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# Structure-stereospecificity relationships of propylene polymerization using substituted *ansa*-silylene(fluorenyl)(amido) titanium complexes

Ryo Tanaka [a], Chie Yanase [a], Zhengguo Cai [b], Yuushou Nakayama [a], Takeshi Shiono [a, *]

[a] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima, 739-8527, Japan

[b] State Key Lab of Chemical Fibers & Polymer Materials, College of Material Science & Engineering, Donghua University, Shanghai 201620, China

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ABSTRACT

*ansa*-Fluorenylamidotitanium complexes bearing various substituents on the nitrogen and fluorene (**2a-d**) were synthesized. The structures of the complexes were characterized by $^{1}H$ and $^{13}C$ NMR, and X-ray crystal analyses were performed for complexes **2a**, **2b** and **2d**. The coordination mode of the fluorenyl group to the metal center was changed from $\eta^3$ to $\eta^1$ when a bulky group was introduced on the nitrogen or 2,3-position of the fluorenyl ring. Syndiotactic-specificity of the catalyst for the propylene polymerization was reduced when bulky group was introduced on the nitrogen. Least-square fitting analysis of the steric pentad distributions revealed that the stereodefect was mainly formed by the chain migration without monomer insertion, which is accelerated by the $\eta^1$-coordination of the fluorenyl group.



## 1. Introduction

Constrained geometry catalysts (CGCs), a series of group 4 metal complexes having an *ansa*-monocyclopentadienylamido ligand, are widely accepted as catalysts of olefin polymerization with various copolymerization ability and stereospecificity since the first example was introduced from industry [1–4]. Among them, fluorenylamido-ligated titanium or zirconium complexes [5–21] are known as catalysts for the copolymerization of ethylene with α-olefins [9,10], α-olefins with styrene [11,12], and norbornene with α-olefins [13–15]. These high copolymerization abilities are ascribed to a $\eta^1$- or $\eta^3$-coordination of the fluorenyl group to the metal center, compared with a $\eta^5$-coordination of the cyclopentadienyl group. These catalysts conduct syndiotactic (*syn*)-specific polymerization of α-olefins because of their high regioselectivity and $C_s$-symmetry [16–21]. However, the qualitative analysis of the relationship between the structure and the stereospecificity has not been performed well.

We previously reported that the introduction of $^{t}$Bu groups on the 3,6-position of the fluorenyl ligand (**1b**) enhanced the *syn*-specificity of α-olefin polymerization compared with the original complex (**1a**) [19]. Razavi et al. also reported that the dichloro derivative of **1b** showed high *syn*-specificity for propylene polymerization [16,17]. However, the introduction of alkyl groups to the 2,3,6,7-position (**1c**) reduced the *syn*-specificity [21], as opposed to the corresponding zirconium complex which showed very high *syn*-specificity [18]. With these expertise of stereospecificity-structure relationships, we were motivated to investigate how the amido and fluorenyl groups affect the propylene polymerization ability of the fluorenylamidotitanium complex. Therefore, we designed new fluorenylamidotitanium complexes **2a-2d** with bulky *N*-alkyl group and/or 2,3-substituted fluorenyl ligand (Fig. 1). Herein, we investigated the relationships between propylene polymerization behavior and the structure of these complexes.

## 2. Experimental section

### 2.1. General

All manipulations were performed under nitrogen gas using standard Schlenk techniques. MMAO was gratefully donated by Tosoh-Finechem Co. Propylene was purchased from Takachiho Chemicals Co. and purified by passing it through dry and deoxygenation columns (DC-A4 and GC-RX, Nikka Seiko Co.). Dry toluene and $Et_2O$ were purchased from Kanto Chemical Co., Inc. and distilled over sodium metal before use. Hexane was dried over 4A molecular sieves overnight and degassed under nitrogen flow before use. Other chemicals were used as purchased. 9-

* Corresponding author.
*E-mail address:* tshiono@hiroshima-u.ac.jp (T. Shiono).

