

# Polymerization of MMA catalyzed by different novel mixed ligand lanthanocene $\{(\text{Cp})(\text{Cl})\text{LnSchiff-base}(\text{THF})\}$ , $(\text{COT})\text{-Ln}(\text{methoxyethylindenyl})(\text{THF})/\text{Al}(i\text{-Bu})_3$ systems

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This article deals that the rare earth metal complexes along with  $\text{Al}(i\text{-Bu})_3$  can catalyze the polymerization of methylmethacrylate (MMA) into high molecular weight poly(MMA) along with narrow molecular weight distributions (MWD). A typical example was mentioned in the case of  $\{\text{Cp}(\text{Cl})\text{Sm-Schiff-base}(\text{THF})\}$  which expresses maximum (conv. % = 55.46 and  $M_n = 354 \times 10^3$ ) efficiency along with narrow MWD ( $M_w/M_n < 2$ ) at  $60^\circ\text{C}$ . The resulting polymer was partially syndiotactic (> 60%). The effect of the catalyst, temperature, catalyst/MMA molar ratio, catalyst/ $\text{Al}(i\text{-Bu})_3$  molar ratio on the polymerization of MMA at  $60^\circ\text{C}$  were also investigated.

**Keywords** MMA, polymerization, novel mixed ligand lanthanocene complexes

## Introduction

Since Ziegler-Natta catalysts were applied for the polymerization of methylmethacrylate (MMA) in the 1960s, many transition metal catalysts, including V, Cr, Co, Mn and Ti catalysts, have been developed.<sup>1-4</sup>

However, not all these catalysts with 30—100 molar ratio of monomer showed high activity, the molecular weight of poly(MMA) was lower than  $25 \times 10^4$ . In 1991, MMA polymerization catalyzed by neodymium catalysts was reported.<sup>5</sup> Later Shen and his co-workers reported that the addition of a small amount of butyl lithi-

um to the  $\text{Y}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$  system could greatly enhance its catalytic activity towards MMA polymerization with high conversion at room temperature.<sup>6</sup> Similarly Yasuda *et al.*<sup>7</sup> reported that polymerization of MMA by bis(cyclopentadienyl)samarium-hydride,  $\{\text{Sm}(\text{C}_5\text{H}_5)_2\text{-H}\}_2$ , in toluene offered the syndiotactic poly(MMA) ( $M_n > 100 \times 10^3$ ) with extremely low polydispersity ( $M_w/M_n = 1.02$ ). But upto now the title complexes have not been tried for the polymerization of polar monomers, especially MMA. So we describe here the first example of high molecular weight, partially syndiotactic poly(MMA) by using the title complexes.

## Experimental

All the operations were carried out under prepurified argon into a 25 mL dry ampule. Toluene was refluxed and distilled over blue sodium benzophenone under argon immediately before use. MMA was washed with dilute NaOH solution until colourless, dried over molecular sieves, then distilled under vacuum.  $\text{Al}(i\text{-Bu})_3$  was purchased and used as such. A general procedure for the polymerization of MMA was as follows<sup>8</sup> (for example, entry 1 in Table 1): Under argon  $\text{Cp}(\text{Cl})\text{Sm-Schiff base}(\text{THF})/\text{Al}(i\text{-Bu})_3$  were charged (1:20) into dry ampule and then 1 mL of toluene was transferred.

