

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

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ABSTRACT: Ring opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) catalyzed by titanium tetrachloride adduct complexes such as $\text{TiCl}_4 \cdot 2\text{L}$ [L = pyridine (1), 2-methylpyridine (2), 2,4,6-trimethylpyridine (3), 3-aminopyridine (4), 2-hydroxypyridine (5)] and CH_3Li as cocatalyst was reported. The polymer was characterized by IR and $^1\text{H-NMR}$ methods. Five influencing factors were also discussed. The catalyst systems $\text{TiCl}_4 \cdot 2\text{L}/\text{CH}_3\text{Li}$ (L = 2-methylpyridine, 2,4,6-trimethylpyridine) appeared to be very active for the ROMP of DCPD. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3247–3251, 2000

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

INTRODUCTION

Ring opening metathesis polymerization (ROMP) of cyclic unsaturated hydrocarbons has been studied extensively over the past several decades^{1–5} following the first report made by Eleuterio⁶ and the famous discovery of homogeneous catalyst by Natta and coworkers.^{7,8} It is not only a major subject in polymer chemistry, but also an area of many recent fascinating developments. The most typical and effective catalyst systems for this kind of polymerization are composed of tungsten, molybdenum, tantalum, rhenium, ruthenium, osmium complexes, and alkylation reagents, such as BuLi , AlEt_2Cl , SnR_4 and others.^{9–11} In 1983, Hercules Company¹² used the RIM technique to

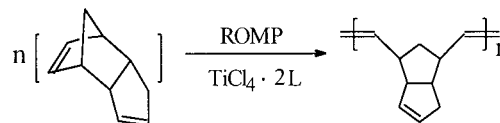
the polymerization of dicyclopentadiene (DCPD) catalyzed by the $\text{WCl}_6/\text{AlEt}_2\text{Cl}$ system to obtain a polymer with a high degree of crosslinking.

Recently, we have reported a study on the ROMP of DCPD and norbornene (NBE) catalyzed by titanocene complexes of the type $\text{Cp}_2\text{TiCl}_2/\text{RMgX}$ ¹³ and substituted titanocene complexes.^{14,15} In addition, our previous work¹⁶ has shown that the catalytic system of the type $\text{TiCl}_4 \cdot 2\text{THF}/\text{CH}_3\text{Li}$ (THF = tetrahydrofuran) exhibits good catalytic activity in the polymerization of dicyclopentadiene and norbornene. Yet there is no report on $\text{TiCl}_4 \cdot 2\text{L}/\text{CH}_3\text{Li}$ (L = organic ligand containing nitrogen as an electron donor atom) as a catalytic system for the ring opening metathesis polymerization of cyclo-olefins especially for polymerization of dicyclopentadiene:

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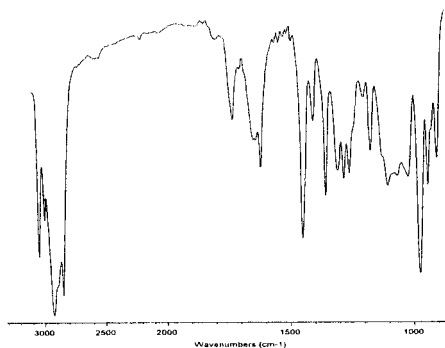


Figure 1 IR spectrum of polymer.

From the data listed in Table I, it is obvious that the catalysts **2** and **3** are more active than the others. The nature of the ligand has great influence on the catalytic activity of the complex. The presence of electron donor groups on the pyridine ring could greatly affect the electron cloud density on the nitrogen atom, which leads to the enhancement of the coordination of ligand to the metal center. Mohring and Coville²⁰ have reported that when the ligand is a better electron donor, it will reduce the positive charge on the metal and then weaken the bonding between the metal and the other ligands, particularly the unstable M–R bond, which will become more reactive. The active center of ROMP is the carbene species^{21,22} that is formed *in situ* under the given polymerization conditions. By taking Mohring's point into account, the coordination of ligand to titanium center reduces the positive charge on the titanium atom, which may weaken the unstable bonding of Ti=C, and then it will become more reactive. In doing so, the catalysts **2** and **3** yield better results in the polymerization of dicyclopentadiene.

