

Ring-Opening Metathesis Polymerization of Dicyclopentadiene Catalyzed by Titanium Tetrachloride Adduct Complexes with Oxygen-Containing Ligands

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ABSTRACT: Ring-opening metathesis polymerization of dicyclopentadiene catalyzed by $\text{TiCl}_4 \cdot 2\text{L}/\text{CH}_3\text{Li}$ system [where L is tetrahydropyran (1), dioxane, 2,5-dimethylfuran, or tetrahydrofurfuryl alcohol] is reported. The obtained polymer was characterized by IR and $^1\text{H-NMR}$. These catalytic systems effectively promoted the polymerization reaction. Seven influencing factors are discussed. When the aging temperature was 0°C , the aging time was 90 min, the polymerization temperature was 60°C , Li/Ti was 1.5–2, and the monomer/catalyst molar ratio ranged between 30 and 50, the polymerization reaction catalyzed by complex **1** yielded better results within a shorter period of time. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 662–666, 2001

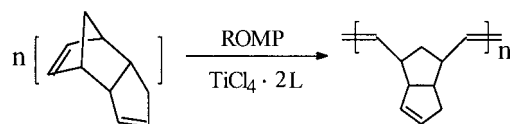
Key words: ring-opening metathesis polymerization (ROMP); dicyclopentadiene (DCPD); titanium tetrachloride adduct complexes; oxygen-containing ligands

INTRODUCTION

Ring-opening metathesis polymerization (ROMP) of cyclic monomers is a relative newcomer to the field of polymer chemistry. This type of reaction has made rapid progress since 1950 and has lately proven to be one of the most investigated subjects in the field of polymer chemistry.^{1,2} Depending on the monomer and the type of catalyst used, a wide range of polyolefin products can be synthesized through ROMP that are destined to have wide industrial applications and have produced great academic interest.

Until now, the most important and effective catalytic systems of ROMP were derived from transition-metal complexes and cocatalysts such as BuLi, EtAlCl_2 , R_3Al , and R_4Sn (where R is Me, Bu, Ph, etc).^{3,4} Because the catalytic activity of this kind of system (e.g., $\text{WCl}_6/\text{AlEt}_2\text{Cl}$) is very high, the reaction injection molding (RIM) technique can be used to polymerize dicyclopentadiene (DCPD).⁵

We reported a study on the ROMP of DCPD and norbornene catalyzed by titanocene complexes of the type $\text{Cp}_2\text{TiCl}_2/\text{RMgX}$ ⁶ and substituted titanocene complexes.^{7,8} In addition, our previous work⁹ has shown that the catalytic system of the type $\text{TiCl}_4 \cdot 2\text{THF}/\text{CH}_3\text{Li}$ (where THF is tetrahydrofuran) exhibits good catalytic activity in the ROMP of DCPD and norbornene:



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Table I Polymerization of DCPD Catalyzed by $\text{TiCl}_4 \cdot 2\text{L}/\text{CH}_3\text{Li}$

Catalyst	Conversion (%)	Activity (g PDCPD/mol Ti · h)	$M_n \times 10^4$	D_n
1	92.2	1016.2	6.06	2.10
2	90.3 ^a	994.8	5.47	2.24
3	51.7	569.6	5.25	2.18
4	3.4	37.5	2.57	2.82

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $T_P = 30^\circ\text{C}$; $t_P = 6$ h; $\text{Li/Ti} = 2$; $\text{M/Ti} = 50$; $C_m = 3.5$ mmol/mL; CH_3Li , 0.36 mL (1.096 mmol/mL); solvent: toluene.

^a $T_A = -20^\circ\text{C}$.

To present the influence of L ligands with different structures on the catalytic activity of the complexes $\text{TiCl}_4 \cdot 2\text{L}$, we studied in detail the behavior of different substituted pyridine ligands¹⁰ in the ROMP of DCPD. It was found that the presence of electron-donor groups on the pyridine ring increased the catalytic activity. In this study, we continued our work on the polymerization of DCPD catalyzed by the oxygen-containing ligand complex, $\text{TiCl}_4 \cdot 2\text{L}/\text{CH}_3\text{Li}$ [where L is tetrahydropyran (**1**), dioxane (**2**), 2,5-dimethylfuran (**3**), or tetrahydrofurfyl alcohol (**4**)].

EXPERIMENTAL

Materials

All the operations concerning the synthesis of the catalysts and polymerization were performed under argon according to the standard Schlenk technique.

