

Precise Isomerization Polymerization of Alkenylcyclohexanes: Stereoregular Polymers Containing Six-Membered Rings along the Polymer Chain

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S Supporting Information

ABSTRACT: Pd and Ni diimine complexes catalyze the isomerization polymerization of alkenylcyclohexanes to afford polymers composed of alternating *trans*-cyclohexane-1,4-diyl rings and oligomethylene spacers with high selectivity. The melting points of the polymers vary from 130 to 226 °C depending on length of the oligomethylene spacer.

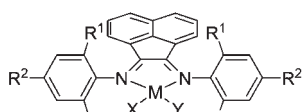
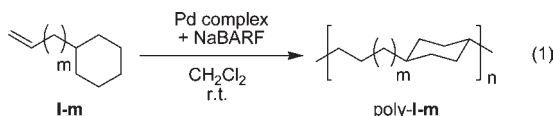
Hydrocarbon polymers whose main chain contains three- to six-membered rings¹ have advantages due to their higher melting or glass-transition temperatures² and optical transparency in comparison with common polyolefins. Coordination polymerization of cyclopentene and norbornene provides the major route to polymers having cyclic repeating units.^{1,3} However, such polymerization is mostly limited to that of monomers with five-membered rings. Six-membered cyclic monomers, such as cyclohexene, are much less reactive than five-membered-ring monomers. We recently found that the polymerization of 4-alkylcyclopentenes via chain-walking reactions catalyzed by Pd diimine complexes yields products composed of *trans*-1,3-cyclopentane rings and oligomethylene spacers and that this process involves selective insertion of the monomer into the CH₂–Pd bond of the growing polymer end rather than the CH–Pd bond.⁴ Further studies revealed that alkenylcyclohexenes do not undergo similar polymerization because of the poor reactivity of their six-membered cyclic olefins. The isomerization of alkenes with a cycloalkyl substituent may also yield polymers with cyclic groups in the chain. Such reactions, however, have not been reported to date. For example, the coordination polymerization of vinylcyclohexane usually produces a polymer with cyclohexyl substituents bonded to the main chain.^{5,6} Here we report that Pd and Ni complexes catalyze the isomerization polymerization of alkenylcyclohexanes to afford polymers with an unexpected

structure. The mechanism and stereoselectivity of the reaction are also discussed.

The Pd and Ni complexes **1–3** catalyze the polymerization of olefins having cyclohexyl groups (**I-*m***; *m* = 0–3, 9) in the presence of NaBARF (BARF = B{C₆H₃(CF₃)_{2-3,5}}₄[−]) or modified methylaluminoxane (MMAO) to produce polymers formulated as $-\text{[CH}_2\text{CH}_2(\text{CH}_2)_m\text{C}_6\text{H}_{10}]_n-$ (poly-**I-*m***), as shown in eq 1.

The results of the polymerization are summarized in Table 1. The polymer of vinylcyclohexane, $-\text{[CH}_2\text{CH}_2\text{C}_6\text{H}_{10}]_n-$ (poly-**I-0**), obtained from the reaction with a monomer-to-catalyst molar ratio of 300:1 (run 1) was practically insoluble in organic solvents and could not be characterized by NMR or gel-permeation chromatography (GPC) measurements. Poly-**I-0** obtained using $[\text{I-0}]/[\text{I}] = 10:1$ was slightly soluble in C₂D₂Cl₄ at 130 °C, probably because of its lower molecular weight in comparison with that from the 300:1 reaction. The ¹³C{¹H} NMR spectrum of the fraction soluble in C₂D₂Cl₄ exhibited three sharp signals at δ 38.6, 35.0, and 33.8 (Figure 1i). The peak positions as well as their comparison with polymers of olefins with longer alkyl groups indicate the structure proposed in Figure 1i. Minor signals may be assigned to repeating units having other structures and/or the terminal groups of the polymer. The polymer of **I-1** was obtained from a reaction in which $[\text{I-1}]/[\text{I}] = 300:1$ (run 3). GPC measurements at 152 °C (soluble fraction) showed M_n to be 18 000. Catalysts **2** and **3** also polymerized **I-1** to form the corresponding polymer (runs 4 and 5). Poly-**I-1** obtained from a reaction in which $[\text{I-1}]/[\text{I}] = 10:1$ had sufficient solubility to enable ¹³C{¹H} NMR measurements. The ¹³C{¹H} NMR spectrum in C₂D₂Cl₄ at 130 °C showed four sharp signals almost exclusively (Figure 1ii). Signals of the CH and CH₂ carbons in the six-membered ring (δ 38.1 and 33.8) were at positions similar to those for the ethylene–butadiene copolymer having *trans*-cyclohexane-1,4-diyl groups (δ 38.45 and 33.94).⁷ Thus, the six-membered rings in poly-**I-1** as well as in poly-**I-0** have *trans*-1,4-disubstituted structures with high selectivity. The chemical shifts of the CH₂ carbon signals in the trimethylene spacer of poly-**I-1** (δ 38.3 and 24.4) were in good agreement with those of the model compound 1,3-dicyclohexylpropane (δ 38 and 25).⁸

