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Role of Tridentate Schiff Base and Methoxyethylindenyl Derivatives of Lanthanocene Complexes for the Synthesis of High Molecular Weight Polymethyl Methacrylate (PMMA)

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Different mixed ligand lanthanocene complexes along with Al(i-Bu)$_3$ are capable of synthesizing partially syndiotactic high molecular weight polymethylmethacrylate. The Schiff base derivative of mixed ligand lanthanocene complexes (1-4) showed better efficiency (Mv = 227 $\times$ 10^3-354 $\times$ 10^3) compared to the methoxyethylindenyl derivative of mixed ligand lanthanocene complexes (5-9) (Mv = 72 $\times$ 10^3, 172 $\times$ 10^3). The effects of the catalyst, temperature, catalyst/MMA molar ratio, and catalyst/Al(i-Bu)$_3$ molar ratio on the polymerization of MMA at 60 °C suggested that ligand size and radius of rare earth metals play an important role in determining the activity of the catalyst.

Key Words: Tridentate Schiff base, lanthanocene, methoxyethylindene lanthanocene, MMA, polymerization.

Introduction

Zieggler and Natta catalysts were applied in 1960 for the polymerization of methyl- methacrylate (MMA). Later many transition metal catalysts, including V, Cr, Co, Mn, and Ti, were developed.[1−3] However, not all these catalysts showed high activity with 30-100 monomer-catalyst molar ratio and the molecular weight of the resulting polymer was less than 25 $\times$ 10^4.According to the literature, a polymer of high molecular weight (M_v > 100 $\times$ 10^3) remained an important target in polymer chemistry. Although various living polymerization systems have been developed, anionic, cationic, group transfer, or metal carbene initiated polymers have never been synthesized.[4−8] After 1991, a series of new rare earth metal catalysts such as Nd(P$_2$O$_4$)$_3$/Al(i-Bu)$_3$, Nd(Oct)$_3$/Al(i-Bu)$_3$, La(acac)$_3$/BuMgCl, Nd(naph)$_3$/BuLi, Nd(i-Pr)$_3$/Al(i-Bu)$_3$[9−10]

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were successfully synthesized. Later it was reported that the addition of a small amount of butyl lithium to the $Y(acac)_3/Al(i\text{-}Bu)_3$ system greatly enhances its catalytic activity.[11] Polymerization of MMA by Bis (cyclopentadienyl) Samarium hydride in toluene yielded the syndiotactic polymer of high molecular weight with extremely low polydispersity.[12] It was also reported that organolanthanoid initiated polymerization of MMA and yielded both syndiotactic and isotactic living polymers of high molecular weight.[13]

A large number of Schiff bases and their complexes have been studied for their interesting properties such as their ability to reversibly bind oxygen[14] and their catalytic activity in the hydrogenation of olefins.[15] Recently Schiff base derivatives of organolanthanoid complexes have been proved a versatile tool for the isomerization of 1,5-hexadiene.[16] We investigated the synthesis of partially syndiotactic high molecular weight Poly(MMA) by using different novel mixed ligand lanthanocene complexes.

Experimental

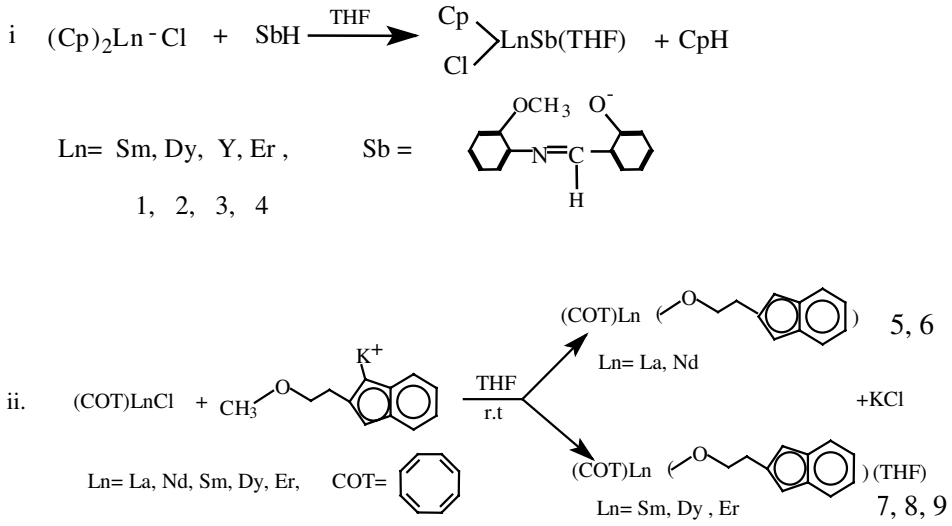
Different mixed ligand lanthanocene {(CP)(Cl) Ln Schiff base (THF)}(Ln=Sm,Dy,Er,Y) and Cyclooctatetraene Ln(methoxyethylindenyl) (THF)(Ln=La,Nd,Sm,Dy,Er) complexes were synthesized according to the literature procedure.[17,18] Newly prepared lanthanocene catalysts were used for the polymerization of MMA carried out under prepurified argon into a 25 mL dry ampoule. MMA was washed with dilute NaOH solution until it was colorless. It was then dried over molecular sieves and distilled under vacuum pressure. A general procedure for the polymerization of MMA was as follows: CP(Cl) Sm Schiff base (THF)/$Al(i\text{-}Bu)_3$ were charged (1:20) under argon into a dry ampoule and 1 mL of dried toluene was added. MMA (1:1000) was syringed (1.05 mL) and the polymerization was initiated at 60 °C in a water bath. After 20 h, the polymerization was quenched with ethanol containing 5% HCl (Table 1). The poly MMA thus obtained was washed with ethanol, dried at 50 °C under vacuum, weighed, and calculated for percentage conversion. 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 $[\eta] = KM_v^{\alpha}$(where Mv is viscosity average molecular weight, K is solvent constant and α is polymer constant).[19] All other complexes were treated in the same way.