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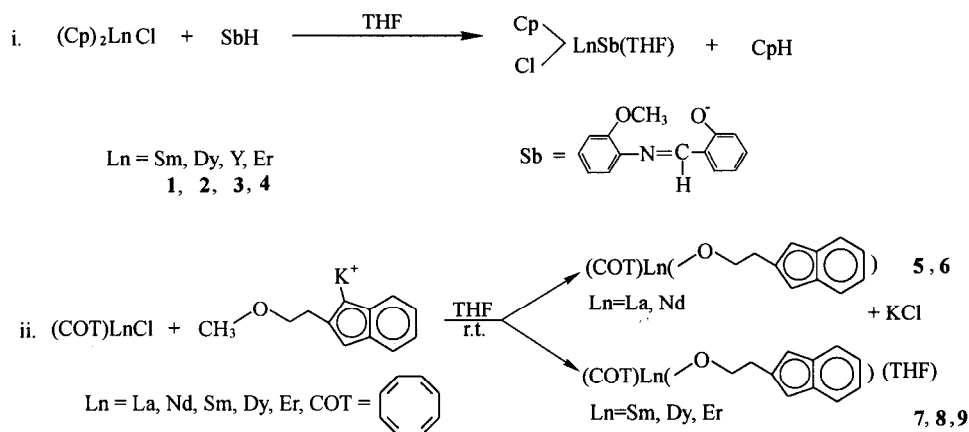
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After this 1.05 mL of MMA (1:1000) was syringed, the polymerization was initiated at 60°C in a waterbath. After 20 h, the polymerization was quenched by ethanol containing 5% HCl. The poly(MMA) thus obtained was washed with ethanol, dried at 50°C under vacuum, (weighed on digital balance and calculated the percentage conversion). Inherent viscosity of poly(MMA) in CHCl<sub>3</sub> was determined at 30°C with an Ubbelohde-type viscometer. The viscosity average molecular weight was calculated with the following equation<sup>9</sup>  $\{\eta\} = 5.5 \times 10^{-3} M_{\eta}^{0.79} (\text{cm}^3/\text{g})$  (where  $M_{\eta}$  = viscosity average molecular

weight). Molecular weight distribution (MWD) values were obtained from GPC chromatograms which were obtained with waters-208LC/GPC, and polystyrene standards for calibration.

## Results and discussion

All the complexes used during this study were newly synthesized in our laboratory by the procedure illustrated below.



For our ease we selected complexes 3 and 7 as a representative for each group to test the effects of catalyst, temperature, catalyst/MMA molar ratio and cata-

lyst/Al(*i*-Bu)<sub>3</sub> molar ratio on the polymerization of MMA. The results of polymerization of MMA by different catalysts are summarized in Table 1.

**Table 1** Effect of catalysts on the polymerization of MMA

No.	Catalyst	Conversion (%)	$M_n \times 10^3$	$M_w/M_n$
1	$\text{Cp}(\text{Cl})\text{Sm}(\text{C}_{14}\text{H}_{13}\text{NO}_2)(\text{THF})$	55.46	354	1.78
2	$\text{Cp}(\text{Cl})\text{Dy}(\text{C}_{14}\text{H}_{13}\text{NO}_2)(\text{THF})$	51.80	274	1.98
3	$\text{Cp}(\text{Cl})\text{Y}(\text{C}_{14}\text{H}_{13}\text{NO}_2)(\text{THF})$	50.52	264	1.82
4	$\text{Cp}(\text{Cl})\text{Er}(\text{C}_{14}\text{H}_{13}\text{NO}_2)(\text{THF})$	43.94	227	1.71
5	$(\text{COT})\text{La}(\text{methoxyethylindenyl})$	34.92	172	2.66
6	$(\text{COT})\text{Nd}(\text{methoxyethylindenyl})$	33.06	148	2.14
7	$(\text{COT})\text{Sm}(\text{methoxyethylindenyl})(\text{THF})$	28.48	141	2.87
8	$(\text{COT})\text{Dy}(\text{methoxyethylindenyl})(\text{THF})$	23.47	126	2.78
9	$(\text{COT})\text{Er}(\text{methoxyethylindenyl})(\text{THF})$	14.44	72	2.37
10	$(\text{Cp})_2\text{Y}(\text{C}_{14}\text{H}_{13}\text{NO}_2)$	20.15	186	2.27
11*	$\text{Al}(\textit{i}\text{-Bu})_3$	33.14	14	-

Reaction conditions: time = 20 h, temperature = 60°C, Cat./MMA = 1:1000, Cat./Al = 1:20. \* blank.

