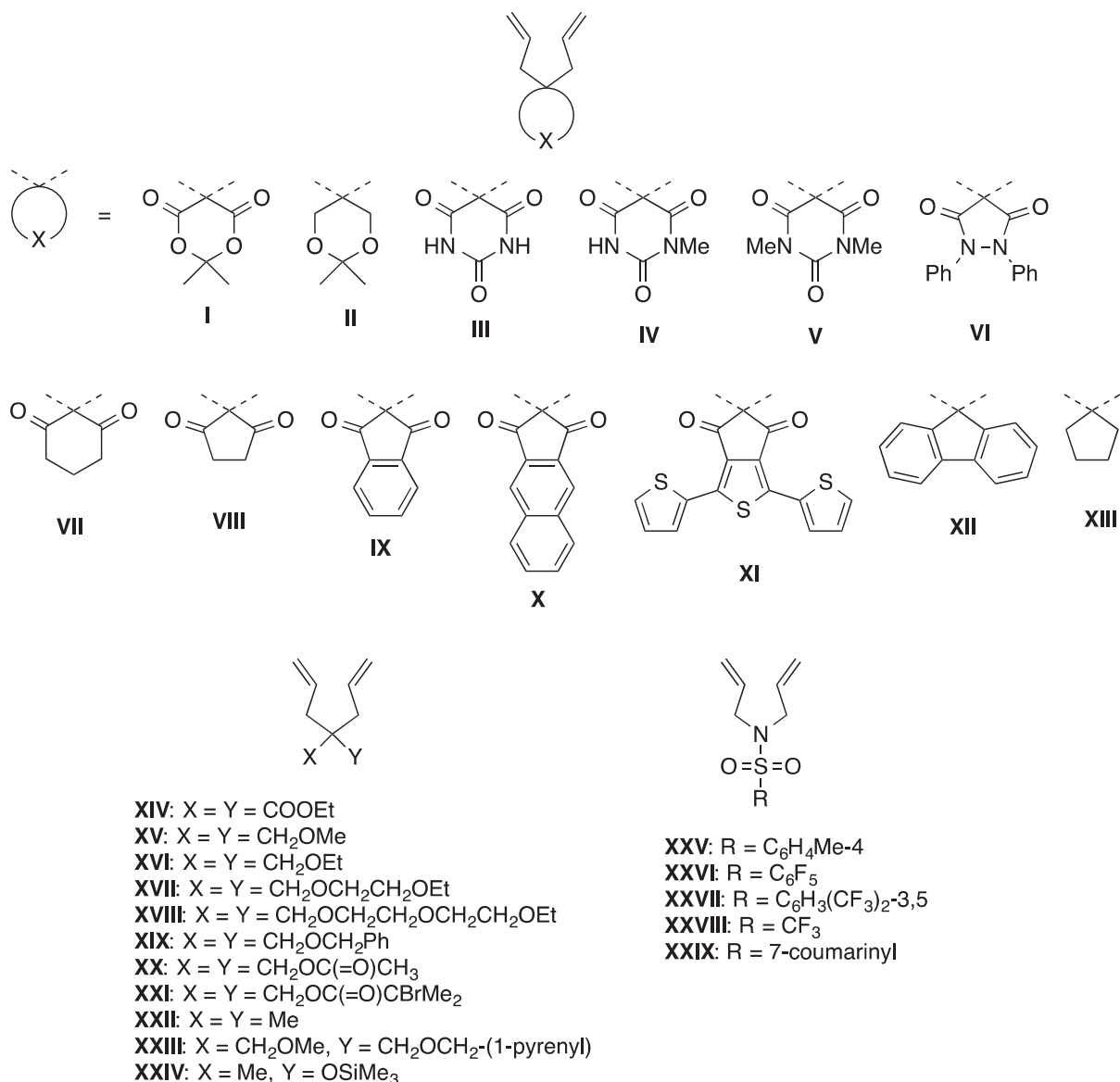
**Scheme 2.** Mechanism of 1-hexene polymerization of catalyzed by diimine Pd complexes.



**Scheme 3.** Catalysts for (i) selective 2,ω-polymerization and (ii) ω,1-polymerization of α-olefins.



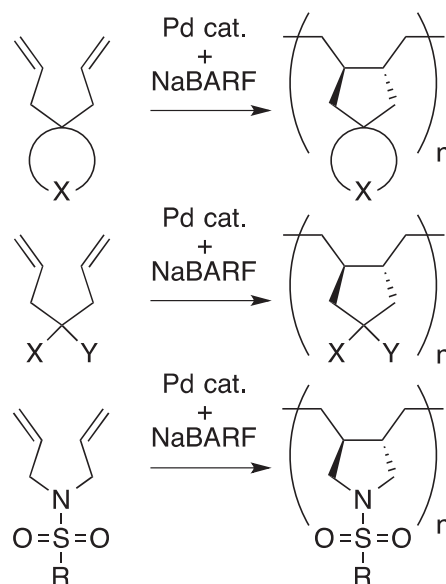
**Chart 1.** Pd complexes used in isomerization polymerization.



**Chart 2.** 1,6-Heptadiene monomers for the cyclopolymerization by Pd-diimine catalysts.

Polymerization via selective 2,1- or 1,2-insertion of  $\alpha$ -olefin followed by chain-walking should provide the polymer composed of the single repeating structure ((ii) or (iii)), but was found in only a limited number of the reports. Nickel/aminobis(imino)phosphorane catalyst system promotes 2, $\omega$ -selective polymerization of  $\alpha$ -olefins and affords the polymer having methyl branches selectively (Scheme 3(ii)) [12,13], which is achieved by proper choice of the substituents on the ligand. Coates reported nickel complexes with diimine ligand having bulky C<sub>2</sub> symmetric structure catalyzed 2, $\omega$ - or  $\omega$ ,1-selective polymerization of  $\alpha$ -olefins [14,15]. Ni complexes with amino-imine ligand are also effective for 2, $\omega$ - and  $\omega$ ,1-selective polymerization of  $\alpha$ -olefins, depending on the substituents on the ligand [16]. We have recently found that dinuclear dipalladium catalyst with cyclic bis(diimine) ligand promotes  $\omega$ ,1-selective polymerization of  $\alpha$ -olefins to afford the polymer with high linearity [17].

