



# Synthesis and thermal properties of poly(oligomethylene-cycloalkylene)s with regulated regio- and stereochemistry

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## Abstract

This article focuses on the synthesis and thermal properties of poly(oligomethylene-cyclopentylene)s and poly(oligomethylene-cyclohexylene)s with regulated regio- and stereochemistry. Pd complexes with diimine ligands promote controlled isomerization polymerization of 4-alkylcyclopentenes to afford polymers with 1,3-*trans*-cyclopentylene groups and oligomethylene spacers alternating along the polymer chain. Pd complexes with a  $C_2$  symmetric structure enable isospecific polymerization of 4-alkylcyclopentenes, and the resultant isotactic polymers show liquid-crystalline properties. Cyclopolymerization of 1,6-heptadiene by bis(imino)pyridine Fe and Co catalysts produces poly(ethylene-1,2-cyclopentylene) with *cis* and *trans*-stereochemistry, respectively. Synthesis of poly(oligomethylene-1,4-cyclohexylene)s with *trans* or *cis* structure can be achieved by Pd-catalyzed isomerization polymerization of alkenylcyclohexanes or methylenecyclohexanes. The polymers with 1,4-*trans*-cyclohexylene show a high melting point that depends on the length of the oligomethylene spacer in the polymer. The thermal properties of the poly(oligomethylene-cyclopentylene)s and poly(oligomethylene-cyclohexylene)s are compared to those of previously reported polymers with different regio- or stereochemistry.

## Introduction

Hydrocarbon polymers with cycloalkane groups have recently attracted increased attention because they often exhibit high thermal stability and optical transparency [1]. The type of linkage and structure of the cycloalkylene groups affect the self-assembly of the polymer chains and the properties of the polymers. Thus, it is highly important to control the regio- and stereoselectivity of the cycloalkylene groups in the synthesis of the polymers. Figure 1 shows the previously reported polymerization for the synthesis of poly(oligomethylene-cyclopentylene)s and poly(oligomethylene-cyclohexylene)s [2–4]. Although there have been several examples of the syntheses of poly(oligomethylene-cyclopentylene)s with 1,2-*cis*, 1,2-*trans*, or 1,3-*cis* structure, selective synthesis of poly

(oligomethylene-1,3-*trans*-cyclopentylene)s has not been reported to date. Examples of the synthesis of polymers bearing cyclohexylene groups with controlled regio- and stereochemistry have also been limited. It has been difficult to obtain the polymers with oligomethylene spacers that are longer than the trimethylene group.

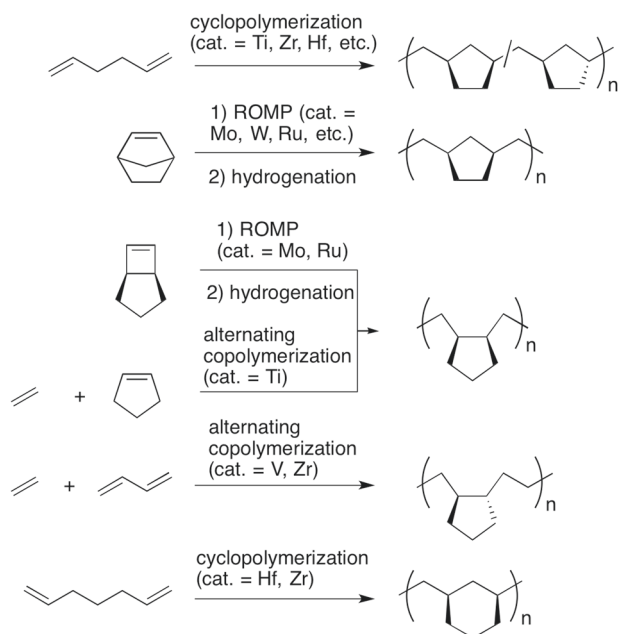
Recently, we reported that late transition metal complexes are effective for cyclopolymerization of 1,6-dienes and isomerization polymerization of cycloolefins and alkenylcycloalkanes to afford poly(oligomethylene-cycloalkylene)s [5–7]. The present article focuses on the synthesis of polyolefins bearing cycloalkylene groups with regulated regio- and stereochemistry, reported by our group as well as others, and on the studies of the thermal properties of these polymers.

