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Published on Web 05/11/2007

Cyclopolymerization of 1,6-Heptadienes Catalyzed by Iron and Cobalt Complexes: Synthesis of Polymers with Trans- or Cis-Fused 1,2-Cyclopentanediyl Groups Depending on the Catalyst

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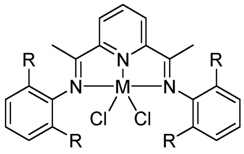
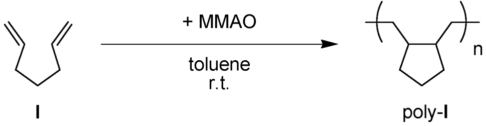
Complexes of early transition metals, namely, Ti, Zr, and Y, catalyze the cyclopolymerization of 1,5-hexadiene and 1,6-heptadiene to produce polymers with 1,3-cyclopetanediyl or 1,3-cyclohexanediyl groups in repeating units.[1,2] The polymerization, however, lacks cyclization selectivity, and the obtained polymers contain trans- and cis-fused rings randomly as well as partial structures having vinyl groups, suggesting an incomplete cyclization of a monomer. The polymers formed via stereoselective cyclopolymerization exhibit unique thermal properties similar to those of stereoregular polynorbornene and poly(1,3-cyclohexadiene).[3] Recently, we have reported that Pd complexes[4] catalyze the cyclopolymerization of 1,6-dienes with ester or ketal groups to yield polymers having polar functional groups,[5] although an unsubstituted 1,6-diene does not polymerize owing to the formation of π-allylic palladium intermediates.[6] In this paper, we report that Fe and Co complexes with bis(imino)pyridine ligands catalyze the cyclopolymerization of both substituted and unsubstituted 1,6-heptadienes with high stereoselectivity.

Catalysts prepared from the bis(imino)pyridine complexes of Fe and Co, **1a**−**c** and **2b**,[7,8] and modified methylaluminoxane (MMAO) initiate the cyclopolymerization of 1,6-heptadiene (**I**) in toluene at room temperature to produce the polymer of the formula -(CH_2-C_5H_8-CH_2)$_n$- (poly-**I**) (eq 1).



1a: M = Fe, R = Cl
1b: M = Fe, R = ^{i}Pr
1c: M = Fe, R = C_6H_{13}
1d: M = Fe, R = Me
2b: M = Co, R = ^{i}Pr



(1)

I poly-**I**

The results are summarized in Table 1 (runs 1−5). The polymer (run 1) does not show the ^{1}H NMR signal corresponding to the pendant 5-pentenyl group, indicating the complete cyclization of the diene monomer during polymerization. Minute signals at δ 5.30−5.50 are close to vinylene hydrogens of 3- and 4-methylcyclohexene,[9] and may be assigned to 2- and/or 3-cyclohexenyl groups at the polymer end.[10] Molecular weight (M_n) is estimated to be 14000 on the basis of the relative intensity ratio of the ^{1}H NMR signals corresponding to the main chain and the terminal cyclohexenyl group.[11] The $^{13}C\{^1H\}$ NMR spectrum shows the signals corresponding to CH and CH_2 carbons of the *cis*-1,2-cyclopentanediyl ring (δ 43.5, 31.0, and 23.0) and much smaller signals corresponding to *trans*-1,2-cyclopentanediyl groups (δ 46.6, 34.7, and 24.3) (Figure 1i).[12] Random copolymerization of the diene with ethylene by Fe catalyst also produces the polymer with cis-five-membered rings.[8] The ratio of cis- and trans-fused five-membered rings of poly-**I** (Figure 1i) is determined to be 95:5 from the peak areas of the CH carbons. Four CH carbon signals corresponding to triads of repeating units appear at almost equal intensities, suggesting an atactic sequence of the polymer. A catalyst prepared from **1b** or **1c** and MMAO catalyzes the formation of the polymer with lower molecular weight and cis−trans ratio (runs 2, 3).

Table 1. Polymerization of 1,6-Heptadienes by Fe and Co Complexes.[a]

run	diene	cat.	[Al]/[cat.]	yield (%)	M_n	M_w/M_n	cis/trans[f]
1	**I**	**1a**	50	98	14000[c] (870[d])	2.4[d]	95:5
2	**I**	**1b**	50	62	3000[c]		70:30
3	**I**	**1c**	50	78	4300[c]		40:60
4[b]	**I**	**2b**	50	87	9300[c] (14000[e])	1.70[e]	<1:>99
5	**I**	**2b**	212	89	10000[c] (2600[d], 10700[e])	1.95[e]	<1:>99
6[b]	**II**	**1d**	50	98	(2700[d])	3.5[d]	>99:<1
7	**II**	**2b**	212	86			<1:>99
8	**III**	**1d**	50	95	4600[c]		65:35

[a] Reaction conditions: Fe or Co complex = 12 μmol, [diene]/[Fe or Co] = 100, solvent = toluene (1.2 mL), reaction time = 5 h, at room temperature; cat. = catalyst. [b] Solvent = toluene (0.6 mL). [c] Determined by ^{1}H NMR. [d] Determined by GPC detected by FTIR (based on polystyrene standard). See ref 9. [e] Determined by GPC detected by RI (based on polystyrene standard). [f] Determined by $^{13}C\{^1H\}$ NMR.