The following scheme was used for the preparation of these novel complexes:

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

No.	Catalyst	Conversion %	$M_v \times 10^3$
1	$Cp(Cl)Sm(C_{14}H_{13}NO_2)(THF)$	55.46	354
2	$Cp(Cl)Dy(C_{14}H_{13}NO_2)(THF)$	51.8	274
3	$Cp(Cl)Y(C_{14}H_{13}NO_2)(THF)$	50.52	264
4	$Cp(Cl)Er(C_{14}H_{13}NO_2)(THF)$	43.94	227
5	(COT)La(methoxyethylindenyl)	34.92	172
6	(COT)Nd(methoxyethylindenyl)	33.06	148
7	(COT)Sm(methoxyethylindenyl)(THF)	28.48	141
8	(COT)Dy(methoxyethylindenyl)(THF)	23.47	126
9	(COT)Er(methoxyethylindenyl)(THF)	14.44	72
10	$(Cp)_2Y$ $(C_{14}H_{13}NO_2)$	20.15	186
11*	Al(i-Bu)3	33.14	14

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



Results and Discussion

One complex from each group was taken as a representative for discussing the polymerization of MMA. For this purpose, complex no. 3, {CP(Cl)Y($C_{14}H_{13}NO_2$)(THF)}, was taken for the tridentate Schiff base derivative of mixed ligand lanthanocene complexes and complex no. 7, {(COT)Sm(Methoxy ethylindenyl)(THF)}, was chosen for the methoxyethyl indenyl derivative of mixed ligand lanthanocene complexes to check the effects of catalysts, temperature, catalyst/MMA molar ratio, and catalyst/Al(i-Bu)$_3$ molar ratio on the polymerization of MMA at 60 °C. Both metals as well as ligands play an important role in determining the activity of the catalysts. The catalysts 1-4 showed a greater increase in the conversion as well as molecular weight than complexes 5-9. The maximum activity (conversion % = 55.46 and Mv = 354 × 10^3) was observed in the case of catalyst 1, while catalyst 9 showed minimum efficiency (conversion % = 14.44 and Mv = 72 × 10^3). Catalyst 10 was tested to compare its activity with the others. It was found that its activity (conversion % = 20.15 and Mv = 186 × 10^3) lies in between the 2 types of catalyzing systems. In the case of complexes 1-4, the ligands have less steric influence on the central metals, which means that the ionic radii play a significant role in determining the efficiency of the catalysts. In the 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 the catalysts resulted in high molecular weight polymethylmethacrylate (PMMA). The result obtained from a blank sample shows that Al(i-Bu)$_3$resulted in PMMA with 33.14% conversion and 14 × 10^3 molecular weight (Table 1).

The effect of temperature (Figure 1a and 1b) illustrates that both catalyzing systems exhibit linear increases in activity with the rise in temperature, which means that the higher the temperature, the greater is the kinetic energy of the reactants. The greater the kinetic energy, the greater is the energy of activation. The greatest efficiency (conversion % = 51.59 and Mv = 416 × 10^3) was observed in the case of catalyst 3 at 70 °C. Catalyst 3 showed greater efficiency than catalyst 7 at all temperatures, which may have been due to the presence of bulky ligands suppressing the activity (Table 2). Similarly, Pan et al.[20] reported that higher temperature favors rapid polymerization of MMA by lanthanoid complexes. The reason is perhaps the increase in activation energy at higher temperature.