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(Chlorodimethylsilyl)fluorene, 1,1,4,4-tetramethyl-2,2,3,3-tetrahydrobenzo[*b*]fluorene and titanium complex **1a** were synthesized according to the literature [20,22]. NMR spectra were recorded by a Varian system500 spectrometer calibrated with residual non-deuterated solvent ($^1$H: $\delta = 7.26$ ppm ($CHCl_3$), 7.15 ppm ($C_6D_5H$)) or solvent ($^{13}$C: $\delta = 128.1$ ppm ($C_6D_6$)). High temperature NMR measurement of the polymer was performed with a JEOL-LA500 spectrometer at 130 °C using 1,1,2,2-tetrachloroethane-$d_2$ as a solvent and for the calibration ($^{13}$C: 74.7 ppm). Molecular weight of the polymer was determined by a Polymer Laboratories PL-GPC210 chromatograph at 140 °C using *o*-dichlorobenzene as an eluent. The calibration was performed by polystyrene standard. Polymer concentration in injecting solution was 1 mg/mL and injection volume was 0.2 mL. X-ray diffraction measurements were performed on a Rigaku R-AXIS RAPID system with Mo Kα radiation ($\lambda = 0.71069$ Å, $2\theta_{max} = 55°$, crystal-to-detector distance = 110 mm). The intensities were corrected for Lorentz and polarization effects. The structures were solved using a combination of direct methods (SHELXS-86) [23] and Fourier synthesis (DIRDIF94) [24], and refined by least-squares (SHELXL-97) [25] on $F_o$ [2]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed using riding models. Least square fitting for the nine stereopentad distributions of the obtained polypropylene (PP) was performed by Microsoft Excel 2010 Solver program.

### 2.2. Synthesis of titanium complexes

#### 2.2.1. Synthesis of adamantyl-substituted fluorenylamino ligand (**3a**)

$^n$BuLi (3.9 mL, 1.6 M solution in hexane, 6.4 mmol) was added dropwise to a solution of 1-adamantylamine (0.88 g, 5.8 mmol) in $Et_2O$ (40 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and the resulting solution was added dropwise to a solution of 9-(chlorodimethylsilyl)fluorene (1.5 g, 5.9 mmol) in $Et_2O$ (30 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature and the solvent was removed in vacuo. The remaining solid was extracted with hexane and the evaporation of the solvent gave yellowish oil of ligand **3a** (2.0 g, 91%). $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 7.82$ (m, 2H), 7.69–7.71 (m, 2H), 7.31 (m,4H), 3.82 (s, 1H), 1.91 (s, 3H), 1.47–1.57 (m, 12H), 0.57 (s, 1H), −0.05 (s, 6H).

#### 2.2.2. Synthesis of 10-chlorodimethyl-1,1,4,4-tetramethyl-1,2,3,4-tetrahydrobenzo[b]fluorene

To a solution of 1,1,4,4-tetramethyl-2,2,3,3-tetrahydrobenzo[*b*]fluorene (2.2 g, 7.9 mmol) in $Et_2O$ (25 mL) was added dropwise $^n$BuLi (5.3 mL, 1.6 M solution in hexane, 8.7 mmol) at 0 °C. After stirring for 4 h at room temperature, the supernatant liquid was removed and the remaining lithium salt was suspended in hexane (25 mL). The suspension was added to a solution of dichlorodimethylsilane (4.7 mL, 40 mmol) in hexane at −78 °C. The resulting mixture was stirred overnight at room temperature and the solvent was removed in vacuo. The solid was extracted with hexane and evapolation of the solvent gave yellowish oil of 10-chlorodimethyl-1,1,4,4-tetramethyl-1,2,3,4-tetrahydrobenzo[*b*]fluorene (2.7 g, 91%). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta = 7.82$ (d, 1H, $J = 10$ Hz), 7.76 (s, 1H), 7.62 (d, 1H, $J = 10$ Hz), 7.57 (s, 1H), 7.36 (dd, 1H, $J = 10$ Hz), 7.27 (m, 1H), 4.00 (s, 1H), 1.74 (s, 4H), 1.33–1.37 (m, 12H), 0.20 (s, 3H), 0.12 (s, 3H).

#### 2.2.3. Synthesis of adamantyl-substituted tetrahydrobenzo[b] fluorenylamino ligand (**3b**)

$^n$BuLi (3.4 mL, 1.6 M solution in hexane, 5.5 mmol) was added dropwise to a solution of cumylamine (0.76 g, 5.0 mmol) in $Et_2O$ (40 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and the solution was added dropwise to a solution of 10-chlorodimethyl-1,1,4,4-tetramethyl-1,2,3,4-tetrahydrobenzo[*b*]fluorene (1.6 g, 4.2 mmol) in $Et_2O$ (30 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature and the solvent was removed in vacuo. The remaining solid was extracted with hexane and the evaporation of the solvent gave yellowish oil of ligand **3b** (1.8 g, 87%). $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 7.98$ (s, 1H), 7.85 (d, 1H, $J = 7$ Hz), 7.75 (s, 1H), 7.71 (d, 1H, $J = 9$ Hz), 7.32 (m, 2H), 3.79 (s, 1H), 1.90 (s, 3H), 1,72 (m, 4H), 1.24–1.56 (m, 24H) 0.46 (s, 1H), 0.09 (s, 3H), 0.03 (s, 3H).

