Polymerization of Methylmethacrylate by Tridentate Schiff Base Derivative of Indenyl and Cyclooctatetraenyl Lanthanoid Complexes Along with Al(*i-Bu*)$_3$ Catalytic System

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Summary: Different types of the tridentate Schiff base, [N-(2-methoxyphenyl) salicylideneamine] derivative of lanthanoid complexes along with Al(*i-Bu*)$_3$ are proved to be versatile tools for the polymerization of methylmethacrylate (MMA). The complexes, derived from indene and tridentate Schiff base ligands, express better efficiency ($M_v = 195 \times 10^3 - 355 \times 10^3$) than the complexes, prepared from cyclooctatetraene (COT) and tridentate Schiff base ligands ($M_v = 105 \times 10^3 - 175 \times 10^3$). The effect of catalyst, temperature, catalyst/MMA molar ratio and catalyst/Al(*i-Bu*)$_3$ molar ratio on the polymerization of MMA at 70 °C are studied. It is observed that ligand size and radius of the metal are important factors in determining the catalytic efficiency of the complexes.

Introduction

The synthesis of high molecular weight ($M_n > 5 \times 10^3$) polymers with narrow molecular weight distribution ($M_w/M_v < 1.05$) is a challenging theme in the modern polymer chemistry. Various living polymerization systems can perform such type of synthesis but no anionic/cationic polymerization, group transfer polymerization or metal carbene initiated polymerization has achieved this goal [1-4].

Earlier Yasuda *et. al.,* [5] reported the synthesis of high molecular mass ($M_v > 1 \times 10^3$) polymethylmethacrylate with low polydispersity ($M_w/M_n = 1.02$) by unique type of the organolanthanoid complex. Similarly Qian *et. al.,* [6] succeeded to prepare predominantly syndiotactic (rr > 70%) polymethylmethacrylate ($M_v = 500 \times 10^3$) with narrow polydispersity ($M_w/M_v = 1.4$) by using 2-propenyl cyclopentadienyl lanthanoid complexes as a single component catalyst. Later on it was found that rare earth metal alkoxides played a key role for the olefin polymerization [7]. In another study it was observed that polymerization of methylmethacrylate (MMA) by *bis*(cyclopentadienyl)samarium hydride in toluene yielded the syndiotactic polymer of high molecular weight with extremely low polydispersity [8].

Schiff base ligands are considered "Privileged ligands" because they are easily prepared by the condensation between aldehydes and imines. The stereogenic centres or other chirality elements can be introduced in the synthetic design. Schiff base ligands coordinate different metals and stabilize them in various oxidation states enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations [9].

Previously several Schiff bases and their complexes were studied for their interesting properties such as their ability to reversibly binding oxygen [10], catalytic activity in the hydrogenation of olefins [11] and isomerization of 1,5-hexadiene [12]. Recently a large number of lanthanoid complexes, derived from different types of Schiff bases have been attempted as they possessed extraordinary catalytic properties. Synthesis of partially syndiotactic high molecular weight polymethylmethacrylate ($M_v = 354 \times 10^3$) by using mixed ligand lanthanoid complexes has been reported earlier [13].

In another study, a high molecular weight poly(*β*-pinene) with high productivity was prepared by using Schiff base nickel complexes blended with methylaluminoxane. It was also found that ligand structure had a substantial effect on the polymerization in terms of the productivity and the molecular weight [14]. Later on it was also observed that Schiff base ruthenium complexes exhibited a high activity and chemoselectivity in a variety of catalytic processes such as ring closing metathesis, alkyne dimerization, enol ester synthesis and ring opening metathesis polymerization [15]. Keeping in mind the importance of Schiff base ligands, present study was carried out to check the effect of catalyst, temperature,

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catalyst/MMA molar ratio and catalyst/cocatalyst molar ratio on the polymerization of MMA by using the complexes, mentioned in the title.

