INVITED REVIEW

Stereo-controlled synthesis of polyolefins with cycloalkane groups by using late transition metals

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Pd complexes with diimine ligands promoted the controlled cyclopolymerization of 1,6-dienes and 1,6,11-trienes to afford polymers containing 1,2-*trans*-cyclopentane groups with well-regulated stereochemistry. The polymerization proceeded with quantitative cyclization of the monomer, even under bulk conditions or in copolymerization reactions with ethylene and α -olefins. The polymerization of monomers with oligomethylene spacers yielded polymers with five-membered rings that are accurately distributed along the polymer chain. 4-Alkylcyclopentenones and alkenylcyclohexanes were also polymerized by Pd-diimine complexes to afford polymers with 1,3-*trans*-cyclopentane groups and 1,4-*trans*-cyclohexane groups, respectively. Pd complexes with a C_2 symmetrical structure promoted the isospecific polymerization of 4-alkylcyclopentenones, and the resultant isotactic polymers showed liquid crystalline properties. The mechanism of the polymerization reaction has been revealed. *Polymer Journal* (2012) 44, 919–928; doi:10.1038/pj.2012.27; published online 25 April 2012

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INTRODUCTION

Recently, hydrocarbon polymers with cycloalkane groups along the polymer chain have attracted a considerable amount of attention because they exhibit high thermal stability and optical transparency.¹ Addition polymerization of cyclic alkenes^{2,3} and metathesis polymerization of norbornenes^{4–6} have been used to synthesize these polymers (Scheme 1). Cyclic groups on the monomer can be introduced into the polymer as *cis*-fused cycloalkane groups.^{7–11} The polymerization of non-conjugated dienes can also be used to synthesize polymers with cycloalkane groups because chain growth is accompanied by monomer ring closure.¹² Early transition metal complexes have been extensively used in cyclopolymerization reactions.^{13–24} The polymers produced via cyclopolymerization often contain both *cis*- and *trans*-isomeric repeating units. Owing to the high oxophilicity of early transition metals, cyclopolymerization reactions of non-conjugated dienes with polar functional groups are relatively scarce.²⁵

Compared with the corresponding homopolymers, the copolymerization of cyclic alkenes with ethylene or α -olefins produces polymers with cycloalkane groups in a relatively low density.^{26–34} The average density of cyclic units along the polymer chain can be controlled by changing the molar ratio of monomers, and the polymer properties also vary accordingly. However, the accurate control of the distribution of cyclic units in the polymer chain has not been achieved. The copolymerization of non-conjugated dienes with ethylene or α -olefins often produces polymers with uncyclized units, because the reactivity of ethylene and α -olefins is greater than

that of non-conjugated dienes, which results in the preferential insertion of monomers over the cyclization of the diene unit at the end of the growing chain.^{35–46}

In contrast to early transition metal complexes, late transition metal complexes are highly active for the oligomerization of ethylene but are not suitable for polymerization. However, in 1995, Brookhart reported that Pd and Ni complexes with diimine ligands show high catalytic activity for the polymerization of ethylene, propylene and α -olefins.⁴⁷ Since the discovery of Brookhart's catalyst, many complexes based on late transition metals have been reported.^{48,49} Although many studies on ethylene polymerization by late transition metal catalysts have been published, only limited examples of propylene or

Scheme 1 Synthesis of polyolefins with cycloalkane groups.

α -olefin polymerization have been presented.⁵⁰ In contrast, Pd and Ni complexes with diimine ligands are effective for α -olefin polymerization.⁵¹

Conventional catalysts such as zirconocenes produce linear polyethylene and polyolefins with alkyl side chains in the polymerization of ethylene and α -olefins, respectively. In contrast, Pd- and Ni-diimine catalysts afford polyethylenes with highly branched structures and poly(α -olefin)s containing non-branched polymethylene repeating units, respectively (Scheme 2 (I)).^{47,52–57} The production of these polymers can be attributed to the occurrence of chain-walking reactions, in which alkylpalladium and alkylnickel species at the growing ends of the polymer undergo repetitive β -hydrogen elimination of vinyl-terminated polyolefins followed by reinsertion of the coordinated olefin into the metal-hydrogen bond (Scheme 2 (II)).