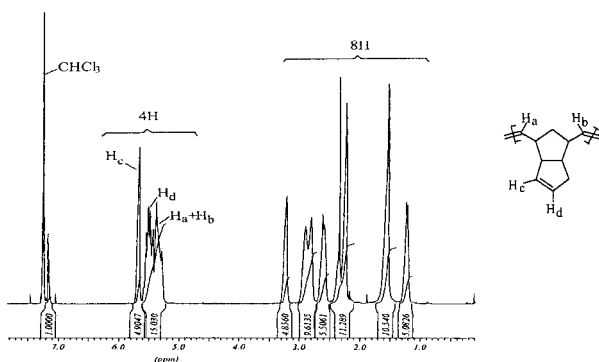


Figure 2 ¹H-NMR spectrum of polymer.

Table II Influence of the Aging Temperature

Catalyst	T_A (°C)	t_p (h)	Conv (%)	Activity (g PDCPD/mol Ti · h)
1	-20	24	0	0
2	-20	24	3.4	14.0
3	-20	24	7.8	32.2
1	0	4	35.7	884.9
2	0	4	55.6	1378.2
3	0	4	91.5	2268.0
1	30	4	4.8	119.0
2	30	4	22.4	555.2
3	30	4	68.1	1690.5

Polymerization conditions: $T_p = 18^\circ\text{C}$; $t_A = 90$ min; monomer/catalyst = 75; Li/Ti = 2; $C_{\text{DCPD}} = 3.5$ mmol/mL; CH_3Li , 0.7 mL (0.8439 mmol/mL); solvent: toluene.

The catalysts **4** and **5** appear not to be effectively active for the polymerization of dicyclopentadiene even though the $-\text{NH}_2$ and $-\text{OH}$ groups are better electron donors than $-\text{CH}_3$. The inactivity of these catalysts could be mainly attributed to undesirable reaction. The methyl lithium may react first with the active hydrogens in the ligands instead of the formation of the carbene species. Thus, the catalyst systems show very low activity for the ROMP of DCPD.

The obtained polymer was characterized by IR and ¹H-NMR. The IR data show the presence of both acyclic C=C double bonds ($\nu_{\text{C=C}} 1650\text{ cm}^{-1}$) and the cyclic C=C double bonds ($\nu_{\text{C=C}} 1620\text{ cm}^{-1}$) of the cyclopentene. On the other hand, there is almost a complete disappearance of the C=C double bonds ($\nu_{\text{C=C}} 1575\text{ cm}^{-1}$)²³ of the norbornene rings (Fig. 1).

Table III Influence of the Aging Time

Catalyst	t_A (min)	Conv (%)	Activity (g PDCPD/mol Ti · h)
1	30	3.6	59.5
2	30	58.4	965.0
3	30	64.7	1069.2
1	60	5.3	87.6
2	60	73.3	1211.3
3	60	86.8	1434.4
1	120	13.8	228.2
2	120	40.9	675.8
3	120	90.2	1490.5

Polymerization conditions: $T_A = 0^\circ\text{C}$; $T_p = 27^\circ\text{C}$; $t_p = 4$ h; monomer/catalyst = 50; Li/Ti = 2; $C_{\text{DCPD}} = 3.5$ mmol/mL; CH_3Li , 0.7 mL (0.8439 mmol/mL); solvent: toluene.

Table IV Influence of the Polymerization Time

Catalyst	t_p (h)	Conv (%)	Activity (g PDCPD/mol Ti · h)	M_n	D_n
1	2	7.6	251.2	66554	2.08
2	2	21.8	720.5	—	—
3	2	31.5	1041.0	—	—
1	4	14.3	236.3	—	—
2	4	51.5	851.0	—	—
3	4	90.2	1490.8	54659	2.24
1	6	50.6	557.5	—	—
2	6	93.6	1031.1	51546	2.06
3	6	99.6	1097.4	50308	2.33

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $T_p = 27^\circ\text{C}$; monomer/catalyst = 50; Li/Ti = 2; $C_{\text{DCPD}} = 3.5$ mmol/mL; CH_3Li , 0.7 mL (0.8439 mmol/mL); solvent: toluene.

These results are confirmed by the $^1\text{H-NMR}$ spectrum (Fig. 2), in which we can identify the protons H_c and H_d of the cyclopentene C=C double bonds and the protons H_a and H_b on the acyclic C=C double bonds. Moreover, the NMR spectrum confirms that, for each monomeric unit that contains 12 hydrogens, there are 4 olefinic hydrogens: there is no loss of C=C double bonds during polymerization. All these results are same as those in the literature²³ and confirm the existence of ROMP of DCPD.