Another feature of the Pd catalysts is their tolerance toward polar functional groups [18,19]. The copolymerization of ethylene or  $\alpha$ -olefins with polar monomers such as acrylates has been rare because the common metal catalysts for olefin polymerization contain highly oxophilic early transition metal center and



**Scheme 4.** Cyclopolymerization of 1,6-dienes.

**Table 1**  
Cyclopolymerization of 1,6-dienes by diimine Pd catalysts.<sup>a</sup>

| run | diene        | Pd       | solvent /mL | time /h | conv. <sup>b</sup> (%) | $M_n^c$             | $M_w/M_n^c$       | $T_g^d$ /°C |
|-----|--------------|----------|-------------|---------|------------------------|---------------------|-------------------|-------------|
| 1   | <b>I</b>     | <b>1</b> | 0.5         | 24      | 56                     | 7900                | 1.51              |             |
| 2   | <b>I</b>     | <b>2</b> | 0.5         | 24      | 95                     | 9200                | 1.75              |             |
| 3   | <b>II</b>    | <b>1</b> | 0.5         | 0.25    | 98                     | 7500                | 1.67              | 90          |
| 4   | <b>III</b>   | <b>1</b> | 0.5         | 24      | 40 <sup>e</sup>        | 23,000 <sup>f</sup> | 1.22 <sup>f</sup> |             |
| 5   | <b>IV</b>    | <b>2</b> | 0.5         | 24      | 77                     | —                   | —                 |             |
| 6   | <b>VII</b>   | <b>2</b> | 0.5         | 72      | 82                     | 2100                | 1.72              | 162         |
| 7   | <b>VIII</b>  | <b>2</b> | 0.5         | 72      | 41                     | 1800                | 1.64              |             |
| 8   | <b>IX</b>    | <b>1</b> | 0.25        | 11      | 85                     | 12,000              | 1.64              | 134         |
| 9   | <b>X</b>     | <b>1</b> | 0.5         | 18      | 42                     | —                   | —                 |             |
| 10  | <b>XII</b>   | <b>1</b> | 0.25        | 0.1     | 65                     | 17,800              | 1.95              | 154         |
| 11  | <b>XIII</b>  | <b>1</b> | 0.5         | 1       | quant.                 | 4200                | 1.56              |             |
| 12  | <b>XIV</b>   | <b>2</b> | 0.25        | 48      | 53                     | 9400                | 1.71              | 20          |
| 13  | <b>XV</b>    | <b>2</b> | 0.5         | 2       | 94                     | 7300 <sup>g</sup>   | 1.81 <sup>g</sup> |             |
| 14  | <b>XXI</b>   | <b>2</b> | 0.5         | 6       | 94                     | 16,200 <sup>g</sup> | 1.92 <sup>g</sup> |             |
| 15  | <b>XXIII</b> | <b>1</b> | 0.25        | 6       | 46                     | 7900                | 1.83              |             |

<sup>a</sup> Reaction conditions: [Pd] = 0.010 mmol, [NaBARF] = 0.012 mmol, [diene] = 0.70 mmol, solvent = CH<sub>2</sub>Cl<sub>2</sub>, r.t.

<sup>b</sup> Determined by <sup>1</sup>H NMR.

<sup>c</sup> Determined by GPC using CHCl<sub>3</sub> as eluent.

<sup>d</sup> Determined by DSC.

<sup>e</sup> Isolated yield.

<sup>f</sup> Determined by GPC using DMF as eluent.

<sup>g</sup> Determined by GPC using THF as eluent.

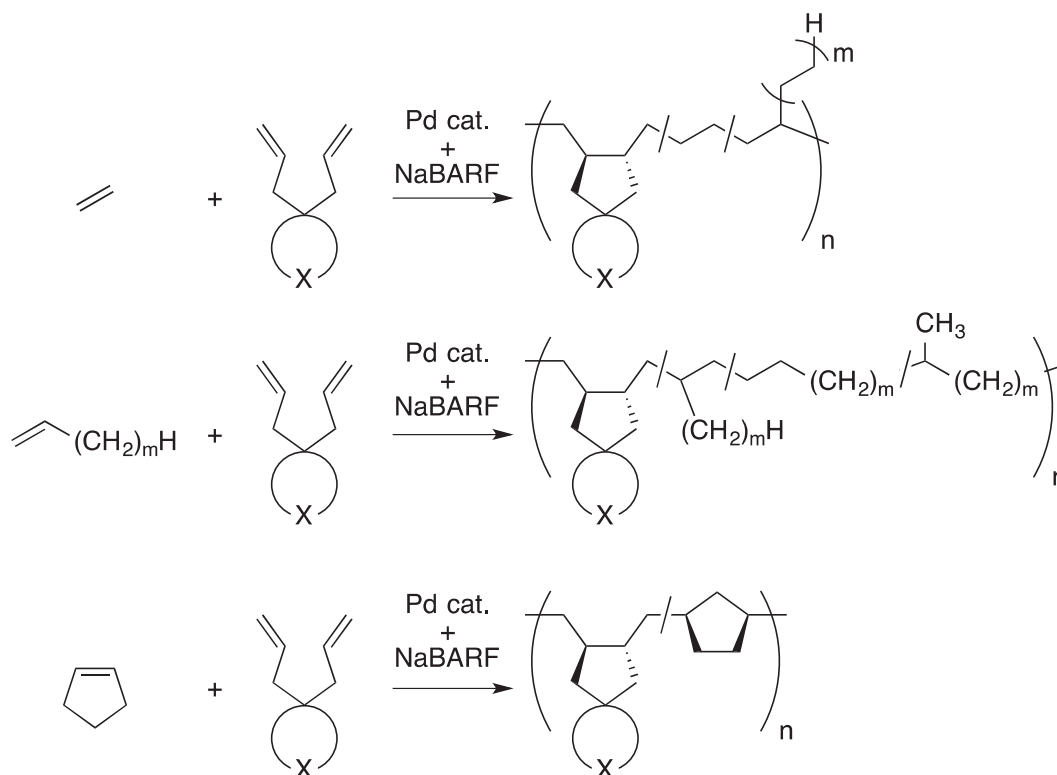
organoaluminum cocatalysts. The diimine Pd catalysts, in contrast, promote copolymerization of ethylene with acrylates to give branched copolymer having the acrylate units at the terminal of the branches [20,21].

Recently, we found that the diimine Pd complexes are effective for the stereoselective cyclopolymerization and isomerization polymerization of alkylcyclopentenones and alkenylcyclohexanes [22–24]. Chart 1 summarizes diimine Pd complexes presented in

this article. The produced polymer contains cycloalkane unit with controlled stereochemistry in regulated intervals along the polymer chain. This article features the controlled isomerization polymerization of dienes, cyclopentenones, alkenylcyclohexanes, trienes, and methylenecyclohexanes by diimine Pd complexes.

## 2. Isomerization cyclopolymerization of non-conjugated dienes and trienes by Pd complexes

1,6-Heptadienes undergo cyclopolymerization in the presence of diimine Pd complex and NaBARF (BARF = B{C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>–3,5}4) to give the polymer with 1,2-*trans*-cyclopentylene unit (Scheme 4) [25–29]. Chart 2 and Table 1 show the representative 1,6-heptadienes used in this study and the results of their cyclopolymerization. The monomer for the cyclopolymerization by the Pd catalysts includes 1,6-heptadienes with cyclic and acyclic esters (**I**, **XIV**, **XX**, **XXI**) and ethers (**II**, **XV**, **XIX**) [25,29], imides (**III**, **IV**, **V**) [27], cyclic diketones (**VII**, **VIII**, **XIX**, **VX**) [27], fluorene (**XII**) [26], and sulfonamides (**XV**, **XVI**, **XVII**, **XVIII**) at 4-position [25,27]. The polymers with functionalized groups such as terthiophene [28], pyrene, and coumarin on the five-membered ring are also obtained from the monomers **XI**, **XXIII**, and **XXIX**. Complex with 2,4,6-trimethylphenyl groups at the diimine nitrogen, **2**, tends to yield the polymer of **I** in high monomer conversion and with higher molecular weight polymer than **1** having 2,6-diisopropylphenyl substituent (Table 1, runs 1 and 2). Monomers **II**, **III** and **IX**, however, polymerized more smoothly by catalyst **1** than catalyst **2**. The polymerization of **IX** catalyzed by **1**/NaBARF takes place smoothly at r.t. to afford the polymer with relatively higher molecular weight ( $M_n$  = 12000 and  $M_w/M_n$  = 1.64). The polymerization of **IX** at –10 °C proceeds in living fashion to give the polymer with narrow molecular weight distribution ( $M_n$  = 9200,  $M_w/M_n$  = 1.12)



**Scheme 5.** Copolymerization of 1,6-heptadienes with ethylene,  $\alpha$ -olefins, and cyclopentene by diimine Pd catalysts.