The catalyst using **2b** and MMAO is also effective for the cyclopolymerization of **I** (run 5). The $^{13}C\{^1H\}$ NMR spectrum of the obtained poly-**I** differs from that of the polymer obtained from the Fe-catalyzed reactions and shows the CH and CH_2 carbon signals corresponding to the *trans*-1,2-cyclopentanediyl rings exclusively (Figure 1ii). The ratio of the two peaks of the CH carbon (δ 46.2 and 46.8) indicates a moderate degree of control in tacticity of the trans-five-membered ring (50% of the major triad), although the microstructure cannot be determined unambiguously. The molecular weight determined from the ^{1}H NMR spectrum (M_n = 10000) agrees well with that determined from GPC using an RI detector and a polystyrene standard (M_n = 10700, M_w/M_n = 1.95).

Scheme 1 shows the summary of pathways proposed for the reaction catalyzed by the Fe and Co complexes. Polymer growth, promoted by the Fe complex, proceeds via the upper route. The intermediate diene-coordinated Fe complex (**A**, M = Fe) undergoes 2,1-insertion of a vinyl group of the monomer into the Fe-polymer bond to yield the olefin-coordinated alkyl intermediate (**B**, M = Fe).[13] Both intermediates favor the chair conformation of the chelate ring, similarly to Fe complexes of 1,6-heptadiene[14] and the alkyl

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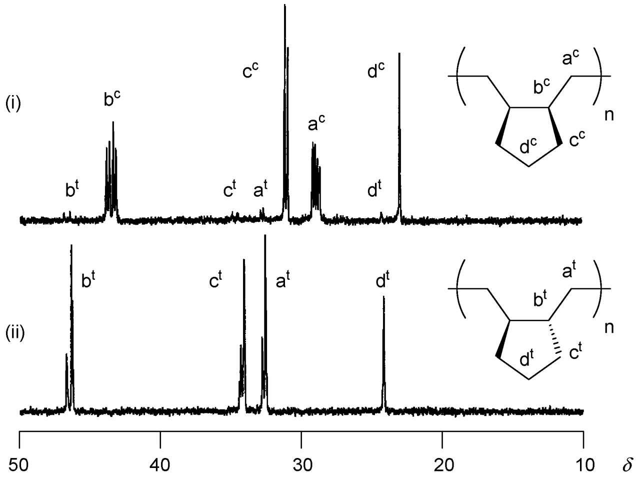
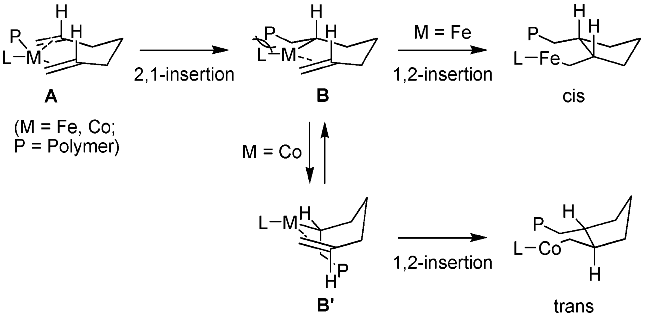


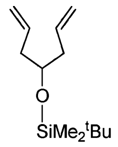
Figure 1. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectra ($\mathrm{C_2D_2Cl_4}$ at 130 °C) of (i) poly-**I**-cis prepared by cyclopolymerization of **I** catalyzed by **1a**/MMAO and (ii) poly-**I**-trans obtained from reaction catalyzed by **2b**/MMAO. The peak with an asterisk is that of the solvent.

Scheme 1. Mechanism of Cyclopolymerization of Diene Catalyzed by Fe and Co Complexes.

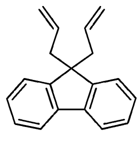


titanium complex with the coordinated pendant vinyl group.[1d,15] A smooth 1,2-insertion of the remaining $\mathrm{C{=}C}$ bond results in the formation of the cis-fused 1,2-cyclopentanediyl ring. In the Co-promoted cyclopolymerization, an olefin-coordinated chelate with a cisoid structure (**B**, M = Co) isomerizes to a transoid structure (**B′**) prior to the cyclization. The subsequent cyclization results in the formation of the thermodynamically favorable trans-fused cyclopentane ring.[16]

Cyclopolymerization reactions of **II** catalyzed by the Fe and the Co complexes show a complete selectivity for the formation of cis- (or trans-) five-membered rings depending on the catalyst (Table 1, runs 6, 7). The Fe catalyst promotes the cyclopolymerization of **III** to yield the polymer containing cis- and trans-fused five-membered rings at 65:35 (Table 1, run 8).



II



III

In summary, the Fe and Co complexes promote a smooth cyclopolymerization of 1,6-heptadienes with high cyclization selectivity. Complementary stereochemistry of the cyclopolymerization catalyzed by the complexes enabled the synthesis of the polymers with cis- or trans-five-membered rings with high stereoselectivity.

Acknowledgment. This work was supported by a Grant-in-Aid for Young Scientist No. 18750094 for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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

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(10) Details on the structure of the polymer end are described in Supporting Information.

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JA0718568