Stereoselective Cyclopolymerization of 1,5-Hexadiene Using Novel Bis(ferrocenyl)zirconocene Catalyst

Makoto Mitani, Kunihiro Oouchi, Michiya Hayakawa, Tohru Yamada, and Teruaki Mukaiyama†
Basic Research Laboratories for Polymer Chemistry, Mitsui Petrochemical Industries, Ltd., Nagaura, Sodegaura, Chiba 299-02
†Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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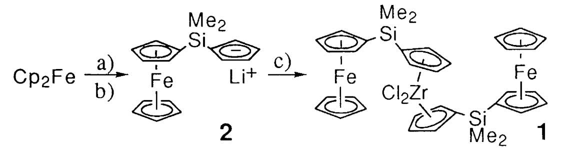
A novel heterotrinuclear zirconium-iron complex **1** was synthesized and crystal structure of **1** was determined by X-ray diffraction method. The complex **1** efficiently catalyzed cyclopolymerization of 1,5-hexadiene in the coexistence of methylaluminoxane to afford trans-poly(methylene-1,3-cyclopentane) with high stereoselectivity (98% trans).

Multinuclear transition-metal complexes are expected to exhibit good catalysis which are not shown by mononuclear complexes.[1] Due to the recent interest of homogeneous group 4 metallocenes for polymerization of olefins,[2] several groups had reported the syntheses of multinuclear group 4 metallocenes.[3,4] In this communication, we would like to report the preparation and the characterization of novel class of heterotrinuclear complex catalyst which was effective in cyclopolymerization of 1,5-hexadiene with high trans-selectivity.



a) i) BuLi, ii) Me_2SiCl_2, 42 %yield, b) i) CpLi, ii) BuLi, 75 %yield, c) 0.5 equiv. $ZrCl_4(THF)_2$, 70 °C, 36 %yield

Scheme 1.

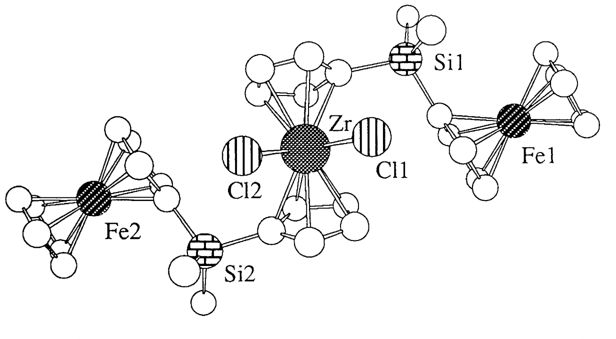
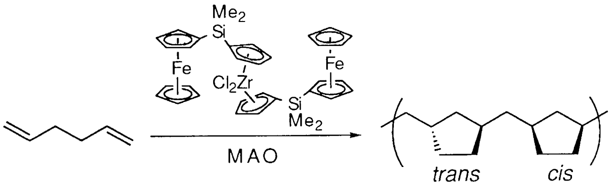


Figure 1. Molecular structure of trinuclear complex **1**.

As shown in Scheme 1, dimethylchloroferrocenylsilane was obtained on treatment of ferrocenyl lithium with the excess amount of dimethyldichlorosilane. Successive reaction with cyclopentadienyl lithium followed by lithiation by BuLi produced lithium salt **2**. The reaction of the lithium salt with 0.5 equivalent of $ZrCl_4(THF)_2$ in THF at 70 °C gave trinuclear zirconium-iron complex **1**. After purification, analytically pure sample of **1** was obtained in 36% yield. Recrystallization from toluene yielded a single crystal of **1** as an orange plate. The crystal structure of the complex was determined by X-ray diffraction method[5] (Figure 1). It is noted that two ferrocenyl moieties are located symmetrically around the central zirconocene and the complex molecule has a C_2 symmetry axis bisecting Cl-Zr-Cl angle. Consequently, the unit cell contained two independent molecules, which is a pair of enantiomers. The ^1H NMR spectra is also consistent with this symmetrical structure.[6] As the bulky ferrocenyl groups prevent free rotation of cyclopentadienyl rings of zirconocene, it is expected that the symmetrical structure would be retained in the reaction solution.

Recently, it was reported that the group 4 metallocenes combined with methylaluminoxane (MAO) performed cyclopolymerization of 1,5-hexadiene as effective catalysts and the stereochemistry of the obtained polymer was influenced by structure of ligands of metallocenes.[7] Then, thus prepared trinuclear zirconium complex **1** was used as catalyst in cyclopolymerization of 1,5-hexadiene (Scheme 2).



Scheme 2.

To a toluene solution of complex **1** and MAO was added 1000 molar amount of 1,5-hexadiene. After stirring for 3 h at 0 °C, poly(methylene-1,3-cyclopentane)(PMCP) was isolated in 27% yield.[8] Analyses by GPC[9] and ^1H NMR[10] indicated that the resulting polymer had high molecular weight (Mw = 31000, Mw: weight average molecular weight) and contained no detectable uncyclized monomer units. It should be noted that the selectivity in ring closure of trans cyclopentane was estimated to be 91% by ^{13}C NMR analysis.[11] Furthermore, it was found that the trinuclear zirconium complex **1** was superior to other

Table 1. Cyclopolymerization[a] of 1,5-hexadiene catalyzed by various zirconocene/MAO systems

