

Titanium Complex Bearing 8-Anilino-1-naphthalenesulfonate Ligand: Synthesis and Catalytic Behavior Toward Ethylene (co-)Polymerization

Hao Zhang,¹ He-Xin Zhang,² Xiao-Ping Cai,³ Xue-Quan Zhang²

¹College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

²Changchun Institute of Applied Chemistry, the Chinese Academy of Sciences, Changchun 130022, People's Republic of China

³Jilin Petrochemical Co. Ltd., PetroChina, Jilin 132021, People's Republic of China

Correspondence to: X.-P. Cai and X.-Q. Zhang (E-mail: zhanghx_china@hotmail.com)

ABSTRACT: A novel titanium complex bearing 8-anilino-1-naphthalenesulfonic acid was synthesized. The effects of cocatalyst and reaction conditions on ethylene polymerization were studied. The synthesized titanium complex exhibited high polymerization activity in the presence of MAO cocatalyst. The synthesized titanium complex/MAO catalyst system showed a uniform active site and was very stable at high polymerization temperature. In addition, the copolymerization of ethylene and norbornene was investigated. With the introduction of norbornene, the catalyst activity slightly decreased with MAO as cocatalyst but increased with TEA as cocatalyst. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: metal-organic catalysts/organometallic; polyethylene (PE); copolymerization

Received 20 February 2012; accepted 6 May 2012; published online

DOI: 10.1002/app.38016

INTRODUCTION

Polymerization of olefins from soluble and well-defined transition-metal complexes is an ever-growing area.^{1,2} Recently, much attention has been paid to nonmetallocene catalysts, including early-,^{3–9} middle-,^{10,11} and late-transition-metal^{12–14} and lanthanide¹⁵ species incorporating noncyclopentadiene-based ligands. Especially, Group 4 nonmetallocene catalysts were used to study polymerization mechanisms, develop structure-property relationships, and prepare polymers with tailored microstructures and desired physical properties. Research on ligand-oriented catalyst design led to the discovery of remarkably active catalysts for olefin polymerization.^{16–21} For example, Group 4 complexes containing monoanionic ligands including amidinate,^{22–24} amide,^{25–29} and alkoxide,^{30,31} for example, were notable due to their high activity for olefin polymerization and unique ability to control polymer microstructures. These catalysts featured an ease of synthesis as a result of strong M–N or M–O bond formation from various chelating ligands.^{32–38} Thus, the catalytic behavior of these complex catalysts as well as the properties of the resultant polyolefins could be finely tuned by modifying the substituents on their ligands. In addition, Group 4 metal complexes supported by dianionic tridentate ligand were known to exhibit outstanding catalytic performance for olefin polymerization.³⁹ A particular example described titanium complexes con-

taining dianionic tridentate [ONS] ligand as efficient catalysts for ethylene polymerization.⁴⁰

Recently, sulfonate ligands have been more frequently used as catalyst supports,^{41,42} few examples of titanium catalyst featuring sulfonate ligand for olefin polymerization have been reported. We suggest that the introduction of anionic sulfonate ligand generally increases the electron density of the transition metal (compared to neutral ligand) and leads to facile formation of the corresponding cationic metal center. This active, cationic metal complex should favor the incorporation of monomer facilitating olefin polymerization. Therefore, the titanium complex bearing 8-anilino-1-naphthalenesulfonate ligand was synthesized and its catalytic behavior for ethylene (co-)polymerization was investigated.

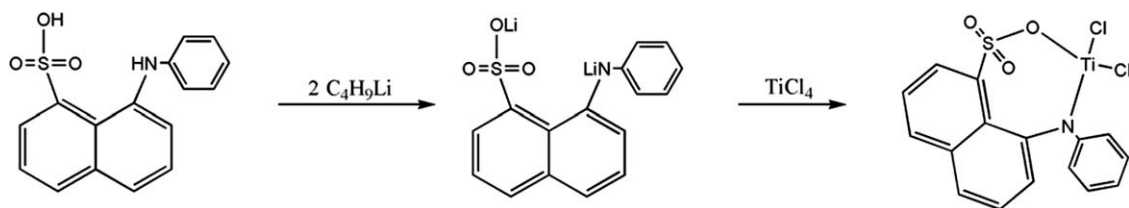
EXPERIMENTAL

General Procedure and Materials

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry nitrogen or argon atmosphere by using standard Schlenk techniques. THF and toluene were distilled from sodium/benzophenone under nitrogen prior to use. Elemental analysis was recorded on an elemental Vario EL spectrometer. The NMR data of the ligand and complex used were obtained on a Bruker 300 MHz spectrometer (300 MHz for ¹H,

Additional Supporting Information may be found in the online version of this article.