Results and Discussion

In order to facilitate the study, one complex from each group was taken as a representative to discuss the polymerization of MMA. Complex **1** was taken as a representative of complexes **1-4** and complex **5** was taken as a representative of the complexes **5-8** to check the effects of catalyst, temperature, catalyst/MMA molar ratio and catalyst/Al(*i-Bu*)$_3$ molar ratio on the polymerization of MMA at 70 °C (Table-1). It was found that both metals as well as ligands played an important role in determining the activity of the catalyst. The catalysts (**1-4**) showed a greater increase in the conversion as well as molecular weight than the catalysts (**5-8**).

Table-1: Effect of catalyst on the polymerization of MMA.

S. No	Catalyst	% conversion	$M_v \times_{10}^3$	M_w/M_v
1	Indenyl SmCl ($C_{14}H_{13}NO_2$).2THF	56.45	355	1.70
2	Indenyl EuCl ($C_{14}H_{13}NO_2$).2THF	53.70	310	1.80
3	Indenyl GdCl ($C_{14}H_{13}NO_2$).2THF	51.45	280	1.75
4	Indenyl ErCl ($C_{14}H_{13}NO_2$).2THF	40.5	195	1.83
5	(COT) Sm ($C_{14}H_{13}NO_2$).2THF	36.46	175	2.14
6	(COT) Eu ($C_{14}H_{13}NO_2$).2THF	34.5	145	2.37
7	(COT) Gd ($C_{14}H_{13}NO_2$).2THF	28.48	130	2.78
8	(COT) Er ($C_{14}H_{13}NO_2$).2THF	18.45	105	2.87
9	$SmCl_3$*	9.5	13	-
10	Al (*i-Bu*)$_3$*	15.5	15	-

Reaction conditions: time = 20 h, cat/MMA =1:1000, cat/Al =1:20, temp. = 70 °C, blank*

The maximum activity (conversion% = 56.45) and M_v (355 × 10^3) were observed in case of catalyst **1** while catalyst **8** showed a minimum efficiency (conversion % = 18.45 and M_v=105 × 10^3). It was attributed to the bulkiness of the cyclo-octatetraene which offered a greater steric hindrance as compared to indene and hence the efficiency of the catalyst (**5**) was suppressed. Since the ionic radius of samarium is comparatively larger than the other attempted metals therefore the efficiency of the catalysts with samarium in both types of the complexes was observed better than those of others (Eu, Gd and Er). The results obtained from blank samples showed that $SmCl_3$ exhibited a very small efficiency (conversion % = 9.5 and molecular weight = 13 × 10^3). Similarly Al(*i-Bu*)$_3$ also showed a negligible efficiency (conversion% = 15.5 and molecular weight = 15 × 10^3) (Table-1).

Both the complexes **1** and **5** showed linear increase in activity with the rise in temperature (Fig. 1a and 1b). The reason is that greater the kinetic energy, greater is the chance to gain the energy of activation and hence greater will be the efficiency of reaction. The greatest efficiency (conv.% = 57.5 and M_v = 472 × 10^3) was observed in case of catalyst **1** at 90 °C. The catalyst **1** expressed better efficiency at all the temperatures than catalyst **5** which might be due to the presence of bulky ligands (Table-2). Pan *et. al.,* found the same trend in the rapid polymerization of MMA by lanthanoid complexes [16]. Similar results have been reported by Qian *et. al.,* by using 2-propenyl substituted cyclopentadienyl lanthanoid complexes as a single component catalyst [6].

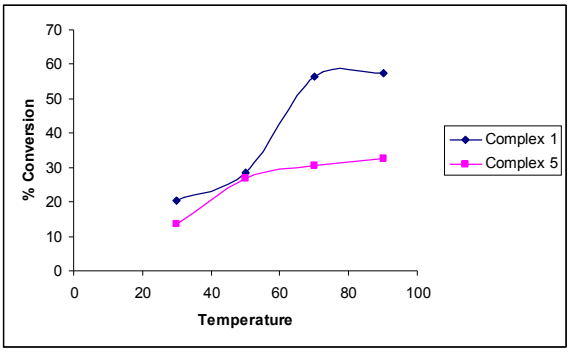


Fig. 1a: Effect of temperature (°C) on the polymerization of MMA with complexes 1 & **5**.

