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Isomerization Polymerization of 4-Alkylcyclopentenes Catalyzed by Pd Complexes: Hydrocarbon Polymers with Isotactic-Type Stereochemistry and Liquid-Crystalline Properties

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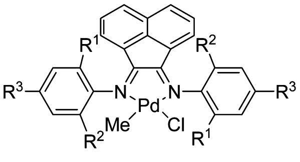
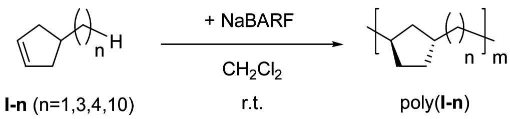
The physical properties of poly(α-olefins) vary to a large degree depending on the alkyl substituents derived from the monomer and the relative stereochemistry of the neighboring repeating units (tacticity). Polymers with five- or six-membered rings in the monomer units have unique thermal and optical properties.[1] Early transition-metal complex-catalyzed polymerization of cyclic olefins and cyclopolymerization of dienes provide these polymers efficiently, although polymerization with regulated tacticity is rare.[2] Ni− or Pd−diimine complexes[3] catalyze the polymerization of α-olefins and cyclopolymerization of dienes with isotactic selectivity[4] when a C_2-symmetric ligand is employed. The polymerization reactions, including cyclopolymerization of monoterminal dienes,[5] involve isomerization of the growing polymer end via a chain-walking process. In this paper, we report polymerization of 4-alkylcyclopentenes catalyzed by Pd complexes to afford polymers with 1,3-disubstituted five-membered rings formed via olefin insertion and chain walking.[6,7] The polymer with regulated tacticity exhibited liquid-crystalline properties.[8]

Pd−diimine complexes **1a** and **1b**, with C_{2V}- and C_2-symmetric ligands,[5] respectively, promote the polymerization of 4-methylcyclopentene (**I-1**) in the presence of NaBARF (BARF = $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$) to produce poly(**I-1**) (eq 1):



1a: $R^1 = R^2 = {}^iPr$, R^3= H
1b: $R^1 = 1\text{-}C_{10}H_7$, $R^2 = R^3$ = Me



(1)

The $^{13}C\{^1H\}$ NMR spectrum of poly(**I-1**) obtained using **1a**/NaBARF [Figure 1(i)] exhibits three peaks (39.32, 39.26, and 39.22 ppm)[9] for the CH_2 (b_1) carbon between two CH carbons, which corresponds to the triad structures with respect to the orientation of three neighboring five-membered rings. The ratio among the peaks (31:47:22) suggests a random or atactic-type arrangement of the five-membered rings. Poly(**I-1**) obtained using **1b**/NaBARF, on the other hand, gives rise primarily to the signal at the lowest field position (39.32 ppm) [Figure 1(ii)]. It is assigned to three monomer units with the same stereochemistry, an *rr* triad, indicating a highly threo-diisotactic structure of the polymer (*rr* > 93%).

The different tacticities of poly(**I-1**) formed by different catalysts affected the crystallographic results. XRD measurements (Cu Kα)[10] on the polymer obtained using **1a**/NaBARF showed an intense diffraction peak at $2\theta = 17.92°$ and a halo pattern, indicating the coexistence of the crystalline and amorphous domains. The isotactic polymer obtained using **1b**/NaBARF exhibited only a single sharp diffraction peak at $2\theta = 18.42°$ and thus contained the crystalline domain almost exclusively at room temperature.

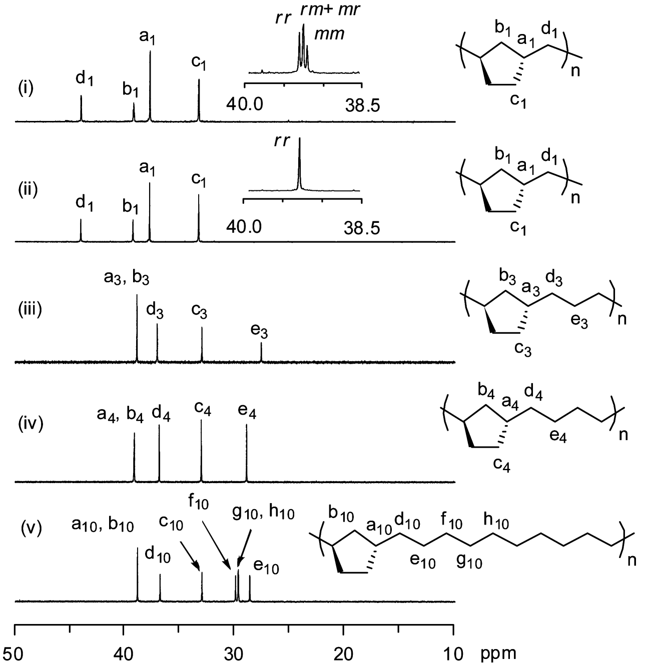


Figure 1. $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$ at 50 °C) of (i) poly(**I-1**) (run 1 in Table 1), (ii) poly(**I-1**) (run 2), (iii) poly(**I-3**) (run 3), (iv) poly(**I-4**) (run 4), and (v) poly(**I-10**) (run 5).