**Table 2**Copolymerization of 1,6-dienes with olefins by diimine Pd catalysts.<sup>a</sup>

| Run            | diene | olefin       | Pd | Time /h | TON <sup>b</sup> |        | incorp. <sup>b,c</sup><br>(mol%) | $M_n^d$ | $M_w/M_n^d$ |
|----------------|-------|--------------|----|---------|------------------|--------|----------------------------------|---------|-------------|
|                |       |              |    |         | diene            | olefin |                                  |         |             |
| 1 <sup>e</sup> | I     | ethylene     | 1  | 12      | 25               | 808    | 3                                | 9500    | 1.48        |
| 2 <sup>f</sup> | I     | ethylene     | 2  | 2       | 34               | 56     | 38 <sup>h</sup>                  | 9300    | 1.32        |
| 3 <sup>g</sup> | I     | propylene    | 1  | 3       | 41               | 164    | 21 <sup>h</sup>                  | 3300    | 1.84        |
| 4 <sup>g</sup> | I     | propylene    | 2  | 4       | 70               | 89     | 41 <sup>h</sup>                  | 10,500  | 2.07        |
| 5              | I     | 1-butene     | 1  | 3       | 34               | 394    | 8                                | 12,600  | 1.97        |
| 6              | I     | 1-butene     | 2  | 3       | 46               | 35     | 57                               | 9200    | 1.62        |
| 7              | I     | 1-hexene     | 1  | 2       | 25               | 70     | 26                               | 9800    | 1.59        |
| 8              | I     | 1-hexene     | 2  | 3       | 24               | 67     | 30                               | 3200    | 1.99        |
| 9              | I     | 1-decene     | 1  | 2       | 22               | 70     | 30                               | 7200    | 1.75        |
| 10             | I     | 1-decene     | 2  | 2       | 19               | 62     | 27                               | 4100    | 1.83        |
| 11             | I     | cyclopentene | 1  | 2       | 23               | 68     | 25                               | 9600    | 1.68        |
| 12             | II    | ethylene     | 1  | 0.5     | 63               | 162    | 28                               | 12,800  | 1.74        |
| 13             | III   | ethylene     | 1  | 3       | 26               | 1274   | 2                                | 11,200  | 1.94        |
| 14             | VII   | ethylene     | 1  | 21      | 29               | 334    | 8                                | 10,000  | 1.37        |
| 15             | X     | ethylene     | 1  | 3       | 36               | 219    | 14                               | 14,600  | 1.54        |
| 16             | XII   | ethylene     | 1  | 0.3     | 45               | 38     | 54                               | 9900    | 2.37        |
| 16             | XII   | propylene    | 1  | 0.3     | 57               | 13     | 82                               | 12,000  | 2.27        |
| 16             | XII   | cyclopentene | 1  | 0.5     | 52               | 36     | 59                               | 14,300  | 2.39        |
| 17             | XXIV  | ethylene     | 1  | 2       | 48               | 352    | 12                               | 6700    | 1.69        |
| 18             | XXIX  | ethylene     | 1  | 12      | 41               | 1335   | 3                                | 4900    | 1.49        |

<sup>a</sup> Reaction conditions: [Pd] = 0.010 mmol, [NaBARF] = 0.012 mmol, [diene] = 0.70 mmol, ethylene, propylene, 1-butene = 1 atm, [1-hexene, 1-decene, cyclopentene] = 0.70 mmol solvent = CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), r.t.

<sup>b</sup> Determined by <sup>1</sup>H NMR of the reaction mixture.

<sup>c</sup> Molar fraction of diene in the copolymer.

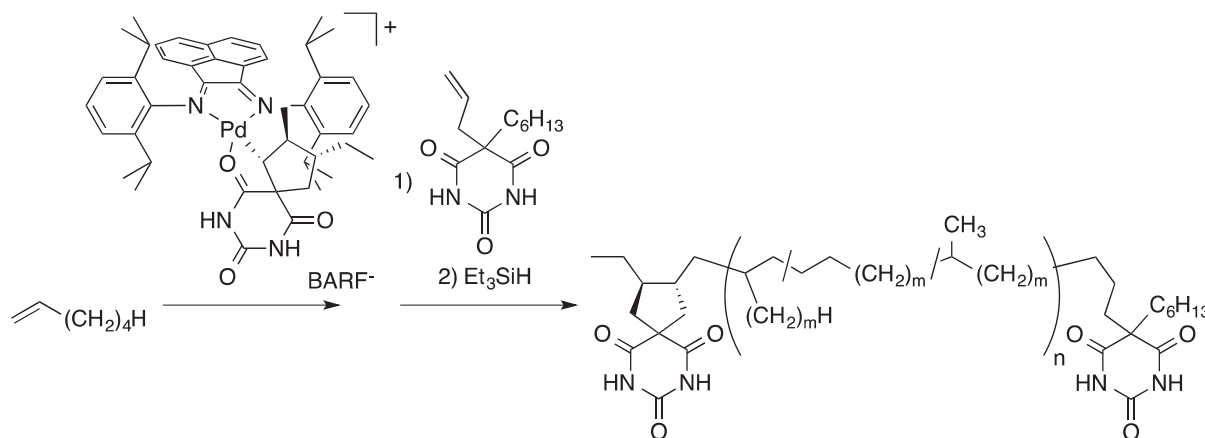
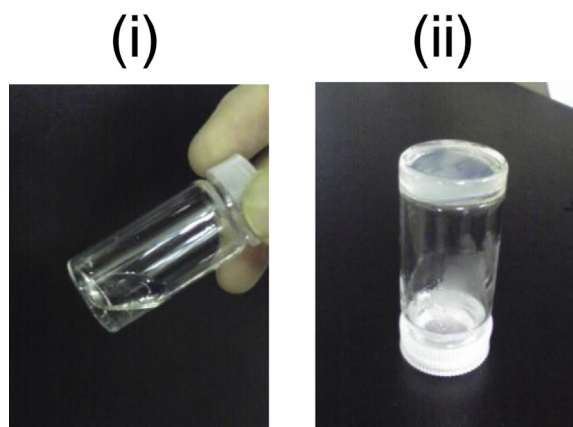
<sup>d</sup> Determined by GPC using CHCl<sub>3</sub> as eluent.

<sup>e</sup> CH<sub>2</sub>Cl<sub>2</sub> = 4 mL.

<sup>f</sup> Ethylene = 0.25 atm.

<sup>g</sup> [diene] = 1.0 mmol.