The copolymerization of ethylene or α -olefins with polar monomers such as acrylates has been difficult to achieve because most catalysts are composed of early transition metal complexes.⁵⁸ In contrast, Pd catalysts promote the copolymerization of ethylene with polar monomers to give functionalized polyethylene.^{59–61}

Recently, we demonstrated that late transition metal complexes are effective for stereoselective cycloolefin polymerization and diene cyclopolymerization reactions.^{62,63} The resulting polymers contain 1,2- or 1,3-disubstituted *trans*-fused cyclopentane rings, which have been difficult to synthesize in a controlled manner by using conventional polymerization catalysts. Various functionalities can be incorporated into cyclopentane rings. The present article describes the scope and limitations of the controlled polymerization of cyclopentenes, dienes and trienes by late transition metal complexes.

CYCLOPOLYMERIZATION OF NON-CONJUGATED DIENES BY Pd COMPLEXES

1,6-Heptadienes undergo cyclopolymerization in the presence of Pd-diimine complexes and NaBARF (BARF = $\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2-3,5)_4$).^{64,65}

The cyclopolymerization reaction proceeds with quantitative cyclization to afford polymers with high molecular weights, even under bulk conditions. In contrast, conventional catalysts frequently afford polymers with uncyclized repeating units and/or cross-linked repeating units as a result of their insufficient cyclization efficiency, especially under bulk conditions.^{66–68}

Scheme 3 shows representative monomers that can be polymerized by Pd complexes. These monomers can be readily synthesized through bis-allylation of active methylene compounds such as malonates (**I-a**, **I-b**) or diketones (**I-f**, **I-g**). Pd catalysis is compatible with polar functional groups such as barbiturates (**I-c**, **d**) and sulfonamides (**I-j**, **I-k**, **I-l**). The stereochemistry of the cyclopentane ring of the polymer is controlled in a *trans*-configuration, as confirmed by the corresponding ^{13}C (^1H) nuclear magnetic resonance (NMR) spectra (Figure 1). Dienes with indanedione groups (**I-f**) and cyclic acetal groups (**I-h**) lead to polymers with sufficient molecular weights and narrow molecular weight distributions, even at lower temperatures. Polymer growth resumes as a result of monomer re-addition after polymerization, and polymers with higher molecular weights are produced, indicating that living cyclopolymerization occurs at low temperatures.

In contrast to the aforementioned monomers, the dienes shown in Scheme 4, including diallyl ether, diallyldimethylsilane, and 4,4-dicyano-1,6-heptadiene, do not afford high mass polymers. Unsubstituted 1,6-heptadiene is not suitable for cyclopolymerization because of the formation of stable π -allyl palladium species that do not promote further polymer growth.⁴⁸

Complexes **1a** and **1b**, which possess a C_{2v} symmetrical structure, produce atactic polymers of **1a**, whereas C_2 symmetrical complexes **1c** and **1d** afford threo-diisotactic polymers with a *rr* of 83% and 66%, respectively (Scheme 5). Recently, Kinbara and Aida⁶⁹ demonstrated that **1e**, a Pd complex containing a cyclic diimine ligand, was effective for the synthesis of threo-disyndiotactic diallylmalonates polymers (Scheme 5). In addition, the resulting polymer has been shown to adopt ordered aggregates.

Scheme 2 (i) Polymerization of ethylene and 1-hexene by Pd-diimine complexes and (ii) the mechanism of chain walking.

Scheme 3 Cyclopolymerization of 1,6-heptadienes by Pd-diimine complexes.

