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# Pd Complex-Promoted Cyclopolymerization of Functionalized α,ω-Dienes and Copolymerization with Ethylene to Afford Polymers with Cyclic Repeating Units

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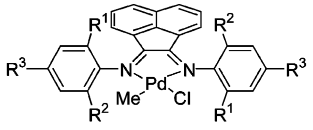
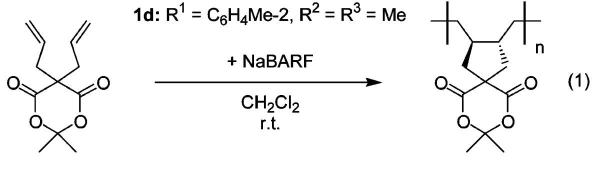
The cyclopolymerization of nonconjugated dienes converts acyclic monomers into polymers with cyclic repeating units. The complexes of the early transition metals Ti, Zr, and Y catalyze the polymerization of 1,5-hexadiene and 1,6-heptadiene to produce polymers with 1,3-disubstituted five- and six-membered cyclic repeating units.[1,2] These polymers, however, consist of both *trans*- and *cis*-fused rings arranged randomly in a polymer chain. Stereoselective cyclopolymerization is of importance because polymers whose cyclic repeating units are arranged in a controlled manner exhibit unique properties.[3] The complexes of late transition metals, such as Ru, Rh, and Pd, have recently been reported to catalyze the cyclization of enynes and dienes.[4] The Brookhart-type Pd catalyst [PdCl(Me)(phen)]-NaBARF (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) catalyzes the cyclizative hydrosilylation and cycloisomerization of diallylmalonates to afford compounds with 1,2-disubstituted *trans*-fused five-membered rings.[5] The combination of the stereoselective ring formation and the insertion of a C=C bond of a diene, which occur alternately, produces the polymers with cyclic repeating units with a high regularity. Such a polymerization of dienes using late-transition-metal catalysts has not yet been reported. In this paper, we report the Pd complex-catalyzed cyclopolymerization of diallyl monomers to produce polymers with five-membered rings as well as the copolymerization of these monomers with ethylene.

A catalyst prepared from the Pd diimine complex (**1a**) and NaBARF[6] initiates the cyclopolymerization of isopropylidene diallylmalonate (**I**) in $CH_2Cl_2$ at room temperature to produce the polymer $-(CH_2-C_5H_6(C_5H_6O_4)\text{-}CH_2)_n-$ (poly-**I**) (eq 1). The results of the polymerization using complexes **1a**−**1d** are summarized in Table 1. Figure 1 shows the $^{13}C\{^1H\}$ NMR spectra of poly-**I** formed by using **1a** (i and ii) and by using new Pd complex **1c** (iii). The former polymer shows the signals of the CH and $CH_2$ carbons of the five-membered ring at δ 46.6−47.1 and 45.8, respectively, while the corresponding signals of the latter appear at δ 46.5 and 45.6. The signal of the carbonyl carbon is observed at δ 172.0 for the polymers. Both polymers are composed of *trans*-1,2-disubstituted five-membered rings because the difference of the peaks due to CH and $CH_2$ carbons (ca. 1 ppm) and the position of the carbonyl carbon peak are quite similar to the model compound with *trans* structure.[7] Figure 1(iii) contains the signal at δ 46.5, suggesting regulated tacticity of the polymer. We assigned the structure rich in isotactic-type tacticity (Scheme 1) for the polymer which was obtained by polymerization catalyzed by **1c** (*rr* = 83%) and by **1d** (*rr* = 62%) because **1c** and **1d** have a $C_2$-symmetric structure. The structure of **1d** was confirmed by X-ray crystallography. Analogous Ni complexes with a $C_2$ symmetry catalyze polymerization of propylene and *trans*-2-butene to produce the isotactic polymers.[8]



**1a:** $R^1 = R^2 = {}^iPr$, $R^3 = H$
**1b:** $R^1 = R^2 = R^3 = Me$
**1c:** $R^1 = 1\text{-}C_{10}H_7$, $R^2 = R^3 = Me$
**1d:** $R^1 = C_6H_4Me\text{-}2$, $R^2 = R^3 = Me$



(1)

**I**　　**poly-I**

To determine the structure of the growing polymer end, an NMR study of the reaction mixture at a low temperature was conducted.