© 2012 Wiley Periodicals, Inc.



Scheme 1. Synthesis of titanium catalyst.

75.5 MHz for ^{13}C) at ambient temperature, with DMSO-d_6 or THF-d_8 as a solvent. The NMR data of the copolymers were obtained on a Varian Unity-400 MHz spectrometer at 135°C , with 1,2-dichlorobenzene- d_4 as a solvent. The norbornene content incorporated was calculated according to the literature.⁴³ The differential scanning calorimeter (DSC) measurements were performed on a Perkin-Elmer Pyris at a rate of $10^\circ\text{C min}^{-1}$. The weight-average molecular weight (M_w) and the molecular weight distribution (MWD) of the resultant polymer were determined at 135°C by a GPC PL-220 type high-temperature chromatograph equipped with three Plgel $10\ \mu\text{m}$ Mixed-B LS type columns. 1,2,4-Trichlorobenzene was employed as the solvent at a flow rate of $1.0\ \text{mLmin}^{-1}$. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

The 8-anilino-1-naphthalenesulfonic acid was purchased from Aldrich. Methylaluminoxane (MAO, Akzo Nobel) and triethylaluminum (TEA, Akzo Nobel) were obtained and used directly. Titanium tetrachloride (TiCl_4) was purchased from Tianjin weichen chemical reagent technology and trade Co. Ltd. Polymerization grade ethylene was directly used.

Procedure for Ethylene Polymerization

The polymerization was carried out in a 0.7 L autoclave equipped with a mechanical stirrer. The reactor was back-filled three times with nitrogen and charged with the required

amount of toluene. At the stipulated temperature, the reaction solution was vigorously stirred under ethylene continues feed for the desired period of time after which the cocatalyst was added to the reactor. After cocatalyst was added, the catalyst was injected and then the polymerization started with a continuous feed of ethylene. The total volume of toluene was 500 mL. After 0.5 h, the polymerization was terminated by adding 10% HCl -methanol solution, and then the mixture was poured into 500 mL of methanol to precipitate the polymer and followed by drying under vacuum at 60°C to its constant weight. Based on the weight of the obtained polymer, the catalyst activity ($\text{kg-polymer}\cdot\text{mol-Ti}^{-1}\ \text{h}^{-1}\ \text{atm}^{-1}$) was calculated.

Synthesis and Characterization of Titanium Complex

The procedure for synthesis of titanium complex bearing 8-anilino-1-naphthalenesulfonate ligand is given in Scheme 1. To a stirred solution of commercial available 8-anilino-1-naphthalenesulfonic acid (2.01 g, 6.72 mmol) in dried THF (100 mL), $n\text{-BuLi}$ (1.13 mL, 13.44 mmol) was added at -78°C . The mixture was stirred for 1 h, allowed to warm to room temperature, and stirred for additional 2 h. After that, the obtained solution was added to TiCl_4 (0.74 mL, 6.72 mmol) at -78°C , then the mixture was warmed to room temperature and stirred for 48 h. The residue, obtained by removing the solvent under vacuum, was extracted with THF ($3 \times 50\ \text{mL}$) and the combined filtrates