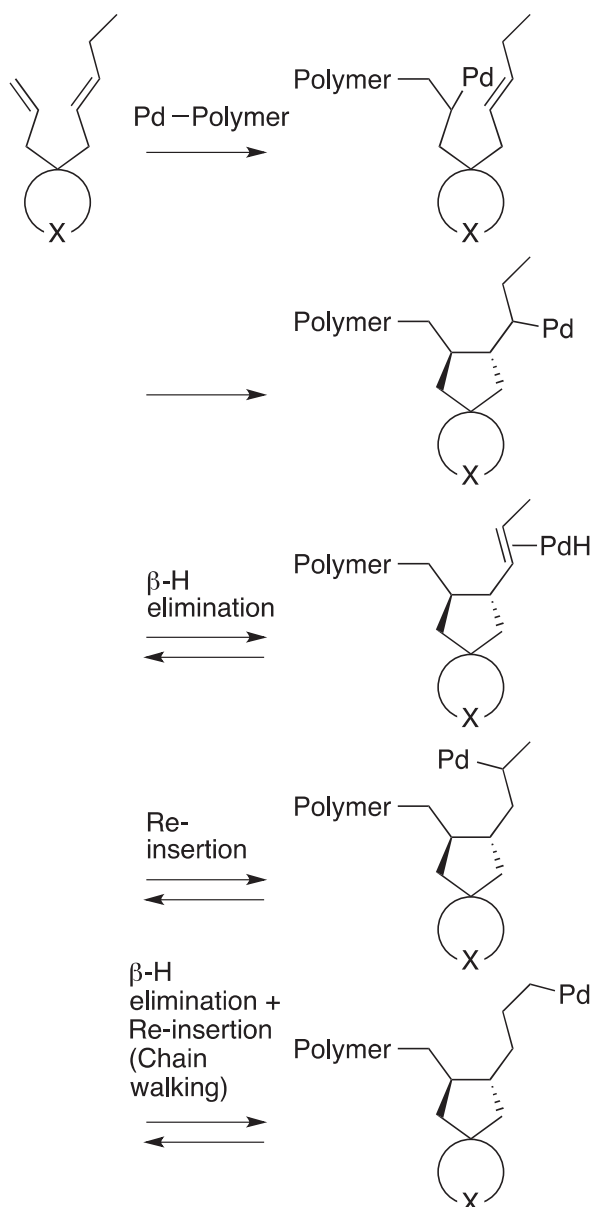
<sup>h</sup> Molar fraction of diene unit in the isolated copolymer.

**Scheme 6.** Synthesis of telechelic polyhexene by using Pd complex with barbituric acid moiety **5b**.**Fig. 1.** Toluene solution of a mixture of barbituric acid-telechelic polyhexene and hexyltriaminopyrimidine, (i) at room temperature, (ii) at  $-20^{\circ}\text{C}$ .

[27]. Polymerization of the monomers without carbonyl group attached to the quaternary carbon on 4-position such as **II**, **XII**, and **XXIII** proceeds faster (65% – quant. conversion within 1 h) than that of the monomers with carbonyl group such as **I** and **III** (40–95% conversion in 24 h). Cyclization of the monomers is quantitative, and no unreacted allyl side chain is contained in the produced polymer. The cyclopolymerization of the monomers in the absence of solvent does not cause cross-linking by the intermolecular reaction, and yields the linear polymer with the regulated structure. Cyclopolymerization of **I** by  $C_2$  symmetric Pd complex **3** affords polymer with threo-diisotactic structure [25], while threo-disyndiotactic polymer of **I** was obtained by using Pd complex with cyclic diimine ligand **4** as the catalyst [30,31].

Copolymerization of ethylene, propylene, 1-hexene, and cyclopentene with those monomers is also possible, affording the corresponding copolymers (Scheme 5, Table 2) [27]. The copolymer of **I** with ethylene and  $\alpha$ -olefins obtained by catalyst **1** contains the repeating unit from **I** in less amount compared to that by catalyst **2**. It is ascribed to that the new insertion of **I** into the Pd–polymer

**Scheme 7.** Isomerization cyclopolymerization of alkyl-substituted 1,6-dienes.



**Scheme 8.** Mechanism of the isomerization cyclopolymerization of alkyl-substituted 1,6-dienes.

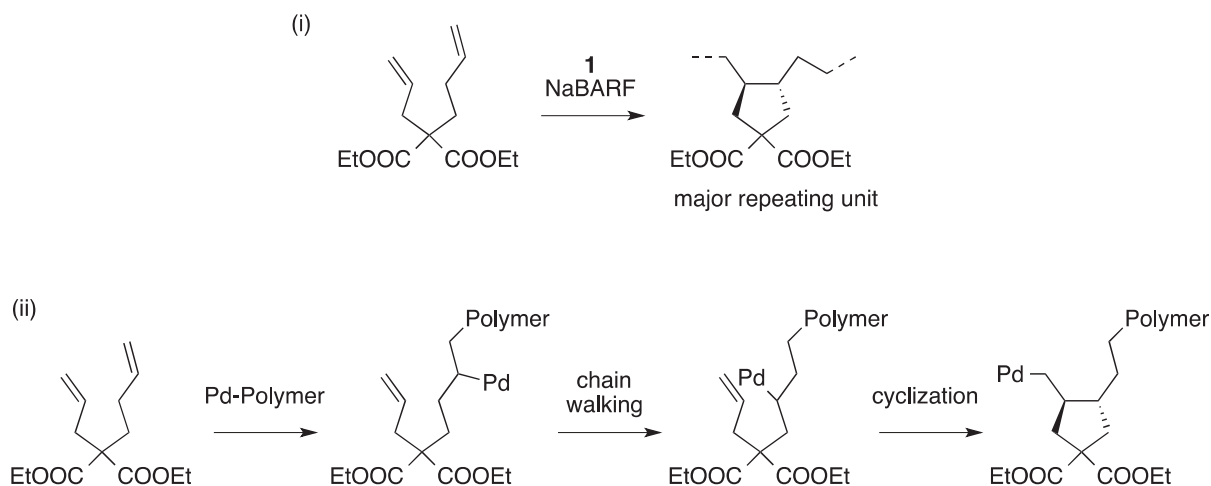
bond is not easier than that of ethylene and propylene in the reaction catalyzed by **1** with bulky substituent. Other diene monomers also undergo copolymerization with the olefins. Copolymerization of ethylene with 5,5-diallylbarbituric acid (**III**) catalyzed by **1**/NaBARF produces the copolymer having 2 mol% of the repeating unit from **III** [27]. Although ethylene polymerization by **1**/NaBARF produced oily products, which are insoluble in DMF, the copolymer of **III** and ethylene is solid at room temperature and soluble in DMF. Thus, introduction of the minor repeating unit from **III** into the polyethylene largely changes its properties. Addition of melamine to the toluene solution of the copolymer leads to gelation, probably due to the multiple hydrogen bonding between barbiturate group and melamine.

An equimolar reaction of Pd complex **1** with diene **I** or **III** leads to successful isolation of the intermediate of the polymerization, **5a** or **5b** (Chart 1) [27]. Pd is attached to the cyclopentane group formed by cyclization of the diene and forms the five-membered chelate ring by the coordination of an ester or imide group of the monomer unit. They correspond to the dormant species of the polymerization, and initiated the polymerization of the dienes. The complexes also promote the polymerization of olefins and yield the polyolefins terminated by the cyclopentane group originally derived from the diene. The polymerization of dienes without carbonyl group at 4-position of the monomer proceeds faster than that of the monomers with carbonyl group. The stable chelate intermediate retards the polymer growth of the monomers with carbonyl groups.