The results explain that both the metals as well as ligands play an important role in determining the activity

of the catalysts. The complexes **1**–**4** showed a greater increase in the conversion as well as molecular weight than complexes **5**–**9**. The maximum activity (conv. % = 55.46 and  $M_n = 354 \times 10^3$ ) was observed in case of catalyst **1** while catalyst **9** showed minimum efficiency (conv. % = 14.44 and  $M_n = 72 \times 10^3$ ). The catalyst **10** was tried to compare its activity with others. It was found that its activity (conv. % = 20.15 and  $M_n = 186 \times 10^3$ ) lies in between the two kinds of the catalyzing systems. Since in case of complexes **1**–**4**, the ligands have less steric influence on the central metals, the ionic radii play a significant role in determining the efficiency of the catalysts. While in case of catalysts **5**–**9**, the bulkiness of the ligands has a pronounced steric effect on the central metals and hence the activity is suppressed greatly. Similarly it was observed that all complexes yield high molecular weight poly(MMA) with somewhat narrow MWD ( $M_w/M_n = 1.71$ – $2.87$ ). Furthermore the result obtained from blank sample indicates that Al(*i*-Bu)<sub>3</sub> yields poly(MMA) (conv. % = 33.14 and  $M_n = 14 \times 10^3$ ). The resulting poly(MMA) was 58.0% syndiotactic.<sup>10</sup> <sup>1</sup>H NMR analysis of the polymer, resulting from the complexes **3**, **7** and **10** indicates that these complexes produce partially syndiotactic poly(MMA) (Fig. 1) which is supported by Li and his coworkers.<sup>11</sup>

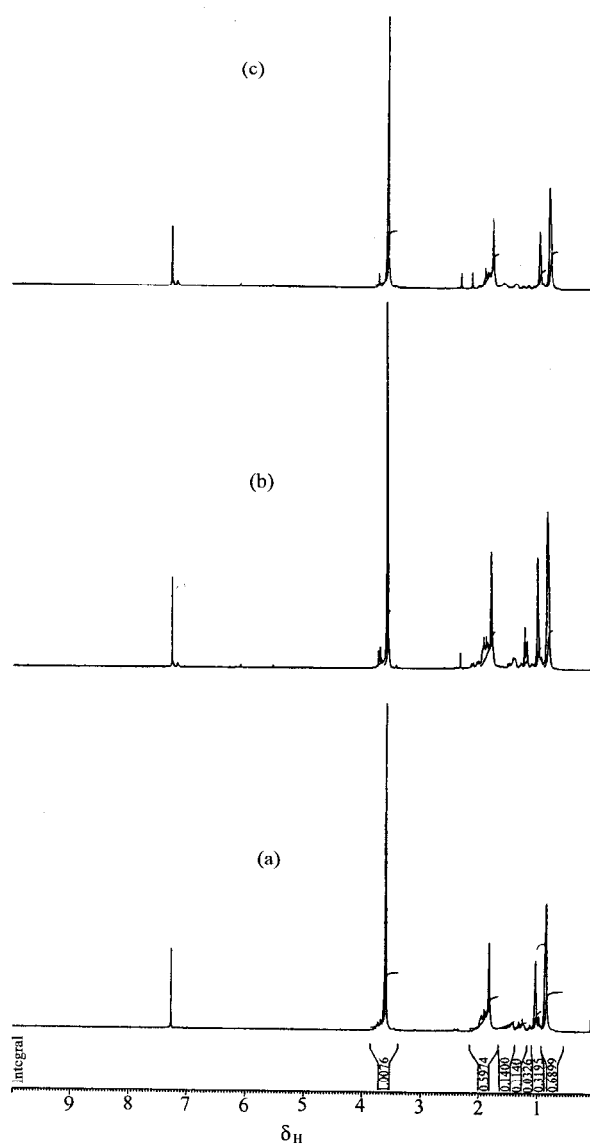
**Table 2** Effect of temperature on the polymerization of MMA

Catalyst	<i>T</i> (°C)	Conversion (%)	$M_n \times 10^3$
<b>3</b>	70	51.59	416
<b>7</b>	70	29.40	148
<b>3</b>	60	50.52	264
<b>7</b>	60	28.48	140
<b>3</b>	50	31.42	191
<b>7</b>	50	14.97	109
<b>3</b>	40	13.80	107
<b>7</b>	40	12.72	99

Reaction conditions: time = 20 h, temperature = 60°C, Cat./MMA = 1:1000, Cat./Al = 1:20.

