

Polymer immobilized silane bridged metallocene catalysts for ethylene polymerization

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Abstract

Ansa-zirconocene complex with an allyl substituted silane bridge $[(\text{CH}_2=\text{CHCH}_2)\text{CH}_2\text{Si}(\text{C}_5\text{H}_4)_2]\text{ZrCl}_2$ (**1a**) has been synthesized and characterized. The molecular structure of **1a** has been determined by X-ray crystallographic analysis. The polymer immobilized metallocene catalyst **1b** is prepared by the co-polymerization of **1a** with styrene in the presence of radical initiator. The result of ethylene polymerization showed that the polymer immobilized metallocene catalyst kept high activity for ethylene polymerization and was a potential supported catalyst for olefin polymerization. © 2002 Published by Elsevier Science B.V.

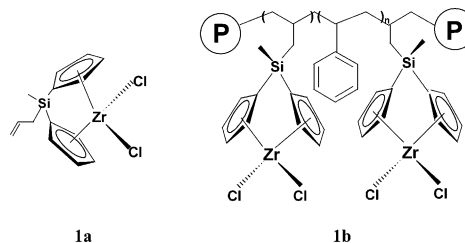
Keywords: Metallocene catalysts; Polymer immobilized metallocene; Silane bridged metallocene; Ethylene polymerization; X-ray structure analysis

1. Introduction

Metallocene catalysts gained widespread importance for polymerization of olefins on account of their high activity and versatility [1–3]. Metallocene catalysts show a single site active center in homogeneous phase and make it possible to tailor the structure of polymers in a precise way. Great industrial interest has arisen in employing them in existing technical process (drop-in technology) to replace the conventional heterogeneous catalysts.

In order to carry out polymerization in slurry, the metallocene have to be supported on an innocuous carrier such as silica, alumina or another inorganic or organic supports [4,5]. Polymer support, although rarely reported, is of great interest in industry and academic research. One approach is the use of the organic support materials like crosslinked polystyrene. It is also possible to fix a ligand on a polymeric support and then build up the catalysts [6–8]. Alt et al. have prepared the self-

immobilized metallocene catalysts for the ethylene polymerisation [9].



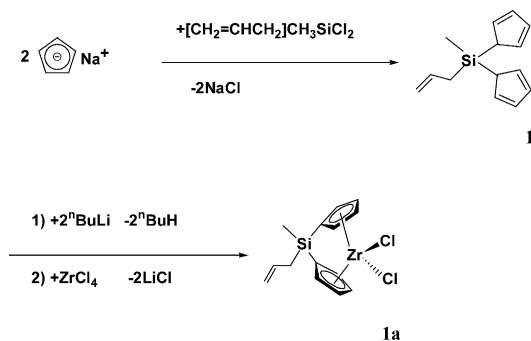
In this paper, we report on the ansa-zirconocene (**1a**) with bridged allyl group and its polymer immobilized catalyst **1b** as well as their catalytic performance for ethylene polymerization.

2. Results and discussion

2.1. Synthesis of the ligand and the metallocene catalyst

The procedure employed to prepare **1a** was modified from that described in the literature [10]. The ligand was obtained without difficulty from a reaction of the appropriate silane with cyclopentadienyl sodium

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(Scheme 1). The substance is as oily liquid and can be used without further purification.

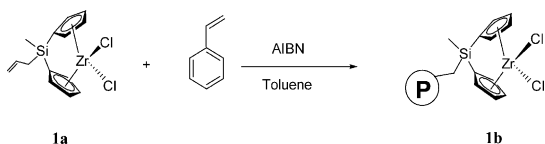
The reaction of **1** with two equivalents of n BuLi results in the formation of the corresponding dianions. The resulting dianions then react with $ZrCl_4$ in DME typically for 2 days at room temperature, giving the corresponding zirconocene complex **1a**. As solids, all metallocene complexes are stable against air and moisture for several days. In contrast, the complexes are unstable in solution, even at low temperature, traces of moisture cause decomposition within a few minutes.

The 1H -NMR spectra measured for **1a** exhibit the characteristic AA'BB' pattern expected for the cyclopentadienyl ring protons. The chemical shift patterns with two resonances at 5.5–6.0 ppm and two resonances at 6.7–7.1 ppm, observed for the cyclopentadienyl protons of complex **1a**.