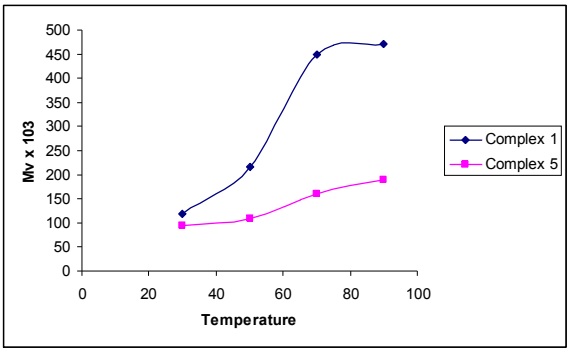


Fig. 1b: Effect of temperature (°C) on the molecular weight (M_v x 10^3) of MMA with complexes **1** & **5**.

Table-2: Effect of temperature on the polymerization of MMA.

Complex no.	Temperature °C	% conversion	$M_v \times 10^3$
1	90°C	57.5	472
5		32.5	190
1	70°C	56.52	450
5		30.42	160
1	50°C	28.5	215
5		26.7	110
1	30°C	20.50	120
5		13.45	95

Reaction conditions: time = 20 h, cat/MMA = 1:1000, cat/Al = 1:20

With increase in MMA concentration, the effect of catalyst/MMA molar ratio (Fig. 2a and 2b)

justifies that both the conversions as well as molecular weight increased in a parallel way. The greatest activity was observed in case of catalyst **1** (conv. % = 65.40 and M_v=395 × 10^3) at 3000 molar ratio of MMA. It also showed greater activity than catalyst **5** (conv.% = 33.47 and M_v= 180 × 10^3) at this molar ratio of MMA (Table-3). The variation may be due to the steric hindrance offered by the cyclooctatetraene as compared to indene. This trend is in line with the earlier reported work [13].

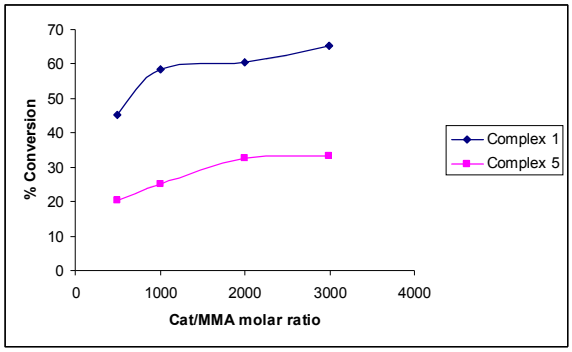


Fig. 2a: Effect of cat/MMA molar ratio on the polymerization of MMA with complex **1** & **5**.

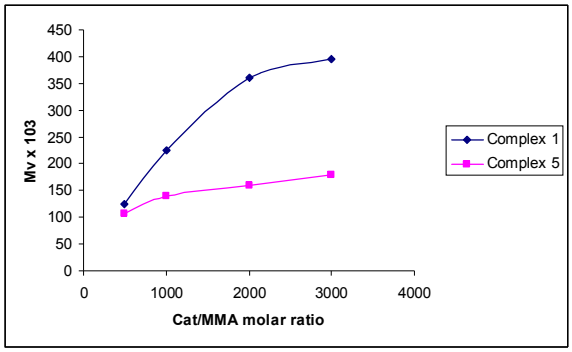


Fig. 2b: Effect of cat/MMA molar ratio on the molecular weight (M_v x 10^3) of MMA with Complex **1** & **5**.

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

Complex no.	Cat/MMA, Mol/Mol	% conversion	$M_v \times 10^3$
1	**500**	**45.15**	**125**
5		**20.50**	**107**
1	**1000**	**58.47**	**255**
5		**25.29**	**140**
1	**2000**	**60.50**	**360**
5		**32.47**	**160**
1	**3000**	**65.40**	**395**
5		**33.47**	**180**