Entry	Complex	*trans*-Selectivity[b] / %	Mw^c / 10^3
1	**1**	91	31
2	Cp_2ZrCl_2	80	22
3	$(Me\text{-}Cp)_2ZrCl_2$	78	33
4	$(Me_3Si\text{-}Cp)_2ZrCl_2$	81	41
5	$(1\text{-}^nBu\text{-}3\text{-}Me\text{-}Cp)_2ZrCl_2$	72	36
6	$Ind_2ZrCl_2{}^d$	64	28
7	$Et(Ind)_2ZrCl_2{}^e$	68	n.d.[f]
8	$Me_2SiCp_2ZrCl_2$	64	4

[a] Polymerization Conditions: [Cat.] = 0.33 mM, [Al]/[Cat.] = 1000, [diene]/[Cat.] = 1000, 0 °C. [b] Ratio of trans ring. Determined by ^{13}C-NMR. [c] Weight average molecular weight. Determined by GPC versus standard polystyrene. [d] Bis(indenyl)zirconium dichloride. [e] Ethylenebis(1-indenyl)zirconium dichloride. [f] Not determined. Obtained polymer was insoluble in toluene .

various metallocenes concerning trans-selectivity in cyclopolymerization (Table 1). For example, the trans selectivity was 80% when $\mathrm{Cp_2ZrCl_2}$ was used at 0 °C, which gave highest value in previous paper.[7c] The complexes having mono-substituted cyclopentadienyl ligands, $\mathrm{(Me\text{-}Cp)_2ZrCl_2}$ and $\mathrm{(trimethylsilyl\text{-}Cp)_2ZrCl_2}$, showed almost the same stereoselectivity as $\mathrm{Cp_2ZrCl_2}$ (Entries 3 and 4 in Table 1). In contrast, the complexes containing bulkier or more rigid ligand systems, di-substituted Cp ligands and the bridged-Cp ligands, gave lower stereoselectivity. Trans stereoselection in cyclization of 1,5-hexadiene is properly explained that the pseudo-chair transition conformer is a favorable transition state on the basis of conformational calculation.[7d] It is reasonable to consider that two ferrocenyl moieties fix zirconocene complex **1** in rigid structure to stabilize pseudo-chair transition state.

Table 2. Effect of polymerization temperature on *trans*-selectivity

Entry[a]	Temperature / °C	*trans*-Selectivity[b] / %	*Mw*[c] / 10^3	*Mw*/*Mn*[d]
1	0	91	31	2.31
2	-30	95[e]	28	2.08
3	-78	98[f]	21	1.73

[a] Polymerization Conditions: [Cat. **1**] = 0.33 mM (Entry 1), 0.50 mM (Entry 2), 0.57 mM (Entry 3), [Al]/[Cat.] = 1000, [diene]/[Cat.**1**] = 1000 (Entries 1 and 2), 5000 (Entry 3). [b] Ratio of trans ring. Determined by ^{13}C NMR. [c] Weight average molecular weight. Determined by GPC versus standard polystyrene. [d] Determined by GPC. [e] Catalyst activity: 5300 g-polymer/mol Cat.•[diene]•h. [f] Catalyst activity: 73 g-polymer/mol Cat.•[diene]•h. By using $\mathrm{Cp_2ZrCl_2}$, ratio of trans ring was 88% and the catalyst activity was 106 g-polymer/mol Cat.•[diene]•h under the same conditions.

The effect of polymerization temperature was also examined by using the trinuclear zirconocene **1** as catalyst (Table 2). When polymerization was performed at -30 °C, the trans-selectivity of obtained cyclopolymer increased up to 95% (Entry 2). At -78 °C, highly stereospecific trans-PMCP was obtained with 98% selectivity (Entry 3). The obtained polymer possessed high molecular weight (*Mw* = 21000), narrow polydispersity (*Mw*/*Mn* = 1.73) and contained scarcely detectable amount of oligomer or uncyclized monomer units. On the contrary, when polymerization was carried out by using $\mathrm{Cp_2ZrCl_2}$ at -78 °C, the obtained polymer had 88% of trans ring and lower molecular weight (*Mw* = ~10000) accompanied with small amount of uncyclized monomer units.

It is noted that highly stereo-controlled trans-PMCP with high molecular weight and fully cyclized structure was formed by stereoselective cyclopolymerization of 1,5-hexadiene using a novel trinuclear bis(ferrocenyl)zirconocene **1**.

References and Notes

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5 The authors would like to thank Prof. Yuji Ohashi, Faculty of Science, Tokyo Institute of Technology, for the measurement of X-ray analysis.

6 Spectroscopic data for **1**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 6.51 (t, 4H), 6.19 (t, 4H), 4.39 (t, 4H), 4.14 (t, 4H), 4.11 (s, 10H), 0.53 (s, 12H).

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8 A typical polymerization was carried out as follows: to a solution of 1.9 mg (2.4 μmol) of **1** in 4.9 ml toluene was added 2.2 ml of 1.1 M solution of MAO (2.4 mmol) in toluene at 0 °C under argon. Then 0.28 ml 1,5-hexadiene (2.4 mmol) was added. After stirring for 3 h at 0 °C, polymerization was quenched by the addition of methanol and the reaction mixture was poured into a large amount of methanol/HCl. The resulting polymer was isolated by filtration and dried *in vacuo*. The yield of obtained polymer was 27% and the catalyst activity was calculated to be 23000 g-polymer/mol Cat.•[diene]•h.

9 GPC analysis: Waters, μ Styragel columns 10^3 and 10^4 Å at 75 °C using toluene as the solvent and calibrated with standard polystyrene.

10 Under the present conditions, the ratio of cyclized monomer units was over 99%.

11 Selectivity of trans / cis was determined from the ratio of the peak areas in ^{13}C NMR spectra of the polymer at 33.3 and 32.8 ppm ($\mathrm{CDCl_3}$, 25 °C, reference TMS = 0, see Ref. 7a).