## Poly(oligomethylene-cyclopentylene)s

Previously reported methods for the synthesis of poly(oligomethylene-cyclopentylene) include (1) cyclopolymerization of 1,5-hexadiene [8–18], (2) cyclocopolymerization of butadiene with ethylene [19], (3) alternating copolymerization of cyclopentene with ethylene [20, 21], and (4) ring-opening metathesis polymerization (ROMP) of norbornene

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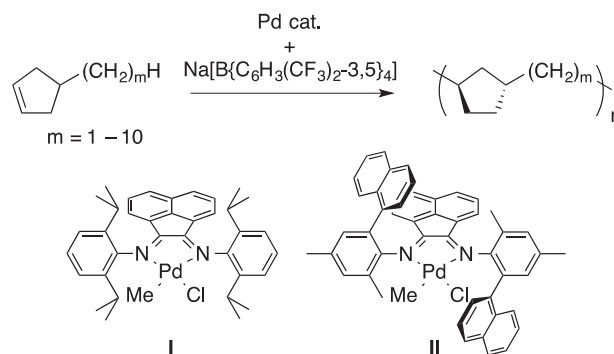
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**Fig. 1** Previous examples of the synthesis of poly(oligomethylene-cyclopentylene)s and poly(oligomethylene-cyclohexylene)s

or bicyclo[3.2.0]hept-6-ene followed by hydrogenation (Fig. 1) [22]. The polymer obtained by ROMP of norbornene has *cis*-fused 1,3-cyclopentylene groups. By contrast, cyclopolymerization of 1,5-hexadiene generally affords the polymer with both *trans*- and *cis*-fused 1,3-cyclopentylene groups, where the *trans/cis* ratio varies from 98/2 to 6/96 depending on the catalyst used. Polymers with 1,2-cyclopentylene groups can be obtained by copolymerization of cyclopentene with ethylene, cyclopolymerization of butadiene with ethylene, and ROMP of bicyclo[3.2.0]hept-6-ene followed by hydrogenation. The 1,2-cyclopentylene groups of the butadiene/ethylene copolymer are predominantly controlled to be in the *trans* configuration. By contrast, the polymer obtained by ROMP of bicyclo[3.2.0]hept-6-ene and subsequent hydrogenation has *cis*-1,2-cyclopentylene groups only. Although 1st generation Grubbs catalyst affords an atactic polymer, the polymer obtained by the chiral Schrock catalyst shows isotactic stereoregularity. Alternating copolymerization of cyclopentene with ethylene also selectively affords a polymer containing *cis*-1,2-cyclopentylene groups only.

Recently, we found that diimine-Pd complexes in combination with  $\text{Na}[\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2-3,5\}_4]$  (NaBARF) are effective for the isomerization polymerization of 4-alkylcyclopentenes (Fig. 2) [23]. The polymerization proceeds via face-selective coordination/addition of the Pd center to the C=C group of the monomer followed by the isomerization of the growing chain end via a chain-walking reaction of the Pd center to the terminal of the alkyl group. Selective insertion of the new monomer into the Pd-CH<sub>2</sub>R



**Fig. 2** Isomerization polymerization of 4-alkylcyclopentenes by Pd catalysts

bond rather than into Pd-CHRR' or Pd-CRR'R'' bonds leads to the formation of the polymer containing *trans*-1,3-cyclopentylene units and oligomethylene spacers alternating along the polymer chain. The polymer obtained by the Pd complex **I** with pseudo-*C*<sub>2v</sub> symmetric structure is atactic and is soluble in chloroform and tetrahydrofuran (THF). By contrast, the polymerization by the pseudo-*C*<sub>2</sub> symmetric Pd complex (**II**) proceeded much faster than that by **I** and afforded the polymer with a highly *trans*-isotactic structure. The isotactic polymer is poorly soluble in common organic solvents at room temperature.

