

Synthesis of Hydroxy-functionalized Ultrahigh Molecular Weight Polyethylene Using Fluorenylamidotitanium Complex

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Electronic Supplementary Information

Abstract Copolymerizations of ethylene and 1-dodecene were conducted with a series of *ansa*-fluorenylamidodimethyltitanium complexes, [*t*-BuNSiMe₂Flu]TiMe₂ (**1a**), [*t*-BuNSiMe₂(2,7-^tBu₂Flu)]TiMe₂ (**1b**), and [(1-adamantyl)NSiMe₂(2,7-^tBu₂Flu)]TiMe₂ (**1c**) activated by modified methylaluminoxane. The activity increased by the introduction of the alkyl groups on the fluorenyl and amido ligands, and **1c** produced the highest molecular weight copolymers. Complex **1c** also promoted copolymerization of ethylene and ^tBu₃Al protected 10-undecen-1-ol with high activity (~2000 kg·mol⁻¹·h⁻¹), affording hydroxy-functionalized ultrahigh molecular weight polyethylene. The hydroxy content of the copolymers obtained was controllable by changing comonomer feed ratio. The introduction of a small amount of hydroxy group can alter the surface properties of polyethylene.

Keywords Single-site catalyst; Ethylene; Polar monomer; Copolymerization; Hydroxy-functionalized polyethylene

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INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) is currently used in a variety of applications as a most important engineering polymer due to its outstanding performance, such as high moduli and strength, toughness, light weight, and excellent chemical resistance^[1]. The introduction of polar functionalized side groups into polyolefin has been expected as a surface modifier to improve its adhesion and compatibility with polar materials^[2, 3]. In addition, the introduction of polar group can also improve mechanical properties of polyolefins. For example, the hydroxy-functionalized isotactic polypropylene showed particular mechanical properties such as a considerably higher modulus and tensile strength in comparison with a pure polypropylene^[4, 5].

The recent developments of the single-site catalysts allow us to conduct copolymerizations of olefin with polar functional monomers via coordination-insertion polymerization to afford functionalized polyolefins. Late transition metal catalysts, which are more tolerant to the functional groups, have been developed to the direct copolymerization of functional monomers with ethylene, although the resulting functionalized polyethylenes have low

molecular weight or branching microstructure^[6–9]. Early transition metal catalysts were also applied for the synthesis of functionalized polyethylene, even though they require more complicated condition to prevent catalyst poisoning. Thus, by adopting allyl monomers with protected polar group, the synthesis of functionalized linear polyethylene with control of the polar monomer content has been achieved^[10–23]. However, most of the copolymerization showed poor copolymerization activity in comparison with corresponding homopolymerization of ethylene. Only few early transition catalysts realized copolymerization of ethylene and allyl comonomer with protected polar group with high activity and good comonomer content^[24–27]. Despite these achievements, the synthesis of functionalized UHMWPE with control of the incorporation of polar group has been far from success.

Herein, we report the synthesis of hydroxy-functionalized UHMWPE with control of the molecular weight and the content of hydroxy group by means of the copolymerization of ethylene and 10-undecen-1-ol (U-OH) complexed by ^tBu₃Al (U-OAl^tBu₂) using a series of *ansa*-dimethylsilylene(fluorenyl)(amido)dimethyltitanium complexes **1** (Chart 1), which is efficient for the living homo- and copolymerization of propylene and norbornene with high activity and good copolymerization ability^[28, 29].

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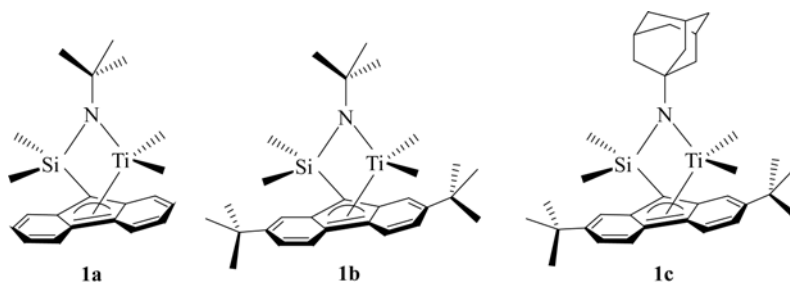