Figure 1 ¹³C(¹H) NMR spectrum of **poly-I-g**

Derivatives of Meldrum's acid are known to undergo unique reactions.⁷⁰ Baxter reported that the pyrolysis of 2,2-dimethyl-1,3-dioxane-4,6-dione-5-spirocyclopropane at 500 °C (0.05 mm Hg) produces ketenes and promotes the release of CO₂ and acetone, which are converted to ketene dimer dispiro-(2.1.2.1)-octane-4,8-dione.⁷¹ Similar reactions of polymers containing Meldrum's acid moieties have been reported by Hawker.^{72,73} **Poly-I-a** obtained using **1e** as a catalyst undergoes a similar thermolysis reaction to afford cross-linked nanofibers.⁷⁴

COPOLYMERIZATION OF NON-CONJUGATED DIENES WITH OLEFINS BY Pd COMPLEXES

Pd–diimine complexes also catalyze the copolymerization of dienes with ethylene or α -olefins (Scheme 6). The diene undergoes quantitative cyclization during the copolymerization reaction to afford polymers with cyclopentane structures. Functionalized cyclopentane rings originating from the diene are located in the main chain of the

copolymer. In contrast, in the copolymerization of ethylene with acrylate by Pd–diimine complexes, the produced polymer adopts a branched structure, and ester groups originating from the acrylate are located at the termini of the branches. Ye reported that copolymers of ethylene and diene adopt a less-branched structure than homopolyethylene produced under similar conditions, owing to the introduction of repeating units from the diene in the copolymer.⁷⁵ Chain-walking reactions across the repeating unit from the diene are suppressed by the presence of *trans*-fused 1,2-cyclopentane rings in the polymer chain.

SYNTHESIS OF TELECHELIC POLYOLEFIN AND FORMATION OF A THERMOREVERSIBLE GEL

Reaction of equimolar amounts of the Pd complex and monomer in the presence of NaBARF and subsequent recrystallization of the products yields **1a–I-a**, a complex containing a five-membered C,O-chelating ring, as revealed by X-ray crystal structure and NMR analysis (Figure 2).

Scheme 4 Monomers that do not undergo smooth cyclopolymerization.

Scheme 6 Copolymerization of ethylene with **1-a** and thermolysis of poly(**1-a-co-ethylene**).

Scheme 5 Stereospecific polymerization of diallylmalonate (**1-a**).

The isolated chelate complex initiates the cyclopolymerization of non-conjugated dienes and the polymerization of α -olefins with quantitative initiation efficiency. The resulting polymer contains the functional group from the chelate complex on the initiating end of the polymer chain. The polymerization of 1-hexene proceeds in living fashion, and another functional groups can be introduced on the terminating end of the polymer by adding functionalized olefin as the terminating reagent.

Figure 2 X-ray crystal structure of **1a-I-a**.

Figure 3 Gelation of telechelic polyhexene (**II**) with triaminopyrimidine in toluene ((i) room temperature and (ii) -20°C).

Thus, polyhexene with barbiturate groups on both termini (**II**) was synthesized by the polymerization of 1-hexene using **1a-I-c** as the initiator and **I-c** and triethylsilane as the terminator (Scheme 7). Barbiturates form triple hydrogen bonds with melamine or 2,4,6-triaminopyrimidine, which have been employed to induce gel formation.^{76,77} For instance, solutions of toluene containing telechelic polymer and melamine or 2,4,6-triaminopyrimidine form thermoreversible gels (Figure 3).

Scheme 8 Isomerization cyclopolymerization of alkyl-substituted 1,6-dienes.

Scheme 7 Synthesis of telechelic polyhexene.

ISOMERIZATION CYCLOPOLYMERIZATION OF MONOALKYL-SUBSTITUTED DIENES BY Pd COMPLEXES

Palladium-diimine complexes promote the polymerization of alkyl-substituted 1,6-dienes to produce polymers with alternating repeating units containing *trans*-1,2-disubstituted cyclopentane rings and oligomethylene spacers (Scheme 8).⁷⁸ The polymers do not show ¹H NMR signals that would arise from the presence of branches. Quantitative cyclopolymerizations of dienes with inner olefins are rare due to their poor reactivity.