#### 2.2.4. Synthesis of cumyl-substituted fluorenylamino ligand (**3c**)

$^n$BuLi (3.8 mL, 1.6 M solution in hexane, 6.0 mmol) was added dropwise to a solution of cumylamine (0.86 mL, 6.0 mmol) in $Et_2O$ (20 mL) at 0 °C. The mixture was stirred for 4 h at room temperature and the resulting solution was added dropwise to a solution of 9-(chlorodimethylsilyl)fluorene (1.5 g, 6.0 mmol) in $Et_2O$ (20 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature and the solvent was removed in vacuo. The remaining solid was extracted with hexane (20 mL x3) and the evaporation of the solvent gave yellowish oil of ligand **3c** (2.1 g, 98%). $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 7.65$ (dd, 2H, $J = 8$ Hz, 1 Hz), 7.40 (dd, 2H, J = 8 Hz, 1 Hz), 7.17-6.89 (brm, 9H), 3.57 (s, 1H), 1.09 (s, 6H), 0.56 (brs, 1H), −0.28 (s, 6H).

#### 2.2.5. Synthesis of cumyl-substituted tetrahydrobenzo[b] fluorenylamino ligand (**3d**)

$^n$BuLi (7.1 mL, 1.6 M solution in hexane, 12 mmol) was added dropwise to a solution of cumylamine (1.6 mL, 11 mmol) in $Et_2O$ (40 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and the solution was added dropwise to a solution of 10-chlorodimethyl-1,1,4,4-tetramethyl-1,2,3,4-tetrahydrobenzo[*b*]fluorene (4.2 g, 11 mmol) in $Et_2O$ (40 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature and the solvent was removed in vacuo. The remaining solid was extracted with hexane and the evaporation of the solvent gave yellowish oil of ligand **3d** (5.0 g, 97%). $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 7.96$ (s, 1H), 7.83 (d, 1H, $J = 9$ Hz), 7,65 (s, 1H), 7.57 (d, 1H, $J = 9$ Hz), 7.45-7.07 (m, 7H), 3.71 (s, 1H), 1.72 (s, 4H), 1.24–1.42 (m, 18H) 0.75 (s, 1H), −0.04 (s, 3H), −0.07 (s, 3H).

#### 2.2.6. Synthesis of fluorenyl-adamantylamido titanium complex (**2a**)

To a solution of **3a** (2.0 g, 5.3 mmol) in $Et_2O$ (30 mL) was slowly added excess MeLi (22 mL, 1.14 M solution in $Et_2O$, 25 mmol) at room temperature and the mixture was stirred for 4 h. The solution of dilithium species was added to a solution of $TiCl_4$ (0.57 mL, 5.3 mmol) in hexane (40 mL) at room temperature, and the resulting red solution was stirred for 1 h. After the solvent was removed, the residue was extracted with hexane (100 mL) and MeMgBr (4.2 mL, 3.0 M solution in $Et_2O$, 13 mmol) was added to the solution. After the resulting brown suspension was stirred for 1 h at room temperature, the solvent was removed and the residue was extracted with hexane (120 mL). The solution was concentrated to approximately 20 mL and cooled overnight at −30 °C to give **2a** as orange crystals (0.87 g, 33%). $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 7.84$ (d, 2H, $J = 9$ Hz), 7.70 (d, 2H, $J = 9$ Hz), 7.24 (dd, 2H, $J = 9$ Hz), 7.13 (dd, 2H, $J = 9$ Hz), 2.00 (s, 6H), 1.97 (s, 3H), 1.54 (s, 6H), 0.72 (s, 6H), 0.00 (s, 6H), $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = 135.1, 129.3, 124.9, 123.8, 82.1, 60.2, 56.9, 47.8, 36.6, 30.8, 6.4$ (2 peaks in the aromatic region should be overlapped with solvent peaks). Anal. Calc. for $C_{27}H_{35}NSiTi$: C, 72.14; H, 7.85; N, 3.12. Found: C, 71.73; H, 7.45; N, 3.28.