Chart 1 The chemical structures of *ansa*-fluorenylamidodimethyltitanium complexes

EXPERIMENTAL

Materials

All operations were performed under nitrogen gas using standard Schlenk techniques or glove-box. All solvents were purified by PS-MD-5 (INNOVATIVE TECHNOLOGY) solvent purification system. Research grade ethylene was purified by passing them through dehydration column of ZHD-20 and deoxidation column of ZHD-20A before use. 1-Dodecene and 10-undecen-1-ol were distilled over calcium hydride before use. MMAO-3A in toluene solution was donated by Tosoh-Finechem Co. $i\text{Bu}_3\text{Al}$ -protected 10-undecen-1-ol was prepared according to the literature procedure^[16]. The titanium complexes **1a**, **1b**, and **1c** were prepared according to the method reported previously^[30, 31].

General Methods

Molecular weight and molecular weight distribution of polymers obtained were determined by a polymer laboratory PL GPC-220 equipped with a triple-detection array consisting of a differential refractive index (DRI) detector, a two-angle (45, 90) light scattering (LS) detector at a laser wavelength of 658 nm and a four-bridge capillary viscosity detector. This system included one guard column (PL# 1110–1120) and three 30 cm columns (PLgel 10 μm MIXED-B 7.5 $\times$ 300 mm). Polymer characterization was carried out at 150 °C using 1,2,4-trichlorobenzene as eluent and calibrated by polystyrene standards.

Nuclear magnetic resonance (NMR) spectra of copolymers were recorded on a Bruker-600 (600 MHz) spectrometer at 110 °C using 1,1,2,2-tetrachloroethane- d_2 as a solvent and the central peak of the solvent (74.47{5.91} ppm) was used as an internal reference.

Differential scanning calorimetry (DSC) analyses were performed on a TA differential scanning calorimeter Q2000

and the DSC curves of samples were recorded under nitrogen flow at a heating rate of 10 K $\cdot\text{min}^{-1}$ from 40 °C to 180 °C.

Copolymerization Procedure

High pressure (co)polymerization reactions were performed in a 1 L Parr Instrument Company autoclave. At first, the reactor was charged with prescribed amounts of hexane, modified methylaluminoxane/2,6-isopropyl-phenol (MMAO/BHT) and corresponding comonomer under nitrogen. Then the mixture was stirred for 10 min at room temperature. Polymerization was initiated by introduction of 1 mL solution of the Ti complex (10 μmol) in hexane under desired ethylene pressure. The polymerization was terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 80 °C until a constant weigh was reached.

RESULTS AND DISCUSSION

We have recently demonstrated the substituent effects of alkyl group on the fluorenyl and amido ligands in propylene polymerization with fluorenylamidotitanium complex (**1a**). The introduction of *tert*-butyl group on the fluorenyl ligand (**1b**) improved the activity (up to $\sim 900 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) with an Al/Ti ratio of 200^[31]. Moreover, the introduction of electron-donating adamantyl substituent on the amido ligand activated by MMAO and 2,6-di-*tert*-butyl-4-methyl phenol (BHT) exhibited remarkably high activity ($\sim 3.1 \times 10^4 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) even with a very low amount of MMAO (Al/Ti molar ratio of 20)^[30]. Thus, we conducted the copolymerization of ethylene and 1-dodecene with complexes **1a**, **1b**, and **1c** in the presence of MMAO/BHT to investigate the ligand substituent effects. The copolymerization results are summarized in Table 1. For comparison, the result of ethylene homopolymerization with **1c** is also shown in Table 1 (entry 7).

Table 1 Copolymerization of ethylene with 1-dodecene by using different titanium complexes^a

Entry	Catalyst	Al/Ti	Yield (g)	Activity ($\text{kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$)	$M_w^b \times 10^{-4}$	M_w/M_n^b	T_m^c (°C)	Incorporation ^d (mol%)
1	1a	1000	14.60	1460	68.3	2.07	127.1	—
2	1b	1000	22.12	2210	78.0	1.77	127.9	—
3	1c	1000	21.91	2200	216.4	1.68	127.6	1.38
4	1c	500	8.38	840	157.7	1.67	—	—
5	1c	800	10.20	1020	151.6	1.55	—	—
6	1c	1500	21.49	2150	222.6	1.84	—	—
7 ^e	1c	1000	20.72	2070	93.5	1.67	134.3	—

