Synthesis, Characterization and Application of Benzyl-substituted Cyclopentadienyl lanthanide Complexes as Catalyst Precursors for the Syndiotactic Polymerization of Methyl Methacrylate

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Benzyl-substituted cyclopentadienyl lanthanide complexes were synthesized and characterized by elemental analysis, MS and IR spectroscopy. The analytical data point out the formation of monomeric, unsolvated complexes. In conjunction with $Al(Et)_3$ as co-catalyst, the title complexes are efficient catalysts for the syndiotactic polymerization of methyl methacrylate. For the complex $(C_6H_5CH_2C_5H_4)_2YCl$, under the optimum polymerization conditions (60 ℃, $n(MMA) : n(catalyst) : n(co-catalyst) = 1000 : 1 : 10$), a predominantly syndiotactic ($rr = 66\%$) polymer of high molecular weight ($M_\eta = 105000$) was obtained.

Keywords   benzyl-cyclopentadiene, organolanthanide complex, methyl methacrylate, syndiotacticity, polymerization

Introduction

Organolanthanide complexes have become important reagents and catalysts for the synthesis of organic molecules and polymers.[1] Ligands based on the cyclopentadienyl moiety and its various substituted forms have largely spearheaded the rapid development of these complexes.[2] The ability to tune electronic and steric features in the cyclopentadienyl type ligands has given rise to greater versatility in the design and modification of catalytic systems aimed at improving catalytic activity and influencing the properties of polymer.[3,4] At present many research groups are involved in ligand modification in order to introduce novel features such as catalytic activity, selectivity and stability, and in determining relationships between new ligands and polymer structures.

In continuation of our studies on ligand modification with the aim of developing new catalyst systems and the establishment of the correlation between Cp-ring substituents and catalyst activity, the benzyl substituent was recognized to be of interest.[5,6] The ligand has electronic properties similar to that of the ω-alkenyl group ligands which we have been exploring, at the same time, it is relatively bulky in size hence is easier to prepare.

Benzyl-substituted Cp complexes of the Group 4 transition metals have been well studied and their per-formance as active catalysts for the polymerization of olefinic monomers have also well documented.[7-11] Bochmann *et al.* have demonstrated the ability of the benzyl substituents to stabilize electrophilic metal centers through π-coordination of the benzylic aryl substituents which is similar to the coordination of the alkenyl-substituted cyclopentadienyl ligands.[12-14] However only a few benzyl cyclopentadienyl lanthanide complexes were synthesized, such as $[(C_6H_5CH_2C_5H_4)_2GdCl(THF)]_2$ and $(C_6H_5CH_2C_5H_4)_2ErCl(THF)$.[15] In this paper, therefore, we present the synthesis and characterization of additional benzyl substituted cyclopentadienyl lanthanide complexes and the study on their catalytic activities in association with aluminum alkyls for the syndiotactic polymerization of MMA.

Experimental

All the operations were carried out under dry argon using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, toluene, and *n*-hexane were dried over sodium/benzophenone and distilled prior to use. Benzyl cyclopentadiene and anhydrous lanthanide chloride were prepared by the published procedures.[16,17] Methyl methacrylate was washed with dilute NaOH solution until colorless, dried over anhydrous $CaCl_2$ and CaH_2, and distilled under reduced pressure into a

Lanthanide complex

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Schlenk flask containing CaH_2. Mass spectra were obtained on an HP5989A mass spectrometer with EI (70 eV). Infrared spectra were recorded on a Nicolet Magna-IR 550 or a Nicolet 5 SXC spectrometer with KBr pellets or Nujol mull. Elemental analyses were performed on an EA 1106 CHN spectrometer.