***Table 1.*** Polymerization of Diallyl Monomers by Pd Complexes[a]

| run | monomer | Pd | solvent (mL) | time (h) | conv. (%) | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | **I** | **1a** | 0.5 | 24 | 56 | 7900 | 1.51 |
| 2 | **I** | **1b** | 0.5 | 24 | 95 | 9200 | 1.75 |
| 3 | **I** | **1c** | 0.25 | 24 | 55 | 4400 | 1.69 |
| 4 | **I** | **1d** | 0.25 | 29 | 78 | 8400 | 1.82 |
| 5 | **II** | **1b** | 0.25 | 48 | 53 | 9400 | 1.71 |
| 6 | **III** | **1a** | 0.5 | 12 | 40 | 3600 | 1.28 |
| 7 | **IV** | **1b** | 0.25 | 24 | 35 | 6200 | 1.56 |

[a] Reaction conditions: Pd complex = 0.01 mmol, NaBARF = 0.012 mmol, [monomer]/[Pd] = 70, solvent = $CH_2Cl_2$, at room temperature.

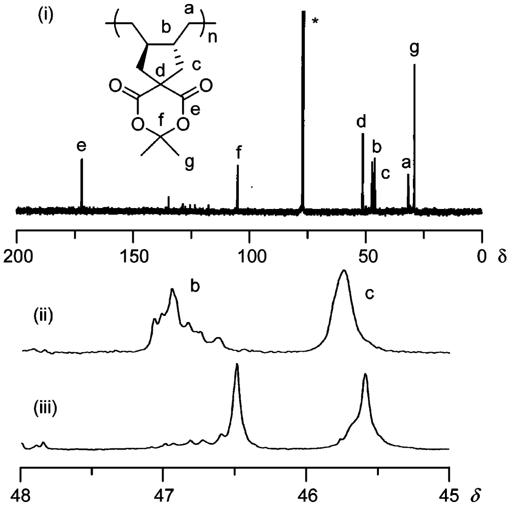
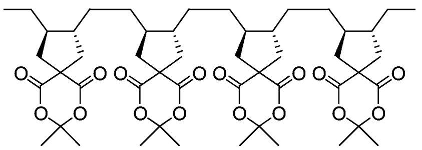


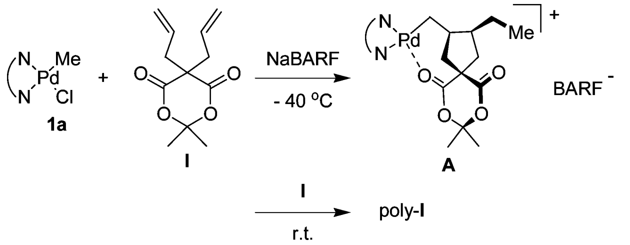
***Figure 1.*** $^{13}C\{^1H\}$ NMR spectra of poly-**I** in $CDCl_3$ at 25 °C. (i) Total and (ii) expanded spectra of poly-**I** prepared by polymerization of **I** in $CH_2Cl_2$ catalyzed by **1a**/NaBARF. (iii) Expanded spectrum of the polymer obtained by the reaction catalyzed by **1c**/NaBARF. The peak with an asterisk is that of the solvent.

10.1021/ja058408p CCC: $33.50

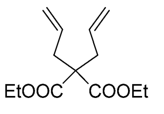
***Scheme 1.*** Isotactic Tetrad of Poly-**I**



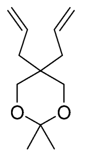
***Scheme 2.*** Equimolar Reaction of **I** with **1a**/NaBARF



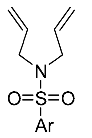
The $^1$H and $^{13}$C{$^1$H} NMR spectra of a mixture of **1a**, NaBARF, and **I** ([**1a**]:[NaBARF]:[**I**] = 1:1.2:20) in $CDCl_3$ at −40 °C showed an exclusive formation of the cyclopentylmethyl palladium complex **A**, as shown in Scheme 2. The insertion of a double bond of **I** into the Pd−Me bond of **1a** and the ensuing intramolecular insertion of the remaining C═C bond resulted in **A**. Two carbonyl carbon signals are observed at $\delta$ 187.3 and 164.4, at which the former signal appears at a significantly lower field than the latter because of the coordination of the carbonyl group to the Pd center.[9] Upon warming the reaction mixture to 20 °C, signals of poly-**I** appear at $\delta$ 172.1, 104.9, 51.0, 45.9, and 28.8, whereas those of the $CH_2$ and CH carbons of the cyclopentylmethyl group attached to Pd appear at $\delta$ 31.5 and 49.5, respectively. These results indicate that the carbonyl-chelated Pd complex **A** initiates polymer growth.[6b] The polymerization of **I** (0.500 M) by **1a** obeys pseudo-first-order kinetics ($k_{obsd} = 1.54 \times 10^{-5}$ s$^{-1}$ at 20 °C). This suggests that the rate-determining step of polymer growth depends on the intermolecular insertion of the C═C bond of **I** into the Pd−C bond of the cyclopentylmethyl palladium polymer end.