Table 1. Polymerization of 4-Alkylcyclopentenes[a]

run	olefin	Pd	time	conv. (%)	M_n	M_w/M_n
1	**I-1**	**1a**	3 h	quant.	10100[b,c]	1.90[b,c]
2	**I-1**	**1b**	5 min	quant.	8200[c,d]	–
3	**I-3**	**1b**	1 h	quant.	3000[e]	2.18[e]
4	**I-4**	**1b**	1.5 h	66	3000[e]	3.38[e]
5	**I-10**	**1b**	36 h	56	5700[e]	2.38[e]

[a] Reaction conditions: Pd complex (0.010 mmol), NaBARF (0.012 mmol), [monomer]/[Pd] = 300, CH_2Cl_2 solvent, r.t. [b] GPC ($CHCl_3$). [c] GPC (*o*-dichlorobenzene) measurements on poly(**I-1**) (runs 1 and 2) were not conducted because of low solubility. [d] Estimated by ^1H NMR. [e] GPC (*o*-dichlorobenzene).

Scheme 1 summarizes a plausible mechanism for the polymerization of **I-1**. Coordination and insertion of the monomer produce a cyclopentylpalladium intermediate (**A**). It does not undergo direct insertion of the monomer into the Pd−secondary alkyl bond but causes isomerization via chain walking to produce the cyclopen-

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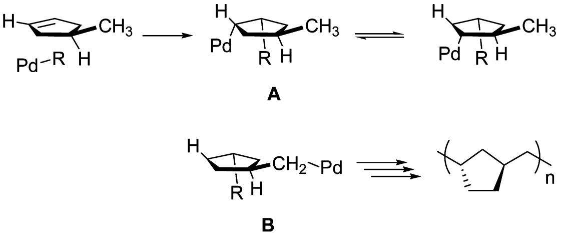
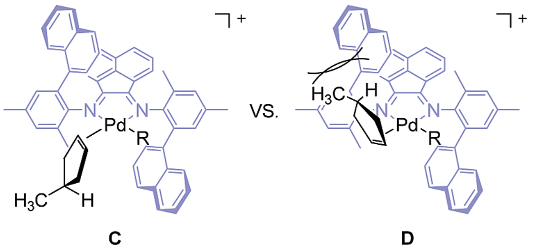
tylmethyl palladium species (**B**).[3] Insertion of a new monomer into the Pd−primary alkyl bond leads to further polymer growth. Formation of a trans five-membered ring in the polymer is explained by assuming preferential coordination of the monomer to Pd at the less-hindered side followed by smooth insertion and chain walking.

Scheme 1. Proposed Mechanism for the Polymerization of **I-1**



Scheme 2 depicts a possible coordination mode of the monomer to the Pd center of **1b** activated by NaBARF. Steric repulsion between the bulky naphthyl substituent and the monomer renders coordination in **C** more favorable than that in **D**. Repetitive coordination in **C** and insertion of the coordinated monomer would result in formation of the isotactic polymer.

Scheme 2. Selective Coordination of **I-1**



Polymerization of 4-alkylcyclopentenes with longer alkyl groups (**I-3**, **I-4**, and **I-10**) catalyzed by **1b**/NaBARF afforded the corresponding polymers poly(**I-3**), poly(**I-4**), and poly(**I-10**) (eq 1 and runs 3−5 in Table 1). On the basis of the $^{13}C\{^{1}H\}$ NMR results [Figure 1(iii)−(v)], the polymers contain *trans*-fused 1,3-cyclopentane rings located at regulated intervals along the linear chain. The long spacers between the five-membered rings did not allow estimation of the tacticity of these polymers by NMR analysis. The polymerization of the monomers with more bulky substituents than **I-1** using the C_2-symmetric catalyst **1b** probably yields poly(**I-3**), poly(**I-4**), and poly(**I-10**) with the regulated tacticity.

Differential scanning calorimetry (DSC) measurements on isotactic poly(**I-1**) and poly(**I-3**) showed monotropic transitions, while poly(**I-4**) and poly(**I-10**) with longer alkylene spacers undergo enantiotropic transitions. Increasing the length of the alkyl spacer leads to lower phase-transition temperatures.[10] These polymers are considered to show liquid-crystalline properties between the transition temperatures. Direct observation of poly(**I-4**) by polarizing optical microscopy also supports the existence of the liquid-crystalline phase (Figure 2). Poly(**I-1**) obtained using **1a**/NaBARF (M_n = 10100 and 4500), however, undergoes only an irreversible glass transition and does not show liquid-crystalline behavior. Recently, Naga *et al.*[8] reported the formation of liquid-crystalline hydrocarbon polymers having five-membered rings from the cyclopolymerization of 1,5-hexadiene, although the stereochemical structure of the polymer has not been clarified and is probably not regulated.

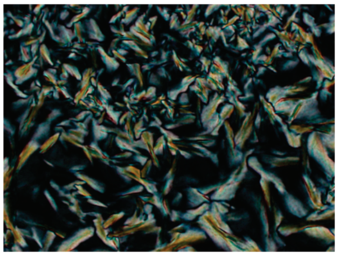


Figure 2. Polarizing optical micrograph of poly(**I-4**) (run 4 in Table 1).

In summary, the polymerization of 4-alkylcyclopentenes catalyzed by Pd complexes affords polymers with *trans*-1,3-disubstituted cyclopentane rings located at regulated intervals along the linear polymer chain. The C_2-symmetric catalyst produced polymers with an isotactic structure that exhibit high crystallinity at low temperature and liquid-crystalline properties upon heating.

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Supporting Information Available: Experimental procedures and NMR spectra, DSC profiles, polarized optical micrographs, and XRD data of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Determined from the $^{13}C\{^{1}H\}$ NMR spectrum at 230 MHz.

(10) The Supporting Information contains complete diffraction and DSC data.

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