

# Ring-opening metathesis polymerization of norbornene catalyzed by substituted titanocene complexes

Yanlong Qian<sup>a,\*</sup>, Danfeng Zhang<sup>a</sup>, Jiling Huang<sup>a</sup>, Haiyan Ma<sup>a</sup>, Albert S.C. Chan<sup>b</sup>

<sup>a</sup> *Laboratory of Organometallic Chemistry, East China University of Science and Technology, Meilong Road 130<sup>#</sup>, Shanghai 200237, China*

<sup>b</sup> *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

Received 24 September 1997; accepted 5 March 1998

## Abstract

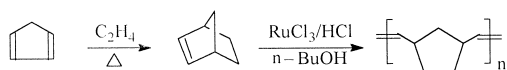
The ring-opening metathesis polymerization (ROMP) of norbornene (NBE) with 11 substituted titanocene dichlorides and MeLi as catalysts was studied. The substituent effect showed that the catalytic activity was generally decreased as the substituents were introduced into the Cp ring. The more bulky the substituents, the lower the activity and the bis-substituted titanocene appeared to have an even lower catalytic activity. The molecular weight of polynorbornene (PNBE) also decreased as substituents are introduced on the Cp ring. But the molecular weight distribution and *cis* structure content have no significant differences compared with non-substituted titanocene complex as catalyst. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Ring-opening metathesis polymerization; Norbornene; Substituted titanocene complexes

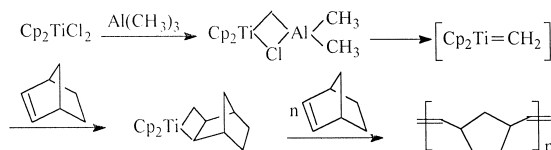
## 1. Introduction

During the past 2 decades, intense research efforts have enabled the ring-opening metathesis polymerization (ROMP) of cycloolefines as an area of many fascinating recent developments. The most effective catalysts for this kind of polymerization are carbene complexes of molybdenum, tungsten, tantalum, rhenium and ruthenium (for general reviews, see Refs. [1–6]). Titanium-based catalyst was also used, for example, in the ROMP of norbornene (NBE) [7–10]. Polynorbornene (PNBE) was the first metathesis polymer marketed in 1976, by CdF-Chemie under the trade name ‘NORSOREX’[5,6]. NBE can be easily synthesized by the Diels–Alder reaction of cyclopentadiene, a by-product of naphtha cracking and petroleum refining, and ethylene, and its polymerization catalyzed by RuCl<sub>3</sub>/HCl yields a thermoplastic powder with very high molecular weight ( $> 2 \times 10^6$ ) with 90% *trans*-double bonds.

\* Corresponding author.



In order to develop a more effective and cheap catalytic system, titanocene derivative catalysts were studied in some detail [7–10]. Grubbs et al. used Tebbe reagent and titanacyclobutanes as catalysts for ROMP of NBE.



Petasis and Fu [7] reported the ROMP of NBE catalyzed by titanium alkylidenes generated from thermolysis of dimethyltitanium. The recent research in our group has dealt with the chemistry of substituted cyclopentadienyl titanium and zirconium complexes [11–23]. Therefore, we have interest to study the substituent effect of titanocene carbene complexes for ROMP. In this paper, we wish to describe the influence of different substituents on Cp ring of in situ prepared substituted dimethyltitanocene complexes on ROMP of NBE.

## 2. Experiments

### 2.1. Materials

NBE was purchased from Aldrich, and purified by distillation over Na.  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{CpCp}'\text{TiCl}_2$  and  $\text{Cp}'_2\text{TiCl}_2$  (Cp =  $\eta^5$ -cyclopentadienyl, Cp' = substituted cyclopentadienyl) were prepared in our laboratory according to the literature [11–23]. Solvents were refluxed over Na and  $\text{Ph}_2\text{CO}$  under argon before use.