^a Polymerization conditions: Ti = 10 μmol , Al/Ti = 1000, ethylene = 0.5 MPa, 1-dodecene = 3.4 mmol, solvent = hexane, total volume = 500 mL, temperature = 0 °C, time = 60 min; ^b Weight-average molecular weight and molecular weight distribution were measured with light scattering (LS) detector in triple-detection GPC measurements; ^c Determined by DSC; ^d Determined by ^{13}C -NMR; ^e Homopolymerization of ethylene

The copolymerization activities of **1b** and **1c** were comparable with that of the homopolymerization of ethylene ($\sim 2000 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$), and their values are higher than that of **1a**, indicating that the alkyl substituents on the fluorenyl and amido ligands were also efficient for the improvement of the activity in the copolymerization of ethylene and 1-dodecene. Comparatively narrow molecular weight distributions of resulting polymers with unimodal GPC curve (Fig. 1) testified the formation of the uniform copolymers in each catalyst system. On the other hand, **1c** gave ultrahigh molecular weight copolymer with the weight average molecular weight (M_w) value of 2.16×10^6 .

The microstructure of the copolymer obtained with **1c** was characterized by ^{13}C -NMR spectroscopy (Fig. 2). The resonances of the methylene carbons and the isolated dodecene signal indicated the production of poly(ethylene-co-dodecene), and the 1-dodecene content was determined according to the published literatures to be 1.38 mol%. The thermal properties of the copolymers were then investigated by DSC, and the results are shown in Table 1. All the copolymers showed lower melting point (T_m) than polyethylene, suggesting that the comonomer was incorporated to the main chain of polyethylene in each catalyst system.

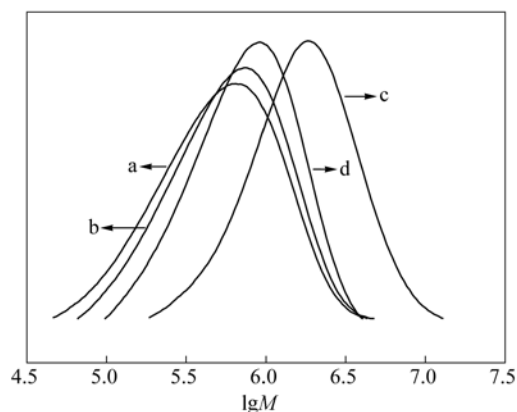


Fig. 1 GPC curves of poly(ethylene-co-dodecene)s and polyethylene obtained with complexes **1a**, **1b**, and **1c**: (a) entry 1, (b) entry 2, (c) entry 3 and (d) entry 7 in Table 1

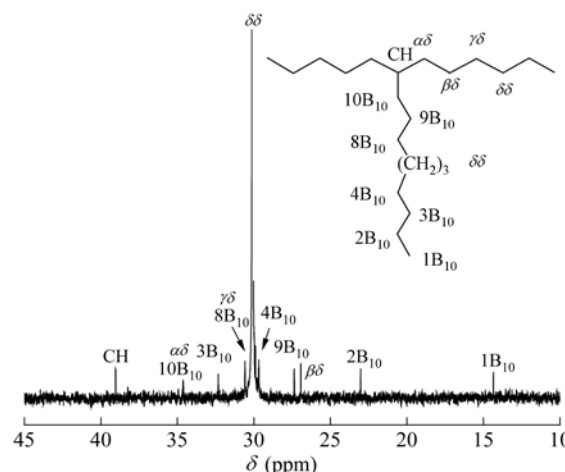


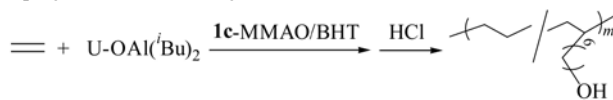
Fig. 2 ^{13}C -NMR spectrum of poly(ethylene-co-dodecene) obtained with complex **1c** (entry 3, Table 1)

The copolymerization activity of **1c** increased by enhancing the Al/Ti ratio from 500 to 1000 and reached constant at the Al/Ti molar ratio of 1000–1500, affording high molecular weight copolymers with narrow molecular weight distributions regardless of Al/Ti ratio employed.