Table 1 shows a summary of the results of the polymerization of alkenylcyclohexanes having longer oligomethylene spacers, namely, **I-2**, **I-3**, and **I-9**. The polymerizations of **I-2** and **I-3** proceeded smoothly to give polymers with molecular weights (M_n) of 9500 and 11 000, respectively (runs 6 and 7). The polymerization of **I-9** also produced the corresponding polymer



Pd complex

- 1: R¹ = ^{*i*}Pr, R² = H, M = Pd, X = Me, Y = Cl
- 2: R¹ = R² = Me, M = Pd, X = Me, Y = Cl
- 3: R¹ = Et, R² = H, M = Ni, X = Y = Br

Received: May 13, 2011

Published: June 27, 2011

Table 1. Polymerization of Alkenylcycloalkanes^a

run	monomer ([monomer]/[cat.])	cat.	yield (%)	M_n^b	M_w/M_n^b
1 ^c	I-0 (300)	1	64	— ^d	— ^d
2 ^c	I-0 (300)	2	quant	— ^d	— ^d
3	I-1 (300)	1	86	18000	2.48
4	I-1 (300)	2	97	21000	1.79
5 ^e	I-1 (100)	3	quant	14000	1.71
6 ^f	I-2 (100)	1	80	9500	1.71
7 ^f	I-3 (100)	1	80	11000	1.86
8 ^f	I-9 (100)	1	75	11000	2.65
9 ^f	II-0 (100)	1	trace		
10 ^f	II-1 (100)	1	trace		

^a Reaction conditions: cat. (0.010 mmol), cocat. = NaBARF (0.012 mmol), solvent = CH₂Cl₂ (1.5 mL), at rt for 20 min, unless otherwise noted. ^b Determined by GPC detected by FTIR based on a polyethylene standard using *o*-dichlorobenzene as the eluent at 152 °C. ^c Reaction time = 1 h. ^d Not available because of the low solubility of the polymer. ^e Reaction conditions: cat. (0.010 mmol), cocat. = MMAO ([Al]/[3] = 300), solvent = toluene (2 mL) at rt for 24 h. ^f Solvent = CH₂Cl₂ (0.5 mL).

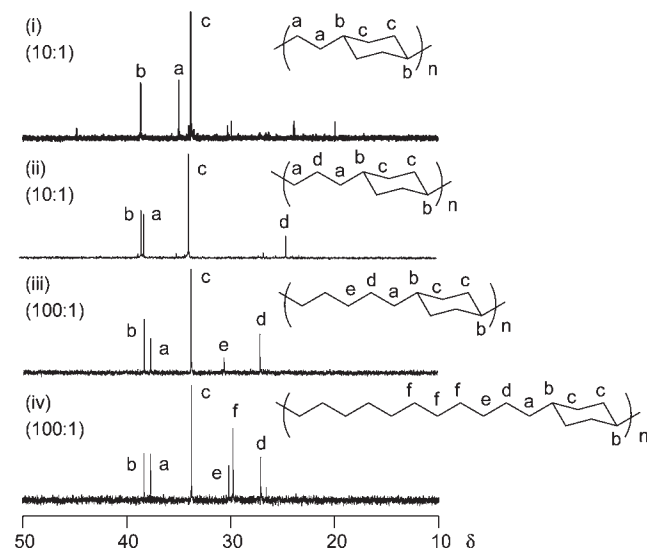


Figure 1. ¹³C{¹H} NMR spectra (C₂D₂Cl₄, 130 °C) of (i) poly-I-0, (ii) poly-I-1, (iii) poly-I-3, and (iv) poly-I-9. Ratios in parentheses correspond to the initial monomer-to-catalyst molar ratio in the polymerization reaction.

in 75% yield in 20 min (run 8). The ¹³C{¹H} NMR spectra of poly-I-3 and poly-I-9 (Figure 1iii,iv) exhibited signals due to *trans* six-membered-ring carbons and CH₂ carbons attached to the ring at positions similar to those for poly-I-1. All of these results indicate a structure composed of *trans*-1,4-disubstituted six-membered rings and oligomethylene spacers, regardless of the length of the spacer. Differential scanning calorimetry (DSC) measurements on poly-I-1–3 and poly-I-9 showed melting transitions (Figure 2), but poly-I-0 did not show a melting point in the range 30–300 °C. Increasing the number of carbons in the alkyl group of the monomer lowered the melting point of the polymer.