The effect of temperature as shown in Table 2, illustrates that both catalyzing systems show linear increase in the activity with the rise of temperature. The greatest efficiency (conv. % = 51.59 and  $M_n = 416 \times 10^3$ ) was seen in case of catalyst **3** at 70°C. The catalyst **3** showed greater activity than catalyst **7** at all temperatures which may be due to the presence of bulky ligands suppressing the activity. These results are in contrast with the previ-

ous work reported by Shen *et al.*<sup>8</sup> that the higher the temperature, the lower the conversion and molecular weight of poly(MMA). Perhaps different catalyst/co-catalyst systems behave differently at different temperatures.



**Fig. 1** <sup>1</sup>H NMR spectra of partially syndiotactic poly(MMA) obtained with (a) Cp(Cl)Y(C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>)(THF)/Al(*i*-Bu)<sub>3</sub>, (b) (COT)Sm(methoxyethylindenyl)(THF)/Al(*i*-Bu)<sub>3</sub>, (c) (Cp)<sub>2</sub>Y(C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>)/Al(*i*-Bu)<sub>3</sub> in toluene at 60°C.

In case of catalyst/MMA molar ratio (Table 3), both conversion as well as molecular weight increase parallel with the increase of MMA concentration. The greatest activity was exhibited by catalyst **3** (conv. % =

54.40 and  $M_n = 395 \times 10^3$ ) at 3000 molar ratio of MMA. The catalyst **3** showed more efficiency than catalyst **7** (conv. % = 33.8 and  $M_n = 181 \times 10^3$ ) at 3000 molar ratio of MMA. The variation may be due to steric hinderance offered by the bulky ligands.

**Table 3** Effect of Cat./MMA molar ratio on the polymerization of MMA

Catalyst	Cat./MMA (mol/mol)	Conversion (%)	$M_n \times 10^3$
3	500	43.10	88
7	500	18.69	107
3	1000	50.52	264
7	1000	28.48	140
3	2000	51.56	355
7	2000	31.46	157
3	3000	54.40	395
7	3000	33.80	181

Reaction conditions: time = 20 h, temperature = 60°C, Cat./Al = 1:20.

The effect of catalyst/Al(*i*-Bu)<sub>3</sub> molar ratio on the polymerization of MMA is described in Table 4. The results explain that catalyst/Al(*i*-Bu)<sub>3</sub> molar ratio proves to be an important factor for the polymerization of MMA. Generally both catalysts exhibit the same characteristics. At first, as the catalyst/Al(*i*-Bu)<sub>3</sub> molar ratio increases, the conversion as well as molecular weight of poly(MMA) increase markedly while the MWD remains in the range ( $M_w/M_n = 1.46$ —2.87) for all the molar ratios of Al(*i*-Bu)<sub>3</sub>. At 20 molar ratio of Al(*i*-Bu)<sub>3</sub>, the catalyst **3** showed the best efficiency (conv. % = 50.52 and  $M_n = 264 \times 10^3$ ). The catalyst **7** also gives better