Based on these results of ethylene-dodecene copolymerization, we conducted copolymerization of ethylene and U-OAl(*i*Bu)₂ using **1c** with an Al/Ti ratio of 1000 by changing comonomer feed ratio. The results are shown in Table 2. The copolymerization activity increased with the increase of the ethylene pressure. Under 1.1 MPa, the copolymerization proceeded so fast that the stirring was stopped within 12 min, and resulting polymer was insoluble in GPC solvent (1,2,4-trichlorobenzene) at 150 °C, probably due to the extremely high molecular weight. We therefore continued copolymerization under 0.5 MPa by increasing comonomer concentration. Each catalyst system showed almost the same activity to give high molecular weight copolymers ($> 1.3 \times 10^6$) with unimodal molecular weight distribution regardless of the comonomer concentration.

The contents of the hydroxy group in the copolymers were determined from the integral ratio of $-\text{CH}_2\text{OH}$ methylene proton at 3.63 ppm in ^1H -NMR spectra (Fig. 3) according to

Table 2 Copolymerization of ethylene and 10-undecene-1-ol with **1c**-MMAO/BHT^a



Entry	Ethylene (MPa)	Comonomer (mmol)	Yield (g)	Activity ($\text{kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$)	$M_w^b \times 10^{-4}$	M_w/M_n^b	Incorporation ^c (mol%)	T_m^d (°C)
1	0.1	4.6	11.82	1180	87.2	1.89	—	—
2	0.3	4.6	13.25	1330	102.9	1.62	—	—
3	0.5	4.6	18.75	1880	114.0	1.40	0.5	124.0
4	0.8	4.6	21.63	2160	157.4	1.42	—	—
5 ^e	1.1	4.6	27.15	9050	— ^f	— ^f	—	—
6	0.5	9.2	19.12	1910	145.6	1.78	1.1	121.7
7	0.5	13.8	20.80	2080	186.5	1.87	1.3	117.8
8	0.5	18.4	19.02	1900	136.6	1.44	1.6	116.8

^a Polymerization conditions: Ti = 10 μmol , Al/Ti = 1000, solvent = hexane, total volume = 500 mL, temperature = 0 °C, time = 60 min; ^b Weight-average molecular weight and molecular weight distribution were measured with light scattering (LS) detector in triple-detection GPC measurements; ^c Determined by ^1H -NMR; ^d Determined by DSC; ^e Polymerization time = 18 min; ^f Insoluble in 1,2,4-trichlorobenzene at 150 °C

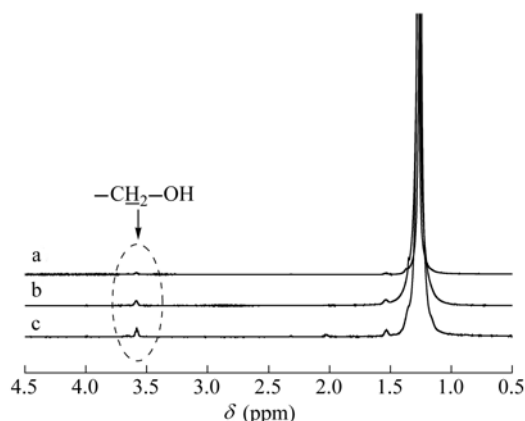


Fig. 3 ^1H -NMR spectra of poly(ethylene-co-10-undecene-1-ol) obtained with complex **1c**: (a) entry 6, (b) entry 7, (c) entry 8 in Table 2

the literatures^[27]. The content increased with the increase of the comonomer feed ratio and reached 1.6 mol% with the highest comonomer concentration (18.4 mmol) in the feed.

The structure of the ethylene/U-OH copolymer was also characterized by ^{13}C -NMR (Fig. 4). The additional signals at 63.46, 33.43, and 26.30 ppm were assigned for α -, β -, and γ -carbon of the hydroxy group labeled as 1B_9 , 2B_9 , and 3B_9 , respectively. The signals of CH , $\alpha\delta$, $\gamma\delta$ and $\beta\delta$ carbons at 38.14, 34.52, 30.49, and 27.26 ppm without any $\alpha\alpha$ carbon signal indicated the absence of U-OH dyad in the copolymer chain.