The use of diimine-Pd catalysts leads to the cyclopolymerization of 1,6-dienes with the substituents on the 4-position to afford the polymer with *trans*-1,2-cyclopentylene groups [24–28]. However, the cyclopolymerization of 1,6-heptadiene without substituents does not proceed by the Pd catalyst because the chain-walking of the Pd center on the 1,6-heptadiene will result in an inactive  $\pi$ -allyl Pd species. In contrast, bis(imino)pyridine Fe and Co complexes smoothly promote the cyclopolymerization of 1,6-heptadiene in the presence of modified methylaluminoxane (MMAO) to afford polymers with 1,2-cyclopentylene groups (Fig. 3) [29, 30]. Cyclization of the monomer occurs quantitatively during the polymerization, and the repeating units with six-membered rings are not included in the produced polymer. The cyclopentylene group of the polymer obtained by the Fe catalyst **III** is controlled in *cis* configuration predominantly (*cis:trans* = 95:5), and the microstructure of the polymer is mostly atactic. By contrast, the Co catalyst **IV** affords the polymer with *trans*-cyclopentylene group exclusively (*trans* > 99%). The microstructure of the polymer is moderately controlled, but its exact tacticity has not been determined.

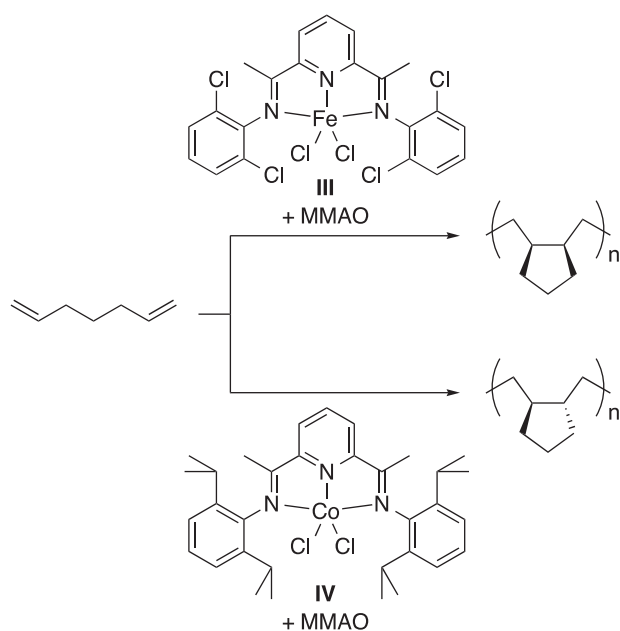
Table 1 shows the summary of the phase-transition temperatures of the poly(oligomethylene-cyclopentylene)s with various regio- and stereochemistries. The polymers with 1,2-*cis*-cyclopentylene groups show high melting points (130 and 182 °C, respectively, for atactic and isotactic polymers (*n* = 2)) [22, 30]. The crystal structure of

isotactic poly(ethylene-1,2-*cis*-cyclopentylene) has been reported [31, 32]. On the basis of X-ray diffraction, geometrical and conformational analyses of a single chain and packing energy calculations, it was revealed that the polymer chains are packed in an orthorhombic unit cell. A high degree of conformational disorder is present in the crystalline state due to the conformational freedom of the cyclopentylene groups. Poly(ethylene-1,2-*trans*-cyclopentylene) does not show a melting temperature in the range between  $-100$  and  $250$  °C but shows a glass transition temperature at  $3.2$  °C [30]. Poly(trimethylene-1,2-*trans*-cyclopentylene) with isotactic structure shows glass transition and melting

temperatures at  $16.3$  and  $182.5$  °C, respectively [19]. The crystal structure of the polymer with the 1,2-*trans*-cyclopentylene unit is unknown.