DCPD was obtained from Shanghai Petroleum Co. (Shanghai, P.R. China) and was purified by vacuum distillation followed by pyrolysis, dimerization, and vacuum distillation. Methyl lithium was prepared according to the literature.¹¹ The catalysts **1**¹² and **2**¹³ were synthesized according to the literature but with some modifications. TiCl_4 was refluxed over copper powder under argon prior to use. Toluene and 2,5-dimethylfuran were refluxed over sodium and benzophenone under argon prior to use. Tetrahydrofurfyl alcohol was refluxed over sodium alcoholate. Chloroform was refluxed over phosphorus pentoxide under argon.

Synthesis of Catalysts

Synthesis of Catalyst 3

To a solution of 2,5-dimethylfuran (33.3 mmol) in CHCl_3 , a solution of TiCl_4 (16.6 mmol) in toluene

was added dropwise at room temperature. A dark red precipitate was produced immediately. The mixture was stirred for another 3 h. Then, it was filtered and washed with CHCl_3 . The solid was dried under vacuum.

Yield: 86.9%. ANAL. Calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_4\text{O}_2\text{Ti}$: C, 37.72%; H, 4.22%. Found: C, 38.13%; H, 4.00%.

Synthesis of Catalyst 4

The procedure was similar to the previous one except that only toluene was used as a solvent and the mixture was stirred at 0°C . A white solid was obtained.

Yield: 95.2%. ANAL. Calcd for $\text{C}_{10}\text{H}_{20}\text{Cl}_4\text{O}_4\text{Ti}$: C, 30.49%; H, 5.12%. Found: C, 30.45%; H, 5.07%.

Polymerization

The ROMP was carried out in a 20-mL, one-necked glass tube that was baked under vacuum and filled with argon several times. We introduced 0.20 mmol of titanium tetrachloride adduct complex, 2 mL of toluene, and 0.36 mL of CH_3Li (1.096 mmol/mL, in ethyl ether) into the tube at 0°C and stirred the mixture for 90 min. Then, 4.2 mL of DCPD in toluene (3.5 mmol/mL) were injected into the tube. The polymerization was carried out at room temperature with agitation for

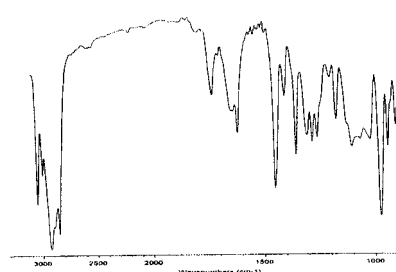


Figure 1 IR spectrum of the polymer.

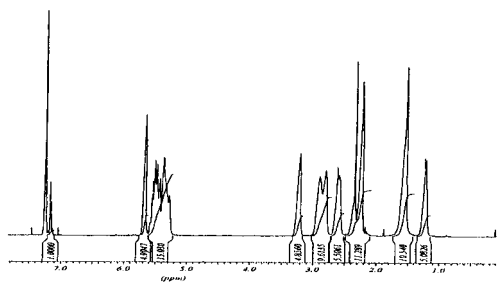


Figure 2 $^1\text{H-NMR}$ spectrum of the polymer.

6 h and quenched with 100 mL of 5% HCl in acetone.

Analysis

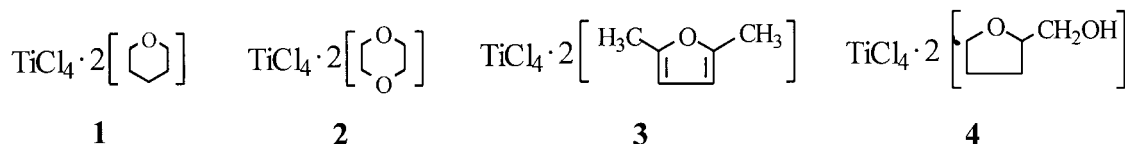
An IR spectrum of the resulting polymer was recorded on a Nicolet Magna-IR550 spectrometer (U.S.), an $^1\text{H-NMR}$ spectrum was recorded in CDCl_3 on a Varian 500-MHz spectrometer, and

gel permeation chromatography analysis was performed on a Water 410RI spectrometer. The retention times were calibrated with a monodispersed polystyrene standard, and high performance liquid chromatography (HPLC)-grade THF was used as the eluant. Elemental analysis was performed with an EA-1106 spectrometer (Craop, Italy).