We have used the catalysts **1**, **2**, and **3** to study the effect of the aging temperature, the aging time, the polymerization time, the molar ratio of the catalyst and cocatalyst, and the molar ratio of

the monomer and the catalyst. The results of our investigation are listed in Tables II–VI.

The aging temperature and the aging time appear to be the main influencing factors in the polymerization of dicyclopentadiene. The data listed in Table II show obviously that when the aging temperature is -20°C , the catalyst **1** remains inactive during the long polymerization process of 24 h, and so do the catalysts **2** and **3**. Increasing the aging temperature gives better results even if the aging time is short, but when the aging temperature is above 0°C , the polymerization reaction appears not to give enough good results. Thus, 0°C is the best aging temperature for catalysts. The data in Table III show that the aging time during 1 to 2 h is better.

The data in Table IV show that the polymerization time has a great influence on the yield of the polymer. The longer the polymerization time, the higher the yield obtained. The time of 6 h is a better condition for the polymerization.

The Li/Ti ratio seems to be an important factor to the polymerization reaction. According to the data in Table V, when $\text{Li/Ti} < 1$ the interaction between the catalyst and the cocatalyst may be incomplete and therefore does not activate efficiently the polymerization reaction. On the contrary, when $1 < \text{Li/Ti} < 2$, the activation of the catalyst is very complete and the polymerization reaction yields better results. However, when $\text{Li/Ti} = 3$, the polymerization does not take place when catalyst **1** is used, and under this condition it produces only an oily product. However, the catalysts **2** and **3** conserve their activity during the polymerization process. When the polymerization reaction catalyzed by the catalyst **3** is

Table V Influence of Li/Ti Molar Ratio

Catalyst	Li/Ti	Conv (%)	Activity (g PDCPD/mol Ti · h)
1	0.5	9.8	242.9
2	0.5	28.5	706.4
3	0.5	34.6	857.6
1	1	32.5	805.6
2	1	41.7	1033.6
3	1	48.3	1197.2
1	2	30.1	746.1
2	2	56.7	1405.5
3	2	92.6	2295.3
1	3	0	0
2	3	54.9	1360.8
3	3	82.2	2037.5

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $T_p = 22^\circ\text{C}$; $t_p = 4$ h; monomer/catalyst = 75; $C_{\text{DCPD}} = 3.5$ mmol/mL; CH_3Li , 0.7 mL (0.8439 mmol/mL); solvent: toluene.

Table VI Influence of Monomer/Catalyst Molar Ratio

Catalyst	Monomer/ Catalyst	Conv (%)	Activity (g PDCPD/mol Ti · h)
2	25	30.6	252.8
3	25	36.8	304.0
2	50	54.6	902.3
3	50	93.7	1548.4
2	75	39.2	971.7
3	75	60.4	1497.2
2	100	69.5	2297.0
3	100	92.3	3050.5

Polymerization conditions: $T_A = 0^\circ\text{C}$; $t_A = 90$ min; $T_p = 22^\circ\text{C}$; $t_p = 4$ h; $\text{Li/Ti} = 2$; $C_{\text{DCPD}} = 3.5$ mmol/mL; CH_3Li , 0.7 mL (0.8439 mmol/mL); solvent: toluene.

carried out at 22°C for 4 h, the yield of the polymer reaches 92.6% at $\text{Li/Ti} = 2$. Friedland and his coworkers²⁴ found for the reaction of TiCl_4 with alkyllithium that when $\text{Li/Ti} < 1$, Ti^{+4} is easily reduced to Ti^{+3} . In addition, when $\text{Li/Ti} > 4$, the complex $\text{TiCl}_4(\text{CH}_3\text{Li})_n$ ($n > 4$) is formed, these two conditions do not favor the formation of titanium carbene, which is the active center for the ring opening metathesis of dicyclopentadiene. Our experimental results have shown that when $\text{Li/Ti} = 2$, the polymerization reaction gives better results if catalysts **2** and **3** are used.

The data in Table VI mainly show that the monomer/catalyst ratio does not have great influence on the polymerization results. However, operation at a ratio ranging between 50 and 75 proves to be favorable for the polymerization.

All of the above results lead to the conclusion that the catalyst **3** shows the highest catalytic activity for the polymerization of dicyclopentadiene.

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