The polymerization of 1-hexene initiated by **5b** followed by end-functionalization by the reaction with olefin having barbituric acid group leads to telechelic polymer (Scheme 6) [27]. A mixture of the telechelic polymer and hexyltri(aminopyridine) in toluene affords thermoreversible gel (Fig. 1).

Diimine Pd complexes are effective for the polymerization of alkyl-substituted 1,6-dienes [32,33]. Although simple cyclizative polymerization of the monomer would produce the polymer with five-membered ring and alkyl side chain, the polymerization by the Pd-catalysis affords the polymers having *trans*-1,2-cyclopentylene unit and oligomethylene spacer alternately along the chain (Scheme 7). The alkyl group is incorporated to the polymer as the oligomethylene spacer of the main chain, and the polymer does not contain alkyl branches as observed by  $^{13}\text{C}$  NMR. The quantitative cyclization was observed during the polymerization in spite of low reactivity of the 1,2-disubstituted olefin in the intermolecular insertion.

Mechanism of the isomerization cyclopolymerization of alkyl-substituted 1,6-dienes is shown in Scheme 8. Vinyl group of the



**Scheme 9.** Isomerization polymerization of 1,7-diene and its plausible mechanism.

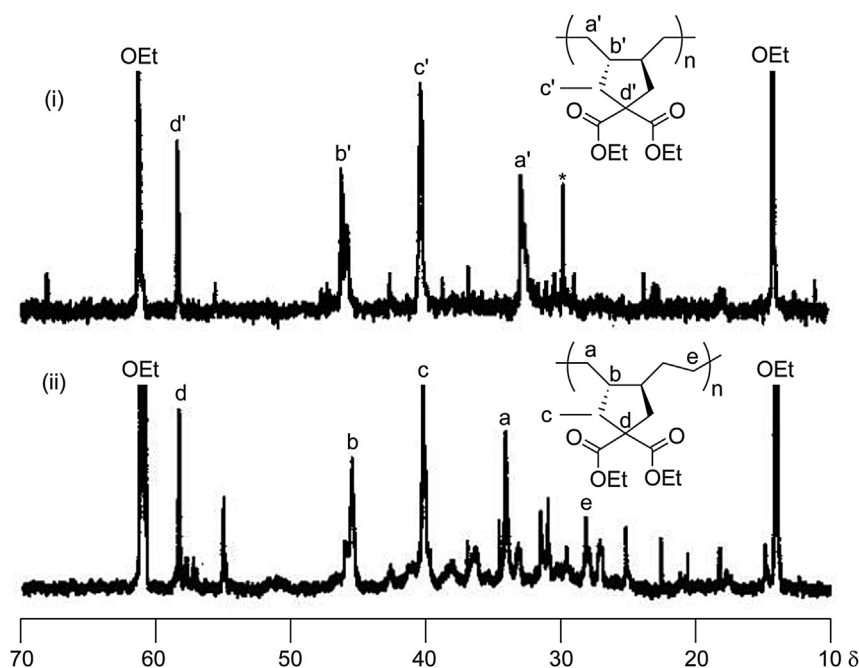


Fig. 2.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of poly(diallyl malonate) and poly(allyl butenyl malonate) produced by **1**/NaBARF.

monomer undergoes 2,1-insertion to the Pd–polymer bond, followed by intramolecular insertion of the vinylene group to form five-membered ring. The Pd center is shifted along the alkyl chain via the chain-walking reaction, and the insertion of another monomer takes place when the Pd center is attached to the terminal of the alkyl group.

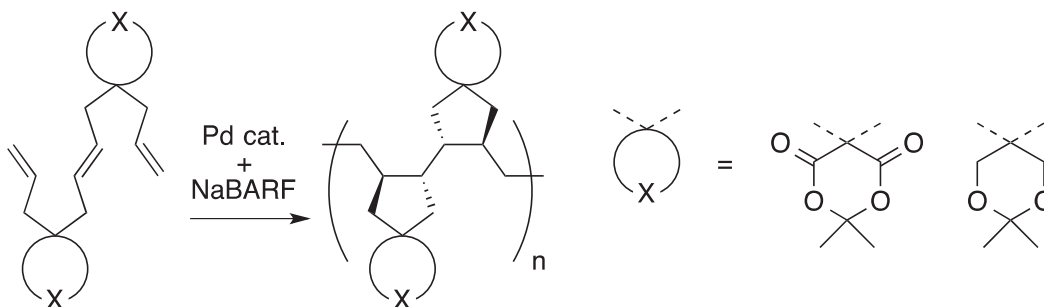
Alkyl-substituted 1,6-dienes with various functional groups such as malonate, cyclic amide, sulfonamide, and cyclic acetal groups also undergo similar cyclopolymerization accompanied by the chain-walking reaction [32]. The polymerization of the diene with acetal group proceeds in living fashion at  $-20\text{ }^\circ\text{C}$  to give the polymer with narrow molecular weight distribution ( $M_w/M_n = 1.20$ ). Polymerization of the 1,6-heptadiene with acetal group followed by the 1,6-octadiene with acetal group affords the corresponding block copolymer, whose glass transition temperature ( $80\text{ }^\circ\text{C}$ ) is lower than those of the homopolymers ( $90$  and  $72\text{ }^\circ\text{C}$ , respectively). Isopropyl- or isobutyl-substituted 1,6-dienes also undergo isomerization cyclopolymerization to afford polymers with regulated methyl branches [33]. However, polymerization of dienes with *sec*-butyl group is of insufficient cyclization efficiency. The cyclized repeating unit of the polymer is equipped with the methyl branch, rather than the ethyl branch. This result indicates that the chain growth takes place when the Pd is attached to methyl

group of  $-\text{CH}(\text{R})-\text{CH}_2-\text{CH}_3$  in the monomer, rather than  $-\text{CH}(\text{R})-\text{CH}_3$ .

Cyclopolymerization of 1,7-octadiene with ester groups is also investigated by using the diimine Pd catalyst (Scheme 9). The polymerization proceeds to attain 64% conversion in 48 h to give the polymer with  $M_n = 3500$  and  $M_w/M_n = 1.72$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the polymer shows major signals at  $\delta$  58.4, 45.5, 40.3, and 34.1, which is close to the chemical shift of the poly(diallylmalonate) (Fig. 2).

Thus, the produced polymer has major repeating unit having *trans*-1,2-cyclopentylene group. There are also other minor signals in the region of  $\delta$  10–60, indicating the presence of minor repeating structures. The formation of *trans*-1,2-cyclopentylene group in the polymerization of 1,7-octadienes is ascribed by the 2,1-insertion of butenyl group of the monomer to Pd–C bond, followed by chain walking of the Pd center to undergo cyclization (1,2-insertion). Selective formation of the five-membered ring is also reported in copolymerization of ethylene with 1,7-octadienes by dinickel catalyst [34] and in Pd-catalyzed cycloisomerization of 1,*n*-dienes [35]. In contrast to the 1,7-octadienes, 1,8-octadienes does not undergo the polymerization to afford polymer.

Trienes having three C=C double bond are expected to undergo polymerization via double cyclization to give polymer with two



Scheme 10. Double cyclizative polymerization of 1,6,11-trienes.

cyclic groups in one repeating unit. However, the reports of the cyclopolymerization of trienes are quite rare [36]. Appropriate alignment of the three C=C double bonds on the monomer molecule is important for the efficient and selective double cyclization of the monomer during the polymerization. Control of the relative stereochemistry of the two cyclic groups in the repeating unit is also an important issue.

