

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

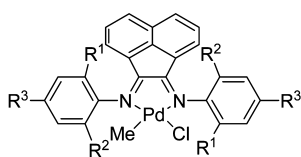
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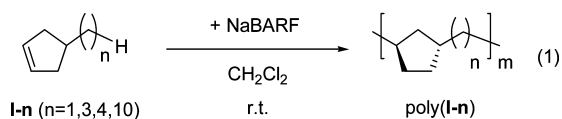
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The physical properties of poly(α -olefins) vary to a large degree depending on the alkyl substituents derived from the monomer and the relative stereochemistry of the neighboring repeating units (tacticity). Polymers with five- or six-membered rings 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 complexes³ catalyze the polymerization of α -olefins and cyclopolymerization of dienes with isotactic selectivity⁴ when a C_2 -symmetric ligand is employed. The polymerization reactions, including cyclopolymerization of monoterminial 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 = [$\{3,5-(CF_3)_2C_6H_3\}_4B\}^-$] to produce poly(**I-1**) (eq 1):



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



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 threeo-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 $K\alpha$)¹⁰ on the polymer obtained using **1a**/NaBARF showed an intense

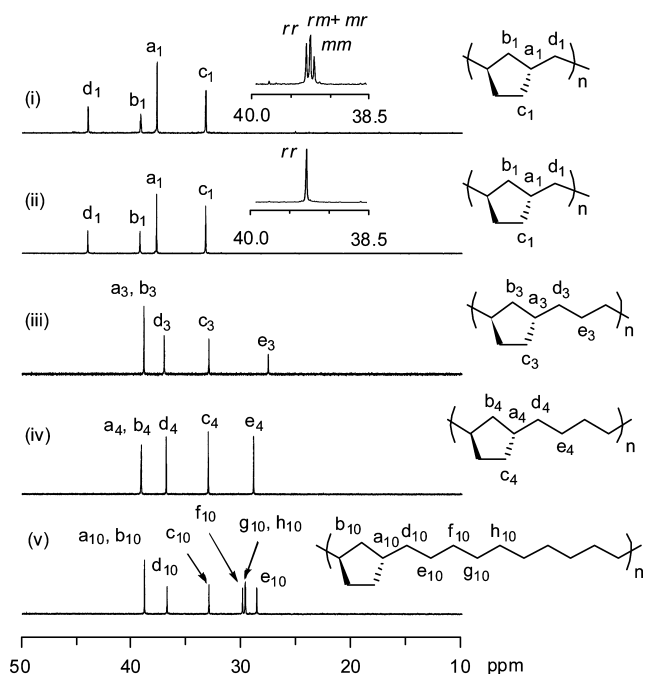


Figure 1. $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$ at 50 °C) of (i) poly(**I-1**) (run 1 in Table 1), (ii) poly(**I-1**) (run 2), (iii) poly(**I-3**) (run 3), (iv) poly(**I-4**) (run 4), and (v) poly(**I-10**) (run 5).

diffraction peak at $2\theta = 17.92^\circ$ 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 $2\theta = 18.42^\circ$ and thus contained the crystalline domain almost exclusively at room temperature.

Table 1. Polymerization of 4-Alkylcyclopentenes^a

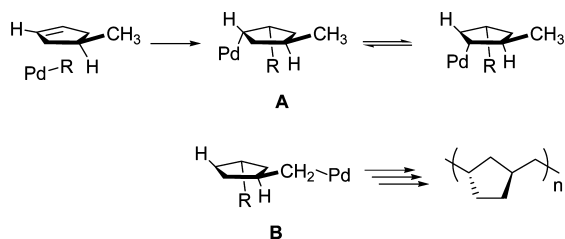
run	olefin	Pd	time	conv. (%)	M_n	M_w/M_n
1	I-1	1a	3 h	quant.	10100 ^{b,c}	1.90 ^{b,c}
2	I-1	1b	5 min	quant.	8200 ^{c,d}	—
3	I-3	1b	1 h	quant.	3000 ^e	2.18 ^e
4	I-4	1b	1.5 h	66	3000 ^e	3.38 ^e
5	I-10	1b	36 h	56	5700 ^e	2.38 ^e

