

Ring-opening metathesis polymerization of norbornene and dicyclopentadiene catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{RMgX}$

Danfeng Zhang^a, Jiling Huang^a, Yanlong Qian^{a,*}, Albert S.C. Chan^b

^a *Laboratory of Organometallic Chemistry, East China University of Science and Technology, Meilong Road 130#, Shanghai 200237, China*

^b *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

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Abstract

The ring-opening metathesis polymerization (ROMP) of norbornene (NBE) and dicyclopentadiene (DCPD) catalyzed by Cp_2TiCl_2 ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) and a series of different RMgX ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, n\text{-C}_6\text{H}_{13}, \text{C}_6\text{H}_5, \text{X} = \text{Cl, Br, I}$) were studied. The catalytic system $\text{Cp}_2\text{TiCl}_2/\text{CH}_3\text{MgI}$ is the most active for the ROMP of NBE and DCPD, but Cp_2TiCl_2 with other Grignards appeared rather low catalytic activity. The mechanism of polymerization with Cp_2TiCl_2 and different Grignard agents was discussed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Ring-opening metathesis polymerization; Norbornene; Dicyclopentadiene

1. Introduction

In the last 20 years, a major advancement in polymer chemistry was the development of ring-opening metathesis polymerization (ROMP) of cycloolefins. The pioneering researches of Grubbs [1] and Schrock [2] have provided valuable mechanistic information and led to the synthesis of new polymeric materials. The most effective catalysts for ROMP were alkylidene complexes ($\text{LnM}=\text{CHR}$) of molybdenum, tungsten, tantalum, rhenium and ruthenium [3]. The titanium-based ‘Tebbe reagent’ ($\text{Cp}_2\text{Ti}=\text{CHR}$) was also used for this kind of polymerization [3–5]. But to our knowledge, so far, there was

still no report on $\text{Cp}_2\text{TiCl}_2/\text{RMgX}$ as a catalytic system for ROMP. In this paper, we report the results of titanium-based catalysts composed from Cp_2TiCl_2 and a series of Grignard agents RMgX for ROMP of norbornene and dicyclopentadiene.

2. Experiments

Norbornene (NBE) was purchased from Aldrich and purified by distillation over Na. Dicyclopentadiene (DCPD) (85%) was obtained from Shanghai Petroleum Chemical and purified by vacuum distillation, pyrolysis, dimerization and vacuum distillation with a purity of 99% in gas chromatography. Cp_2TiCl_2 and all kinds of

* Corresponding author.

RMgX were synthesized in our laboratory according to the literature. All solvents were refluxed over Na and distilled prior to use under argon.

Polymerization was carried out in a sealed glass tube under argon. The following typical procedure was used. Into a 20 ml glass tube, 0.10 mmol Cp_2TiCl_2 and 0.5 ml dry toluene were introduced at 0°C , then 0.20 mmol RMgX was injected into it and stirred for 30 min. After that, a solution of 10.00 mmol NBE (5.00 mmol/ml) or DCPD in toluene was injected into the tube which was then placed in an oil bath at 80°C . After 24 h agitation, it was terminated with excess of 5% HCl in acetone.

The inherent viscosity was determined in THF at 30°C by Ubbelodhe viscosimeter. ^1H NMR spectrum was recorded by using Gemini-300 in CDCl_3 . Cis content of C=C bond in the polymer was calculated according to ^1H NMR data.

3. Results and discussion

3.1. Polymerization of NBE

The results of polymerization of NBE catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{RMgX}$ are listed in Table 1.

Table 1 shows that $\text{Cp}_2\text{TiCl}_2/\text{CH}_3\text{MgI}$ is the most effective catalytic system, and the catalysts composed from Cp_2TiCl_2 and other Grignards appear rather low activity. But the difference of R in RMgX seems to be no significant effect on $[\eta]$ and cis-content.

Table 1
Polymerization of NBE by $\text{Cp}_2\text{TiCl}_2/\text{RMgX}^a$

RMgX	Cont. (mmol/ml)	Time (h)	Conv. (%)	$[\eta]$ (l/g)	Cis. (%)	Activity (g PNBE/molTi h)
CH_3MgI	1.5462	6	100	0.0958	32	1823
$\text{C}_2\text{H}_5\text{MgBr}$	1.1981	24	29	0.1175	36	113
<i>i</i> - $\text{C}_3\text{H}_7\text{MgCl}$	0.9400	24	31	0.1044	39	121
<i>n</i> - $\text{C}_4\text{H}_9\text{MgCl}$	0.9984	24	26	0.1129	46	101
<i>n</i> - $\text{C}_6\text{H}_{13}\text{MgBr}$	0.8397	24	32	0.1076	52	125
$\text{C}_6\text{H}_5\text{MgBr}$	0.9173	24	34	0.1540	39	143
1- $\text{C}_3\text{H}_5\text{MgBr}$	0.6557	24	22	0.0582	40	89

^aPolymerization condition: monomer/catalyst = 100; NBE: 10.00 mmol (5.00 mmol/ml); Cp_2TiCl_2 : 0.10 mmol; RMgX: 0.20 mmol; Aging: 0°C , 30 min; Polymerization: 80°C .