Recently, we found that Pd diimine complexes promote polymerization of 1,6,11-dodecatrienes having functional groups, such as cyclic acetal groups and cyclic ester groups (Scheme 10) [37]. Double cyclization takes place quantitatively during the polymerization. The produced polymers contain two *trans*-1,2-cyclopentylene units in every repeating unit, and the relative stereochemistry between the two five-membered rings is controlled in racemo structure. Polymerization of the triene with acetal group produces the corresponding polymer with narrow molecular weight distribution. The polymer obtained by using **1a** is rich in *racemo*-syndiotactic sequence (91%). The acetal group of the polymer can be hydrolyzed in the presence of trifluoroacetic acid. Triene with acyclic ether or ester groups also undergoes cyclopolymerization in the presence of Pd complex. Trienes with sulfonamide group or fluorenylidene group, in contrast, do not undergo the polymerization, although the diene with the same functional groups were reported to undergo the smooth cyclopolymerization.

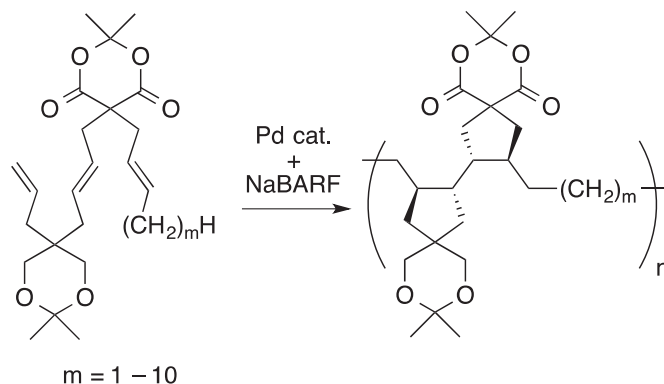
Similarly to the polymerization of alkyl-substituted 1,6-dienes, alkyl-substituted 1,6,11-trienes undergo double cyclizative polymerization accompanied by chain walking (Scheme 11) [38]. The produced polymer contains bis(cyclopentylene) unit and oligomethylene spacer alternatingly along the polymer chain. The polymerization of the triene monomers having cyclic acetal group at 4-position and cyclic ester group at 9-position affords the polymer with cyclopentane group attached with those functional groups in alternating manner.

1,6,13-Heptadecatrienes undergo double cyclizative polymerization accompanying isomerization not only after the second cyclization of the monomer, but also after the first cyclization (Scheme 12) [39]. 1,2-*trans*-Cyclopentylene group was formed in both cyclization steps. The produced polymers have two different functionalized cyclopentylene groups in every repeating unit, and the two neighboring five-membered rings of the polymer are separated by ethylene and pentamethylene spacers, alternatingly. The 1,6,13-heptadecatriene monomers with cyclic acetal groups at 4-position and the cyclic acetal, cyclic ester, acyclic ester, or sulfonamide groups at 11-position undergo polymerization to produce the polymers with  $M_n > 10000$ . This is in contrast to that 1,6,11-dodecatrienes with acyclic ester or sulfonamide groups does not yield the high molecular weight polymer. Choice of the functional group at 4-position is essential for the smooth double cyclizative polymerization of trienes.

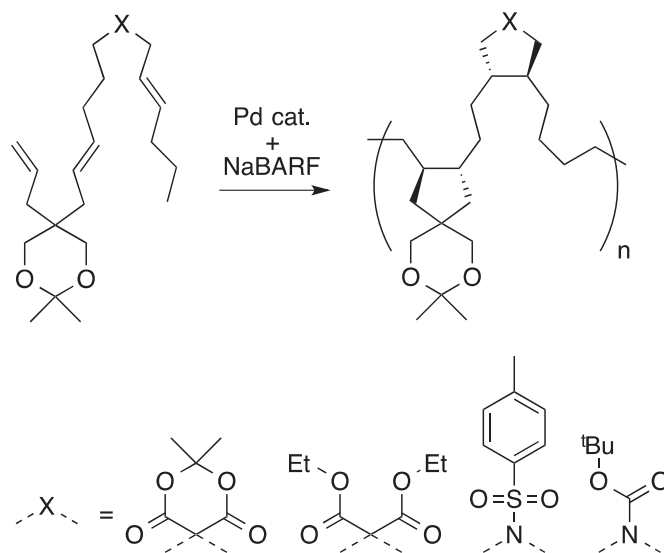
Differential scanning calorimetry (DSC) of the polymers of the dienes and trienes show good correlation between glass transition temperature of the polymer and number of methylene groups of the polymer chain per two five-membered rings.

### 3. Isomerization polymerization of cycloolefins and olefins having cyclic substituent

Polymerization of cyclopentene by diimine Ni and Pd catalysts affords the polymer with *cis*-1,3-cyclopentylene unit [40]. Pd catalysts also bring about polymerization of 4-alkylcyclopentenenes. The produced polymer contains *trans*-1,3-cyclopentylene unit and oligomethylene spacer alternatingly along the polymer chain (Scheme 13) [41]. The polymerization involves face-selective coordination of the Pd center to the C=C group of the monomer, its



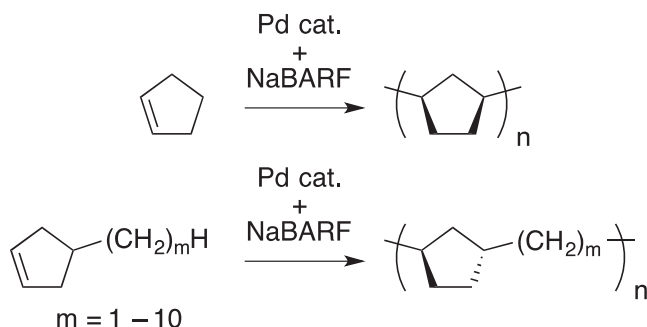
**Scheme 11.** Double cyclizative isomerization polymerization of alkyl-substituted 1,6,11-trienes.



**Scheme 12.** Double cyclizative isomerization polymerization of 1,6,13-trienes.

insertion to the growing terminal, and chain-walking reaction of the Pd center (Scheme 14). Selective insertion of a new monomer to the Pd-CH<sub>2</sub> bond renders formation of the polymer without branch.