RESULTS AND DISCUSSION

In this section, we assume T_A ($^\circ\text{C}$) is the aging temperature, t_A (min) is the aging time, T_p ($^\circ\text{C}$) is the polymerization temperature, t_p (h) is the polymerization time, conversion (%) is the monomer conversion, Li/Ti is the cocatalyst and catalyst molar ratio, M/Ti is the monomer and catalyst molar ratio, M_n is the molecular weight, and D_n is the molecular distribution.

The structures of the catalysts are as follows:



The results of the ROMP of DCPD catalyzed by the catalysts **1**, **2**, **3**, and **4** are illustrated in Table I. From the data listed in Table I, we found that catalysts **1** and **2** were more active than the others, and the catalytic activity of complex **4** was very poor. The nature of the ligand has great influence on the catalytic activity of the complex. In the case of catalyst **3**, the lone pair of electrons of the oxygen atom participates in the formation of aromaticity, which leads to less coordination of oxygen to the titanium center compared with the

ligands of catalysts **1** and **2**. According to Mohring and Coville¹⁴ and our previous work,¹⁰ this kind of coordination will increase the activity of carbene species. Thus, catalyst **3** showed less activity than catalysts **1** and **2**.

Regarding catalyst **4**, the presence of active hydrogen in the ligand made the undesirable reaction of methyl lithium and the hydrogen dominant instead of the formation of carbene species. The molar ratio of Li/Ti was almost 0.

From the previous results, we concluded that the enhancement of the coordination of the ligand

Table II Influence of Li/Ti

Run	Li/Ti	Conversion (%)	Activity (g PDCPD/mol Ti · h)
1	0.5	0.3	3.3
2	1.0	82.9	913.3
3	1.5	95.3	1049.1
4	2.0	92.1	1014.6
5	2.5	29.2	321.6
6	3.0	0.0	0.0

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $T_p = 37^\circ\text{C}$; $t_p = 6$ h; M/Ti = 50; $C_m = 3.5$ mmol/mL; CH_3Li , (1.096 mmol/mL); solvent: toluene.

Table III Influence of t_A

Run	t_A (h)	Conversion (%)	Activity (g PDCPD/mol Ti · h)
7	0.5	63.1	2085.4
8	1.0	71.3	2356.4
9	1.5	89.7	2974.3
10	2.0	55.3	1824.3
11	4.0	42.3	1398.0
12	6.0	31.6	1044.3

Polymerization conditions: $T_A = 0^\circ\text{C}$; $T_p = 37^\circ\text{C}$; $t_p = 2$ h; Li/Ti = 1.5; M/Ti = 50; $C_m = 3.5$ mmol/mL; CH_3Li , (1.096 mmol/mL); solvent: toluene.

Table IV Influence of T_A

Run	T_A (°C)	Conversion (%)	Activity (g PDCPD/mol Ti · h)
13	-20	0.0	0.0
14	0	96.1	3176.1
15	20	61.3	2025.9
16	30	0.0	0

Polymerization conditions: $t_A = 90$ min; $T_p = 18^\circ\text{C}$; $t_p = 2$ h; Li/Ti = 1.5; M/Ti = 50; $C_m = 3.5$ mmol/mL; CH_3Li , (1.096 mmol/mL); solvent: toluene.

to the titanium center would increase the activity of the complex.

The obtained polymer was characterized by IR (Fig. 1) and $^1\text{H-NMR}$ (Fig. 2). All the data were same as those in the literature¹⁵ and from our previous work concerning nitrogen-containing ligands,¹⁰ and the data confirmed the existence of ROMP of DCPD in the given polymerization conditions.

Furthermore, we used catalyst **1** to study the influencing parameters on the ROMP of DCPD. The results of our experiments are listed in Tables II–VIII.

From the data listed in the tables, it is obvious that the ROMP of DCPD was affected by many factors. The data in Table II show that the amount of methyl lithium greatly affected the results of the polymerization. Our experiment results show that the operation at Li/Ti = 1.5–2 yielded better results.

In the same way, t_A (Table III) and T_A (Table IV) seem to have had a great influence on the polymerization reaction. The polymer yield increased when t_A ranged between 0.5 and 1.5 h;

Table V Influence of t_p

Run	t_p (h)	Conversion (%)	Activity (g PDCPD/mol Ti · h)
17	0.5	55.2	7279.5
18	1.0	68.5	4527.9
19	1.5	71.4	3146.4
20	2.0	78.3	2587.8
21	2.5	80.1	2146.3
22	4.0	87.9	1452.6
23	6.0	91.3	1005.8
24	10	93.8	620.0

Polymerization conditions: $T_A = 0^\circ\text{C}$; $T_p = 37^\circ\text{C}$; $t_A = 60$ min; Li/Ti = 1.5; M/Ti = 50; $C_m = 3.5$ mmol/mL; CH_3Li , (1.096 mmol/mL); solvent: toluene.