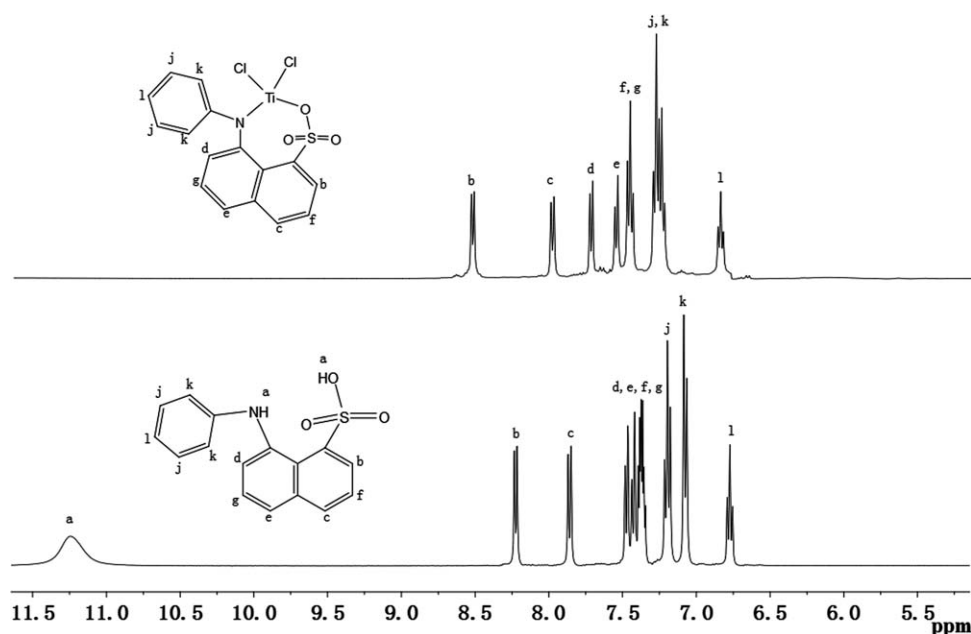


Figure 1. $^1\text{H-NMR}$ spectra of 8-anilino-1-naphthalenesulfonic acid and the obtained titanium complex.

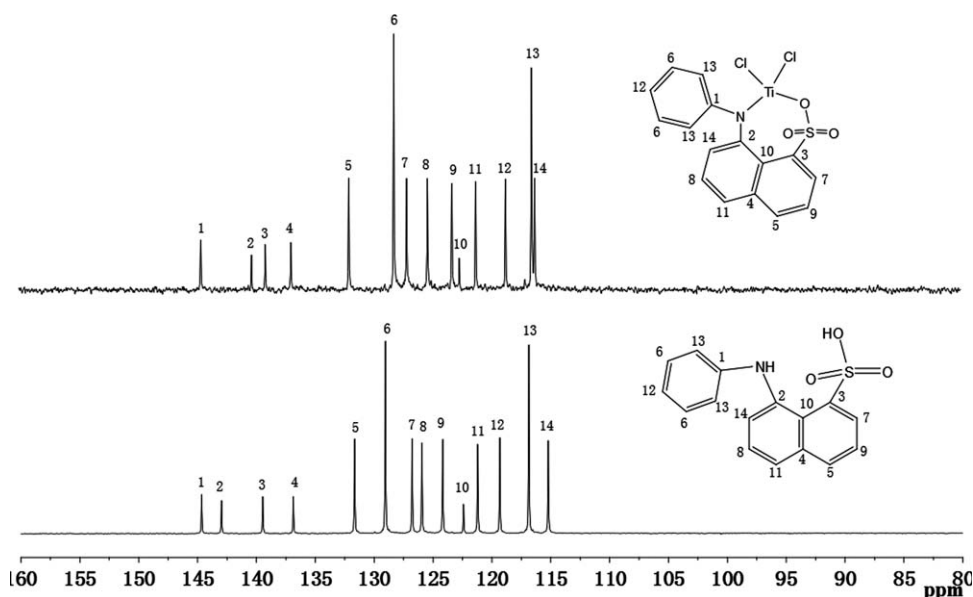


Figure 2. ^{13}C -NMR spectra of 8-anilino-1-naphthalenesulfonic acid and the obtained titanium complex.

were collected. The extracted titanium complex was precipitated in ethyl ether and filtered under N_2 . The solid was collected and dried in vacuum. The yield of the dark green titanium complex was 2.13 g (76%).

The dark green titanium complex was identified by elemental analysis. Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{NO}_3\text{STi}$: C: 46.18%; H:

2.67%; N: 3.37%; Ti: 11.50%; S: 7.71%. Found: C: 45.98%; H: 2.60%; N: 2.96%; Ti: 11.15%; S: 7.07%.