Synthesis of the complex $(C_6H_5CH_2C_5H_4)_2LnCl$ (Ln = Y, Er, Yb)

The general synthetic procedure for the complexes $(C_6H_5CH_2C_5H_4)_2LnCl$ is in analogy to $(C_6H_5CH_2C_5H_4)_2ErCl(THF)$.[15] Typically, Benzylcyclopentadiene (8 g, 0.051 mol) was added to a suspension of potassium metal (2.5 g, 0.064 mol) in THF (80 mL) at −20 ℃. The reaction mixture was stirred overnight at room temperature. A solution of benzylcyclopentadienyl potassium in THF was obtained. To a suspension of YCl_3 (0.74 g, 3.8 mmol) in THF (30 mL) was added benzyl cyclopentadienyl potassium 18.6 mL (0.4086 N, 7.6 mmol) in THF at room temperature. After stirring for 24 h, the reaction mixture was centrifuged, and the solvent was removed under reduced pressure and the residue was extracted twice with ether (40 mL×2). The ether extract was concentrated and a little amount of *n*-hexane was added, then it was kept at −30 ℃ to give fine yellowish micro crystals (yield 65%). The complexes were characterized by elemental analyses, MS and IR spectroscopy. Analytical data are presented below:

$(C_6H_5CH_2C_5H_4)_2YCl$ (**1**) is yellow crystalline solid (yield 65%). IR (KBr) *v*: 3130 (m), 3100 (m), 3050 (m), 2980 (m), 2900 (m), 2850 (w), 1940 (w), 1870 (w), 1810 (w), 1720 (m), 1650 (m), 1600 (m), 1490 (s), 1450 (m), 1430 (w), 1360 (w), 1265 (w), 1200 (w), 1150 (w), 1070 (w), 1050 (w), 1030 (m), 960 (w), 940 (w), 890 (w), 830 (w), 760 (s), 74 (m), 700 (s) cm^{-1}; MS *m/z* (%): 399 [(M−Cl)$^+$, 1], 279 [(M−$C_6H_5CH_2C_5H_4$)$^+$, 2], 156 ($C_6H_5CH_2C_5H_5^+$, 75), 91 ($C_7H_7^+$, 100). Anal. calcd for $C_{24}H_{22}YCl$: C 65.29, H 5.11; found C 64.77, H 5.49.

$(C_6H_5CH_2C_5H_4)_2ErCl$ (**2**) is pink crystal (yield 38%). IR (Nujol) *v*: 3050 (s), 3020 (s), 2980 (s), 2910 (s), 2310 (w), 1945 (w), 1875 (w), 1805 (w), 1720 (m), 1650 (s), 1600 (s), 1490 (s), 1450 (s), 1430 (m), 1375 (m), 1300 (m), 1260 (m), 1190 (m), 1150 (m), 1070 (m), 1050 (s), 1030 (s), 950 (m), 930 (m), 890 (m), 830 (m), 760 (s), 730 (s), 700 (s) cm^{-1}; MS *m/z* (%): 511 (M$^+$, 4), 476 [(M−Cl)$^+$, 31], 356 [(M−$C_6H_5CH_2C_5H_4$)$^+$, 41], 156 ($C_6H_5CH_2C_5H_5^+$, 60), 91 ($C_7H_7^+$, 100). Anal. calcd for $C_{24}H_{22}ErCl$: C 56.17, H 4.33; found C 55.71, H 4.66.

$(C_6H_5CH_2C_5H_4)_2YbCl$ (**3**) is red crystalline solid (yield 62%). IR (KBr) *v*: 3150 (m), 3100 (m), 3050 (m), 2980 (m) 2930 (m), 1940 (w), 1870 (w), 1810 (w), 1720 (m), 1715 (m), 1650 (s), 1600 (m), 1490 (m), 1450 (m), 1430 (w), 1360 (m), 1250 (w), 1170 (w), 1150 (w), 1070 (w), 1050 (w), 1030 (m), 930 (w), 910 (w), 830 (w), 760 (m), 740 (m), 700 (s) cm^{-1}; MS *m/z* (%): 364 [(M−$C_6H_5CH_2C_5H_4$)$^+$, 8], 209 [(M−($C_6H_5CH_2C_5H_4$)$_2$)$^+$, 1], 156 ($C_6H_5CH_2C_5H_5^+$, 89), 91 ($C_7H_7^+$, 100). Anal. calcd for $C_{24}H_{22}YbCl$: C 54.54, H 4.28; found C 54.38, H 4.80.