2.2. Preparation of **1b**

The allyl groups in **1a** can be co-polymerized with styrene under the condition of radical initiator (AIBN) to result in corresponding polymer immobilized metallocene catalysts **1b** (Scheme 2). In order to co-polymerize the complexes with styrene sufficiently, it was indispensable to control the temperature in the range of 79–81 °C. The higher temperature would lead to enhancement of the rate of homo-polymerization of styrene [11]. When the co-polymerization is complete, the mixture solvent of hexane and toluene (3:1) was used to precipitate the polymer immobilized metallocene catalysts and wash away the remnants of **1a**, which did not co-polymerize with styrene.

A GPC study of the resultant polymer immobilized metallocene catalyst displays a molecular weight distribution no more than 1.4 ($M_n = 6437$; $M_w = 9554$;



polydispersity = 1.33). The narrow MWD indicates that the length of every polymer chain is identical. The uniform of composition and shape of polymer is a prerequisite as support materials of catalyst. So this results show that polymer immobilized metallocene is a potential supported catalyst.

The process of the formation of the polymer immobilized metallocene catalyst was investigated by XPS. The results show the binding energy of Si_{2p} (101.9 eV) in **1b** has a 1.2 eV dramatically increase comparing to that of the corresponding catalyst **1a** (100.7 eV). The XPS results confirm that the olefin substituent on the silicon atom has a strong interaction with styrene, causing the catalyst molecule fixed in the polymer chain. An alternative explanation is that the catalyst molecule may be imbedded in the polymer, resulting in the variation of the chemical surrounding of the silicon atom that can change the binding energy.

It is difficult to distinguish the structure of polymer immobilized catalyst **1b** by the normal characterization methods such as IR- and 1H -NMR. The low content of active centers make the IR- and 1H -NMR characterization inefficiently.

3. Molecular structure of **1a**

Single crystals of **1a** suitable for X-ray crystal structure determination were obtained by slow diffusion hexane into a toluene solution. Fig. 1 gives an ORTEP view of the structure of **1a** together with selected bond

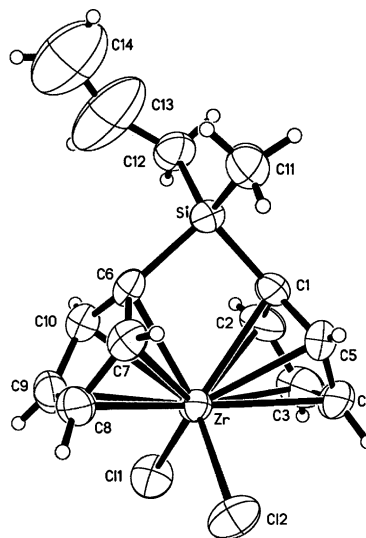


Fig. 1. Molecular structure of **1a**. Selected bond lengths (Å) and angles (°): Zr-Cl(1) 2.438(2), Zr-Cl(2) 2.4361(14), Zr-Cp1(c) 2.197(4), Zr-Cp2(c) 2.207, Si-C1 1.863(5), Si-C6 1.861(5), Si-C11 1.846(5), Si-C12, 1.853(5), C13-C14 1.293(2), C11-Zr-C12 98.36(5), Cp1(c)-Zr-Cp2(c) 125.3(1), C1-Si-C6 93.9(2), C11-Si-C12 113.8(3), Si-C12-C13 112.5(4), C12-C13-C14 153.6(14), Cp1-Cp2 59.5 (1) (Cp1: C1-C5, Cp2 C6-C10, Cp(c): Cp(centroid))

distances and angles for the coordination geometry of the Zr atom. The geometry around the Zr atom is distorted tetrahedron formed by two Cl atoms and two Cp rings. The Zr atom, Si atom and two bridge-head carbon atoms are in the same plane which is nearly upright with the two C₅ ring planes. The Zr–Cl bond lengths amount to 2.438(2) (Zr–Cl(1)) and 2.4361(14) Å (Zr–Cl(2)). The Cl(1)–Zr–Cl(2) angle is 98.36(5)°, and the Cp(centroid)–Zr–Cp(centroid) angle is found at 125.3(1)°. The bond lengths between zirconium and the carbon atoms of the cyclopentadienyl rings are in a range between 2.470(5) and 2.537(5) Å (C3, C4, C5, C1, C2) and 2.556(4) and 2.475(4) Å (C8, C9, C7, C6, C10) respectively. Most of the other structural features are similar to those observed in [(CH₃)₂Si(C₅H₄)₂]ZrCl₂ [12].