^1H -NMR (300 MHz, $\text{C}_4\text{D}_8\text{O}$, δ , ppm): 8.52 [*d, b-H*, 1H], 7.98 [*d, c-H*, 1H], 7.72 [*d, d-H*, 1H], 7.55 [*d, e-H*, 1H], 7.47 [*t, f* and *g-H*, 2H], 7.29 [*m, 2(j-H)*, 2H], 7.25 [*m, 2(k-H)*, 2H], 6.85 [*t, l-H*, 1H].

Table I. Polymerization Results by Resultant Titanium Complex^a

Run	Cocat.	Al/Ti	P_E (bar)	Temp. ($^\circ\text{C}$)	Yield (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m ($^\circ\text{C}$)
1	MAO	50	7	70	2.7	30.9	38.6	2.6	130.9
2	MAO	100	7	70	3.3	37.7	17.7	2.9	130.8
3	MAO	200	7	70	3.9	44.6	13.6	2.9	132.3
4	MAO	400	7	70	7.1	81.1	9.4	2.4	132.4
5	MAO	1000	7	70	15.4	176.0	7.4	2.0	132.4
6	TEA	50	7	70	1.5	17.1	32.4	3.7	134.1
7	TEA	100	7	70	0.9	10.3	19.7	15.4	134.8
8	TEA	200	7	70	0.6	6.9	19.5	7.9	133.6
9	TEA	400	7	70	0.8	9.1	17.8	24.2	132.3
10	MAO	400	7	30	3.4	38.9	45.8	3.1	130.8
11	MAO	400	7	50	3.7	42.3	24.7	3.1	130.3
12	MAO	400	7	90	8.8	100.6	7.6	3.5	133.5
13	MAO	400	1	70	2.7	216.0	6.6	1.8	132.2
14	MAO	400	3	70	4.9	130.7	7.8	3.5	131.4
15	MAO	400	5	70	6.3	100.8	7.4	1.9	132.1
16 ^d	MAO	400	7	70	5.6	64.0	9.1	2.8	122.2
17 ^d	TEA	400	7	70	1.5	17.1	n.d. ^e	n.d. ^e	129.4

^aPolymerization conditions: catalyst 2.5×10^{-5} mol, solvent 500 mL toluene, 30 min, 500 rpm.

^b $\text{kg-polymer} \cdot \text{mol-Ti}^{-1} \cdot \text{h}^{-1} \cdot \text{atm}^{-1}$.

^c $\times 10^{-4}$ g mol⁻¹, determined by GPC data in 1,2,4-trichlorobenzene versus polystyrene standard.

^dEthylene/norbornene copolymerization, norbornene: 5 g.

^eNot detected.

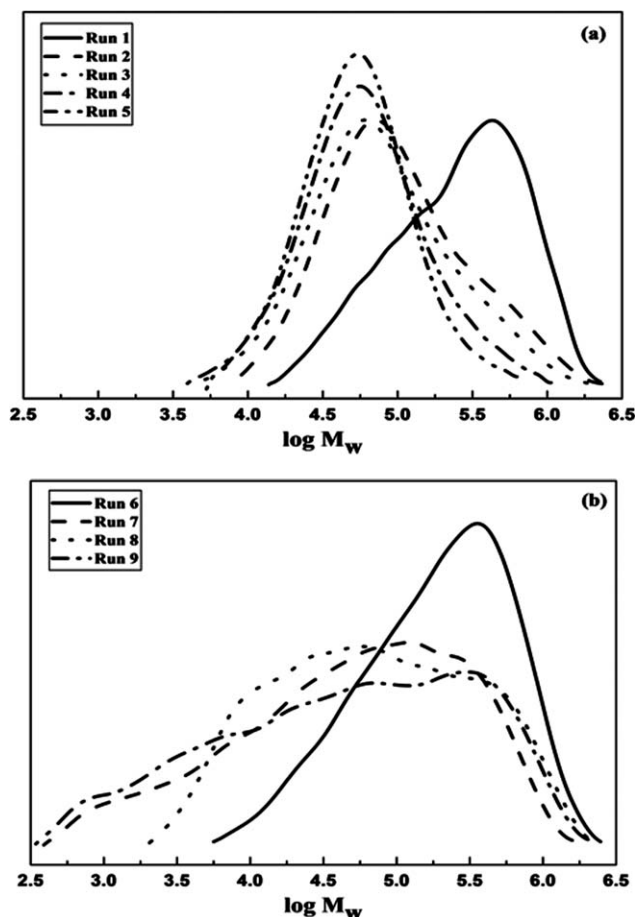


Figure 3. GPC profiles of the resulting polyethylenes: (a) MAO as cocatalyst and (b) TEA as cocatalyst.