Reaction conditions: time = 20h, cat/Al = 1:20, temp. = 70 °C

The effect of catalyst/**Al** (i-Bu)$_3$ molar ratio was proved to be an important factor for the polymerization of MMA (Fig. 3a and 3b). Generally, both the catalytic systems expressed similar pattern. At the beginning, as the catalyst/Al(i-Bu)$_3$ molar ratio increased, the conversion (%) as well as molecular weight of poly(MMA) increased in a parallel manner. At 20 molar ratio of Al(i-Bu)$_3$, catalyst **1** exhibited the best efficiency (conv.%=52.50 and M_v=268 × 10^3) while the catalyst **5** showed better activity (conversion %= 30.10 and M_v=145 × 10^3) at this molar ratio of the Al(i-Bu)$_3$ than those of others but less than catalyst **1** which was due to the bulkiness of the cyclooctatetraene as compared to indene and the difference in the ionic radii of the attempted metals (Sm, Eu, Gd, Er). Further increase in the Al(i-Bu)$_3$ molar ratio caused a fall in the conversion(%) as well as the molecular weight of Poly(MMA) (Table-4) which was due to the fact that Al(i-Bu)$_3$ at higher concentration may act as (a) chain transfer agent and hence may terminate the further polymerization. Earlier it was found that a low concentration of Al(i-Bu)$_3$ favoured high conversion with greater molecular weight Poly(MMA) [17]. Both the catalyzing systems resulted predominantly syndiotactic polymethymethacrylate (> 70%)

Table-4: Effect of **Cat**/Al(i-Bu)$_3$ molar ratio on the polymerization of MMA.

complex no.	cat/MMA, mol/mol	% conversion	$M_v \times 10^3$
1	**10**	**25.20**	**243**
5		**20.10**	**120**
1	**20**	**52.50**	**268**
5		**30.10**	**145**
1	**30**	**50.87**	**210**
5		**25.26**	**125**
1	**40**	**48.90**	**170**
5		**20.60**	**120**

Reaction conditions: time = 20 h, temp.= 70 °C, Cat/MMA = 1:1000.

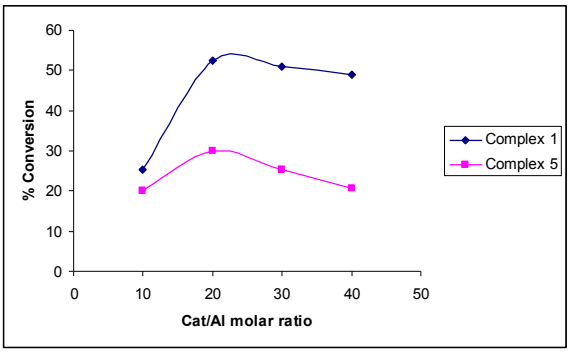


Fig. 3a: Effect of cat/Al molar ratio on the polymerization of MMA with complexes **1** & **5**.

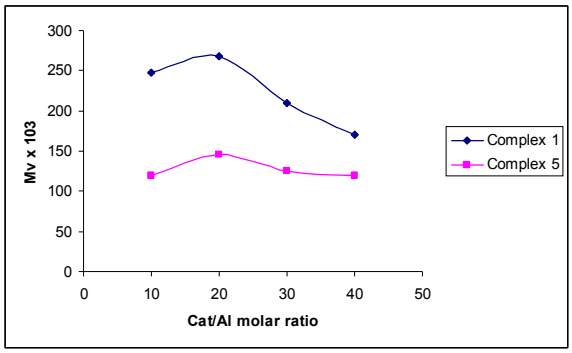


Fig. 3b: Effect of cat/Al molar ratio on the molecular weight (M_v x 10^3) of MMA with complexes **1** & **5**.

Experimental

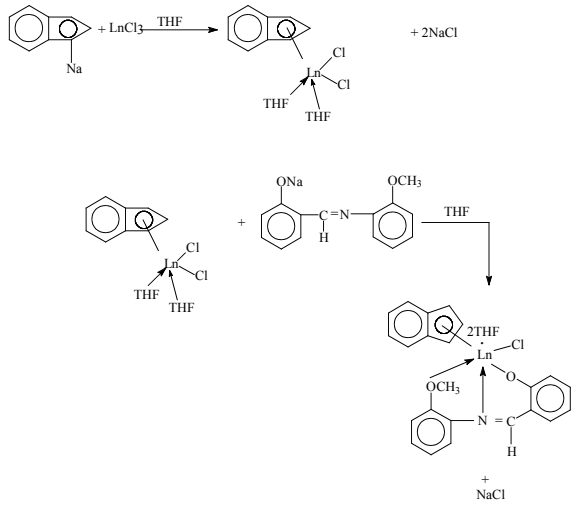
The tridentate schiff base {*N*-(*2-methoxy-phenyl*) salicylideneamine} was prepared by the condensation of equimolar quantities of purified salicylaldehyde and anisidene in toluene at room temperature. The resulting Schiff base was purified by recrystallization in petroleum ether, dried and was used subsequently. The tridentate schiff base derivative of indenyl and cyclooctatetraenyl lanthanoid complexes were synthesized by using the standard procedure [18, 19] and were characterized with the help of elemental analysis and MS technique (Schemes 1 and 2).