Synthesis of the complex $(C_6H_5CH_2C_5H_4)_2SmCl$ (4)

To a suspension of $SmCl_3$ (0.76 g, 2.96 mmol) in THF (30 mL) was added 14.4 mL (5.92 mmol) of benzyl cyclopentadienyl potassium in THF at room temperature. After stirring for 24 h, the reaction mixture was centrifuged, and the solvent was removed under reduced pressure. The residue was extracted with ether (50 mL) and toluene (50 mL). The solvent was evaporated and the residue was washed twice with *n*-hexane (20 mL) to obtain 1.31 g (89%) of orange oil. IR (KBr) *v*: 3130 (m), 3100 (m), 3050 (s), 2950 (s), 2980 (s), 2900 (s), 2850 (m), 1940 (w), 1870 (w), 1810 (w), 1720 (w), 1650 (w), 1600 (m), 1490 (s), 1450 (m), 1430 (w), 1360 (w), 1340 (w), 1295 (w), 1250 (w), 1200 (w), 1170 (w), 1150 (w), 1110 (w), 1070 (m), 1050 (w), 1030 (m), 980 (w), 960 (w), 940 (w), 910 (w), 830 (w), 810 (w), 760 (m), 740 (m), 700 (s) cm^{-1}; MS *m/z* (%): 462 [(M−Cl)$^+$, 100], 342 [(M−$C_6H_5CH_2C_5H_4$)$^+$, 1], 156 ($C_6H_5CH_2C_5H_5^+$, 57), 91 ($C_7H_7^+$, 70). Anal. calcd for $C_{24}H_{22}SmCl$: C 58.08, H 4.48; found C 58.37, H 4.29.

Polymerization of MMA

All polymerizations were performed in a sealed ampoule. The required amounts of reagents were introduced into the ampoule by a syringe. After introducing the catalyst and the co-catalyst, the monomer MMA (usually 1 mL) was charged. Polymerization was carried out at a constant temperature for an appropriate period of time, and quenched by the addition of acidified ethanol (5% HCl). The polymer was washed twice with ethanol and dried to constant weight at 50 ℃ in a vacuum oven.

Characterization of the polymer

Inherent viscosity of PMMA in $CHCl_3$ was determined at 30 ℃ with an Ubbelohde-type viscometer. Viscosity average molecular weight was calculated using Mark-Houwink equation $[\eta] = 5.5 \times 10^{-3} M_{\eta}^{0.79}$ (cm^3/g) (where M_{η} = viscosity average molecular weight). The tacticity of PMMA obtained under different polymerization conditions was determined by ^1H NMR spectra (from the peak of α-methyl, *mm*, *mr* and *rr* at δ 1.17, 0.98 and 0.78 respectively). ^1H NMR spectra were recorded on a Bruker AVANCE 500 MHz NMR spectrometer at room temperature in $CDCl_3$.

## Results and discussion

Synthesis and characterization

The title complexes were easily obtained by metathesis reactions involving the lanthanide trichloride and the potassium salt of the substituted cyclopentadiene as shown in Scheme 1.

The ionic radius of the lanthanide metal is important for obtaining isolable complexes. Only complexes of lanthanides with relatively smaller ionic radius (Ln = Y,

Scheme 1

Ln = Y (**1**), Er (**2**), Yb (**3**), Sm (**4**)
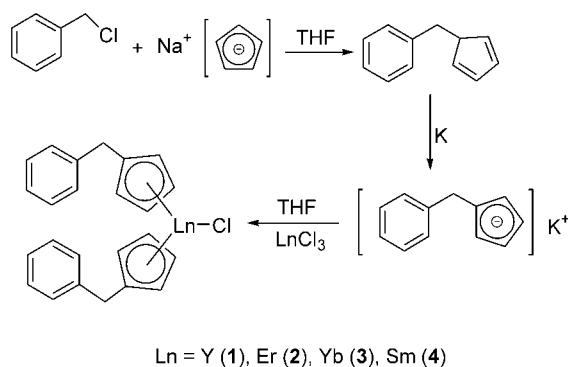
Er, Yb, Sm) were isolated. Until now, we did not succeed in synthesizing bis(benzylcyclopentadienyl)-lanthanide chloride of the larger lanthanides (Ln＝La, Nd). The erbium and ytterbium complexes were obtained as reddish micro crystals, while yttrium complexe was formed as a pale yellowish powder. In contrast, the medium sized samarium metal could only yield orange oil. Therefore, it is clear that the physical nature and colors of the complexes are influenced by the nature of the central metal in relation to the nature and size of the attached ligand. All the four complexes have no melting points and tend to decompose above 100 ℃. They are sensitive to air and moisture. Solubility also varies slightly depending on the central metal, but they are generally soluble in polar solvents (THF, ether) and insoluble in hydrocarbon solvents such as *n*-hexane. The complexes of yttrium and samarium are soluble in toluene.