The thermal properties of the copolymers determined by DSC are also shown in Table 2. The T_m values were lower than that of polyethylene and decreased with the increase of the hydroxy content in the copolymer chain (Fig. S1, in the electronic supplementary information, ESI). In addition, the $-\text{OH}$ group peak at 3355.2 cm^{-1} in the FTIR spectra (Fig. S2, in ESI) and lower thermal decomposition temperature of the copolymer in comparison with polypropylene (Fig. S3, in ESI) also demonstrated the existence of hydroxyl. These results indicated the formation of the hydroxy-functionalized polyethylene.

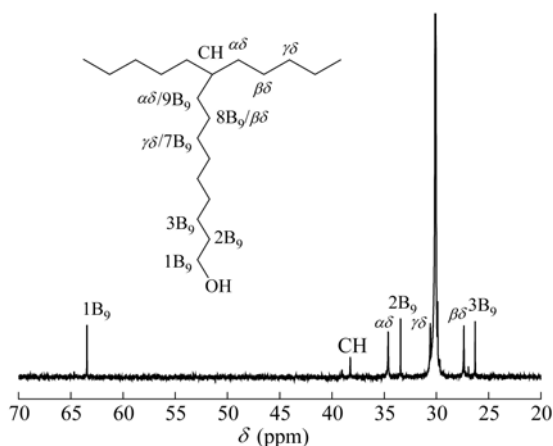


Fig. 4 ^{13}C -NMR spectrum of poly(ethylene-co-10-undecene-1-ol) obtained with complex **1c** (entry 8, Table 2)

We therefore determined the water contact angle (WCA) of the hydroxy-functionalized polyethylene films to evaluate the surface properties of these copolymers (Fig. 5). The WCA of non-functional polyethylene is 105° . When the hydroxy incorporation was 0.5 mol% and 1.1 mol%, the WCA values were determined to be 95° and 90° , respectively. The result testified that a small amount of hydroxy group can dramatically alter the surface properties of polyethylene.

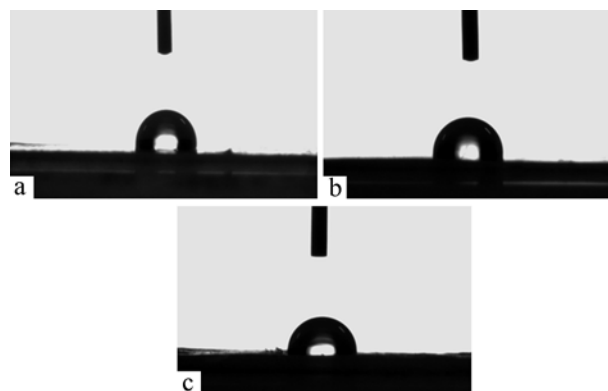


Fig. 5 The water contact angles for polyethylene and hydroxy-functional polyethylenes: (a) entry 7, Table 1; (b) entry 3, Table 2; (c) entry 6, Table 2

CONCLUSIONS

In conclusion, the results of the copolymerizations of ethylene and 1-dodecene with $[\text{t-BuNSiMe}_2\text{Flu}]\text{TiMe}_2$ (**1a**), $[\text{t-BuNSiMe}_2(2,7\text{-tBu}_2\text{Flu})]\text{TiMe}_2$ (**1b**) and $[(1\text{-adamantyl})\text{NSiMe}_2(2,7\text{-tBu}_2\text{Flu})]\text{TiMe}_2$ (**1c**) activated by MMAO/BHT indicated that the introduction of electron-donating alkyl groups on the fluorenyl or amido ligands improved activity (up to $\sim 2200\text{ kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$). Complex **1c** gave ultrahigh molecular weight copolymers with narrow molecular weight distribution. Complex **1c** was applied for the copolymerization of ethylene with 10-undecene-1-ol. The system showed high copolymerization activity ($\sim 2000\text{ kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) to produce hydroxy-functionalized ultrahigh molecular weight copolymers. The hydroxy content of the copolymer obtained was controllable by changing comonomer feed ratio. The WCA value decreased with increasing the hydroxy content in the copolymer.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-018-2046-6>.

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