^{13}C -NMR (75.5 MHz, $\text{C}_4\text{D}_8\text{O}$, δ , ppm): 144.55 [s, 1-C, 1C], 140.24 [s, 2-C, 1C], 139.07 [s, 3-C, 1C], 136.90 [s, 4-C, 1C], 131.98 [s, 5-C, 1C], 128.16 [s, 2(6-C), 2C], 127.07 [s, 7-C, 1C], 125.29 [s, 8-C, 1C], 123.23 [s, 9-C, 1C], 122.59 [s, 10-C, 1C], 121.21 [s, 11-C, 1C], 118.67 [s, 12-C, 1C], 116.46 [d, 2(13-C), 2C], 116.19 [d, 14-C, 1C].

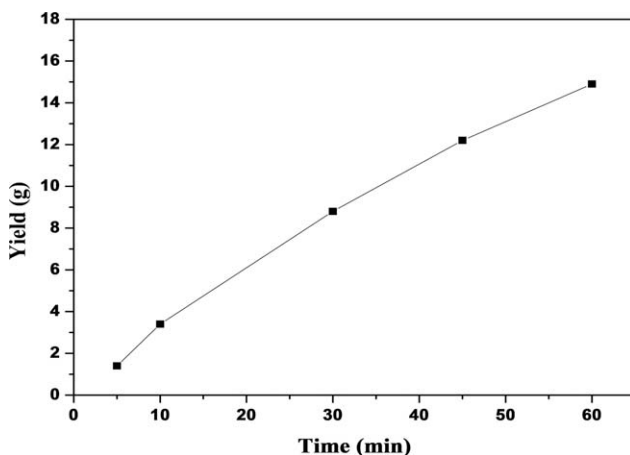


Figure 4. Plots polymer yield versus polymerization time for polymerization at 90°C .

However, attempts to obtain single crystals of the titanium complex have so far been unsuccessful. Thus, investigation involving exact structural determination for this complex remains worthy of further study.

8-Anilino-1-naphthalenesulfonic acid and the obtained titanium complex were characterized by ^1H -NMR and ^{13}C -NMR, and the spectra were shown in Figures 1 and 2 (8-anilino-1-naphthalenesulfonic acid was dissolved in DMSO-d_6 and the obtained titanium complex was dissolved in THF-d_8 at ambient temperature). According to the ^1H -NMR spectra, the resonance signal of active hydrogens ($=\text{NH}$ and $-\text{SO}_3\text{H}$) disappeared after reaction. The HH-COSY NMR spectra of ligand and titanium complex are given in Supporting Information.

RESULTS AND DISCUSSION

The performance of the synthesized titanium complex in ethylene polymerization was evaluated after activation with MAO. The synthesized titanium complex was typically investigated by changing various reaction parameters such as the type and concentration of the cocatalyst, Al/Ti molar ratio, polymerization temperature, and pressure. The polymerization results are summarized in Table I.

The titanium complex with MAO as cocatalyst performed with an activity over $30.0 \text{ kg-PE}\cdot\text{mol-Ti}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ (Runs 1–5), which was several times higher than that with TEA as cocatalyst (Runs 6–9). The catalytic activity increased gradually with higher Al/Ti ratios, with MAO cocatalyst, and the maximum of $176.0 \text{ kg-PE}\cdot\text{mol-Ti}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ (Run 5) was observed at the highest Al/Ti ratio of 1000. On the contrary, when TEA was used as cocatalyst, the catalytic activity reduced gradually with the increase of Al/Ti ratio, and the maximum of $17.1 \text{ kg-PE}\cdot\text{mol-Ti}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ (Run 6) was observed at the lowest Al/Ti ratio. Correspondingly, the M_w of the obtained polyethylenes with MAO or TEA as cocatalyst is found to decrease gradually with increasing Al/Ti ratio, which indicated that transferring to the aluminum was the major chain transfer pathway. Narrow MWD and low M_w were observed with MAO as cocatalyst, but broad MWD and high M_w were observed with TEA as