Similar to the cyclopolymerization of 1,6-heptadienes, alkyl-substituted 1,6-dienes with various functional groups such as malonate, cyclic imide, tosylamide and cyclic acetal groups also undergo cyclopolymerization. The polymerization of dienes with acetal groups proceeds in a living fashion at -20 °C to produce polymers with narrow molecular weight distributions ($M_w/M_n = 1.20$). The polymerization of 1,6-heptadiene followed by 1,6-octadiene affords the corresponding block copolymer. This material possesses a glass transition temperature of 80 °C, which is in between the glass transition temperature of the homopolymers (90 °C and 72 °C, respectively). Diene monomers with isopropyl or isobutyl groups can also be used, and the resulting polymers possess methyl branches

at regular intervals.⁷⁹ However, the polymerization of dienes with sec-butyl groups displays insufficient cyclization efficiency.

MECHANISM OF CYCLOPOLYMERIZATION

Scheme 9 depicts the proposed mechanism of cyclopolymerization. 2,1-Insertion of the olefinic group of the diene results in the formation of 5-hexenylpalladium intermediates (**A**), which undergo subsequent intramolecular 1,2-insertion of the remaining alkenyl group to form cyclopentylmethylpalladium intermediate **B**. The cyclization occurs in a *trans*-selective manner. Similar *trans*-selective cyclizations of 1,6-diene have also been observed in Pd-catalyzed cyclization hydrosilylation reactions.^{80,81} Intermediate **B** may react with another monomer in a similar manner, resulting in chain growth; however, intermediate **B** also undergoes chain-walking reactions to produce cyclopentylpalladium intermediate **C**.

Although intermediates **B** and **C** are in equilibrium, the equilibrium resides largely toward the formation of **C**. However, dienes and olefins cannot insert into the CH-Pd bond of intermediate **C**, and insertion occurs only after the isomerization of **C** to **B**. In the polymerization of alkyl-substituted 1,6-diene, the new monomer inserts exclusively into the CH₂-Pd bond of intermediate **B'**, which

Scheme 9 Mechanism of cyclopolymerization of (i) 1,6-heptadienes and (ii) alkyl-substituted 1,6-dienes.

results in the formation of polymers with controlled repeating sequences.

DOUBLE CYCLOPOLYMERIZATION OF NON-CONJUGATED TRIENES BY Pd COMPLEXES

In contrast to the cyclopolymerization of non-conjugated dienes, cyclopolymerizations of trienes are rare.⁸² The ordered and quantitative reaction of three C=C double bonds during chain growth is required for the formation of polymers with controlled structures. Recently, we found that Pd–diimine complexes are effective for the polymerization of 1,6,11-dodecatrienes with functional groups such as cyclic acetals and cyclic esters (Scheme 10).⁸³ Double cyclization occurs quantitatively during polymerization. The resulting polymers contain two *trans*-1,2-cyclopentane rings in each repeating unit, and the relative stereochemistry between the two five-membered rings is controlled in the racemic structure.

The polymerization of trienes with acetal groups produces polymers with narrow molecular weight distributions. The polymer obtained using **1a** is rich in racemo-syndiotactic sequences (91%). The acetal group of the polymer can be easily hydrolyzed in the presence of trifluoroacetic acid. In contrast to these monomers, trienes with sulfonamide or fluorenylidene groups do not undergo

polymerization; however, cyclopolymerization reactions of dienes with the same functional groups proceed smoothly.

ISOMERIZATION POLYMERIZATION OF 4-ALKYLCYCLOPENTENE

The polymerization of cyclopentene by zirconocenes or Pd- and Ni-diimine catalysts affords polymers with *cis*-fused 1,3-cyclopentane rings. Reports on the polymerization of substituted cyclopentanes are relatively rare.⁸⁴ We found that Pd-catalyzed polymerization of 4-alkylcyclopentenes is an efficient method for synthesis of polymers with *trans*-fused 1,3-cyclopentane rings (Scheme 11 (I)).⁸⁵ Isomerization occurs during chain growth, and polymers with oligomethylene-1,3-*trans*-cyclopentane repeating units are produced. The length of the oligomethylene spacer is determined by the length of the alkyl group on the monomer.