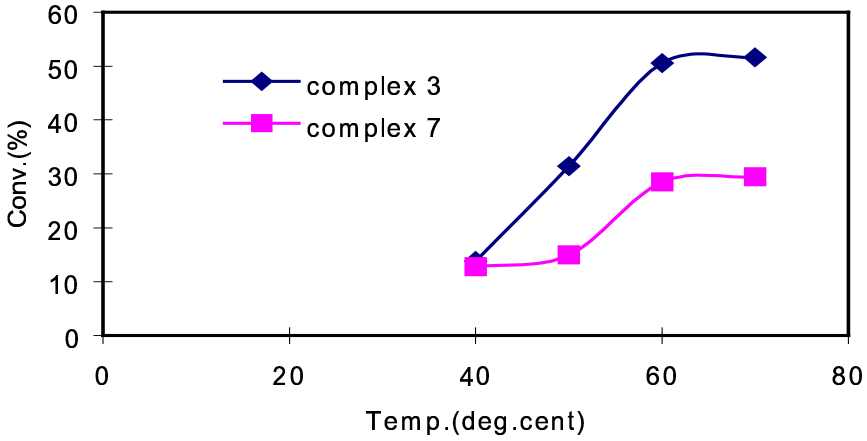


Figure 1a. Effect of temperature on the polymerization of MMA.

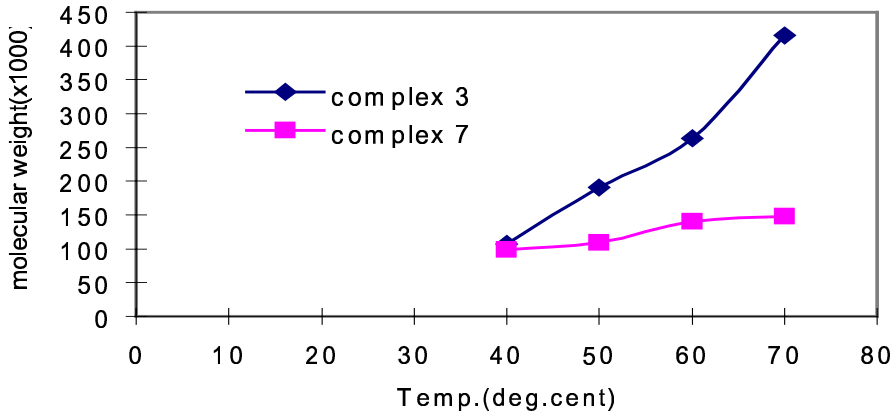


Figure 1b. Effect of temperature on the molecular weight of poly(MMA).

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

Catalyst	Temp. °C	Conversion %	$M_v \times 10^3$
3	70	51.59	416
7		29.40	148
3	60	50.52	264
7		28.48	140
3	50	31.42	191
7		14.97	109
3	40	13.80	107
7		12.72	99

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

The effect of catalyst/MMA molar ratio (Figure 2a and 2b) shows that conversions as well as molecular weight increase parallel the increase in MMA concentration. The greatest activity was observed with catalyst 3 (conversion % = 54.40 and Mv = 395 $\times$ 10^3) at 3000 molar ratio of MMA. Catalyst 3 exhibited greater activity than catalyst 7 (conversion % = 33.8 and Mv = 181 $\times$ 10^3) at 3000 molar ratio of MMA (Table 3). The variation may be due to the steric hindrance from the bulky ligands.

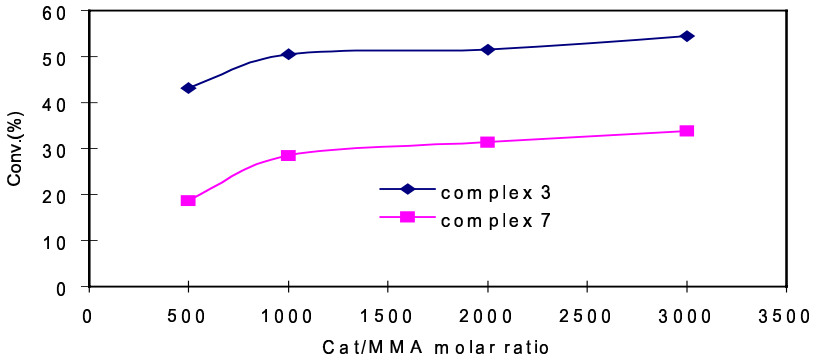


Figure 2a. Effect of cat/MMA molar ratio on the polymerization of MMA.