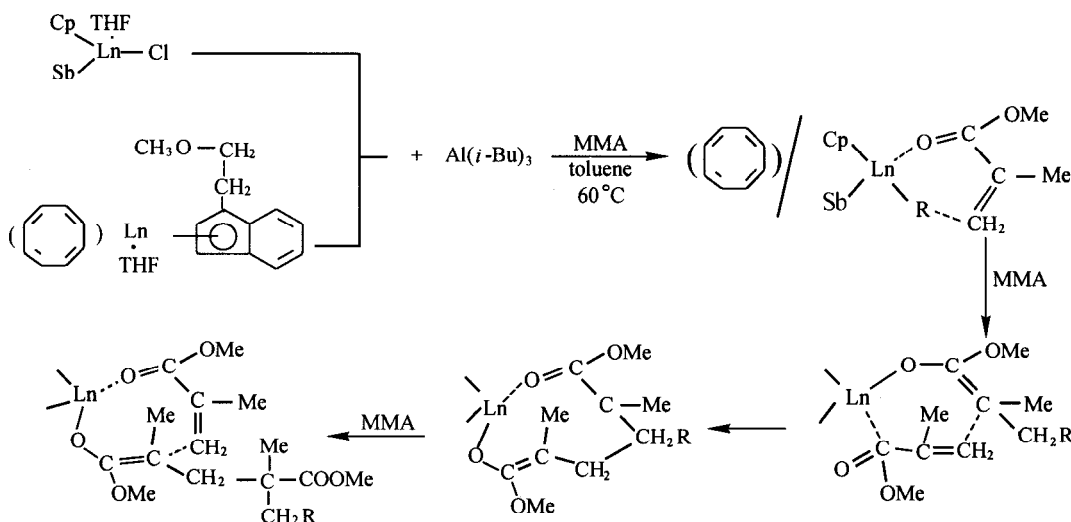
activity (conv. % = 28.48 and  $M_n = 140 \times 10^3$ ) at 20 molar ratio of Al(*i*-Bu)<sub>3</sub> than those of other molar ratios of Al(*i*-Bu)<sub>3</sub>. The further increase of Al(*i*-Bu)<sub>3</sub> molar ratio causes a fall of conversion as well as molecular weight of Polt(MMA) which may be Al(*i*-Bu)<sub>3</sub> at higher concentration may act as chain transfer agent and hence may terminate the further polymerization. Earlier Li and his coworkers<sup>12</sup> reported that low concentration of Al(*i*-Bu)<sub>3</sub> favours high conversion with high molecular weight poly(MMA). The resulting poly(MMA) was partially syndiotactic (*ca.* 80%).

The catalyzing systems used during this study are new type of Ziegler-Natta type catalysts while the proposed mechanistic pathway is presumed to be similar as reported earlier by Yasuda and Ihara<sup>12</sup> which is illustrated by the following scheme.

**Table 4** Effect of Cat./Al(*i*-Bu)<sub>3</sub> molar ratio on the polymerization of MMA

Catalyst	Cat./Al (mol/mol)	Conversion (%)	$M_n \times 10^3$	$M_w/M_n$
3	10	24.47	244	1.61
7	10	19.72	118	2.27
3	20	50.52	264	1.82
7	20	28.48	140	2.87
3	30	49.63	83	1.68
7	30	21.79	136	2.30
3	40	49.57	73	1.46
7	40	16.60	133	2.46

Reaction conditions: time = 20 h, temperature = 60°C, Cat./MMA = 1:1000



## Conclusion

From this article we can derive conclusion that partially syndiotactic polymer of high molecular weight ( $M_n > 100 \times 10^3$ ) with somewhat narrow MWD ( $M_w/M_n < 2$ ) can be obtained by such type of catalyzing systems. Further study is to improve the catalytic efficiency of these complexes.

## References

1. Kapur, S.L.; Deshpande, A.B., *J. Scient. Ind. Res.*, **31**, 254(1972).
2. Akimoto, A., *J. Polym. Sci. Polym. Chem.*, Part A-1 **10**, 3113(1972).
3. Koide, N.; Imura, K.; Pakeda, M., *J. Macromol. Sci., Chem. A*, **9**,961(1975).
4. Kothandaraman, H.; Palannivelu, K., *Eur. Polym. J.*, **21**, 815(1985).
5. Zhang, W.; Wang, W.; Lin, L.P.; Shen, Z.Q., *J. Zhejiang Univ. (Natural Sci.)* (in Chinese), **25**, 114 (1991).
6. Liu, J.-F.; Sun, J.-Q.; Shen, Z.-Q., *Chem. Res. Chin. Univ.*, **9**, 148(1993).
7. Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yakota, K.; Miyake, S.; Kai, Y.; Kenehisa, N., *Macromolecules*, **28**, 7134(1993).
8. Liu, J.-F.; Shen, Z.-Q.; Sun, J.-Q., *Eur. Polym. J.*, **32**, 883(1996).
9. Canton, H.J.; Meyerhoff, G., *Z. Electrochem.*, **56**, 904(1952).
10. Sun, J.Q., *ACTA Polym. Sin.*, **1**, 96(1998).
11. Li, Y.F.; Ward, D.G.; Reddy, S.S.; Collins, S., *Macromolecules*, **30**, 1875(1997).
12. Yasuda, H.; Ihara, E., *Macromol. Chem. Phys.*, **196**, 2417(1995).

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