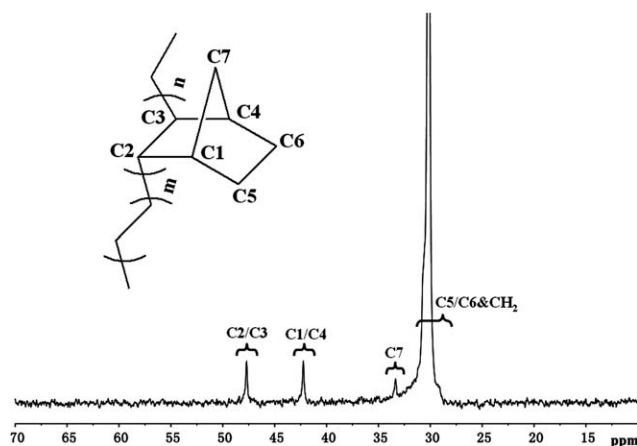


Figure 5. ^{13}C -NMR (1,2-dichlorobenzene- d_4 , 135°C , 100.40 MHz) spectrum of the copolymer obtained by MAO as cocatalyst (Run 16).

cocatalyst. Additionally, MWD became broader at higher TEA concentrations, which was possibly due to the disruption of the active centers by large amount of TEA. The GPC curves of the obtained polyethylenes with MAO or TEA in the different Al/Ti molar ratios are given in Figure 3. According to the narrower MWD of polyethylene obtained at higher MAO/Ti molar ratios, common active species are present displaying similar catalytic processes.⁴⁴

In the case of Al/Ti molar ratio higher than 400 (MAO as cocatalyst), the polymerization reactor was overloaded. Thus, the effects of reaction temperatures and pressures on ethylene polymerization behavior were investigated at Al/Ti = 400. The catalyst activity steadily increased at higher temperatures (Runs 4 and 10–12), whilst the M_w of the resulting polyethylenes gradually decreased. Figure 4 plots the curve of polymer yield versus polymerization time for polymerization at 90°C. The polymer yield increased steadily with polymerization time at 90°C. These results indicated that the obtained titanium complex was stable at high polymerization temperature (90°C). The ethylene polymerization was also conducted under different ethylene pressures (Runs 4 and 13–15). The polymer yield was raised with an increase in ethylene pressure, attributable to the higher monomer concentration around the active Ti centers at higher pressure. In contrast to TEA as cocatalyst, the polyethylene generated in the presence of MAO cocatalyst was much narrower (Runs 1–4 vs. Runs 6–9). In general, the resultant polyethylenes exhibiting high M_w with unimodal MWD, suggests uniform and active catalyst species over the course of polymerization.

The copolymerization of ethylene–norbornene was carried out using the synthesized titanium complex with TEA or MAO as cocatalyst and the results are illustrated in Table I (Runs 16 and 17). The complex, after activation with MAO, is an active catalyst for the copolymerization of ethylene–norbornene (Run 16). However, the activity of copolymerization was lower than that of ethylene homopolymerization (Run 4 vs. Run 16). In contrast, the catalytic activity slightly increased with the introduction of norbornene comonomer for TEA as cocatalyst (Run 9 vs. Run 17).

The T_m values for the resultant copolymers decreased with the introduction of norbornene and the T_m value of the resultant copolymer made by MAO as cocatalyst was much lower than that of the copolymer produced by TEA as cocatalyst (Run 16 vs. Run 17). Changes in the M_w and MWD were insignificant with the introduction of comonomer. ¹³C-NMR spectra (Figure 5, 100.40 MHz for ¹³C, dissolved in 1,2-dichlorobenzene-d₄ at 135°C) of the copolymer revealed 3.2% and 0.4% molar incorporation of norbornene for MAO and TEA, respectively.

