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Highly Active Copolymerization of Ethylene and Dicyclopentadiene with [(η^1-t-BuN)SiMe$_2$(η^1-C$_{29}$H$_{36}$)]TiMe$_2$(THF) Complex

Kei Nishii,[1] Shigetaka Hayano,[1] Yasuo Tsunogae,*[1] Zhengguo Cai,[2] Yuushou Nakayama,[2] and Takeshi Shiono*[2]
[1] *R&D Center, Zeon Corporation, 1-2-1 Yako, Kawasaki-ku, Kawasaki 210-9507*
[2] *Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527*

(Received February 26, 2008; CL-080218; E-mail: tsunogae@zeon.co.jp)

A new *ansa*-fluorenylamidodimethyltitanium complex **1** was synthesized and applied for ethylene–dicyclopentadiene copolymerization using modified methylaluminoxane (MMAO) as a cocatalyst at 50 °C. **1**–MMAO exhibited the remarkable catalytic activity for the copolymerization and gave a copolymer with high glass-transition temperature of 191 °C.

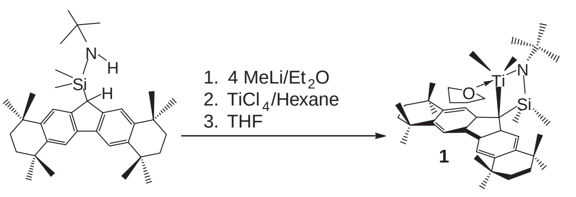
Single-site catalysts[1] are effective catalysts for the copolymerization of α-olefins and cycloolefins.[2] Cycloolefin copolymers provide a new class of amorphous plastics with a range of glass-transition temperature (T_g), good thermal stability, high transparency, and low water absorption. Recently, some of single-site Group 3 and 4 catalysts were found to be highly active for the copolymerization of ethylene with norbornene (NB).[3,4] A high activity and a control of the NB contents for the copolymerization of ethylene with NB have been achieved by using various catalyst systems.[2a] However, only a few catalysts can show a high activity and a control of the dicyclopentadiene (DCP) contents for the copolymerization of ethylene with DCP. Hou and co-workers reported that di(alkyl)mono(cyclopentadienyl)scandium activated with [X][B(C$_6$F$_5$)$_4$] (X = Ph$_3$C or PhNMe$_2$H) showed the high activity for the copolymerization of α-olefins with DCP.[5] Tardif and Kaita recently reported that (2-R-Ind)$_2$ScN(SiMe$_3$)$_2$ (R = H or alkyl group) combined with [Ph$_3$C][B(C$_6$F$_5$)$_4$]/(i-Bu)$_2$AlH conducted homo- and copolymerization of DCP with ethylene.[6] On the other hand, Miller and co-workers recently reported that sterically expanded *ansa*-fluorenylamidodichlorozirconium complex, [(η^1-t-BuN)SiMe$_2$(η^1-C$_{29}$H$_{36}$)]ZrCl$_2$(Et$_2$O), activated with MAO showed very high activity for the polymerization and copolymerization of α-olefins.[7a,7b]

We have previously reported that *ansa*-fluorenylamidodimethyltitanium complexes in the presence of suitable activator conducted homo- and copolymerization of NB[8a,8b] with ethylene[8c–8e] or propylene[8f] and gave the random or block[9] copolymers with high T_g value. In this paper, we report the synthesis of [(η^1-t-BuN)SiMe$_2$(η^1-C$_{29}$H$_{36}$)]TiMe$_2$(THF) (**1**) and the preliminary results of ethylene–DCP copolymerization with **1**–MMAO.

The synthetic route of **1** is summarized in Scheme 1. The ligand of t-BuNHSiMe$_2$(C$_{29}$H$_{37}$) was prepared according to the literature.[7a] The complexation of the ligand and TiCl$_4$ was conducted by the method reported by Resconi and co-workers[10a] and our previous paper[10b] to directly obtain the corresponding dimethyl complex, and the complex was isolated as dark reddish-orange single crystals.[11,12] The X-ray structure of **1** with crystal solvent[13] is shown in Figure 1. The Ti atom of **1** is in a trigonal-bipyramidal environment and THF ligand located in the axial position.[7a,7c] The bond lengths: Ti(1)–C(21), –C(1), and –C(2) of [(η^1-t-BuN)SiMe$_2$(η^3-C$_{13}$H$_8$)]TiMe$_2$ (**2**), in which the C$_{13}$H$_8$ group coordinates to the Ti atom with a η^3-manner, are 2.415(3), 2.253(3), and 2.418(3) Å, respectively.[10b] On the other hand, the Ti(1)–C(2) and Ti(1)–C(21) lengths of **1** are 3.050(2) and 2.845(2) Å. Assignments from the literature place the threshold for Ti–C bonding between 2.105 and 2.557 Å.[10b] Thus, these results suggest that the C$_{29}$H$_{36}$ ligand in **1** coordinates to the Ti atom in a η^1-manner.

Polymerization of DCP was carried out at 50 °C with **1**–MMAO, and the results are summarized in Runs 1 and 2 of Table 1. In the absence of ethylene, we observed DCP homopolymerzation in toluene at 50 °C, although all runs were polymerized in a low activity. We have recently reported that **2**–dMAO[14] conducted the homopolymerization of DCP at 40 °C (activity = 3-kg polymer/[mol Ti·h], $M_n = 1.9 \times 10^3$, $M_w/M_n = 1.4$).[8e] **1**–MMAO showed more than 4 times higher activity of **2**–dMAO. GPC analysis of the poly(DCP) obtained with **1**–MMAO revealed bimodal molecular weight distributions, thus indicating the presence of at least two catalytically active species (Table 1, Run 2).