### 2.2. Polymerization

Polymerization was carried out in a sealed glass tube which was baked under vacuum, and flushed with argon for several times. Thus, 0.10 mmol titanocene complexes and 0.5 ml dry toluene and 0.20 mmol  $\text{CH}_3\text{Li}$  (1.2493 mmol/ml) were introduced into the tube under argon at  $0^\circ\text{C}$ , and stirred for 30 min. Then, 2.0 ml solution of 10.00 mmol NBE (5.00 mmol/ml) in toluene was injected into the tube, which placed in oil bath at  $80^\circ\text{C}$ . The polymerization was carried out with agitation for 6 h and terminated with 100 ml 5% HCl in acetone.

### 2.3. Analysis

$^1\text{H}$  NMR spectra was recorded in  $\text{CDCl}_3$  on a Gemini-300 instrument. GPC analysis was performed on Waters-244 spectrometer. The retention times were calibrated with monodispersed polystyrene standards, and HPLC-grade THF was used as the eluant.

### 3. Results and discussion

In order to study the substituent effect of titanium-based catalysts on ROMP of NBE, a series of substituted titanocene complexes (1–11) have been synthesized, and used with MeLi (molar ratio of Li/Ti is 2) in situ to prepare dimethyl titanocene for the ROMP of NBE. The polymerization results are listed in Table 1.

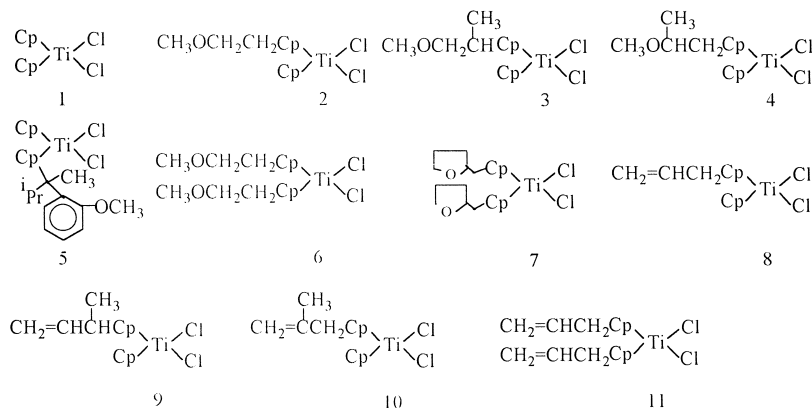


Table 1 shows that the catalytic activities were generally decreased as the substituents were introduced into the Cp ring. The more bulky the substituents, the lower the conversion. The bis-substituted titanocene catalysts appear to have an even lower catalytic activity. The molecular weight of PNBE also decreased as the substituents introduced on the Cp ring of catalysts. The decrease both in catalytic activity and molecular weight may be mainly attributed to steric effect. The bulky substituents on Cp ring do not favor the coordination of C=C bond of NBE to Ti atom. From the view of Mohring and Coville [24], if the ligand is a better electron donor, it will reduce the positive charge on the metal, and thus weaken the bonding between the metal and all other ligands, particularly the unstable M–R bond which will become more reactive. In the case of oxygen-containing substituents on Cp ring, it may be regarded as electron donor, and therefore should be favorable to

Table 1  
Ring-opening metathesis polymerization of NBE catalyzed by substituted titanocene complexes

Catalyst	Conv. (%)	$M_n (\times 10^4)$	$M_w (\times 10^4)$	$M_w/M_n$	<i>cis</i> (%)	Activity (g PNBE/mol Ti h)
1	85	5.3	12.4	2.34	37	1332
2	90	5.2	8.5	1.64	45	1405
3	80	4.9	10.1	2.06	40	1252
4 <sup>a</sup>	44	2.8	7.0	2.49	41	173
5 <sup>a</sup>	34	6.0	17.4	2.90	41	133
6	13	—	—	—	41	198
7	8	—	—	—	38	125
8	50	3.1	8.0	2.58	42	783
9	71	2.9	6.3	2.16	44	1117
10	19	1.7	3.8	2.23	43	300
11 <sup>a</sup>	4	—	—	—	44	55

Conditions: monomer/catalyst = 100; NBE: 10.00 mmol (5.00 mmol/ml); catalyst: 0.10 mmol; CH<sub>3</sub>Li: 0.20 mmol (1.2493 mmol/ml); aging: 0°C, 30 min; polymerization: 80°C, 6 h.