Pd complex **1** affords the atactic polymer, which is soluble in chloroform and THF at room temperature. DSC of the isotactic polymer shows only one phase transition due to melting point. The polymerization of 4-methylcyclopentene by the Pd complex with C<sub>2</sub> symmetric diimine ligand (**3**), proceeds much faster than that by **1**. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the obtained polymer shows highly threo-diisotactic structure. DSC of the stereoregulated polymer shows stepwise phase transition at two temperatures, indicating liquid crystalline properties. The liquid crystalline properties of the polymer is also confirmed by polarizing microscope. The temperature range of the phase transition between liquid crystalline phase and solid phase or isotropic phase can be controlled by the length of the oligomethylene spacer of the polymer (Fig. 3). Liquid crystalline polyolefin are very limited [42,43]. Polymer with 1,3-cyclopentylene groups with *trans*- and *cis*-stereochemistry, synthesized by cyclopolymerization of 1,5-hexadiene catalyzed by C<sub>2</sub>-symmetric zirconocene catalyst, has been reported to have liquid crystalline properties. As the polymer of 4-alkylcyclopentene with

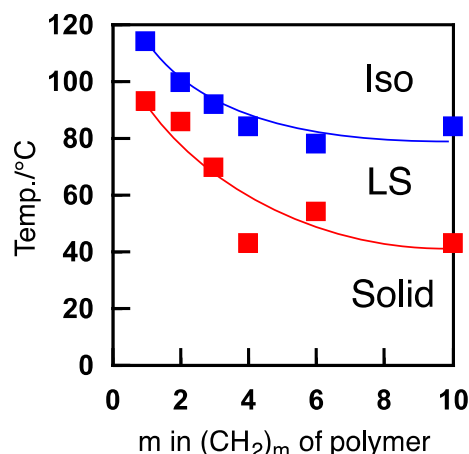


**Scheme 13.** Polymerization of cyclopentene and 4-alkylcyclopenten-1-yls by Pd complexes.

atactic structure is not liquid crystalline, the stereo-regular five-membered rings may render the ordered alignment of the polymer chain to realize liquid crystalline properties.

Pd-catalyzed polymerization of alkenylcyclohexanes gives the polymer composed of alternating 1,4-*trans*-cyclohexylene unit and oligomethylene spacer (Scheme 15) [44]. The produced polymers show high melting point ranging from 226 to 130 °C, depending on the length of the oligomethylene spacer in the repeating unit (Fig. 4).

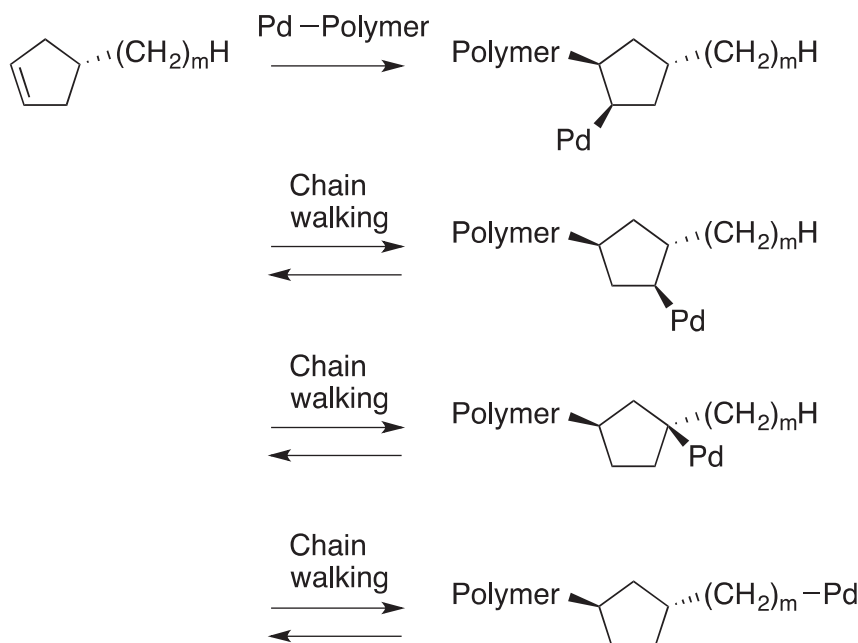
The polymerization mechanism involves 2,1-insertion of the monomer to the cyclohexyl–Pd bond of the growing chain end, chain walking of the Pd center along the cyclohexane ring, and selective insertion of the new monomer when the Pd center is attached to the 4-position of the cyclohexyl group (Scheme 16). In the Pd-catalyzed isomerization polymerization of  $\alpha$ -olefins, dienes, and alkylcyclopenten-1-yls, the monomers undergo selective insertion into –CH<sub>2</sub>–Pd bond rather than –CH(R)–Pd bond. Selective formation of *trans*-1,4-cyclohexylene unit in the polymer indicates that no plane-inversion takes place during the chain walking of Pd center along the cyclohexane ring. The polymerization of vinylcyclopentane and allylcyclopentane does not proceed by the Pd



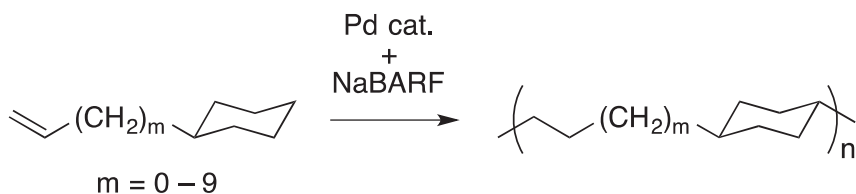
**Fig. 3.** Relationship between length of oligomethylene spacer in the poly(4-alkylcyclopentene) and its phase transition temperature.

catalyst, although they are expected to afford the polymer having cyclopentylene unit. Pd catalyzed reaction of bicyclo[3.2.0]hept-6-ene afforded high mass polymer whereas that of bicyclo[4.2.0]oct-7-ene results in isomerization or oligomerization [45,46]. These results may indicate the chain walking into six-membered ring takes place much easier than that into five-membered ring, which enables the efficient isomerization polymerization of alkenylcyclohexanes as well as the addition polymerization of bicyclo[3.2.0]hept-6-ene (Scheme 17).

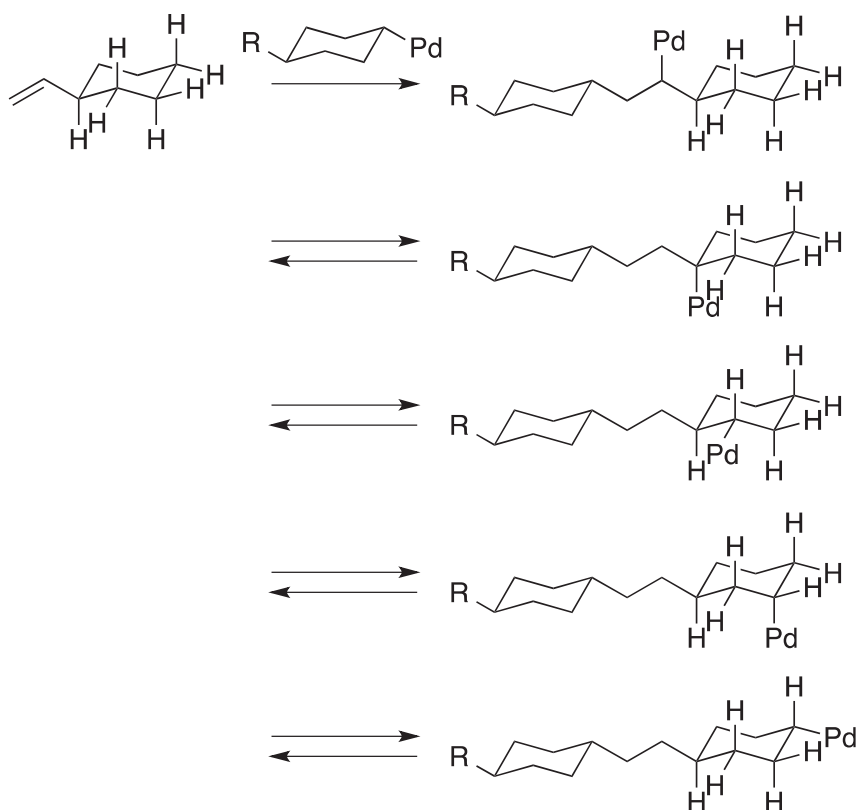
Methylenecyclohexanes are known to have low reactivity for coordination polymerization due to their 1,1-disubstituted olefin structure. Pd catalysis allows efficient isomerization polymerization of methylenecyclohexanes to give the polymer with methylene-1,4-*trans*-cyclohexylene repeating structure (Scheme 18) [47]. Alkyl-substituted methylenecyclohexanes also undergo isomerization polymerization in the presence of Pd catalysts. 4-



**Scheme 14.** Mechanism of the polymerization of alkylcyclopenten-1-yls by Pd complexes.



Scheme 15. Isomerization polymerization of alkenylcyclohexanes.