^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-

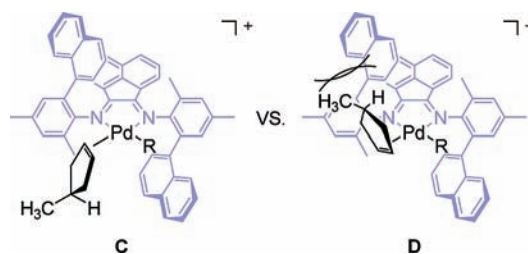
tylmethyl palladium species (**B**).³ Insertion of a new monomer into the Pd–primary alkyl bond leads to further polymer growth. Formation of a *trans* five-membered ring in the polymer is explained by assuming preferential coordination of the monomer to Pd at the less-hindered side followed by smooth 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 ¹³C{¹H} 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 C₂-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 C₂-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>.

References

- (1) (a) Janiak, C.; Lassahn, P. G. *Macromol. Rapid Commun.* **2001**, *22*, 479. (b) Natori, I.; Imaizumi, K.; Yamagishi, H.; Kazunori, M. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1657. (c) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (d) Ballesteros, O. R.; Venditto, V.; Auremma, F.; Guerra, G.; Resconi, L.; Waymouth, R. M.; Mogstad, A. *Macromolecules* **1995**, *28*, 2383.
- (2) (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (b) Lavoie, A. R.; Ho, M. H.; Waymouth, R. M. *Chem. Commun.* **2003**, 864.
- (3) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (d) Leatherman, M. D.; Brookhart, M. *Macromolecules* **2001**, *34*, 2748. (e) McCord, E. F.; McLain, S. J.; Nelson, L. T. J.; Ittel, S. D.; Tempel, D.; Killian, C. M.; Johnson, L. K.; Brookhart, M. *Macromolecules* **2007**, *40*, 410.
- (4) (a) Pappalardo, D.; Mazzeo, M.; Antinucci, S.; Pellicchia, C. *Macromolecules* **2000**, *33*, 9483. (b) Cherian, A. E.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2003**, 2566. (c) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 13770. (d) Park, S.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2006**, *128*, 3510. (e) Rose, J. M.; Deplace, F.; Lynd, N. A.; Wang, Z.; Hotta, A.; Lobkovsky, E. B.; Kramer, E. J.; Coates, G. W. *Macromolecules* **2008**, *41*, 9548. A C₂-symmetric Ni–diimine complex has been reported to promote polymerization of α -olefins with high levels of ω ,2-regiochemistry. See: (f) Rose, J. M.; Cherian, A. E.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 4186.
- (5) Okada, T.; Park, S.; Takeuchi, D.; Osakada, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6141.
- (6) For 1,3-polymerization of cyclopentene, see: McLain, S.; Feldman, J.; McCord, E. F.; Gardner, K. H.; Teasley, M. F.; Coughlin, E. B.; Sweetman, K. J.; Johnson, L. K.; Brookhart, M. *Macromolecules* **1998**, *31*, 6705.
- (7) Polymerization of 4-methylcyclopentene was reported to show high stereoselectivity. See: McLain, S. J.; McCord, E. F.; Bennett, A. M. A.; Ittel, S. D.; Sweetman, K. J.; Teasley, M. F. U.S. Patent 6,258,908, 1999; WO 9950320, 1999; *Chem. Abstr.* **1999**, *131*, 272335w.
- (8) For the report of liquid-crystal polyolefins, see: Naga, N.; Yabe, T.; Sawaguchi, A.; Sone, M.; Noguchi, K.; Murase, S. *Macromolecules* **2008**, *41*, 7448.
- (9) Determined from the ¹³C{¹H} NMR spectrum at 230 MHz.
- (10) The Supporting Information contains complete diffraction and DSC data.

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