<sup>a</sup>24 h.

the activity. On the other hand, the coordination between the oxygen atom in the side chain of Cp ring and central titanium atom inhibits the coordination of monomer to Ti. Therefore, combination of above two factors led to the slightly decreased activity. In the case of alkenyl substituents on the Cp ring, not only the substituent itself sterically affects coordination of NBE to the metal, but also competitive coordination of two C=C bonds of substituent on Cp ring and monomer to Ti is unfavorable to the polymerization. That is the reasonable explanation for even lower activity of alkenyl-substituted titanocene catalysts, shown in Table 1.

As the activity decreased, the molecular weight also slightly decreased. But the steric hindrance and intramolecular coordination of substituted titanocene catalysts seem to have no significant effect on the molecular weight distribution and *cis* structure content.

## Acknowledgements

Financial support for this work from the National Natural Science Foundation of China (29572044) is gratefully acknowledged. This project is also supported by State Key Laboratory of Coordination Chemistry, Nanjing University. We also thank 3M for the scholarship.

## References

- [1] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.
- [2] R.H. Grubbs, Comp. Organomet. Chem. 8 (1982) 499.
- [3] A.J. Amass, Comp. Polym. Sci. 4 (1989) 109.
- [4] R.H. Grubbs, Adv. Polym. Sci. 102 (1992) 47.
- [5] D.S. Breslow, Prog. Polym. Sci. 18 (1993) 1141.
- [6] R. Ohm, C. Stein, in: M. Grayson (Ed.), Encyclopedia of Chemical Technology, 3rd edn., Vol. 18, Wiley-Interscience, New York, 1982, pp. 436–442.
- [7] N.A. Petasis, D.-K. Fu, J. Am. Chem. Soc. 115 (1993) 7208.
- [8] L.R. Gilliom, R.H. Grubbs, J. Am. Chem. Soc. 108 (1986) 733.
- [9] D. Jeremic, Q. Wang, R. Quyoum, M.C. Baird, J. Organomet. Chem. 497 (1995) 143.
- [10] T.R. Howard, J.B. Lee, R.H. Grubbs, J. Am. Chem. Soc. 102 (1980) 6876.
- [11] Y. Qian, J. Huang, X. Chen, G. Li, W. Chen, B. Li, X. Jin, Q. Yang, Polyhedron 13 (1994) 1105.
- [12] Y. Qian, G. Li, W. Chen, B. Li, X. Jin, Transition Met. Chem. 15 (1990) 478.
- [13] Q. Huang, Y. Qian, G. Li, Y. Tang, Transition Met. Chem. 15 (1990) 483.
- [14] Y. Qian, G. Li, W. Chen, B. Li, X. Jin, J. Organomet. Chem. 373 (1989) 185.
- [15] Q. Huang, Y. Qian, Y. Tang, J. Organomet. Chem. 368 (1989) 277.
- [16] Q. Huang, Y. Qian, Transition Met. Chem. 14 (1989) 315.
- [17] Y. Qian, G. Li, Polyhedron 12 (1993) 967.
- [18] Y. Qian, J. Huang, Macromol. Symp. 105 (1996) 205.
- [19] Y. Qian, J. Huang, T. Huang, S. Chen, Transition Met. Chem. 21 (1996) 393.
- [20] Y. Qian, K. Hong, H. Zong, J. Huang, Polym. Adv. Technol. 7 (1996) 619.
- [21] Y. Qian, R. Guo, J. Huang, K. Jones, Chin. Chem. Lett. 7 (1996) 1139.
- [22] Y. Qian, R. Guo, J. Huang, Q. Yang, Polyhedron 16 (1997) 195.
- [23] Y. Qian, J. Yang, W. Sun, Y. Ling, J. Huang, Chin. Chem. Lett. 8 (1997) 305.
- [24] P.C. Mohring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.