Copolymerization of ethylene and DCP was carried out at 50 °C with **1**–MMAO (Scheme 2). The results are summarized



Scheme 1. Synthesis of complex **1**.

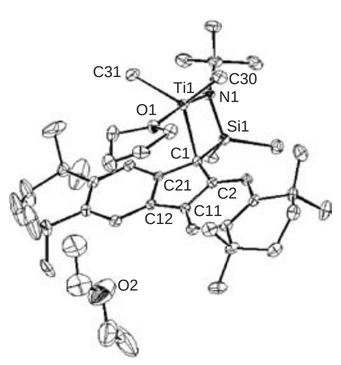
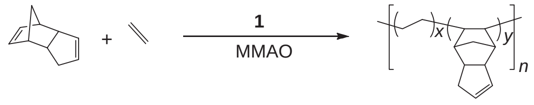


Figure 1. ORTEP drawing of **1**·OEt$_2$ (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)–C(1) = 2.198(2); Ti(1)–N(1) = 1.9149(19); Ti(1)–O(1) = 2.1936(17); C(1)–Ti(1)–N(1) = 80.60(9); C(1)–Ti(1)–O(1) = 89.49(7); N(1)–Si(1)–C(1) = 95.36(10); N(1)–Ti(1)–O(1) = 169.66(9).

Table 1. Copolymerization of ethylene and DCP with **1**–MMAO^{a}

Run	Cat. /μmol	DCP /mmol	t /min	Yield /g	Activity^{b}	M_n^{c} ($\times 10^4$)	M_w/M_n^{c}	DCP cont.^{d} /mol %	T_g^{e} /°C
1^{f}	**1**/2	40	120	trace					
2^{f}	**1**/20	40	120	0.50	13	36.9, 1.1	1.45, 2.75	100	n.d.^{g}
3	**1**/2	40	4	1.32	9900	18.7	2.55	30.7	132
4	**1**/2	50	5	2.05	12300	18.1	2.97	49.3	180
5	**1**/20	40	3	4.70	4700	6.9	2.76	54.2	191
6	**2**/20	40	3	1.63^{h}	1600	2.2	6.15	50.0	190

^{a}Polymerization conditions: solvent = toluene; total volume = 50 mL; MMAO = 2.0 mmol (Runs 1, 3, and 4); MMAO = 8.0 mmol (Runs 2, 5, and 6); Ethylene = 1 atm; $T = 50$ °C. ^{b}Activity in kg polymer/(mol Ti·h). ^{c}Determined by GPC in $CHCl_3$ at 40 °C against polystyrene standard. ^{d}DCP content, determined by ^{1}H NMR. ^{e}Determined by DSC. ^{f}Ethylene = 0 atm; total volume = 15 mL. ^{g}n.d. = not determined. ^{h}Toluene soluble portion: 1.63 g; toluene insoluble portion: 2.92 g.



Scheme 2. Copolymerization of ethylene and DCP with **1**.

in Runs 3, 4, and 5 of Table 1. For comparison, the result of **2**–MMAO is also shown in Run 6 of Table 1. Both systems showed the extremely high activity and produced a large amount of copolymer in a few minutes to stop the stirring. The ethylene–DCP copolymers produced with **1** were soluble in $CHCl_3$. On the other hand, ethylene–DCP copolymer produced with **2** contained $CHCl_3$-insoluble portion. Solvent fractionation experiment revealed a relatively large amount of homopolymer impurity in the resultant copolymer produced with **2**.[15] This distinction between **1** and **2** could be ascribed to the structure of complexes. We assume that **1** provides more open nature of active species due to the η^1 coordination between Ti and $C_{29}H_{36}$ ligand that favors easy access of DCP to propagate. GPC analysis of the copolymer (Table 1, Run 6) indicated a broad molecular weight distribution ($M_w/M_n = 6.2$), which suggested a partial thermal degradation of the molecular catalyst or a side reaction with alkylaluminium species during copolymerization. In addition, the incorporation of DCP in the copolymer produced was relatively high (50 mol %) and showed the high T_g value at 190 °C. The catalytic activity of **1** increased as DCP monomer feed was increased in the range of 40–50 mmol. The DCP contents and T_g value of the resulting copolymers also increased as the DCP monomer feed was raised. The highest catalytic activity of 12,300-kg polymer/(mol Ti·h) was achieved with a DCP incorporation of ca. 49.3 mol % (Table 1, Run 4). In the DEPT135° spectrum, although the clear assignment of each peak was not accomplished, the presence of bridged methylene carbon (C10)[12] indicates that the structure of copolymer obtained (Table 1, Run 5) is completely different from that of alternating copolymer obtained by scandium complex.[5a] All of the copolymer products were amorphous with T_g values in the wide range of 132–191 °C.

In summary, we have reported a synthesis of **1** from the $C_{29}H_{36}$ ligand in a facile method. A highly active copolymerization of ethylene and DCP with titanocene–MMAO system has been achieved for the first time. Extremely high T_g value and DCP content (DCP = 54 mol %) have been accomplished with this new catalytic system. Further studies into the mechanistic details of this system and the polymerization of other α-olefins are under progress.

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11 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC 678132.

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

13 **1** cocrystallized with solvent, packing one diethyl ether molecule into the cleft of each $C_{29}H_{36}$ ligand.

14 dMAO: Me_3Al-free dried methylaluminoxane.

15 The ethylene–DCP copolymer was soluble in toluene, whereas homopolyethylene was insoluble.