All the four complexes were characterized by elemental analyses, mass spectra and infrared spectroscopy. The analyses of all complexes conform to the general formula $(C_6H_5CH_2C_5H_4)_2LnCl$, in which the metal is a seven-coordinate center. No evidence of coordinated solvent molecules was observed. Although, in the complex $(C_6H_5CH_2C_5H_4)_2ErCl(THF)$ determined by X-ray crystallography THF coordination was observed,[15] it is probable in our case that the coordinated THF was lost during workup and high vacuum drying of the complexes. In fact, it is not uncommon for crystals to loose all or part of their coordinated solvent molecules under vacuum. In the IR spectra of the complexes which show characteristic absorption peaks consistent with the proposed structure, the mono-substituted phenyl group has absorptions around 1463, 750—740, and 700 cm^{-1}. The absorption at 700 cm^{-1} is particularly very strong in all the four complexes. The strength of the intensity of these absorptions is unchanged from what is expected for normal aromatic compounds.[18] There is no shift in the peak position towards lower frequency as is observed for fully coordinated bonds.[19] This indicates that an interaction between the central metal and the pendant phenyl groups is not evident in the four lanthanide complexes. This result is in agreement with the X-ray structural analyses of $(C_6H_5CH_2C_5H_4)_2ErCl(THF)$, in which

the pendant phenyl substituent is not coordinated with the central metal.[15]

Polymerization of MMA

Polymerization of MMA was carried out with the title complexes and triethyl aluminium as cocatalyst. The result is presented in Table 1. All the complexes show activity to the monomer. The result indicates that the ionic radius of the central lanthanide metal influences the catalytic activity of the complexes. The catalytic activity increases with the decrease in the radius of the central metal. The Er complex produced the highest monomer conversion of 100% and $M_\eta＝350\times10^3$. The reason may be that the combination of a sterically bulky ligand in association with a small metal center stabilizes active centers such as $Cp_2'LnR$ or $Cp_2'LnH$ which are more active than $Cp_2'Ln(\mu\text{-}R)_2AlR_2$. Also the bulk size of the ligand suppresses chain transfer processes which lead to high molecular weight.

Table 1 Influence of the metal (Ln) on the polymerization of MMA catalyzed by $(C_6H_5CH_2C_5H_4)_2LnCl$ complexes

Ln	Conversion/%	$M_\eta \times 10^{-3}$
Sm^a	20	205
Y^a	37	357
Er^b	100	350
Yb^b	61	231

Conditions: $n(MMA) \colon n(Ln) \colon n(Et_3Al)＝1000 \colon 1 \colon 10$, time＝24 h, temp.＝60 ℃, monomer 1 mL; ^{a} as solution in toluene (1 mL); ^{b} bulk polymerization.

Based on these initial observations, we conducted a more detailed study on the yttrium complex to establish the optimum conditions of polymerization. This is because Y is of average size (ionic radius 1.62), fitting right at the middle of the lanthanide series in terms of ionic radius, therefore it is believed that a detailed study on it will be a representative of the entire series. The effects of such factors as temperature, time of polymerization and variation in catalyst, cocatalyst concentration were studied. The result is presented in Table 2.

The influence of variation in MMA/catalyst molar ratio is presented in Figure 1. As the amount of monomer increases (decrease in initiator concentration), the conversion of monomer also increases accordingly, while the molecular weight of the polymer obtained decreases. The observation is different from our observation on the polymerization activated by pendant allyl-Cp lanthanide complexes.[5,6] Increasing conversions at higher MMA concentration is due to the stability of the active species. The recorded activity of the present system is lower than what was observed for the polymerization systems initiated by $Y(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$ as single component catalyst.[20] This is much likely due to steric factors arising from the larger size of the benzyl group, which will electronically improve catalyst performance through resonance stabilization, but will also

impose steric restrictions on incoming monomers. The observed decrease in molar mass is due to the increase in chain transfer to monomer from the active center. The rate of chain transfer increases with the rise in MMA concentration.