Table 2
Polymerization of DCPD by $\text{Cp}_2\text{TiCl}_2/\text{RMgX}^a$

RMgX	Cont. (mmol/ml)	Conv. (%)
CH_3MgI	1.5462	75
$\text{C}_2\text{H}_5\text{MgBr}$	1.1981	< 1
<i>i</i> - $\text{C}_3\text{H}_7\text{MgCl}$	0.9400	< 1
<i>n</i> - $\text{C}_4\text{H}_9\text{MgCl}$	0.9984	< 1
<i>n</i> - $\text{C}_6\text{H}_{13}\text{MgBr}$	0.8397	< 1
1- $\text{C}_3\text{H}_5\text{MgBr}$	0.6557	< 1

^aPolymerization condition: monomer/catalyst = 75; DCPD: 14.06 mmol (3.50 mol/l); Cp_2TiCl_2 : 0.19 mmol; RMgX: 0.38 mmol; Aging: -20°C , 90 min; Polymerization: 80°C , 24 h.

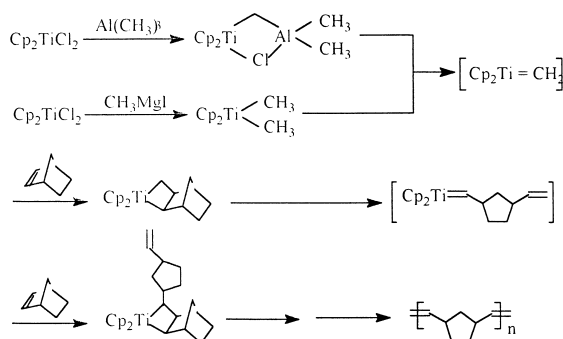
3.2. Polymerization of DCPD

The polymerization of DCPD was also carried out by $\text{Cp}_2\text{TiCl}_2/\text{RMgX}$ and the results are shown in Table 2.

Table 2 shows that only $\text{Cp}_2\text{TiCl}_2/\text{CH}_3\text{MgI}$ appears to have some activity, and the others seem to have nearly no activity.

3.3. Mechanism discussion

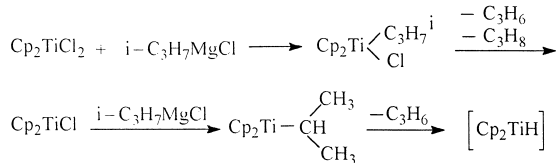
It was reported that 'Tebbe reagent' had been shown to be a titanium carbene precursor, which reacts with 1-olefin and a Lewis-based to form a stable, crystalline titanacyclobutanes. Both titanium carbene and titanacycles are the catalysts for ROMP [4,6,7]. Therefore, the mechanism of ROMP of NBE or DCPD catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{CH}_3\text{MgI}$ may be proposed similarly (see Scheme 1). But in the case of other Grignard agents instead of CH_3MgI , there was no possibility to form a titanium carbene species.



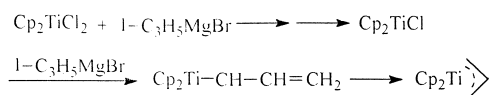
Scheme 1.

The reaction of Cp_2TiCl_2 with different Grignard agents is very complicated and it has been proven that such reaction may be followed in quite different ways [8–14].

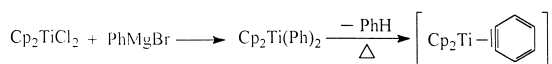
(1) In the case of RMgX with $\beta\text{-H}$, such as $\text{R} = \text{C}_2\text{H}_5$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $n\text{-C}_6\text{H}_{13}$, after reduction, alkylation and $\beta\text{-H}$ elimination, it gave in-situ a titanocene hydride [8], for example:



(2) In the case of $1\text{-C}_3\text{H}_5\text{MgBr}$, after reduction and $\sigma\text{-}\pi$ bond transformation, it formed a Cp_2Ti -allyl complex [9,10]:



(3) In the case of PhMgBr , after alkylation and thermolysis, it seems to yield a titanocene benzyne complex [11–14]:



In our previous work, it had been described that titanocene hydride and allyl complex are

good catalysts for olefin isomerization, but not for polymerization [8–10]. It is generally considered that metallocene carbene complexes are the effective catalysts for ROMP. But the above-mentioned titanocene hydride, allyl and benzyne complexes cannot be transformed into carbene species. Therefore, it is understandable that the systems titanocene dichloride with Grignard agents, except CH_3MgI , catalyzed the polymerization of NBE and DCPD with a low activity, and such polymerization may be assumed to follow a different mechanism with ROMP.

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