Table VI Influence of T_p

Run	T_p (°C)	Conversion (%)	Activity (g PDCPD/mol Ti · h)
25	0	3.4	33.7
26	12	8.3	82.3
27	40	68.7	681.2
28	60	96.2	954.3
29	80	80.6	799.5
30	100	78.8	781.0

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $t_p = 4$ h; Li/Ti = 1.5; M/Ti = 30; $C_m = 3.5$ mmol/mL; CH_3Li , (1.096 mmol/mL); solvent: toluene.

longer t_A led to the decrease of the yield. Operation at a low temperature of -20°C or at a high temperature of 30°C did not favor the polymerization reaction. Our results prove that, when T_A is 0°C and t_A is 1.5 h, the polymerization reaction yields better results.

t_p (Table V) and T_p (Table VI) appear to be the main influencing factors in the ROMP of DCPD. From a kinetic point of view, raising the temperature increases the rate of the chemical reaction. Our study proves that operation at a lower temperature does not favor the polymerization reaction. A high temperature does increase the rate of the reaction, but the data in Table VI show a decrease in the polymer yields; this could be attributed to the presence of an undesirable side reaction. Amass and Tuck¹⁶ investigated the kinetic polymerization of cyclopentene with $\text{WCl}_6/(\text{iso-C}_4\text{H}_9)_3\text{Al}$ in toluene and found that the longer the t_p is, the higher the conversion of cyclopentene will be, but the activity decreases rapidly as the reaction proceeds. We also found in our studies that the data listed in Table V lead to the same

Table VII Influence of MTi

Run	M/Ti	Conversion (%)	Activity (g PDCPD/mol Ti · h)
31	15	96.2	190.8
32	30	94.7	375.7
33	50	79.4	524.7
34	70	69.1	639.5
35	80	59.3	627.2
36	100	52.6	695.4
37	120	42.7	677.4
38	150	30.8	610.8

Polymerization conditions: $T_A = -3^\circ\text{C}$; $T_p = 37^\circ\text{C}$; $t_A = 90$ min; $t_p = 10$ h; Li/Ti = 1.5; $C_m = 3.5$ mmol/mL; CH_3Li , (1.096 mmol/mL); solvent: toluene.

Table VIII Influence of Monomer Concentration

Run	C_m (mmol/mL)	Conversion (%)	Activity (g PDCPD/mol Ti · h)
39	2.3	33.4	1324.6
40	3.5	64.0	2538.2
41	4.5	89.6	3553.5
42	6.0	92.8	3675.0

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $T_P = 60$ ($^\circ\text{C}$); $t_P = 60$ min; $\text{Li/Ti} = 1.5$; $\text{M/Ti} = 30$; CH_3Li , (1.096 mmol/mL); solvent: toluene.

conclusion. When the polymerization reaction is carried out at 60°C for 4 h, the yield of the polymer reaches 96%.

The quantity of DCPD injected into the reaction system seems to have a significant effect on the activity of the catalyst. A quick look at Table VII shows that the greater the amount of monomer added, the smaller the yield of the polymer obtained. As M/Ti increases, the concentration of the active centers of the catalyst decreases, which obviously leads to the decrease in the yield of polydicyclopentadiene (PDCPD). Finally, the data in Table VIII show that the yield of PDCPD increases with an increase in the monomer concentration (C_m) under the condition of a constant M/Ti ratio. Increasing the C_m , that is, increasing the concentration of the active species, leads to an increase in the yield of PDCPD.

From the previous results and discussion, the following conclusions can be made. The synthesis of these adduct complexes has created a convenient method to perform the ROMP of DCPD. The nature of the ligands does affect the activity of the catalyst and the molecular weight of PDCPD. However, these factors do not have a significant impact on the molecular weight distribution of the polymer. Many parameters do have a great influence on the course of the polymerization reaction. Controlling and optimizing these param-

eters make it possible to increase the yield of PD-CPD. When the conditions are $\text{Li/Ti} = 1.5\text{--}2$, $\text{M/Ti} = 30\text{--}50$, $T_A = 0^\circ\text{C}$, $T_P = 60^\circ\text{C}$, and $C_m = 3.5$ mmol/mL, the polymerization yields better results in a short period of time.

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