**II**

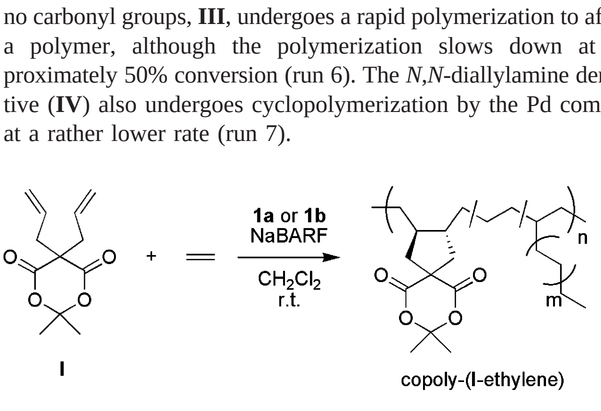


**III**



**IV**
(Ar = $C_6H_4Me$-4)

The results of the Pd-catalyzed cyclopolymerizations of **II**−**IV** are included in Table 1. The slow cyclopolymerization of **II** (run 5) indicates the importance of the cyclic structure of isopropylidene diallylmalonate for smooth polymerization. A diallyl monomer with no carbonyl groups, **III**, undergoes a rapid polymerization to afford a polymer, although the polymerization slows down at approximately 50% conversion (run 6). The *N*,*N*-diallylamine derivative (**IV**) also undergoes cyclopolymerization by the Pd complex at a rather lower rate (run 7).



(2)

The addition of **I** to a $CH_2Cl_2$ solution of **1b** in ethylene atmosphere initiates the copolymerization of **I** with ethylene to produce the polymer $-((CH_2-C_5H_6(C_5H_6O_4)-CH_2)_n-(CH_2CH_2)_m)-$ (copoly−(**I**−ethylene)) (eq 2). The reaction at atmospheric ethylene pressure ($[\mathbf{I}]_0 = 0.175$ M) produced a copolymer containing 3 mol % repeating units from **I**, whereas content from **I** increased to 42% at a higher **I** concentration ($[\mathbf{I}]_0 = 2.8$ M) and a reduced ethylene pressure (0.25 atm). The $^{13}$C{$^1$H} NMR spectra of the copolymers show signals at $\delta$ 47.0 and 46.5, which respectively correspond to the CH carbons of the cyclopentane units of $-CH_2-C_5H_6(C_5H_6O_4)-CH_2-CH_2-C_5H_6(C_5H_6O_4)$-$CH_2-$ and $-CH_2-C_5H_6(C_5H_6O_4)-CH_2-CH_2CH_2-$ in a random sequence of monomer units from **I** and ethylene.

In summary, Pd complexes promote smooth cyclopolymerization to give a polymer with *trans*-1,2-disubstituted five-membered rings. The chelating coordination of a carbonyl group to the Pd center stabilizes the cyclopentylmethyl intermediate and induces the further insertion of a C═C bond into the Pd−C bond, instead of $\beta$-hydrogen elimination, thereby leading to polymer growth. **I** also undergoes copolymerization with ethylene to give a polymer with up to 42% **I** incorporated.

**Acknowledgment.** This work was supported by a Grant-in-Aid for Young Scientist No. 16750091 for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

**Supporting Information Available:** Experimental procedures for the synthesis of ligands and Pd complexes, polymerization and copolymerization, NMR data including assignment of polymer end signals and estimation of tacticity, and X-ray crystal structure analysis of a Pd complex (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) *trans*-3,4-Dimethylcyclopentane-1,1-dicarboxylate shows the signals due to CH, $CH_2$, and CO carbons at $\delta$ 43.2, 42.0 (difference 1.2 ppm), and 173.8, while the corresponding carbons of the *cis* isomer appear at $\delta$ 41.2, 36.8 (difference 4.4 ppm), and 173.5, 173.7. See: (a) Perch, N. S.; Pei, T.; Widenhoefer, R. A. *J. Org. Chem.* **2000**, *65*, 3836. (b) Curran, D. P.; Shen, W. *J. Am. Chem. Soc.* **1993**, *115*, 6051.

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(9) Addition of MeCN to **A** ([MeCN]/[**A**] = 10) shifts the carbonyl carbon signal to $\delta$ 172.0 and 171.1 and appearance of the carbon signals of MeCN coordinated to Pd at $\delta$ 104.8 and 12.1.

JA058408P