The polymerizations of I-0, I-1, and I-3 catalyzed by 1/NaBARF obeyed zeroth-order kinetics with respect to the monomer concentration. The kinetic constants were found to be 6.9×10^{-6} , 4.0×10^{-5} , and $2.9 \times 10^{-5} \text{ M s}^{-1}$, respectively, at 0 °C. The results suggest

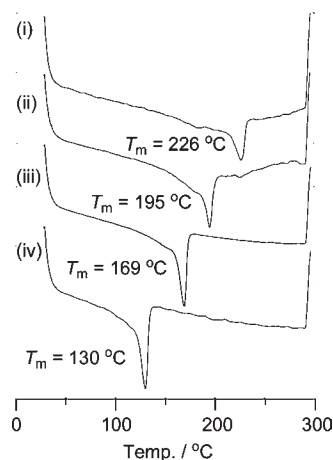


Figure 2. DSC profiles of (i) poly-I-1, (ii) poly-I-2, (iii) poly-I-3, and (iv) poly-I-9.

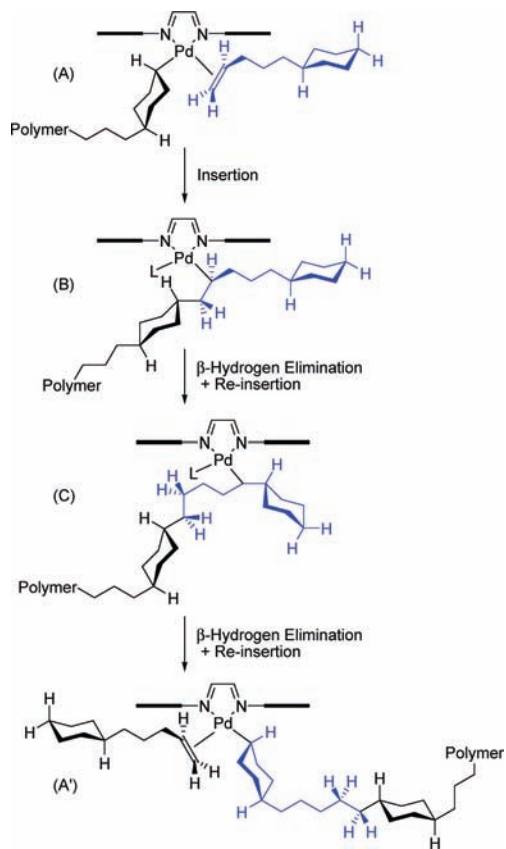
that the rate-determining step of the polymerization is not coordination/insertion of the monomer but isomerization of the growing polymer end by chain walking. Chain-walking reactions in olefin polymerization using Pd catalysts have been proposed to be much faster than insertion.⁹ Kinetic results independent of the monomer concentration are rare in coordination polymerization using Pd catalysts.^{10,11}

Analogous isomerization polymerizations of monomers with five-membered rings, such as vinylcyclopentane (II-0) and allylcyclopentane (II-1), yielded only trace amounts of uncharacterized polymers (runs 9 and 10), although they were expected to give polymers via the reactions of 4-ethyl- and 4-propylcyclopentenes catalyzed by Pd complexes.⁴ In contrast, 3-methylcyclohexene did not polymerize in the presence of the Pd catalysts. The Pd-catalyzed polymerization of 4-alkylcyclopentenes afforded polymers composed of alternating *trans*-cyclopentane-1,3-diyl groups and oligomethylene spacers, whereas polymers containing *trans*-cyclohexane-1,4-diyl groups and oligomethylene spacers were obtained from alkenylcyclohexane rather than alkylcyclohexene.

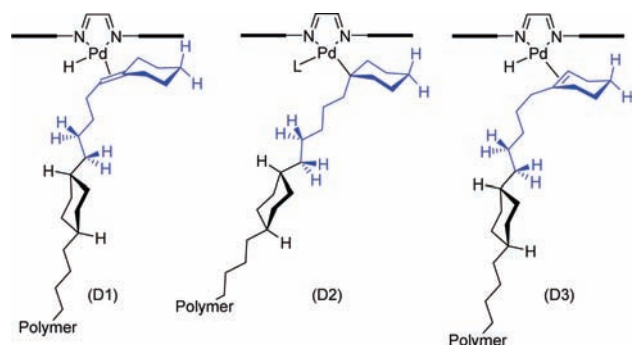
Olefin polymerization catalyzed by Ni and Pd complexes involves the isomerization of the growing polymer end, as proposed by Brookhart and co-workers.¹² The details have been investigated by their research group as well as others.¹³ We reported the polymerization of dienes, trienes, and cycloolefins using a Pd catalyst, in which the preferential insertion of the monomer into the CH₂–Pd bond rather than the CH–Pd bonds enables apparent selective chain walking.^{4,14} The polymerization in this study also involves the selective insertion of vinyl groups of monomers into a CH–Pd bond of the six-membered ring because the polymers are composed of 1,4-disubstituted six-membered rings and oligomethylene spacers.