CONCLUSIONS

The novel titanium complex bearing 8-anilino-1-naphthalene-sulfonic acid was synthesized. After activation with MAO, the synthesized titanium complex showed fairly good activity toward ethylene (co-)polymerization, but low activity toward ethylene polymerization with TEA as cocatalyst. Narrow MWD and low M_w were observed with MAO as cocatalyst, while broad MWD and high M_w were observed with TEA as cocatalyst.

Furthermore, the titanium complex/MAO catalyst system showed a uniform active site and was stable at high polymerization temperature. In addition, the incorporation rate of norbornene was affected by the type of cocatalyst. Further investigation of the olefin polymerization copolymerization of such complex is ongoing.

REFERENCES

1. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428.
2. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *10*, 1169.
3. Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.
4. Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134.
5. Lamberti, M.; Pappalardo, D.; Zambelli, A.; Pellicchia, C. *Macromolecules* **2002**, *35*, 658.
6. Hustad, P. D.; Tian, J.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 3614.
7. Milano, G.; Cavallo, L.; Guerra, G. *J. Am. Chem. Soc.* **2002**, *124*, 13368.
8. Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 11578.
9. Hu, W. Q.; Sun, X. L.; Wang, C.; Gao, Y.; Tang, Y.; Shi, L. P.; Xia, W.; Sun, J.; Dai, H. L.; Li, X. Q.; Yao, X. L.; Wang, X. R. *Organometallics* **2004**, *23*, 1684.
10. Kohn, R. D.; Haufe, M.; Kociok-Kohn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337.
11. Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. *J. Chem. Commun.* **2002**, **1038**.
12. Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
13. Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
14. Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
15. Bambirra, S.; Leusen, D. V.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, **637**.
16. Long, Y. Y.; Ye, W. P.; Shi, X. C.; Li, Y. S. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 6072.
17. He, L. P.; Liu, J. Y.; Pan, L.; Li, Y. S. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7062.
18. Stelzig, S. H.; Tamm, M.; Waymouth, R. M. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 6064.
19. Sudhakar, P. *J. Polym. Sci. Part A: Polym. Chem.*, **2008**, *46*, 444.
20. Napoli, M.; Mariconda, A.; Immediata, I. Longo, P. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4725.
21. Nomura, K.; Zhang, H.; Byun, D. J. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4162.

22. Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307.
23. Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 2106.
24. Volkis, V.; Shmulinson, M.; Averbuj, C.; Lisovskii, A.; Edelmann, F. T.; Eisen, M. S. *Organometallics* **1998**, *17*, 3155.
25. Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.
26. Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.
27. Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.
28. Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308.
29. Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *Chem. Commun.* **1998**, **313**.
30. Linden, A.; J. Schaverien, C.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.
31. Fokken, S.; Spaniol, T. P.; Kang, H. C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069.
32. Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, **1263**.
33. Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327.
34. Mitani, M.; Furuyama, R.; Mohri, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293.
35. Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576.
36. Matsui, S.; Fujita, T. *Catal. Today* **2001**, *66*, 63.
37. Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Organometallics* **2001**, *20*, 4793.
38. Yoshida, Y.; Saito, J.; Mitani, M.; Takagi, Y.; Matsui, S.; Ishii, S.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Chem. Commun.* **2002**, **1298**.
39. Xu, T.; Liu, J.; Wu, G. P.; Lu, X. B. *Inorg. Chem.* **2011**, *50*, 10884.
40. Zhang, J.; Lin, Y. J.; Jin, G. X. *Organometallics* **2007**, *26*, 4042.
41. Anselment, T. M. J.; Wichmann, C.; Anderson, C. E.; Herdtweck, E.; Rieger, B. *Organometallics* **2011**, *30*, 6602.
42. Ravasio, A.; Boggioni, L.; Tritto, I. *Macromolecules* **2011**, *44*, 4180.
43. Arndt-Rosenau, M.; Beulich, I. *Macromolecules* **1999**, *32*, 7335.
44. Xiao, T. P. F.; Zhang, S.; Li, B. X.; Hao, X.; Redshaw, C.; Li, Y. S.; Sun, W. H. *Polymer* **2011**, *52*, 5803.