Scheme 16. Mechanism of isomerization polymerization of vinylcyclohexane.

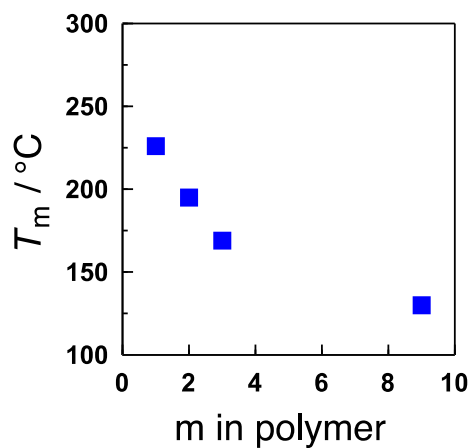
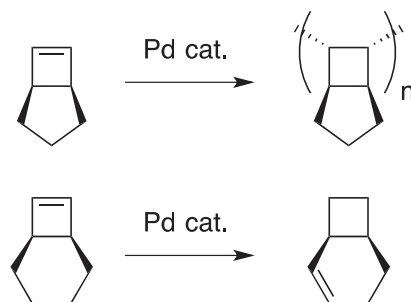
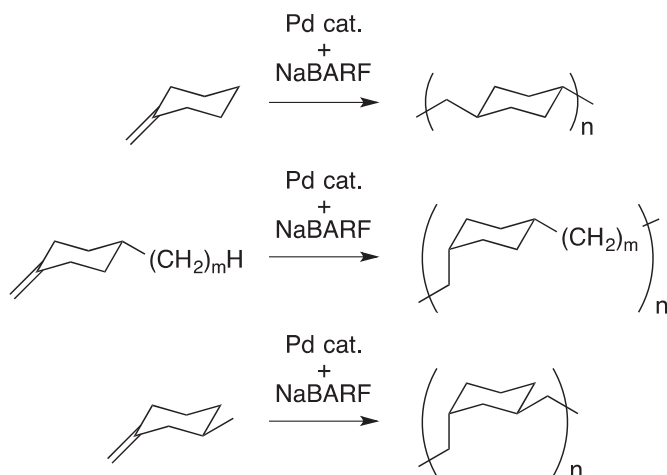


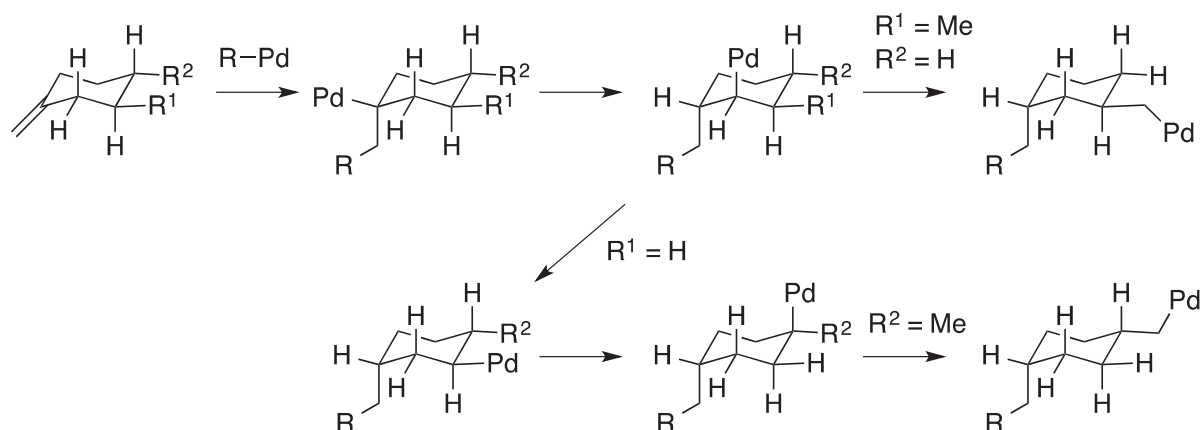
Fig. 4. Relationship between length of oligomethylene spacer in the poly(alkenylcyclohexanes) and its melting point.



Scheme 17. Pd-catalyzed reaction of bicyclo[3.2.0]hept-6-ene and bicyclo[4.2.0]oct-7-ene.



**Scheme 18.** Isomerization polymerization of methylenecyclohexanes.



**Scheme 19.** Mechanism of isomerization polymerization of methylenecyclohexanes.

Alkyl-1-methylenecyclohexanes afford the polymer with *cis*-1,4-cyclohexylene group, whereas the polymer of 3-methyl-1-methylenecyclohexane contains the repeating unit with *trans*-1,3-cyclohexylene group. The polymer of 2-methyl-1-methylenecyclohexane has a complicated structure and its full characterization of the structure of the polymer is not feasible.

The polymerization mechanism of methylenecyclohexanes is shown in [Scheme 19](#). The monomer adopts the chair conformation with the equatorial methyl group. Growing polymer end adds to the monomer from the equatorial direction, followed by the chain walking of the Pd center within the cyclohexane ring. The polymerization of 3-methyl-1-methylenecyclohexane proceeds via  $\gamma$ -C–H activation, and the insertion of a new monomer takes place to the –CH<sub>2</sub>–Pd bond. The polymerization mechanism of non-substituted methylenecyclohexane and 4-methyl-1-methylenecyclohexane includes the chain walking of the Pd center to the 4-position of the cyclohexane group and methyl group on 4-position, respectively, followed by the insertion of a new monomer.

#### 4. Summary

We have developed that Pd-catalyzed isomerization polymerization of dienes, trienes, and alkylcyclopentenes provides a new

and effective method for synthesis of the polymers with *trans*-five-membered rings. Cyclopolymerization of dienes allows incorporation of various functional groups, such as cyclic ester, acetal, and imide groups on the cyclopentylene group of the polymer. Isomerization cyclopolymerization of trienes enable the synthesis of polymers having two different functionalized cyclopentylene groups in alternating manner along the polymer chain. Stereoregular polymers obtained by isotactic polymerization of 4-alkylcyclopentenes are liquid crystalline, and their phase transition temperature can be controlled by the length of alkyl group of the monomer. Isomerization polymerization of alkenylcyclohexanes and methylenecyclohexanes produces the polymers with *trans*- or *cis*-fused six-membered rings, which show high melting point. Further design of new monomers suited to the Pd-catalyzed isomerization polymerization will enable the synthesis of polymers with controlled alignment of cycloalkane groups and/or functional groups along the polymer chain.

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