4. Catalytic activity

The performance of the catalysts was evaluated on basis of ethylene polymerization in toluene. Table 1 compares the polymerization productivity of **1a** with **1b** at identical conditions. The data show that the increment of Al/Zr (molar ratio) leads to great increase in activity, but extreme concentration of MAO may hinder the ethylene insertion, making the active centers embedded and useless, and thus the activity decrease. The polymer immobilized metallocene **1b** are found to be more active than **1a**. The mechanistic explanation given that is the fixation of the catalyst molecule on the polymer chain may reduce the bimolecular deactivation, improving the activity of **1b**. In addition, the polymer immobilized metallocene catalyst **1b** is soluble in toluene and its catalytic mechanism is similar to **1a**. Work is now in progress to further investigate the influence of the behavior of the polymer chain on the activity of the polymer immobilized metallocene catalyst.

The PE produced by **1b** (*t* = 25 °C, [Al]/[Zr] = 2750) was characterized by DSC and GPC. The DSC results (T_m = 130.1 °C, T_c = 115.0 °C) show that the PE has

high crystallinity (>70%), resulting from the highly linear structure of PE. The GPC data (*M*_w = 60 500, *M*_n = 12 800, *M*_w/*M*_n = 4.7) suggest that the active species formed in the polymer immobilized catalyst are not uniform. The origin of the behavior is not clear at present. Both metal species with different environment and access to the substrate can play a certain role.

5. Experimental

5.1. General procedures

All reactions and manipulations were carried out under purified argon using Schlenk-tube techniques. The use of dry solvents is necessary. The cyclopentadienyl sodium was prepared by literature procedure [14]. ZrCl₄ (Aldrich), ⁿBuLi (Aldrich, 1.6 M in C₆H₁₄), (CH₂=CHCH₂)CH₃SiCl₂ (Aldrich) were used as purchased without further purification. IR spectra were recorded on Bio-Rad FT-135 spectrometer. The ¹H-NMR was recorded in C₆D₆ at 25 °C on Unity-400 spectrometer. Elemental analyses were carried out on elemental Vario EL spectrometer.

5.2. Preparation of [(CH₂=CHCH₂)CH₃Si(C₅H₄)₂]ZrCl₂ (**1a**)

The reaction was initiated by the dropwise addition of 1.0 ml (6.88 mmol) of allyldichloromethylsilane into a 50-ml DME solution (–78 °C) containing 13.76 mmol of freshly prepared C₅H₅Na. The reaction mixture was then stirred at room temperature (r.t.) overnight. The reaction mixture was then cooled in EtOH/dry CO₂ slush bath to –78 °C and 8.60 ml (13.76 mmol) of a 1.6 M solution of ⁿBuLi in C₆H₁₄ was added dropwise. The mixture was then warmed to r.t. and stirred for 24 h. Finally the mixture was transferred to a DME solution of zirconium tetrachloride (1.604 g, 6.88 mmol) at r.t. and then was stirred for 48 h. The solvent was removed in vacuum and the residue was dissolved in C₆H₅CH₃.

Table 1
Ethylene polymerization for catalysts **1a** and **1b**

Entry	Polymerization conditions			Productivity (10 ⁻⁵ g PE/mol Zr h)	
	Temperature (°C)	[Al]/[Zr] (molar ratio)	[Zr] (M × 10 ⁻⁶)	Catalyst 1a	Catalyst 1b
1	25	1100	2.0	1.05	4.23
2	25	1650	2.0	1.65	4.80
3	25	2200	2.0	4.15	5.05
4	25	2750	2.0	1.50	8.74
5	25	3300	2.0	1.40	2.45
6 ^a	25	1500		3.73 [13a]	
7 ^b	25	200			1.72 [13b]

^a Cp₂ZrCl₂ as catalyst [13a].

^b Cp₂ZrCl₂ supported in the SiO₂ as catalyst [13b].