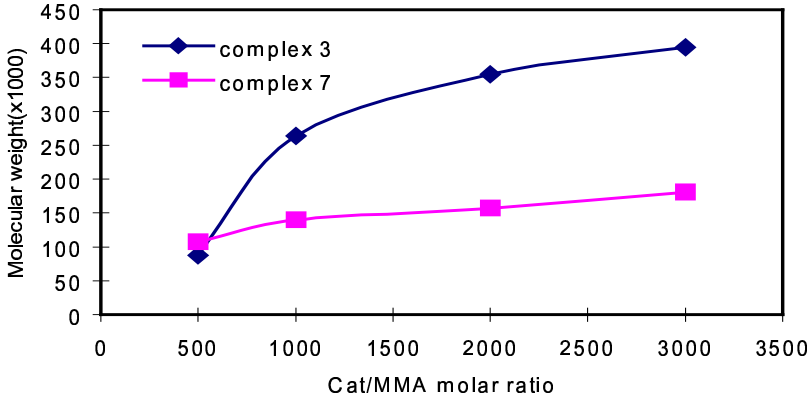


Figure 2b. Effect of cat./MMA molar ratio on the molecular weight of poly(MMA).

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

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

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

The catalyst/Al(i-Bu)$_3$ molar ratio proves to be an important factor for the polymerization of MMA (Figure 3a and 3b). Generally, the 2 catalytic systems show similar characteristics. At first, as the catalyst/Al(i-Bu)$_3$molar ratio increases, the conversion as well as molecular weight of Poly(MMA) increase markedly. At the 20 molar ratio, catalyst 3 showed the best efficiency (conversion % = 50.52 and Mv = 264 × 10^3) while catalyst 7 also showed better activity (conversion % = 28.48 and Mv = 140 × 10^3) at this molar ratio of the Al(i-Bu)$_3$ than the other molar ratios. The further increase in the Al(i-Bu)$_3$ molar

ratio causes a fall in conversion as well as in the molecular weight of Poly(MMA) (Table 4), which may have been due to the fact that Al(i-Bu)$_3$ at higher concentration may act as a chain transfer agent and hence may terminate further polymerization. Earlier it was reported that a low concentration of Al(i-Bu)$_3$ favors high conversion with high molecular weight Poly(MMA).[21] Both catalyzing systems synthesized partially syndiotactic polymethymethacrylate (> 60%).

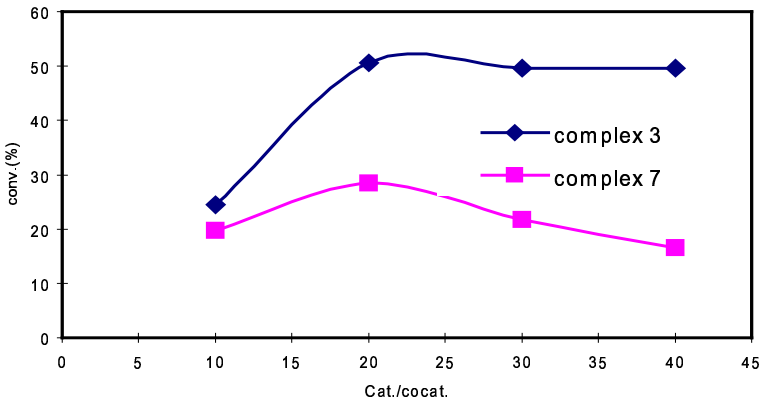


Figure 3a. Effect of cat./cocat.on the polymerization of MMA.

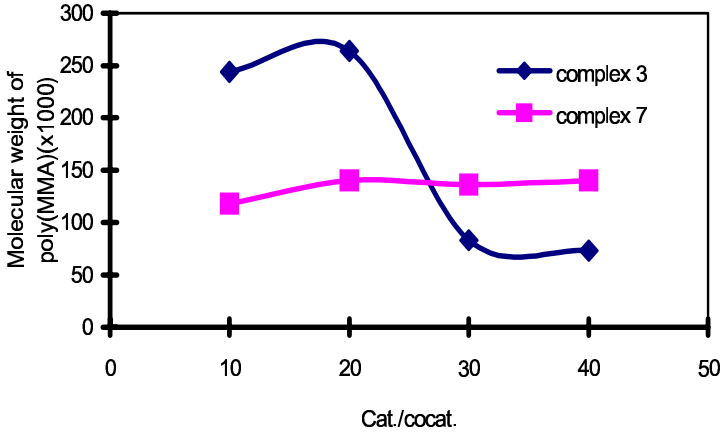


Figure 3b. Effect of cat./cocat. molar ratio on molecular weight of poly(MMA).

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

Catalyst	Cat/Al mol/mol	Conversion %	$M_v \times 10^3$
3	10	24.47	244
7		19.72	118
3	20	50.52	264
7		28.48	140
3	30	49.63	83
7		21.79	136
3	40	49.57	73
7		16.60	133

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

Conclusion

Novel mixed ligand lanthanocene complexes were prepared for the polymerization of MMA. The tridentate Schiff base derivative of lanthanocene complexes in general showed better efficiency than the methoxyethylindenyl derivative of lanthanocene complexes. Further it is possible to prepare partially syndiotactic high molecular weight ($M_v > 100 \times 10^3$) Poly(MMA) by using such types of catalytic system.

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