The polymers bearing the 1,3-*cis*-cyclopentylene groups also show high melting points of  $171$  and  $134$  °C, respectively, for the polymers with methylene and ethylene linkage between the cyclopentylene units [1, 33]. The atactic polymers with the 1,3-*trans*-cyclopentylene unit showed a phase transition due to the glass transition and/or melting in DSC measurements [33]. By contrast, two phase transitions were observed in the DSC measurements of the isotactic polymers [23]. Polymers with shorter oligomethylene spacers ( $n = 1$  and  $3$ ) showed monotropic transitions, while those with longer oligomethylene spacers undergo enantiotropic transitions. Isotactic poly(oligomethylene-1,3-*trans*-cyclopentylene)s are liquid-crystalline in the range between these two phase-transition temperatures as observed by polarizing microscopy. The phase-transition temperature between the liquid-crystalline phase and the solid phase or isotropic phase can be varied by changing the length of the oligomethylene spacer of the polymer.

Thermal and crystal structure characterizations of poly(ethylene-1,2-cyclopentylene)s with *trans*- and *cis*-structures and with different tacticity have been reported [33, 34]. Regardless of the stereochemistry, the polymers adopt similar disordered crystalline structures, and the polymer chains were found to be packed in a hexagonal arrangement. The polymers with high *cis* structure show higher melting points, which is in line with the shorter distance between the polymer chains for the polymer with a higher *cis* content. The crystallinity of the polymer increases as the stereoregularity of the polymers becomes higher. It has been reported that low molecular weight polymers with 1,3-cyclopentylene groups with predominantly *trans*-stereochemistry, synthesized by the cyclopolymerization of



**Fig. 3** Cyclopolymerization of 1,6-heptadiene by Fe and Co catalysts

**Table 1** Phase-transition temperatures of poly(oligomethylene-cyclopentylene)s ( $\{-\text{CH}_2\}_n\text{-C}_5\text{H}_8\text{-}\}_m$ )

	<i>Cis</i>	<i>Trans</i>
1,2-	$0.4$ °C ( $T_g$ ), $130$ °C ( $T_m$ ) ( $n = 2$ , atactic) [30] $17$ °C ( $T_g$ ), $182$ °C ( $T_m$ ) ( $n = 2$ , isotactic) [22]	$3.2$ °C ( $T_g$ ) ( $n = 2$ ) [30] $16.3$ °C ( $T_g$ ), $182.5$ °C ( $T_m$ ) ( $n = 3$ , isotactic) [19]
1,3-	$45$ °C ( $T_g$ ), $171$ °C ( $T_m$ ) ( <i>cis</i> = 86%, $n = 1$ , atactic) [33] $134$ °C ( $T_m$ ) ( $n = 2$ ) [1]	$25$ °C ( $T_g$ ), $86$ °C ( $T_m$ ) ( <i>trans</i> = 81%, $n = 1$ , atactic) [33] $4$ – $21$ °C ( $T_g$ ) ( $n = 1$ , atactic) [23] $93$ , $114$ °C ( $n = 1$ , isotactic) [23] $77$ °C ( $T_m$ ) ( $n = 2$ , atactic) [23] $86$ , $100$ °C ( $n = 2$ , isotactic) [23] $74$ °C ( $T_m$ ) ( $n = 3$ , atactic) [23] $70$ , $92$ °C ( $n = 3$ , isotactic) [23] $81$ °C ( $T_m$ ) ( $n = 4$ , atactic) [23] $43$ , $84$ °C ( $n = 4$ , isotactic) [23] $81$ °C ( $T_g$ ) ( $n = 6$ , atactic) [23] $54$ , $78$ °C ( $n = 6$ , isotactic) [23] $86$ °C ( $T_m$ ) ( $n = 10$ , atactic) [23] $43$ , $84$ °C ( $n = 10$ , isotactic) [23]

“ $n$ ” is the number of methylene units in a repeating unit

1,5-hexadiene by  $C_2$ -symmetric zirconocene catalyst, are also liquid crystalline [35, 36]. As the polymer of 4-alkylcyclopentene with atactic structure is not liquid crystalline, the isotactic structure would be important for the ordered alignment of the polymer chain necessary for the liquid-crystalline properties. The polymer obtained by the cyclopolymerization of 1,5-hexadiene using a racemic  $C_2$ -symmetric zirconocene catalyst shows Schlieren-like texture, indicating a nematic liquid crystal [35]. On the other hand, a fingerprint texture of the polymer produced by the optically active catalyst indicates a cholesteric liquid crystal [36]. The detailed phase structure of the isotactic poly(oligomethylene-cyclopentylene)s is currently not clear.