These catalysts along with Al(*i-Bu*)$_3$ were used for the polymerization of MMA. It was carried out under prepurified argon into a 25 ml dry ampule. The MMA was purified by washing with dilute NaOH solution, dried over molecular sieves and distilled under vacuum. A general procedure is explained for the synthesis of complex **1**; Indenyl(Cl)Sm Schiff base (THF)/Al(*i-Bu*)$_3$ were charged (1:20) under argon into a dry ampule and 1 mL of well dried and refluxed toluene was added. MMA (1:1000) was syringed (1.1 mL) and the polymerization was initiated at 70 °C in a water bath. After 20 h, the polymerization was quenched with ethanol containing 1%HCl (Table-1). The poly(MMA) thus obtained was washed with ethanol, dried at 50 °C under vacuum, weighed and % conversion was measured. The inherent viscosity of poly(MMA) in $CHCl_3$ was determined at 30 °C with an Ubbelohde type viscometer. The viscosity average molecular weight was calculated with the help of the Mark-Houwink equation

$[\eta] = KM_v^{\alpha}$

M_v is viscosity average molecular weight, K is a solvent constant and α is a polymer constant [20].

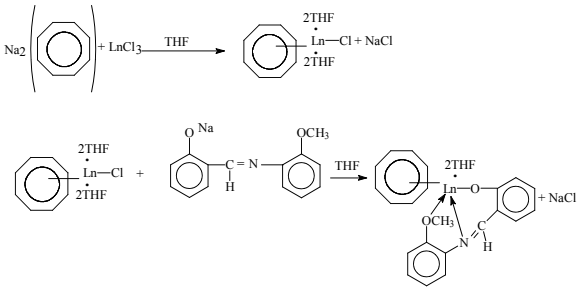
All other complexes were treated in the same way.



where Ln = Sm **(1)**, Eu **(2)**, Gd **(3)**, Er **(4)**

$C_{31}H_{35}NO_4ClSm$(Complex 1) : m/z(%):372.5(M^+-Indenyl-THF-Cl 100) , 483.5 (M^+-Schiff base-THF-Cl 56.5), 115 (indenyl 2.7), 226 (Schiff base 1.5), 72 (THF 2.5) Anal.$C_{31}H_{35}NO_4ClSm$.Calcd: C, 55.48 ; H , 5.22 ; N, 2.08. Found: C, 55.52; H, 5.02; N, 2.06.

Scheme 1



where Ln = Sm **(5)**, Eu **(6)**, Gd **(7)**, Er **(8)**

$C_{30}H_{35}NO_4Sm$ (Complex 5): m/z(%): 425 (M^+-COT-THF 5.7), 448 (M^+-Schiff base-THF 2.5), 203 (COT 100), 226 (Schiff base 5.5) 72 (THF 1.5). Anal.$C_{30}H_{35}NO_4Sm$. Calcd: C, 57.78; H, 5.62; N, 2.25. Found: C, 57.74; H, 5.60; N, 2.21

Scheme 2

Conclusion

Both types of tridentate Schiff base derivative of lanthanoid complexes are proved to be successful tools for the polymerization of methyl-methacrylate (MMA). Comparatively the tridentate

Schiff base derivative of indenyl samarium chloride complex (**1**) showed better efficiency than tridentate Schiff base derivative of cyclooctatetraenyl lanthanoid complex (**5**) under all the tested conditions. Such type of the lanthanoid complexes can be applied to prepare regiospecific poly (MMA) successfully.

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