Table 2 Polymerization of MMA catalyzed by ($C_6H_5CH_2$-$C_5H_4)_2$YCl/Et_3Al catalyst system

n(MMA) : n(Cat.)	Temp./℃	Time/h	Conv./%	$M_\eta \times 10^{-3}$
500	60	24	18	442
1000	60	24	37	357
1500	60	24	43	93.5
2000	60	24	45	63.2
1000	0	24	14	5.4
1000	20	24	21	38.4
1000	80	24	56	212.8
1000	60	18	25	71.0
1000	60	30	45	176

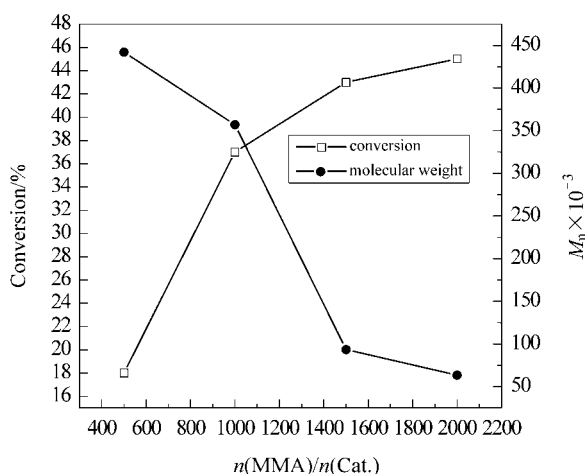Conditions: n(Cat.) : n(Co-cat.)=1 : 10, monomer 1 mL, toluene 1 mL.

Figure 1 Influence of MMA/catalyst molar ratio on polymerization of MMA catalyzed by ($C_6H_5CH_2C_5H_4)_2$YCl/Et_3Al catalyst system.

The influence of temperature on the polymerization of MMA catalyzed by the title catalyst system is presented in Figure 2. MMA conversion increases with a rise in temperature, and the molecular mass of polymer also increases with an increase of temperature and reaches maximum at 60 ℃, from which it begins to decrease. The observation is also different from the record for the polymerization system initiated by pendant allyl-Cp lanthanide complexes as single component catalyst in which the catalytic activity declines with a temperature rise.[6] These indicate that even for long time, the high-temperature environment does not hinder the catalyst efficiency. In the polymerization system, some reactions competing with the insertion of monomer are also activated by the rise in temperature. These reac-

tions may be chain termination or coordination of the benzyl group. Schwecke and Kaminsky[16] noted that the benzyl group also acts by competing with the monomer for the available coordination site during polymerization. The benzyl group coordinates to the active site for a short period (labile behavior) thereby blocking the free coordination site to incoming monomer. This may be responsible for the fall in molar mass and syndiotactic selectivity moving from 60 to 80 ℃ (as showed in Table 3).
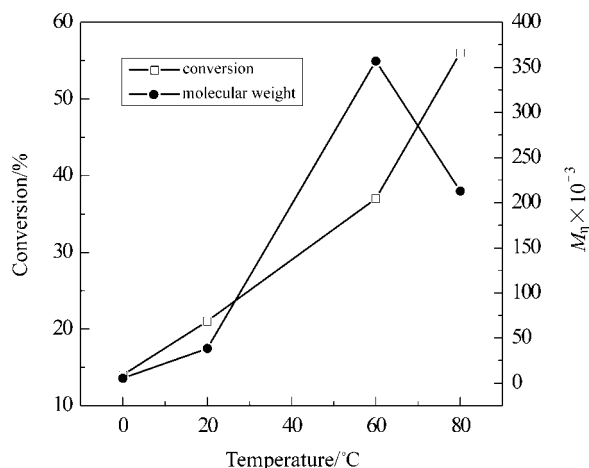

Figure 2 Influence of polymerization temperature on polymerization of MMA catalyzed by ($C_6H_5CH_2C_5H_4)_2$YCl/Et_3Al catalyst system