Scheme 1 shows the polymer growth mechanism proposed for I-3. The polymerizations of the other monomers also proceed via the same mechanism. The 4-alkylcyclohexylpalladium intermediate (A) undergoes selective 2,1-insertion of the vinyl group of the monomer into the CH–Pd bond. The 1,2-insertion does not take place, probably because of the steric repulsion between the cyclohexyl group attached to Pd and the monomer substituent. Intermediate B does not undergo direct insertion of a new monomer¹⁰ but instead undergoes a chain-walking reaction via β -hydrogen elimination and reinsertion of the olefin-terminated polymer, giving the new intermediate C and then intermediate

Scheme 1. Plausible Mechanism of Polymerization of I-3



Scheme 2. Possible Intermediates Formed in Going from C to A' in Scheme 1



A'. Because chain walking within the cyclic group takes place on the same side of the ring as a result of the stereochemical requirement of β -hydrogen elimination,¹⁵ the six-membered ring attached to Pd in A and A' should have the trans configuration.

β -Hydrogen elimination from C and further reaction to yield A' should proceed via the less-stable intermediates D1–D3 shown in Scheme 2. The tertiary alkyl–Pd bond of D2 and the trisubstituted olefin π -bonded to Pd in D1 and D2 destabilize these intermediates sterically. These unstable intermediates probably cause the isomerization from C to A' to be the rate-determining step of the total reaction in Scheme 1; this possibility enables the zeroth-order-kinetics results to be rationalized.¹⁶

In this work, we have presented isomerization polymerization occurring with high selectivity during the insertion of the monomer. The 2,1-insertion of the monomer takes place selectively, in contrast to the polymerization of α -olefins using the same catalyst. Here the monomer inserts into a CH–Pd bond at the 4-position of the cyclohexyl group rather than into the other CH–Pd bonds of the growing polymer chain. This mechanism is in contrast to those for the isomerization polymerizations reported to date, which show either apparent selectivity for insertion of the monomer into the CH₂–Pd bond instead of the CH–Pd bond or no such selectivity. The steric requirements of β -hydrogen elimination during the polymerization result in a single stereoisomeric polymer containing *trans*-cyclohexane-1,4-diyl groups.¹⁷ This selective isomerization polymerization has been developed for the copolymerization of alkenylcyclohexanes as well as the copolymerization of these monomers with ethylene and α -olefins, the results of which will be presented in the future.

ASSOCIATED CONTENT

S Supporting Information. Experimental procedures and NMR spectra of polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

The author is grateful to Prof. Kohtaro Osakada of Tokyo Institute of Technology for helpful discussions and suggestions. This work was supported by a Grant-in-Aid for Young Scientist (22685012) for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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(10) We conducted a kinetic study of the cyclopolymerization of 1,6-dienes catalyzed by Pd complexes and observed apparent zeroth-order kinetics of the reaction only at a high monomer concentration (1.0 M). The kinetics in this study was measured at a monomer concentration much lower than that required for pseudo-zeroth-order conditions. See: Park, S.; Okada, T.; Takeuchi, D.; Osakada, K. *Chem.—Eur. J.* **2010**, *16*, 8662.

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(16) Alkenylcyclopentanes do not polymerize smoothly under the same conditions. This can be ascribed to the low stability of the intermediate with cyclopentyl or cyclopentene as the ligand (corresponding to **D2** and **D3** in Scheme 2). Further studies of the reaction pathway and intermediates are needed to clarify this issue.

(17) Polymers with 1,4-disubstituted cyclohexanediyl groups in the polymer chain were prepared by stepwise reactions involving anionic

polymerization of cyclohexadiene and subsequent hydrogenation of the resulting polymer or cationic polymerization of β -pinene followed by hydrogenation. The former polymer has *cis*-cyclohexane-1,4-diyl groups, and the stereoselectivity of the latter is unclear. See ref 2 and: Satoh, K.; Sugiyama, H.; Kamigaito, M. *Green Chem.* **2006**, *8*, 878. Polymers containing *trans*-cyclohexane-1,4-diyl groups in part were prepared by copolymerization of ethylene with 1,3-butadiene. See ref 7.