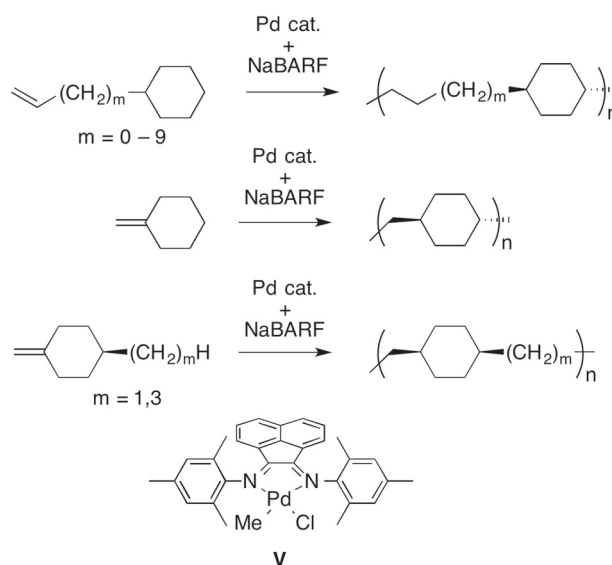
### Poly(oligomethylene-cyclohexylene)s

Synthesis of poly(oligomethylene-1,3-cyclohexylene)s has been achieved by zirconocene-catalyzed cyclopolymerization of 1,6-heptadiene, where the *trans/cis* selectivity of the cyclohexylene group could not be controlled [9]. By contrast, some Hf and Zr catalysts enable *cis*-specific polymerization of the 1,6-heptadiene polymer (Fig. 1) [37–39]. Polyolefins with 1,2-cyclohexylene groups can also be synthesized by copolymerization of ethylene with cyclohexene by half-titanocene catalysts, where the incorporation of the cyclohexene unit reaches up to 16.2 mol% [40]. Cationic polymerization of  $\beta$ -pinene followed by hydrogenation affords the poly(isobutylene-1,4-cyclohexylene) [41]. ROMP of bicyclo[2.2.2]oct-2-ene [42] or bicyclo[4.2.0]octa-7-ene [43] produces the unsaturated hydrocarbon polymer bearing six-membered rings, but the subsequent hydrogenation has not been performed.

Attempted synthesis of polymer with the 1,2-cyclohexylene group by cyclopolymerization of 1,7-octadiene by the bis(imino)pyridine Co catalyst **IV**/MMAO results in no reaction. The reaction of 1,7-octadiene by the bis(imino)pyridine Fe catalyst **III**/MMAO produced oily product (up to 73% yield). Its  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows the absence of vinyl carbon signals and the presence of many unassigned signals, including olefinic signals ( $\delta$  124–131). Thus, the structure of the product has not been confirmed, and its molecular weight is low. Synthesis of the polymer with the six-membered ring was also attempted by the isomerization polymerization of 3-methylcyclohexene by diimine-Pd catalysts. The reaction by using catalyst **2**/NaBARF attained quantitative conversion of 3-methylcyclohexene.  $^{13}\text{C}\{^1\text{H}\}$  NMR analysis of the product showed the signals due to olefinic carbons at  $\delta$  121, 126, and 131–133. The relative intensity of the olefin signals and those due to an aliphatic region indicate that the product is 7-8 mer.