A plausible mechanism for the polymerization reaction includes face-selective coordination and insertion of the monomer into the Pd-alkyl intermediate to form a cyclopentylpalladium species and selective insertion of a new monomer into the Pd-CH₂ bond of the intermediate that forms after chain walking (Scheme 11 (II)).

Pd complex **1c**, which contains a C₂ symmetric diimine ligand, promotes isospecific polymerization reactions. The highly threo-diisotactic polymer shows liquid crystalline properties, as analyzed by polarizing microscopy and differential scanning calorimetry (DSC), whereas atactic polymers do not show such properties. The temperature of the transition between the liquid crystalline phase and solid phase or isotropic phase can be controlled by the length of the

Scheme 10 Double cyclopolymerization of 1,6,11-trienes and hydrolysis.

Figure 4 Relationship between the length of the oligomethylene spacer in the poly(4-alkylcyclopentene) (*m*) and the phase transition temperature of the polymer (square, from solid phase to mesophase; circle, from mesophase to isotropic phase).

Scheme 11 (i) Polymerization of 4-alkylcyclopentenes by Pd complexes and (ii) the mechanism of polymerization.

Scheme 12 (i) Polymerization of alkenylcyclohexanes by Pd complexes and (ii) the mechanism of polymerization.

oligomethylene spacer of the polymer (Figure 4). Examples of liquid crystalline polyolefins are very limited.^{86,87} The presence of stereo-regular five-membered rings may order the alignment of the polymer chain, which produces a material with liquid crystalline properties.

ISOMERIZATION POLYMERIZATION OF ALKENYLCYCLOHEXANE

Although Pd catalysts are effective for the isomerization polymerization of alkylcyclopentenes, the polymerization of 3-methylcyclohexene does not proceed in the presence of the catalysts. In contrast, alkenylcyclohexanes undergo smooth isomerization polymerization to afford polymers containing *trans*-fused 1,4-cyclohexane rings (Scheme 12 (I)).⁸⁸ The intervals between adjacent cyclohexane rings in the polymer are determined by the length of the oligomethylene spacer between the vinyl and cyclohexyl group of the monomer. The active species in the polymerization reaction is a cyclohexyl Pd complex, which undergoes selective 2,1-insertion of the monomer followed by chain walking of the resulting intermediate. In contrast to the isomerization polymerization of alkyl-substituted dienes and 4-alkylcyclopentene, intermediates containing a Pd-CH₂ bond do not form in the polymerization of alkenylcyclohexane. The insertion of another monomer into an intermediate containing a 4-alkylcyclohexyl-Pd bond occurs selectively to yield a polymer with *trans*-fused 1,4-disubstituted six-membered rings (Scheme 12 (II)).

SUMMARY

We have shown that Pd-catalyzed cyclopolymerizations of dienes and trienes and isomerization polymerizations of alkylcyclopentenes and alkenylcyclohexanes are effective methods for the synthesis of polymers with *trans*-fused cycloalkane groups. In the cyclopolymerization of dienes and trienes, various functional groups such as cyclic esters, acetals and imides can be incorporated into the cyclopentane group of the polymer. Further modification of the functional groups in the polymer is also possible. Through the chain-walking isomerization of growing termini, polymers containing a regular distribution of cyclopentane or cyclohexane groups can be synthesized.

The melting temperature and/or glass transition temperature of polymers with *trans*-fused five-membered rings are comparable to those that of polymers with *cis*-fused rings.^{89,90} In addition, stereo-regular polymers with *trans*-1,3-cyclopentane rings show liquid crystalline properties. Further design of novel monomers will allow the synthesis of polymers with unique cyclic structures.

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