Filtration to remove Li salts and cooling the filtrate gave the crystals of the complex **1a** (colorless solid powder). Yield: 0.772 (30%); IR (KBr, cm^{-1}): 3105, 3091, 3068, 2997, 2967, 2899, 1626, 1400, 1369, 1360, 1323, 1261, 1170, 1156, 997, 926, 898; $^1\text{H-NMR}$ (C_6D_6): δ 6.89 (2H, t, $2\text{C}_5\text{H}_4\text{-}\beta\text{H}$), 6.85 (2H, t, $2\text{C}_5\text{H}_4\text{-}\beta\text{H}$), 5.71 (1H, m, $-\text{CH}=\text{}$), 5.67 (2H, t, $2\text{C}_5\text{H}_4\text{-}\alpha\text{H}$), 5.63 (2H, t, $2\text{C}_5\text{H}_4\text{-}\alpha\text{H}$), 5.02 (1H, m, $\text{CH}_2=\text{}$), 4.99 (1H, m, $\text{CH}_2=\text{}$), 1.77 (1H, d, $-\text{CH}_2-\text{}$), 1.75 (1H, d, $-\text{CH}_2-\text{}$), 0.24 (3H, s, SiCH_3). Anal. Calc. for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{SiZr}$: C, 44.88; H, 4.28. Found: C, 45.15; H, 4.60%.

5.3. X-ray crystal structure analysis for **1a** Section 6

Single crystals were sealed in thin-walled glass capillaries under an atmosphere of Ar. The intensity data of both compounds was collected with a Siemens P4 diffractometer using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$, graphite monochromator); the stability of the primary beam was controlled by monitoring three check reflections every 100 reflections. Corrections for Lp factors and for absorption based on ψ -scan technique were applied.

1a: $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{SiZr}$, Mr = 374.48, Dc = 1.612 g cm^{-3} , yellow prisma of the dimension $0.42 \times 0.38 \times 0.36 \text{ mm}$, Triclinic space group $P\bar{1}$, with lattice parameters $a = 7.7246(11)$, $b = 8.490(2)$, $c = 12.816(4) \text{ \AA}$, $\alpha = 102.70(2)$, $\beta = 94.27(2)$, $\gamma = 107.78(2)^\circ$ and $Z = 2$; unit cell volume $V = 771.6(3) \text{ \AA}^3$, absorption coefficient $\mu = 1.116 \text{ mm}^{-1}$, reflections collected: 3452, independent reflections: 2695 ($R_{\text{int}} = 0.0257$); structure solution with direct methods (SHELXTL PLUS (VMS)); refinement with 164 parameters converged at $R_1 = 0.0399$, and $wR_2 = 0.1026$ [$I > 2\delta(I)$]; Good-of-fit 1.089, max./min. residual electron density was $0.875/-0.598 \text{ e\AA}^{-3}$.

5.4. Preparation of the Polymer immobilized metallocene **1b**

The polymer immobilized metallocene catalyst **1b** was prepared by radical co-polymerization in $\text{C}_6\text{H}_5\text{CH}_3$ at 80°C for 12 h using AIBN as an initiator. Toluene (100 ml), styrene (10 ml), metallocene **1a** (2 mmol) were added into Schlenk tubes under vigorous stirring and the reaction mixture was then slowly warm to 80°C . The reaction began when initiator AIBN (0.5 g) was added. After evaporation of large part of solvent, C_6H_{14} was added to precipitate the polymer. The supernatant liquid was decanted and the polymer precipitate was washed with $\text{C}_6\text{H}_{14}/\text{C}_6\text{H}_5\text{CH}_3$ (3:1 V/V) mixture until forming the solid powder. After sufficient washing, the polymer precipitate was dried under vacuum at 40°C for 5 h. The dried polymer (7.3 mg Zr/g) was then ground into fine powder and stored under Ar_2 for future use.

5.5. Characterization of **1b**

The Zr content of the polymer immobilized metallocene catalyst was determined by ICP-AES using POEMS spectra of TJA Corporation. Molecular weights were determined by Gel Permeation Chromatograph using a Waters 410 instrument (solution in THF at 35°C).

5.6. Ethylene polymerization

Ethylene polymerization was performed in a 200-ml Schlenk-type glass reactor fitted with a mechanical stirrer. After heating and evacuating the reactor for about 50 min, ethylene, $\text{C}_6\text{H}_5\text{CH}_3$ (50 ml), MAO were led into the reactor sequentially. Polymerization started when the solution of catalyst was introduced. After reaction for 1 h, an acetic ethanol solution was quickly added to terminate the polymerization. The precipitated polymer was collected and washed with ethanol for several times and dried under vacuum at 40°C for 24 h.

5.7. Polymer analyses

M.p.s were determined by DSC with a Perkin-Elmer 7 series Thermal Analysis System. Molecular weight of polymers was determined by Gel Permeation Chromatograph using PL-GPC 220 of Polymer Laboratory in Changchun Institute of Applied Chemistry.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 173925 for compound **1a**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://ccdc.cam.ac.uk>).

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