Table 3 Tacticity of PMMA produced by ($C_6H_5CH_2C_5H_4)_2$YCl/Et_3Al catalyst system

n(MMA) : n(Ln) : n(Et_3Al)	Temp./℃	Time/h	*mm*/%	*mr*/%	*rr*/%
1000 : 1 : 10	80	24	7	35	58
1000 : 1 : 10	60	30	11	31	58
1000 : 1 : 10	60	24	0	34	66
2000 : 1 : 10	60	24	0	37	63
1000 : 1 : 5	60	24	5	33	62

The result of the influence of variation in time of the polymerization is presented in Figure 3. The conversion of monomer increases directly with time. With the decrease of monomer, the rate of increase of conversion becomes gradually slower. The molar weight of polymer also increases with time, and it begins to decrease as time extends beyond 24 h. This may be attributed to a combination of factors that are all time dependent, such as degradation of the active site.

Table 4 presents the result of the influence of varying the co-catalyst concentration on the polymerization of MMA. In Ziegler-Natta type catalyst initiated polymerizations, the aluminum compounds used as co-catalysts serve the dual function of initiating the active species by alkylating the catalyst and extending its life span by acting as a scavenger for moisture and other impurities. From the data in Table 4 it is very clear that
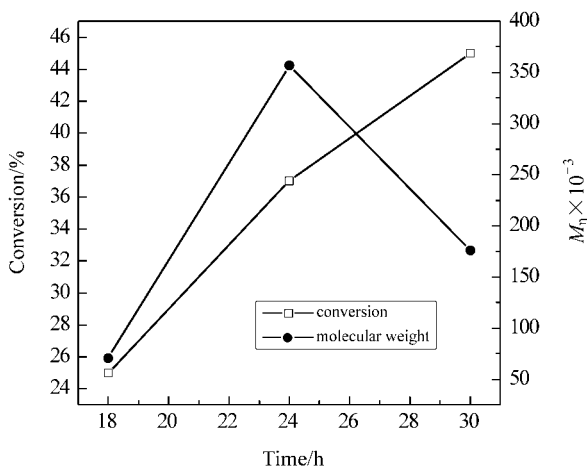
Figure 3 Influence of time on the polymerization of MMA catalyzed by $(C_6H_5CH_2C_5H_4)_2YCl/Et_3Al$ catalyst system.

the amount of cocatalyst is not very significant as the conversion of MMA to polymer varies within a small range (29%—41%) irrespective of the amount of co-catalyst, while the molecular mass is negatively affected by an increase in cocatalyst concentration beyond a 10 fold molar excess. The probable reason may be that the excess cocatalyst increases the rate of termination by polymer chain transfer to the alkyl group, otherwise known as overalkylation. Therefore, it is clear that the present catalyst system is not dependent on the amount of cocatalyst, and a minimal amount of cocatalyst to initiate polymerization is all that is needed for the process to be self-sustaining.

Table 4 Influence of cocatalyst/catalyst molar ratio on the polymerization of MMA catalyzed by $(C_6H_5CH_2C_5H_4)_2YCl/Et_3Al$ catalyst system

n(Co-cat.) ：n(Cat.)	Conversion/%	$M_\eta \times 10^{-3}$
5	29	307
10	37	357
15	29	75.8
20	41	25.6

Conditions: n(MMA)：n(Cat)＝1000, temp.＝60 ℃, time＝24 h, monomer 1 mL, toluene 1 mL.

By established procedure, tacticity of PMMA obtained under different polymerization conditions was determined by ^{1}H NMR spectra of the polymers in $CDCl_3$ (from the assignment of α-methyl proton peaks for *mm*, *mr* and *rr* at δ 1.17, 0.98 and 0.78 respectively).[21] The result is summarized in Table 3. This indicates that long polymerization time and very high polymerization temperature lower the syndioselectivity of the present catalyst system, while the concentrations of

catalyst and cocatalyst has no noticeable influence on the amount of syndiotactic poly(MMA) produced.

Conclusions

Benzyl-substituted cyclopentadienyl lanthanide complexes of the relatively smaller ionic radius lanthanide metals have been synthesized and successfully characterized. And the analytical data point out the formation of monomeric and unsolvated complexes. In conjunction with Al(Et)₃ as a co-catalyst, these complexes are efficient catalysts for the syndiotactic polymerization of MMA.

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