In contrast to the above attempts, synthesis of poly(oligomethylene-*trans*-1,4-cyclohexylene)s can be achieved by the isomerization polymerization of alkenylcyclohexanes by diimine-Pd catalysts **V**/NaBARF (Fig. 4) [44]. The polymerization mechanism involves 2,1-insertion of the monomer to the cyclohexyl-Pd active 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. Diimine-Pd catalysts are also effective for the isomerization polymerization of methylenecyclohexane to give poly(methylene-1,4-*trans*-cyclohexylene) [45]. Note that coordination polymerization of methylenecyclohexane has been difficult due to the bulky structure of the monomer. 4-Alkyl-1-methylenecyclohexanes undergo isomerization polymerization by the Pd catalyst to afford the polymers bearing the 1,4-*cis*-cyclohexylene group and oligomethylene spacer.

Table 2 summarizes the thermal properties of the poly(oligomethylene-cyclohexylene)s with various regio- and stereochemistries. It has been reported that DSC analysis of isotactic poly(1,3-*cis*-cyclohexylene-methylene) by a heat/cool/heat cycle at the rate of 10 °C/min showed  $T_g$  and  $T_m$  at 103.9 and 179.0 °C, respectively, in the first scan but only  $T_g$  in the second scan [37]. This result was ascribed to the slow crystallization kinetics of the polymer in an amorphous glassy state due to its high  $T_g$  value. Actually, DSC analysis at the rate of 1 °C/min showed  $T_g$  and  $T_m$  at 92.2 and 208.5 °C in the fourth scan [38]. Poly(oligomethylene-1,4-cyclohexylene)s (either *trans* or *cis* structure) with  $n < 3$  did not show a transition or melting temperature in the 30–300 °C range. Poly(1,4-*trans*-cyclohexylene-oligomethylene)s with



**Fig. 4** Isomerization polymerization of alkenylcyclohexanes and methylenecyclohexanes by Pd catalyst

**Table 2** Phase-transition temperatures of poly(oligomethylene-cyclohexylene)s ( $\{-(\text{CH}_2)_n-\text{C}_6\text{H}_{10}-\}_m$ )

	<i>Cis</i>	<i>Trans</i>
1,2-	No example	No example
1,3-	92.2 °C ( $T_g$ ), 208.5 °C ( $T_m$ ) ( $n = 1$ , isotactic) [38]	No example
1,4-	162 °C ( $T_g$ ) ( $n = 4$ ) [45]	226 °C ( $T_m$ ) ( $n = 3$ ) [44] 195 °C ( $T_m$ ) ( $n = 4$ ) [44] 169 °C ( $T_m$ ) ( $n = 5$ ) [44] 130 °C ( $T_m$ ) ( $n = 11$ ) [44]

“ $n$ ” is the number of methylene units in a repeating unit

$n \geq 3$  show high melting points ranging from 226 to 130 °C, depending on the length of the oligomethylene spacer in the repeating unit [44]. In particular, the melting point of poly(trimethylene-1,4-*trans*-cyclohexylene) (226 °C) is the highest among those of the previously reported poly(oligomethylene-cycloalkylene)s. By contrast, poly(tetramethylene-1,4-*cis*-cyclohexylene)s shows only a glass transition temperature at 162 °C [45]. These results may be due to the high crystallinity of the polymer with the 1,4-*trans*-cyclohexylene group compared to that with the 1,4-*cis*-cyclohexylene structure.

## Summary

Fe- and Co-catalyzed cyclopolymerization of 1,6-heptadiene and Pd-catalyzed isomerization polymerization of 4-alkylcyclopentenes and alkenylcyclohexanes enable the synthesis of poly(oligomethylene-cycloalkylene)s with controlled regio- and stereochemistry. Some of the polymers are unprecedented, and the liquid-crystalline properties of the polymers with 1,3-*trans*-cyclopentylene group and the very high thermal stability of the polymers with the 1,4-*trans*-cyclopentylene group were revealed. Controlled synthesis of the polymers with 1,2- or 1,3-*trans*-cyclohexylene groups and the thermal properties of such polymers are still unknown. Further development of the synthetic method for poly(oligomethylene-cycloalkylene)s will enable a deeper understanding of the effect of cycloalkylene units on the self-assembly of the polymer chain and the thermal properties of the polymer.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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